UNIVERSITAT ROVIRA I VIRGILI

LEXICAL AND SEMANTIC PROCESSING DURING THE TRANSLATION PROCESS IN HIGHLY PROFICIENT BILINGUALS: BEHAVIORAL AND ELECTROPHYSIOLOGICAL MEASURES.

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Lexical and Semantic Processing During the Translation Process in Highly Proficient Bilinguals: Behavioral and Electrophysiological Measures

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Doctoral Thesis

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Dedication

I Cornelia, dedicate this work to my beloved father, Romul Victor Moldovan, and to my principal PhD supervisor Dr. Rosa Sánchez-Casas who both passed away unexpectedly in 2012. Each in their own very different way were an integral part of this work, and such an important support and so proud of me working on this project. Words cannot express my gratitude for the wonderful time spent with them, what I was able to learn and knowing I could succeed at many particular aspects, but especially I express my appreciation for some of their words that touched my heart/mind and in difficult moments gave me strength.

While supervising my masters and PhD project, Rosa introduced me into the research field and closely watched my steps. I saw her not only a great professional and leader, but also a model of an intensely dedicated worker in the field, with a special ability and dedication for working with students. Beyond the knowledge gained, I was enriched in many other aspects that were and continue to be very important for me in the process of becoming a researcher. Her special way to encourage my steps, her ability to work on my thinking and stress the importance to take initiatives in research, her interest in improving my English and to open my perspective in the field… are only some of the aspects, that gave me the courage "to fly" (in her words) with direction and the strength to conclude this project. I fondly remember many pleasant moments when we enjoyed research results. In fact, all the experimental work of this dissertation was done under her supervision. I am sure that she would be very glad to see the entire work-product of this PhD project.

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Presentation

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It is estimated that almost half of the entire world population, under certain definitions, is bilingual (i.e., a person who acquired and use two languages, Grosjean, 2010). Bilinguals can be found on every continent, and across the entire spectrum of human existence.

Speaking two languages rather than just one has obvious neurocognitive benefits. In the last decades, cognitive psychologists and neuroscience researchers have provided solid evidences showing that the advantages of bilingualism are much more relevant than being able to converse with a wider range of people. Bilingualism can have a profound effect on the plasticity of the brain, affecting cognitive functions that are not exclusively related to language (e.g., Bialystok, Craik, Grady, Chau, Ishii, Gunji & Pantev, 2005), even contributing to the preservation of the brain against dementia in old age (see Bialystok, Craik, Green, & Gollan, 2009, or Bialystok, Craik, & Luk, 2012, for reviews). The bilingual brain is not necessarily a smarter brain, rather it is more resourceful and flexible than a monolingual brain probably because it has learned to manage and control the language in use and keep out the other language. Thus, in a context where two languages are used the bilingual has to develop the ability to switch between them. This ability, in its turn, increases the mental flexibility to switch between tasks with less cost than for monolinguals. The bilingual brain also has to learn to focus attention on the target language and inhibit or suppress the influence of the other language. This might produce positive consequence on inhibitory control processes.

The consequences of bilingualism for both linguistic and non-linguistic processing are a result of a lifelong experience in managing attention to two languages and in avoiding interferences from the non-target language. This ability would not be necessary if a bilingual mind consisted of two independent language systems. However, substantial evidence shows that this is not how the bilingual mind is organized. Instead, the two languages of bilinguals seem to be always active to some extent and there is an interaction between them all the times. Over the last decades the study of the cross-languages influences on language processing has become a central topic in research on bilingualism (see Kroll, Dussias, Bogulski & Valdes-Kroff, 2012; Schwartz & Van Hell, 2012; van Hell & Tanner, 2012; van Assche, Duyck, & Hartsuiker, 2012, for recent reviews). The accumulated evidence suggests that cross-language interactions are not a matter of all or nothing; rather they have to be considered in relation to different variables that can determine how the two languages are connected and activated during word processing. These variables are related either to characteristics of the words (i.e., types of words' relations across languages) or to characteristics of the bilinguals (i.e. proficiency, age of acquisition, context of acquisition and language use, etc.).

The studies included in the present thesis address this issue by focusing on the influence of lexical and semantic variables on the translation process in highly proficient and balanced bilinguals. Most research conducted in this field has tested the effects of the native or first language (L1) on the processing of the weaker second language (L2) and has focused on non-proficient and/or relatively proficient bilinguals. Additionally of being unbalanced, this type of bilinguals usually live immersed in a L1 context, in which they use one language much more than the other. The results obtained with these bilinguals might not be generalized to other populations. In fact, it has been shown that even a short period of L2 immersion could attenuate the influence of L1 over L2 (e.g., Linck, Kroll and Sunderman, 2009). Thus, it is very relevant to study bilinguals in different immersion contexts to fully characterize cross-languages lexical and semantic activation.

The main contribution of this thesis is the study of cross-languages interactions and influences in a population of highly proficient and balanced Catalan-Spanish bilinguals who acquired both languages in early childhood and who live in an immersion context whereby both languages are actively used on a regular basis (both Catalan and Spanish are official languages in Catalonia). The study of this particular type of bilinguals will provide the opportunity of characterizing cross-languages interaction processes in a context that favors the constant activation of both languages.

In this Thesis, I present four studies in which behavioral and electrophysiological measures were used to address several specific topics concerning lexical and semantic activation in bilinguals, within the framework of the most relevant models of bilingual memory. In the Introduction, a general overview about bilingual memory, as well as several research questions about bilingual language processing, are presented. Afterwards, I introduce some of the most representative models of bilingual memory, which have inspired the experiments of this Thesis. Then, I introduce the specific issues addressed in this Thesis, within the framework of the abovementioned models. After the Introduction, the Experimental Section is included. Finally, by taking into consideration the results of the four studies, I present a General Discussion and provide several conclusions in relation with the issues addressed and with the predictions of the models of bilingual memory.

I. Introduction

1. Introduction

1.1 BILINGUAL MEMORY

1.1.1 MEMORY ORGANIZATION: EARLIEST VIEWS

One central issue addressed in Psycholinguistics has been whether the two languages of a bilingual are represented in a common memory system or rather each language is stored in a separate system. This issue lead initially to two different views: the language-specific view which assumed independent memory stores for each known language and a language nonspecific view that posited an integrated memory store for both languages. The language-specific view claimed that separate language stores can be selectively accessed depending on the language set information (Gerard & Scarborough, 1989; Macnamara, 1967; Macnamara & Kushnir, 1971; Scarboroough, Gerard & Cortese 1984; Soares & Grosjean, 1984). This proposal was typically associated with the existence of a switching mechanism that guides the linguistic input to the appropriate set of language-specific representations (Macnamara, 1967). According to this view, no cross-language interactions or influences would be expected when the language of the incoming information is predictable. Conversely, the language-nonspecific view, by assuming an integrated memory, holds that the representations of both languages are activated to some degree when bilinguals are using one of them and that this activation causes cross-languages interactions/influences (Altenbero & Cairns, 1983; Beauvillain & Grainger, 1987; Bijeljac-Babic, Biardeau & Grainger 1997; Caramazza & Brones 1979). There were early evidences supporting both a selective access and a nonselective access (see Grosjean, 1998, for a review). However, subsequent reviews of the early findings pointed out that the issue of selective vs nonselective access should not be confounded with a representational issue. That is, it is possible to have a shared memory with selective access as well as separate memories for different languages with nonselective or parallel access. Aside from this confounding, a possible reason of the inconsistencies between the results of these early studies was that the authors did not take into account relevant variables such as proficiency or that they did not distinguish between different levels of representation (Kroll & Tokowicz, 2005; Van Heuven, Dijkstra &

Grainger, 1998). In the following section, I will firstly address the issue of the levels of representation and then I will introduce the models of bilingual memory that have inspired the studies included in this Thesis, all of them proposing different levels of representation.

1.1.2. Word Levels of Representation

There is a common consensus among the models of bilingual memory that the mental representation of a language includes a *lexical* and *a semantic/conceptual system* (see Section 1.2). Here I refer to the representation of the individual words and their meaning rather than to larger units of language such as sentences or phrases. The term *lexical* literally means "having to do with words" and includes the whole set of words in a person's vocabulary, the *lexicon* (Francis, 2005). The lexical level refers to the verbal and grapheme labels of words, such as phonology and orthography. Further, every word must have a meaning. This fact connects the lexical level with the semantic level where the meaning of the words is represented (i.e., *word meaning* representation/ or *semantic representation*). Word meaning refers to the aspects of a word that give significance to it and relate it to its *concept*. Concepts define a nonlinguistic psychological representation of the entities in the world. In other words, concepts imply the cognitive knowledge of what kinds of things there are in the world, and what properties these things have. According to this approach, people construct a mental description or representation of world objects, events, etc., that allows them to understand their meaning. Words subtract their meaning from the mental description that concepts pick up from the world. For instance, if I have a mental description of what *cat* means, I can retrieve it to identify *cats*. I can use this information to classify the *cat* as *being an animal, having four legs, etc*. and also to find commonalities between *cat* and other animal exemplars such as *dog*. I also can distinguish between *cat* and *dog,* as being different exemplars because in the conceptual structure my concept of each animal is different. Therefore, the meaning of an individual word such as *cat* might be described through a series of properties, such as: *"has four legs" etc.*, which could be also linked to the conceptual structure. Clearly, the processing of a word meaning involves cognitive mechanisms that enable people to process the similarity and the differences between concepts. The point is that at the conceptual level, it might be that similarity is also relevant as an organizational principle. Otherwise, it would be quite difficult to find similarities and differences between *cat* and *dog*. Then the relationship between language and concepts could be expressed as follows: since we represent our information about the world in terms of concepts, language needs to make contact with those concepts in order to provide meaning to words. Given these considerations, the psycholinguistic interest in meaning has focused on the study of how word meaning is mapped onto the conceptual structure. Probably, there is not a one-to-one mapping. For instance, whereas synonyms should be connected to the same concept, homonyms would be connected to different concepts). Further, there are concepts not associated with any particular word. Such concepts can be expressed in sentences and their meaning is extracted from the entire sentence. Although concepts are more complex than the meaning of a given word, for empirical purposes it would be very difficult to study the aspects of a concept that have nothing to do with words. In this sense, many studies use the terms semantic and conceptual as being interchangeable, others exclusively use one term or the other, and others do not specify the differences between the semantic representation and concepts (see Vigliocco & Vinson, 2007, for a distinction between semantics and concepts). In the present dissertation, I use the terms: "meaning", "semantic" and "concepts" as being interchangeable.

I have provided a simple essay about what "*word meaning*" might be. It is important to mention that a main focus of interest in Psycholinguistics has been the issue of "*How word meaning is represented?*". Some influential theories of semantic memory have conceived meaning as being represented in a semantic network. In such a network, cat and dog can be considered as individual concepts linked to each other through other related concepts that represent common properties (e.g., has four legs, etc.), the so-called localist view (Anderson, 1983; Collins and Loftus, 1975). Other theories hold that meaning is distributed across the network, rather than considering an individual word as a concept. According to this view, *cat* and *dog* could be described in terms such as: *they are living-things; have four legs*; thus, *cat* and *dog* are linked to one another in the semantic network through these overlapped features-the so-called distributed view (Minsky, 1975; Moss, Hare, Day, & Tyler, 1994; Norman & Rumelhart, 1975; Plaut, 1995; Rosch & Mervis, 1975; Smith, Shoben, & Rips, 1974). Regardless of whether meaning is represented in a holistic or a decomposable manner, the above theories point out that the semantic representation of words is based on features/properties and that activation is spread across concepts depending on their common properties. It is worth noting that these theories were developed in the monolingual domain. However, bilingualism adds complexity to the representational issue. For instance, it has been suggested that the conceptual overlap between translation equivalents is greater for concrete words than for abstract words (De Groot, 1992), this fact having consequences for bilingual word processing (Schoonbaert, Duyck, Brysbaert, & Hartsuiker, 2009). In what follows I will present the most relevant models of bilingual memory. Although all of them include a semantic level of representation, the extent to which they provide details about the organization of this level differs across models. What they have in common is the inclusion of a lexical and a semantic level of representation. The semantic level is shared between languages whereas the lexical level can be also shared between languages (e.g., Dijkstra & Van Heuven, 1998) or there can be two independent lexical levels, one for each language (e.g., Kroll & Stewart, 1994).

1.2. BILINGUAL MODELS OF WORD PROCESSING

1.2.1. BASIC QUESTIONS

A bilingual, by definition, is a person that has acquired and uses two languages, a first language (L1) and a second language (L2) (Grosjean, 1998). The L1 has a lexical and a semantic level of representation. Words in L1 can effectively access meaning during processing. Then, principally, learning a L2 implies that a learner acquires a vocabulary or new lexical word forms in L2 (De Groot & Van Hell, 2005) with the final goal of being able to access meaning in a manner effectively similar to that reached in L1. Having this picture in mind, of two languages with two lexicons where each word (either in L1 or L2) is able to access meaning in some way, the issues of shared *vs*. not shared levels (in terms of languages structure) and selective *vs*. not selective access (in terms of lexical access/or processing) have to be addressed in relation with several variables that can modulate meaning access. For instance, type of bilinguals, context of acquisition of L2, age of acquisition, characteristics of the tasks and of the types of words and relations tested, etc. These factors draw attention to the complexity of the issues of representation and processing in bilinguals and raise some basic questions that researchers have addressed during the last years. Some of these questions are the following:

In relation with representation:

1. Do bilinguals develop an independent lexical store for the new vocabulary of L2 or do they integrate the new L2 forms into the same lexical store as the first language (L1)? If they develop an independent store for L2 words, how are the L1 and L2 stores linked to each other?

2. How is meaning represented across languages? Are L1 and L2 represented in the same system, different systems, or in a partially overlapping system?

3. How are different types of words represented at each level?

4. How are age of acquisition and proficiency in L2 plotted on the bilingual structure system? Is the bilingual memory a static system or does the internal organization change as a function of shifts in proficiency, for instance?

5. How are the lexical and semantic levels interconnected? To what extent do characteristics of the words (i.e., frequency of use of the words) or of the bilinguals, such as age of acquisition and proficiency, modulate the connections between the lexical and semantic levels?

6. Does the bilingual system contain a mechanism to inhibit the non-target language and facilitate the processing of the language in use?

In relation with language processing:

1. Which is the role of L1 on the acquisition of L2? For instance, do bilinguals use L1 in order to access meaning (i.e., by associating L2 words with their L1 translations) or do they develop a strategy during learning that encourages a direct connection with semantics (e.g., by associating L2 words with a picture, for instance)?

2. Which are the characteristics of the words that modulate cross-language processing (e.g., cognate status, concreteness). On the other hand, is L1 meaning transferred to L2? If not, how is meaning accessed when there is not a total correspondence between L1 and L2?

3. How do variables of the bilinguals such as: age of L2 acquisition, proficiency, learning context or language immersion affect L2 processing? Over time, do bilinguals maintain always their L1 dominance (i.e., in terms of greater proficiency in L1 than in L2) or could L2 become more dominant? If this is possible, under what circumstances?

4. How do different tasks and modality (comprehension vs. production) capture similarities and differences in cross-languages processing?

5. What is the role of the executive function on cross-languages processing?

During the last few decades, considerable progress has been made in our understanding of languages' representation and processing. Several models of bilingual memory have been proposed, which have guided the research in the field dealing with the above issues. At present, there is not a unique model that is able to provide a theoretical framework for all the issues that the co-existence of two languages in the bilingual mind poses. This fact is quite understandable due to the complexity of linguistic and cognitive aspects, as well as the variability that exists among types of bilinguals, contexts of L2 acquisition, etc. In this respect, models of bilingual memory focus on different aspects of L1 and L2 representation and processing. For instance, the issue of selective vs nonselective lexical access has been addressed mainly within the framework of the BIA model (Dijkstra & Van Heuven, 1998; Grainger & Dijkstra, 1992). On the other hand, both the Revised Hierarchical Model (RHM, Kroll and Stewart, 1994) and the Distributed Representational Model (DRM, proposed by De Groot 1992a, 1992b) have focused on the issue of meaning access from L1 and L2. Whereas the DRM has paid more attention to the characterization of cross-languages meaning representation and to the characteristics of the words that can modulate meaning access, the RHM has focused on the characteristics of bilinguals (i.e., proficiency) also affecting this access.

There is a consensus among the models that the semantic level is shared between languages (see Kroll & De Groot, 1997, for review). There is less agreement concerning whether the words of the two languages of the bilinguals at the lexical level are represented in two distinct lexicons, one for each language, or in an integrated lexicon including the two languages. Moreover, the structure and processing that the models propose are also influenced by the source from which they emerge in the case where they are not entirely new models, rather an extension from the monolingual domain to the bilingual field. This is the case of BIA. Since it emerged from connectionist monolingual models, it is quite reasonable that it proposes an integrated lexicon. Conversely, the RHM was developed for bilinguals, not coming from a monolingual model. Thus, it is logical that it focused from the beginning on the dynamic nature of word processing in bilinguals as L2 proficiency develops as well as on the effect that proficiency has on the entire functional organization of bilingual memory. In spite of the differences between the aforementioned three models, they are complementary rather than to exclude one another, at least in two aspects. The first is that together they provide a more complete picture of bilingual memory than each one separately. This is because one exhibits more insight on lexical access (BIA), another on semantics (DRM) and the other on L2 proficiency (RHM). Second, being specialized either in lexical or semantic access or in bilinguals' proficiency, these models enable researchers to ask specific questions in relation with those issues. In the next section I will describe in detail the three models, presenting some of the main evidence supporting them.

1.2.2. The Bilingual Interactive Activation Models (BIA and BIA+)

The Bilingual Interactive Activation model (BIA) proposed by Dijkstra and Van Heuven (1998) is an extension to the bilingual field of one of the most influencing localist models of lexical access in monolinguals, the Interactive Activation (IA) model of McClelland & Rumelhart (1981). In localist models, the network is divided into layers of units corresponding, for instance, to letter features, letters and words. The IA model was proposed to account for visual word recognition (i.e., the process to connect a written word to its meaning, the so- called lexical access). Visual word recognition in the IA model is initiated by a visual input (i.e., a word or a non-word) and proceeds bottom-up from letter features to letters to words. For instance, when a monolingual reader is presented with an input word *cat*, words such as *cap* or *car* become also activated since they share the first two letters with *cat*. Once the reader sees that the final letter of the word is *"t"*, the word is matched with the lexical representation of *cat* and the activation of the competitors (e.g., *cap* and *car*) is shut off. As it can be seen from the above, the IA model (see also, Forster, 1976; Paap, Newsome, McDonald, & Schvaneveldt, 1982) assumes a one-to-many mapping from input representation to lexical representations. This key assumption is on the heart of BIA, which proposes that not only words from the language in use, but also words in the non-target language of the bilingual, are also activated during word recognition, thus proposing a nonselective access.

BIA model Structure and Processing

The BIA model (see Figure 1) consists of four layers (or levels) of nodes. The first layer contains the features of letters, the second individual letters, and the third the entire word in each of the two languages (i.e., Dutch and English). Furthermore, in the fourth layer BIA implements a node for each language with a mechanism for coding which language the word belongs to (i.e., Dutch and English). Arrows with triangular heads represent excitatory connections and those with circular heads inhibitory connections. Word recognition, according to BIA, evolves in different steps or cycles, beginning with a bottom-up, nonselective activation as a response to an input string and ending with a language-specific top-down inhibition of words of the non-target language, which can ultimately allow recognition in the intended language. Thus, the activation first flows up from features, to letters, to words and language nodes. Therefore, when a string is presented, letter features become active for each position of a letter in the string. At each position (i.e., pos1, pos2, etc., representing a 4-letter word) letters are activated when they are consistent with a given feature whereas they are inhibited when there is no correspondence between features and letters. Similarly each letter activates words that have that letter in the same position and inhibits those that do not contain the letter in the same position. At the word level, words from both languages are activated and compete with each other to achieve the highest activation. At this level the nodes of both languages (Dutch and English) are interconnected and they can mutually inhibit each other's activation. This inhibition at the word level is termed lateral inhibition and is represented by the external arrow with a circle head in the figure. Connecting the words of the two languages at the level of word representation, BIA implements an interactive lexicon with a nonselective and parallel access (i.e., bottom-up). Moreover, the lateral inhibition proposed at this level regulates competition and inhibition between the two languages' words. The activated word nodes send excitatory feedback to their constituent letters to reinforce their activation. Additionally, the two language nodes (i.e., Dutch and English) of the fourth layer collect the activation of each lexicon and once they become activated their function will be to suppress the activation of the non-target lexicon (i.e., a top-down mechanism).

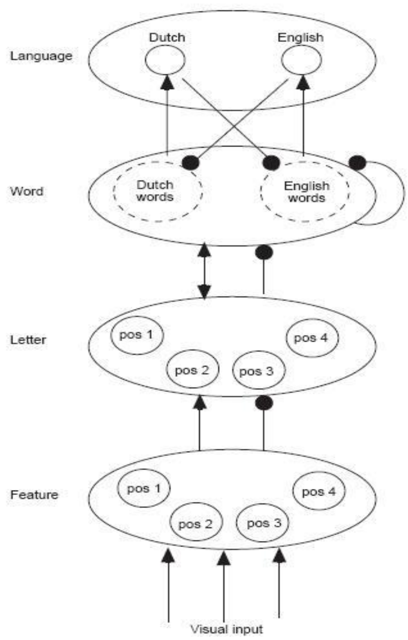


Figure 1. The Bilingual Interactive Activation (BIA) model (Dijkstra & Van Heuven, 1998). Arrowheads indicate excitatory connections; black filled circles indicate inhibitory connections.

As can be seen from the above, according to BIA, letters and words are not processed in isolation, but in the context of the words that contain the respective letters as well as of the language to which these words belong. In this way the activation flows between layers in a number of different cycles and the activation of each node is calculated. After a complex interactive process of activation and inhibition within and between levels, the lexical candidate corresponding to the input word will reach the recognition threshold. The time for a word to be recognized depends, on one hand, on the frequency of this word and, on the other hand, on the number and frequency of orthographically similar words that exists in the two lexicons of the bilingual.

Key assumptions of BIA

1. *An integrated lexicon:* The lexical items of the bilinguals' two languages are represented in the same memory system.
2. *Nonselective access:* During the initial process of the recognition of a target word (i.e., a word belonging to a language in use), orthographically similar words from the two lexicons of the bilingual become active and compete for selection until the top-down mechanism inhibit the non-target language and the bilingual effectively recognizes the target word.
3. *An asymmetry between the first language (L1) and the second language (L2)*: The model assumes an asymmetry between L1 and L2 processing in relation to subjective frequency. The subjective frequency of a word refers to the number of times that a bilingual encounters, use/or is exposed to a word. Many studies in this field have tested unbalanced bilinguals (less proficient in L2 than in L1). As Thomas and van Heuven (2005) pointed out, the subjective frequency of L2 words for unbalanced bilinguals is lower than that of L1 words, due to their reduced exposure to the former with respect to the later. These differences between L1 and L2 use are captured by BIA, which proposes that L1 words are activated faster and reach the recognition threshold earlier than L2

words. In addition, the representation is larger for L1 than for L2 at both the word level and the language nodes. As a result, L1 words would strongly inhibit L2 words than vice versa.

BIA predictions

1. If lexical access is nonselective, then during word recognition the two languages will be co-activated at some point. As a consequence, the processing of words that share orthographic form across languages will be affected. Thus, these words would be recognized faster/or slower than words that are not similar in form.
2. If there is an asymmetry between L1 and L2 processing produced by differences in use, unbalanced bilinguals will comprehend L2 words slower and less accurately than L1 words.

Some empirical evidence

Several studies have addressed the issue of selective vs. nonselective lexical access by exploiting different types of words that share form across-languages: a) *interlexical homographs,* which are words with the same written form across two languages but with a different meaning in each language (e.g., the English-Spanish interlexical homograph *pan*, which means *bread* in Spanish); (Dijkstra, Van Jaarsveld & Ten Brinke, 1998); b) *orthographic/phonological neighbors*, which are words of the same length in both languages but the word in one language differs from the word in the other language by only one letter/phoneme and has a distinct meaning (e.g., English-Spanish: *card-cara [face]*); (Coltheart, Davelaar, Jonasson & Besner, 1977; Van Heuven, et al., 1998) and c) *cognate words*, which are translation equivalents with full or partial form and meaning overlap across-languages (e.g., English-Spanish *tomato-tomate*) (De Groot & Nass, 1991; Sánchez-Casas, Davis & García-Albea, 1992; Van Hell & De Groot, 1998a; Van Hell & Dijkstra, 2002).

1) *Homographs:* The rationale of studying homographs, according to BIA, is as follows: if homographs are recognized faster or slower than control words that occur exclusively in one language (e.g., the English-Spanish homograph *pan* [bread] vs. any control word, like *libro* [book]), it would be an evidence that the two languages are co-activated at some point during word processing, thus supporting a nonselective access. Contrarily, the lack of differences between the response patterns for homographs and the matched controls would provide support for selective access in bilinguals. To test this assumption, Dijkstra et al., (1998)

conducted a study, including three experiments, with Dutch-English bilinguals. In the first experiment, participants were presented with a list of words that included English-Dutch homographs (e.g., *room* meaning *cream* in Dutch), cognates (e.g., *film;* English-Dutch) as well as English control words (i.e., non-cognates). Then the participants were asked to perform an English lexical decision task (LDT) (i.e., participants had to categorize letter strings as words or non-words in English). In this first experiment there were not differences between homographs and controls. In contrast, cognates were responded faster than control words, supporting a nonselective access. The authors then reasoned that the list composition and the task demands might have contributed to invalidate the homograph effects. That is to say, because of the instruction in the LDT to respond to English words and also due to the absence of exclusively Dutch items in the experiment, the English lexicon would have been very active and diminished the activation of Dutch words. Conversely, the cognate effects could be explained in terms of their semantic overlap. Then in the second experiment the authors removed the cognates and added exclusively Dutch words to the stimulus list. Participants had to respond "no" to the last type of stimuli since they were not English words. The results of Experiment 2 showed a longer latency for homographs than for controls (i.e., inhibition) which was interpreted as a competition between the two readings of the homographs. In other words, participants in reading homographs are not able to ignore the non-target language reading (i.e., Dutch). Finally, Experiment 3 was very similar to Experiment 2 with the difference that participants were asked to perform a mixed LDT (i.e., to respond "yes" when the letter string was a word either in Dutch or in English). It was expected that the inhibition found in Experiment 2 turned into facilitation in the mixed LDT, due to the fact that participants had to respond as soon as one of the reading of the homographs became available. The results of Experiment 3 revealed facilitation, as predicted. Overall this study is important since it pointed out that words similar in form across languages are activated, supporting a nonselective access. Furthermore, it revealed that the type of effects (i.e., inhibition or facilitation) is modulated by factors such as list composition and task demands. Further studies conducted with homographs reported findings in the same direction (Dijkstra, Moscoso del Prado Martín, Schulpen, Schreuder, & Baayen, 2005; Dijkstra, Timmermans, & Schriefers, 2000; Kerkhofs, Dijkstra, Chwilla, & De Bruijn, 2006). In addition, word frequency was described as another variable modulating the homograph effect, being the magnitude greater for low-frequent homographs than for high-frequent ones (De Groot, Delmar and Lupker, 2000).

2) *Orthographic neighbors:* Their influence on cross-languages processing has been addressed from different lines of research. One of these lines, directly related with the topics addressed in the present thesis, has tested words similar in form across-languages (e.g., *cara* [*face*]-*card* in Spanish-English) in translation recognition tasks (Link, Kroll & Sunderman, 2009; Sunderman & Kroll, 2006; Sunderman & Priyah, 2012). These studies will be reviewed in the final section of this introduction, when I present the main objectives of the Thesis. Another line has focused on "neighborhood density effects", namely the degree in which the number of neighbors (i.e., neighborhood density) in the non-target language could affect the performance of bilinguals in the target language (Grainger & Dijkstra 1992; Van Heuven et al., 1998). For instance, Van Heuven et al., (1998) performed a study with bilinguals of Dutch (L1) and English (L2) by manipulating the number of orthographic neighbors within and between languages in a series of experiments using two different tasks: LDT and a progressive demasking task (PDT). In the PDT task, the presentation of a target word is alternated with that of a mask. During this alternation process, the time presentation of the mask progressively decreases while that of the target word increases and participants are asked to push a button as soon as they can identify the word. An increase in the number of neighbors within the target language produced constant inhibitory effects in Dutch while in English facilitation effects were found. Across languages, the authors found that increasing the number of neighbors in the non-target language slowed word recognition in both Dutch and English. The cross-language effects (from Dutch neighbors on English target words) disappeared in an English monolingual group used as control. The results were first interpreted as providing evidence that, with respect to orthographic codes, the bilingual lexicon is integrated and the access is nonselective in nature. Concerning the differential effect of English (facilitation) and Dutch (inhibition) neighbors, it was interpreted in the BIA framework as due to the bilinguals' lower use of English (relative to Dutch) and the asymmetric top-down inhibition (see also Thomas & Van Heuven, 2005, for review). Further evidence of nonselective access has come not only from words that are orthographically similar across languages, but also from words that share phonology (Brysbaert, Van Duyck & Van de Poel, 1999; Jared & Kroll 2001).

BIA was able to account for the above reviewed results obtained with words orthographically similar across languages. However, in its initial formulation, it could explain neither the effects of phonological similarity nor task demands (Dijkstra et al., 1998). In addition, a semantic level was lacking. Dijkstra and Van Heuven (2002) updated BIA to BIA+ (see Figure 2) to account for overcome these limitations.

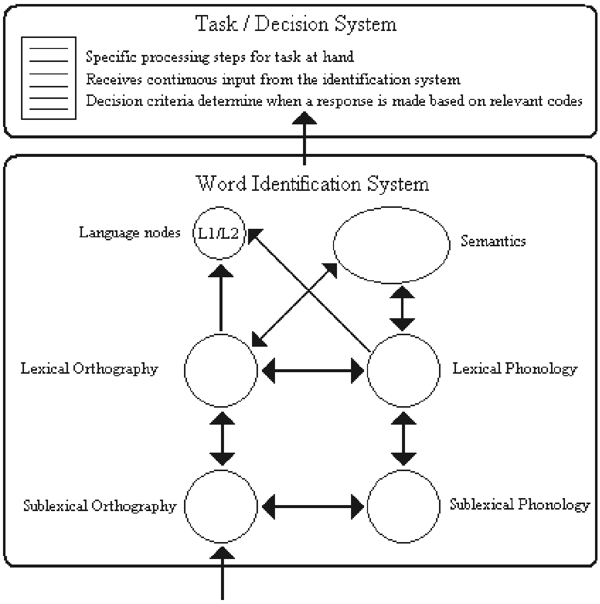


Figure 2. The BIA+ model. (Adapted from Dijkstra & Van Heuven, 2002). Arrowheads indicate excitatory connections; black filled circles indicate inhibitory connections. In BIA+, L1 is the first language and L2 the second language.

The BIA+ model contains two layers. The first layer, "the word identification system", in addition to the orthographical representation of the word, also incorporates phonology and semantics. This first layer provides output to the second layer, a task/decision system. In separating lexical processing from the task system, the assumption of BIA+ is that lexical processing proceeds exclusively from the word identification system. Nonlinguistic context effects (e.g., task instructions, expectancy, etc.) can affect the way in which the information of the word system is used but not the activation state of the words (Dijkstra, 2005). The relationship between layers is represented in BIA+ by the upward directed arrow that connects the two systems.

3) *Cognates:* A number of studies has addressed the issue of nonselective activation by exploiting cognates, that is, words that share form and meaning across languages (e.g., *tomato-tomate*; English-Spanish); (De Groot & Nas, 1991; Dijkstra, Grainger & Van Heuven, 1999; Dijkstra & Van Heuven, 2002; Duyck, Van Assche, Drieghe & Hartsuiker, 2007; Lemhöfer & Dijkstra, 2004; Sánchez-Casas et. al., 1992; Van Hell & De Groot, 1998a; Van Hell & Dijkstra, 2002). These studies have demonstrated that cognates are recognized and produced faster than non-cognate words (i.e., the *cognate facilitation effect*). This cognate facilitation effect, which is considered a reliable proof of language nonselective activation, has been accounted for by the most influential models of bilingual memory. In particular, BIA+ (Dijkstra & van Heuven, 2002; Dijkstra et al., 2010) assumes that cognates are only different from noncognates in that they share orthographic and phonological characteristics with their translation equivalents. According to this account, the presentation of a cognate produces an activation of the overlapping semantic and orthographic/phonological representations of both languages leading to an advantage in recognition over non-cognates. Other proposals explain cognate facilitation effects as a result of the stronger associative lexical links (Kroll & Stewart, 1994; Kroll et al., 2010) or the larger number of shared semantic features across languages (de Groot, 1992a; van Hell & de Groot, 1998) when compared to non-cognates. Finally, it has also been proposed that cognate words are characterized by a special kind of morphological representation (Sánchez-Casas & García-Albea, 2005).

Whichever is the reason of the facilitative effects of cognates, they suggest, together with the findings reported with homographs/homophones and cross-language neighbors, that both languages of bilinguals are active to some degree when they use one of them (see Kroll, Dussias, Bogulski, & Valdes Kroff, 2012; Kroll & De Groot, 2005, for reviews). This non-selective activation has been observed across a wide range of paradigms and tasks, either when bilinguals process words in L1 or in L2 (see Schwartz & Van Hell, 2012; Van Assche, Duyck, & Hartsuiker, 2012; Van Hell & Tanner, 2012, for recent reviews). Cross- languages interactions have been reported even in languages that do not share the same script, like Chinese and English (Thierry & Wu, 2007). Moreover, there is evidence that deaf readers of English activate the translations of English words in American Sign Language (ASL), thus demonstrating that ASL signs are active during printed word recognition in deaf bilinguals who are highly proficient in both ASL and English (Morford, Wilkinson, Villwock, Piñar, & Kroll, 2011). It is worth noting, however, that the nonselective access is not a matter of all or nothing, rather it has to be considered in relation with a series of modulating factors concerned with either characteristics of the words or of the bilinguals tested. In what follows, I will describe the two remaining models of bilingual memory that have inspired the experiments of this Thesis, the DRM (De Groot, 1992 a,b) and the RHM (Kroll & Stewart, 1994). Both models deal mainly with semantic access from L1 and L2 words and have taken into consideration, in any way or another, the aforementioned factors that can modulate across languages activation.

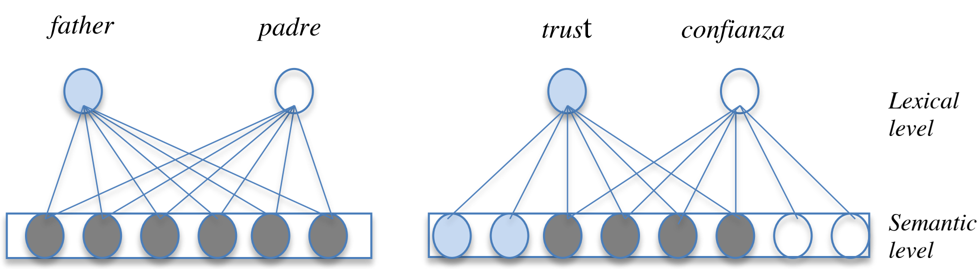
1.2.3. The Distributed Representational Model (DRM)

The Distributed Representational Model (DRM, Figures 3 and 4) proposed by de Groot (1992a,b), is a model of bilingual memory representation, focused on how meaning is represented and accessed from both languages of a bilingual. It is a distributed model, which postulates that meaning is distributed across a set of features (i.e., each feature represents a node in the semantic network), and each feature can be part of the meaning of multiple concepts. As a consequence, there is an overlap between features of different words in the semantic network. The degree of feature overlap on the semantic representations would determine the extent to which meaning is shared across languages, which in turn is dependent on word type (De Groot, 1992a,b; Van Hell & De Groot, 1998a). Thus, according to De Groot, different types of representations could coexist in bilingual memory for different types of words.

A relevant distinction to be made is between concrete and abstract words. The representations of concrete words would be more integrated across languages whereas the representations of abstract words would overlap to a lesser extent. The reason would be that an important difference between concrete and abstract words is that the former have higher context availability than the later (De Groot, Dannenburg, Van Hell, 1994; Schwanenflugel & Shoben, 1983). It is easier to form an image for concrete words than for abstract words, an image that in a majority of cases is very similar across languages. In contrast, abstract words are more dependent on the cultural context in which they are acquired. Thus, De Groot, (1992a,b) proposed two versions of their bilingual memory model, one for concrete translation equivalents and another for abstract translation equivalents. In the case of concrete words, the model assumes that translation equivalents have the same meaning (e.g., *father-padre* [English-Spanish]. Concerning abstract translation pairs, they would share part of their meaning, but they would also have a part of their meaning which is specific for each language (e.g., *trust-confianza* [English-Spanish]).

DRM Structure and Processing

Figures 3 and 4 depict the representation of concrete and abstract translation equivalents between English and Spanish. The model assumes two levels of representation: a lexical level and a semantic level. The circles represent nodes and the lines are the connections between nodes (i.e., between the lexical and the semantic levels). Concerning concrete words, there is a single node for the English word *father* and another for its Spanish translation *padre* at the lexical level. In contrast, meaning information is distributed at the semantic level through different nodes (in the example I have chosen arbitrarily to represent it with six nodes). These nodes represent different features that constitute the concept *father-padre*. Therefore, the lexical nodes *father* and *padre* are connected individually with the same six nodes in the semantic network, totally sharing their meaning across languages. Abstract words have a similar representation as the concrete words with the only difference that they share only a subset of nodes in the semantic level. For instance, the English-Spanish translation pair *trust-confianza*, might be represented at the semantic level as having arbitrarily eight nodes, four of which would be shared across languages (i.e., the nodes filled in grey). Additionally, there would be other non-shared nodes, representing the particular meaning that each word has in its own language. The proposal of non-full overlapped representations of abstract words between languages implies that they would have some language-specific conceptual representation. In other words, the extent to which meaning is shared or integrated across languages (and in its turn, the access to word meaning from both languages), depends on the type of word. This fact is important since it draws attention to the relevance of the characteristics of the words in determining the organization of bilingual memory. It is worth mentioning in this line of argumentation that not only concrete words have a greater conceptual overlap than abstract words across languages, but also cognates would have a more similar meaning than non-cognates (De Groot, 1992a,b).



Figures 3 and 4. The Distributed Representational Model (DRM, De Groot, 1992a,b) for concrete (e.g., *father-padre*; English-Spanish) and abstract words (e.g., *trust-confianza*; English-Spanish).

According to the DRM, comprehension begins with the presentation of a word in a given language (e.g., *father* or *padre*). Upon the presentation of the concrete word *father,* for example, each of the semantic nodes that represent its features would receive activation via its connection with the lexical node (i.e., bottom-up) (see de Groot, 1992a, Figure 2). Therefore, all the nodes representing the meaning of *father* and *padre* at the semantic level would become active, assuming that meaning is integrated across languages and that concrete words have a full overlap on the semantic representation. If we look at the translation process, activation will spread from the lexical representation of a word in one language (e.g., *father*) to that of the word in the other language (e.g., *padre*) through the conceptual level, as a result of the activation of the semantic nodes shared between languages. The same process would take place with abstract words (e.g., *trust-confianza*), the difference being that the degree of cross-languages activation might be lower than with concrete words, as it would be modulated by the amount of shared nodes.

Key assumptions of DRM

1. *An integrated semantic level:* The degree to which sematic representations are shared across languages depends on word type.
2. *Cross-languages interaction and influence:* They would depend on the amount of activation, which in its turn is a function of the degree of semantic overlap.

Predictions

1. If bilingual word processing is determined by the degree of semantic overlap between languages, the time it takes a bilingual to perform a cross-languages task as well as the errors committed and the magnitude of the experimental effects observed would be modulated by the degree of semantic similarity.

Some empirical evidence

In a series of experiments, De Groot and colleagues obtained support for the DRM (De Groot 1992a,b; De Groot, et al., 1994; Van Hell & De Groot, 1998). They observed that the time it took to translate and recognize pairs as translation equivalents was faster for concrete and cognate words than for abstract and non-cognate words. Similarly, they reported that the highest degree of equivalence of associations between languages in a bilingual word association task was for cognate and concrete words.

Additional evidences for the DRM have been accumulated during the last decade. In this line of research, the study of meaning access from the two languages has mostly relied on *priming paradigms,* namely *translation priming* and *semantic priming* (see Basnight-Brown & Altarriba, 2007 or Schoonbaert et al., 2009, for reviews). In these paradigms, participants are typically presented with a first word (i.e., the prime) followed by a second word (i.e., the target) and they are asked to make a decision about the target (e.g.., a lexical decision task, LDT). In translation priming, the *prime-target* pairs are translation equivalents (e.g., *dog-perro*; English-Spanish) while in semantic priming they are two words related in meaning, one in each language (e.g., *dog-gato* [*cat*]; English-Spanish). The theoretical assumption, in line with DRM, is that when the target and the prime are semantically related (e.g.., because they share a subset of features), the presentation of the prime activates part of the target representation. That is, the features shared by the prime and the target are activated, thus leading to faster responses in comparison to when the prime and the target are semantically unrelated (e.g., *dog-mesa* [*table*]; English-Spanish); (Fischler, 1977). The usual finding with these paradigms, when testing unbalanced bilinguals, is that there is an asymmetry between directions. That is, priming is stronger from L1 to L2 than in the other direction (Dimitropoulou, Duñabeitia, & Carreiras, 2011; Midgley, Holcomb, & Grainger, 2009; Schoonbaert et al., 2009). For instance, Schoonbaert et al., (2009) investigated cross-language translation and semantic priming effects in a series of experiments by comparing concrete and abstract non-cognate words. Unbalanced Dutch (L1)-English (L2) bilinguals performed a LDT in the two translation directions. The authors obtained reliable priming effects in both translation directions, the effects being larger in the L1-L2 direction. Furthermore, the size of the priming effects was larger for translation priming than for semantic priming, and it was slightly greater (although not significantly) for concrete words than for abstract words. These results constitute a support for the DRM, since concrete words are assumed to have a greater conceptual overlap than abstract words (De

Groot, 1992). Furthermore, translation equivalents would share a great amount of conceptual nodes than cross-language semantically related words. With respect to the translation direction asymmetry, Schoonbaert et al., argued that the magnitude of priming effects depends on the proportion of the target's conceptual nodes that are activated by the prime. If we consider that for unbalanced bilinguals, the semantic representation of any word is richer in L1 than in L2, it seems clear that L1 would activate more conceptual nodes than L2. Conversely, for highly proficient bilinguals, the richness of semantic representations (and as a consequence the proportion of conceptual nodes activated) would be the same for L1 and L2 words. In fact, there are solid evidences of symmetrical priming effects between L1-L2 and L2-L1 in highly proficient and balanced early bilinguals (Duñabeitia, Dimitropoulou, Uribe-Etxebarria, Laka & Carreiras, 2010; Duñabeitia, Perea & Carreiras, 2010; Guasch, Sánchez-Casas, Ferré & García-Albea, 2011; Perea, Duñabeitia & Carreiras, 2008). In this line of research, of special relevance for the present work is the study of Guasch et al. (2011), conducted with Catalan-Spanish bilinguals. The authors manipulated the degree of semantic similarity between primes and targets by using prime-target pairs more or less related in meaning (i.e., *ruc-caballo* [*donkey-horse*] vs *ruc-oso* [*donkey-bear*]. Guasch et al. observed that priming effects were symmetrical between directions and that they depended on the degree of meaning similarity between primes and targets, both in a TDL and in a semantic categorization task.

It is worth mentioning here that the evidence supporting the DRM not only provides from priming studies, but also from research using other types of tasks, such as translation recognition. In this task participants are presented with pairs of words and have to decide whether the second word in the pair is the correct translation of the first one. For instance, there are a series of studies that have focused on words with multiple translations (e.g., the Spanish word "*muñeca*" can be translated into English as both: "*doll*" and "*wrist*"). The common finding is that these words are translated slowly than words with a single translation (Boada, Sánchez-Casas, Gavilán, García-Albea & Tokowicz, 2012; Degani & Tokowicz, 2010; Tokowicz, Kroll, De Groot & Van Hell 2002). These results would support the DRM, as there is presumably a lower overlap in meaning across languages for words with multiple translations that for single-translation words. Accordingly, people rate the former as less semantically similar than the later (Degani, Prior & Tokowicz, 2011). Additional evidence has been obtained in studies using translation recognition in which the critical conditions include distractors which have some type of relation with the correct translations, thus producing an interference effect when participants have to reject them. For instance, Ferré et al. (2006) and Guasch et al. (2008), by using pairs more and less related in meaning (i.e., the same pairs tested in the abovementioned study of Guasch et al., 2011), reported that the amount of interference obtained depended on the degree of semantic similarity between the correct translation and the distractor, as it could be predicted from the DRM.

As it can be seen from the above, there is strong evidence supporting the DRM and the assumption that the degree of meaning overlap modulates cross-languages interactions and influences. It has also become clear that not only variables related with the type of words are relevant in determining the pattern of effects (i.e., concreteness, degree of meaning similarity, number of translations, etc.), but also the characteristics of the bilinguals, in particular their relative proficiency in their two languages. In the following section, I will present the last model that has inspired the present work and which has, among their most relevant contributions, the inclusion of an interesting view of how the organization of bilingual memory changes as proficiency increases.

1.2.4. THE REVISED HIERARCHICAL MODEL (RHM)

The RHM was developed from the Word Association and the Concept Mediation Model (Potter, So, Von Eckhardt, & Feldman, 1984; Figures 5 and 6). The Word Association Model (WAM) and the Concept Mediation Model (CMM) addressed the issue of the architecture of bilingual memory by focusing on the nature of the interconnections between L1 and L2 and the conceptual system. The question was how the new L2 vocabulary fits into the lexical/conceptual system that exists for words and concepts in L1. Both models postulated two separate lexical stores, one for L1 and another for L2, and a common conceptual system. In WAM, the L2 lexical representation (e.g., *cat* in English) was linked to the L1 lexical representation (e.g., *gato* [*cat*] in Spanish) only through lexical links, whereas in the CMM the bilingual two lexical stores (i.e., for L1 and L2) were connected through a shared conceptual representation. The critical difference between these two models concerned the route of access to meaning when bilinguals understand an L2 word. WAM sustained that words in L2 are learned by lexical associations with their equivalents in L1. Then, the mapping of L2 word forms to meanings would require mediation via the L1 translation equivalents. In contrast, CMM claimed that new L2 words are directly linked to their meaning and the activation of L1 translation equivalents is not necessary for comprehension. To test the models, Potter et al. (1984) compared picture naming in L2 with translation of L1 words into L2 words, and found support for the CMM. In that study, translation and picture naming were equally fast for two groups of subjects with different proficiency levels. However, subsequent research debated this conclusion and pointed to a possible developmental shift for L2 learners: from reliance on word association in the very early acquisition period to concept mediation in a later, more fluent period (e.g., Chen & Leung, 1989; Kroll & Curley, 1988). Kroll & Stewart (1994) proposed the RHM to accommodate these developmental changes that occur during L2 learning by integrating aspects of the two models proposed by Potter et al., (1984), along with additional ideas about the asymmetrical relation between L1 and L2.

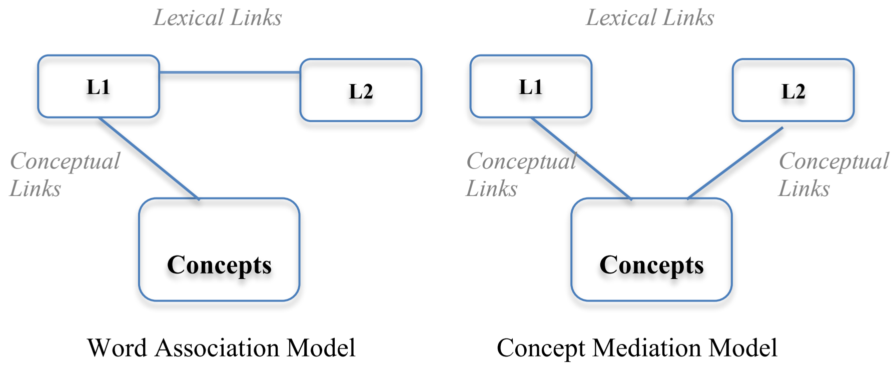


Figure 5 and 6: The Word Association and Concept Mediation Models (adapted from Potter, et al., 1984). In the Word Association Model (i.e., left figure) second language words (L2) are lexically associated to their translation equivalents in the first language (L1). In the Concept Mediation Model (i.e., right figure) each language (L1 and L2) are directly connected to the concepts.

RHM Structure and Processing

The RHM (see Figure 7) proposes two separate, interconnected lexicons, one for each language (L1 and L2), in addition to a shared integrated conceptual system that is connected to both lexicons. The L1 lexicon is seen as being larger than the L2 lexicon, since it is assumed that the bilingual would have a larger vocabulary in their native language than in the other. The connections between L1 and the conceptual system appear to be bidirectional and very strong, since acquiring a first language would imply an encoding process between the language lexicon and the corresponding concepts. When a bilingual acquires an L2, especially if it occurs later in life, L2 would be integrated in the memory system by developing a pathway that is attached to the L1 lexicon through which the L2 gains access to the conceptual system (i.e., the access is similar to that proposed by the Word Association model). This pathway is reflected in the RHM by a solid and directional line between the L2 and L1 lexicons. The opposite link between L1 and L2 is assumed to be weaker, since the learner will know many words in L1, which do not have an L2 translation equivalent. Finally, the connection between L2 and the conceptual system is weak at the early stage of acquisition, and it would increase in strength as the bilingual improves their proficiency in L2.

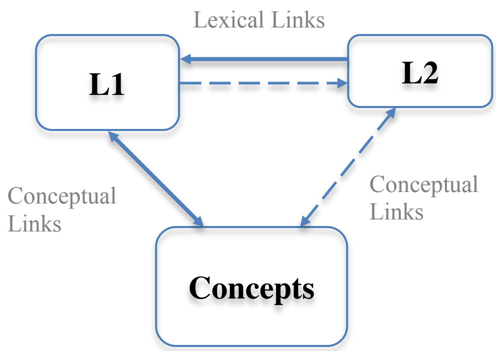


Figure 7: The Revised Hierarchical Model (RHM, adapted from Kroll and Stewart, 1994). Words in the two languages (L1 and L2) are connected via lexical and conceptual links. Solid lines represent stronger connections and dotted lines represent weaker connections.

As it can be seen from the above, changes in proficiency have a central role in determining how meaning is accessed from the two languages. Thus, at the initial stages of L2 acquisition, access to meaning would rely on the activation of L1 translation equivalents. As proficiency in L2 increases and direct L2 lexical-to-conceptual mappings develop, the lexical dependence on L1 would decrease. Thus, if L1 translation equivalents are activated during meaning access in highly proficient bilinguals, their influence would be small. A last consideration is that he RHM was a model developed to account mainly for translation and it was initially proposed for sequential bilinguals (i.e., bilinguals that learned L2 once L1 was acquired). However, since the development of proficiency can be seen as a gradual process, RHM has inspired a line of research focused not only on sequential bilinguals, but also on different types of bilinguals ranging from those beginning to learn a language to highly proficient simultaneous bilinguals.

Key assumptions of the RHM

1. *An asymmetry between L1 and L2 lexicons and connections at early stages of L2 acquisition*. This asymmetry would be reduced as proficiency develops.
2. *A different route of meaning access* during translation processes for proficient and non-proficient (beginner) bilinguals.

RHM predictions

1. If the strength of lexical connections between L1 and L2 and between the two lexicons and the conceptual level is not the same across directions, translating from L2 to L1 (backward direction) is predicted to be faster than translation from L1 to L2 (forward direction), since it is more likely to occurs via the direct lexical pathway. In contrast, forward direction is expected to occur more slowly as it would be performed through the conceptual route. For the same reason, this direction would be more affected by semantic manipulations than backward translation.
2. If during the early stages of acquisition, L2 words access meaning via L1 lexical links, then learners would be more influenced by manipulations involving L1 translation equivalents (e.g., the presentation of words similar in form to the L1 translations) than by semantic manipulations. Conversely, the performance of proficient bilinguals during translation is expected to be more affected by semantic manipulations (e.g. the presentation of words similar in meaning to the correct translations) than by manipulations involving the L1 translation equivalents, since they are assumed to use to rely more on the conceptual route than on the lexical route.

Some empirical evidence:

During the last decades there has been a considerable amount of research testing the predictions of the RHM, which can be classified according to its main interest. The first line of research has dealt with the first prediction and has tested whether there is an asymmetry between the two translation directions during translation recognition. The second line has focused on the second prediction and has examined the degree to which the effects of semantic manipulations and formal manipulations (i.e., those involving the L1 translation equivalents) depend on L2 proficiency.

Concerning the first line of research, Kroll and Stewart (1994) investigated translation performance of highly proficient Dutch-English bilinguals in the context of word lists that were blocked by semantic category or randomly mixed. Their findings revealed two important results: First, translation from L1 to L2 was slower and less accurate than translation from L2 to L1. Second, while backward translation (i.e., the direction hypothesized to be lexical mediated) was unaffected by the semantic context of the lists, translation in the forward direction was slower in the condition of semantically categorized lists than in the mixed conditions. Subsequent studies provided further evidence that bilinguals translate faster from L2 to L1 than from L1 to L2 (Kroll, Michael, Tokowicz & Dufour, 2002; Sánchez-Casas et. al., 1992; Tokowicz & Kroll, 2007) as well as that semantic variables affect the forward direction much more than the backward direction, as the RHM predicted (Sholl, Sankaranaarayanan & Kroll, 1995). However, further research revealed that semantic variables could affect both directions of translation (De Groot and Poot, 1997; La Heij, Hooglander, Kerling & Van der Velden, 1996, see Kroll & Tokowicz, 2005 for a review). According to Kroll, van Hell, Tokowicz, & Green (2010) the last results does not itself refuse the RHM, since most of the semantic effects were obtained through the comparison of concrete and abstract words, and it appears that word concreteness may engage both lexical and semantic factors (e.g., Reilly & Kean, 2007).

The topic of the asymmetry between the two translation directions has been addressed not only from translation studies but also from research relying on cross-language priming (i.e., both translation priming and semantic priming). If we focus on semantic priming, the RHM might predict more effects from L1 to L2 than the other way around, since only the former is conceptually mediated. In contrast, concerning translation priming, RHM would predict more priming from L2 to L1 than vice versa, since the model assumes strong associative lexical link in this direction that can be quickly activated. The results reported in the literature are not consistent, either for translation priming or for semantic priming. Although the most usual finding in both paradigms is a stronger effect in the L1-L2 direction than in the reverse, there are also reports of symmetric priming and even of larger priming effects from L2 to L1 than from L1 to L2 (see for instance Altarriba & Basnight-Brown, 2007 or Duñabeitia et al., 2010, for comprehensive reviews). Researchers have provided different accounts for this inconsistent pattern of results, mostly related with differences between studies in the methodology and tasks used. For instance, Altarriba & Basnight-Brown (2007) underlined that one of the difficulties to generalize across studies lays in the variability of the participants regarding their mode of language acquisition, age of acquisition, etc. They outlined various recommendations, such as the need to include more information about the language history of bilingual participants in the studies and the use of complementary (and more objective) measures to assess language proficiency, for example, different tests that are aligned with the issues under investigation (i.e., reading tests for visual reading studies, etc.). These authors emphasized that a more accurate assessment of language proficiency would provide a better identification of which language is dominant for a given speaker. Similarly, van Hell and Kroll (2012) pointed out some factors related to the language experience that could explain the mixed results of translation priming experiments. For instance, findings reporting symmetry might be explained by the high proficiency of the bilinguals in both languages. Further, the immersion context can be very relevant. Thus, if a bilingual lives immersed in an L2, he could become more dominant/or proficient in this language and this fact could explain the reversed asymmetry (i.e., a stronger translation priming from L1 to L2 than the other way around) reported in some studies (e.g., Altarriba & Basnight-Brown, 2007). Van Hell and Kroll (2012) and Muller (2005) also pointed out that it is quite difficult to reach clear conclusions about several issues related to the mappings of word form to meaning in bilinguals on the basis of behavioral data alone. These authors recommend the use of electrophysiological measures such as event-related potentials (ERPs), a highly sensitive measure of on-line processing, to complement behavioral measures.

A second group of studies has addressed the second prediction of the RHM, by testing bilinguals at different stages of L2 proficiency (Ferré, Sánchez-Casas, García-Albea & Guasch, 2006; Guasch, Sánchez-Casas, Ferré & García-Albea, 2008; Guo, Misra, Tam & Kroll, 2012; Linck, et al., 2009; Sunderman & Kroll, 2006; Talamas, Kroll & Dofour, 1999). For instance, Talamas, et al. (1999) examined the role of L1 mediation in L2 processing during translation. They used a translation recognition task in which the critical conditions involved the presentation of word pairs that were not correct translations (i.e., participants had to reject them). These authors used a new type of relationship, in which the word in L1 was similar in form to the L1 translation equivalent. To illustrate, I will use as an example a learner who has to translate from English (L2) to Spanish (L1). According to the RHM, this learner would use the lexical route in order to access meaning. Therefore, when the learner is presented with the English word *"blind", "blind"* activates the Spanish L1 translation equivalent *"ciego"* (i.e., at the lexical level). Talamas et al. anticipated that words similar in form to the L1 translation equivalents, such as the Spanish word "*cielo*" ("*sky"*), would also be activated and would be able to produce interference. This would be the case if participants are mainly using the lexical route, but not if they are using the conceptual route. Talamas et al. presented participants with a first word in one language followed by a second word in another language and they had to decide whether the second word was the correct translation of the first one (*e.g., blind-ciego*). The critical pairs in their study were non-translation pairs, which could be related in form to the L1 translation equivalent (*e.g., blind-cielo [sky]*); semantically related (*e.g., blind-sordo [deaf]*) or unrelated (*e.g., blind- dueño [owner]*). The time it took a participant to reject the related pairs as non-correct translations was compared to the time to reject pairs that were completely unrelated to each other. The difference in reaction times as well as in the percentage of errors between the related and unrelated conditions was the so-called interference effect. Importantly, Talamas et al. compared two groups of English-Spanish bilinguals differing in their L2 (Spanish) proficiency. Their findings showed that proficient bilinguals were more affected by the semantic relations (i.e., they showed more interference effects with these relations) than by the form relations, whereas the reverse pattern was found for the less proficient group. These results concerning non-proficient bilinguals, which support the RHM, have been subsequently replicated in different studies (Ferré, et al., 2006; Guasch, et al., 2008; Sunderman & Kroll, 2006). Regarding proficient bilinguals, although there are results in the same line as those of Talamas et al. (1999), which would support the RHM (e.g., Linck et al., 2009; Sunderman & Kroll, 2006), there are also evidences that translation equivalents are activated during translation recognition (Ferré, et al., 2006; Guasch, et al., 2008). These evidences will be reviewed in the following section, as they are very relevant for the purposes of the present work.

In the present section I have presented the three models that constitute the theoretical framework of this Thesis as well as the evidences supporting them. During the last decade, conflicting findings for the models have emerged and new questions have appeared. This Thesis has been developed with the aim to address some of those questions. In the following section, I will present the topics which are the focus of this work and I will justify the relevance of their study for a further understanding of the translation process in highly proficient and balanced bilinguals.

1.3. MEANING ACCESS IN HIGHLY PROFICIENT BILINGUALS

Once I have introduced the bilingual models that inspired the experimental part of this dissertation, I will now mention, briefly, the major topics that will be addressed in this thesis. I will focus on the performance of highly proficient bilinguals in a translation recognition task. Except for one study (i.e., the Spanish database of semantic similarity), all the empirical studies of this dissertation examined highly proficient Catalan-Spanish bilinguals performing this task. The bilinguals studied acquired both Catalan and Spanish early in childhood, and live in a context whereby both languages are actively used on a daily basis. The study of this particular type of bilinguals will provide the opportunity of characterizing cross-language interaction processes in a context that favors the constant activation of both languages. In what follows, I will present the main topics that constitute the focus of the present work.

1.3.1. ON THE ISSUE OF L1 TRANSLATION EQUIVALENTS

There is currently a debate on whether L1 translation equivalents are activated only in less proficient, and not in highly proficient bilinguals as a means to access the meaning of L2 words as the RHM holds. However, it could be possible that under some specific circumstances highly proficient bilinguals activate L1 translation equivalents. This is one of the central topics that I address in the experimental part of this dissertation. In what follows, I will briefly introduce it.

According to the RHM, highly proficient bilinguals access meaning directly from L2, which implies that access to the meaning of L2 words is no longer mediated through the L1 translation equivalents (see the RHM section for more details). A series of behavioral studies on translation recognition found that the presentation of words related in form to the L1 translation equivalents affected the performance of highly proficient bilinguals, suggesting that they were activating the L1 translation equivalent. For instance, Ferré et al. (2006) addressed the issue of meaning access on translation recognition (i.e., from L2 to L1) by testing three groups of Catalan (L2)-Spanish (L1) bilinguals who differed in their level of proficiency and in their age of L2 acquisition. The authors examined early (having acquired L2 at childhood), and late (having acquired L2 after puberty) highly proficient bilinguals, and a group of late non-proficient bilinguals. The authors, following Talamas et al. (1999), used the translation recognition task that included Catalan-Spanish translation pairs (e.g., *ruc-burro* [*donkey*]) and non-translation pairs. The critical non-translation pairs were manipulated such that there were *(a)* translation neighbors, that is, pairs in which the Spanish word was related in form to the Spanish translation of the Catalan word (e.g., *ruc-berro* [*donkey-watercress*], where the Spanish word *berro* is similar in form, but not in meaning to *burro*, the Spanish translation of the Catalan word *ruc*); *(b)* pairs in which the Spanish word was semantically related to the Catalan word (e.g., *ruc-caballo* [*donkey-horse*]), and *(c)* pairs in which the two words were neither related in form nor in meaning (e.g., *ruc-domingo* [*donkey-Sunday*]). Although the RHM did not make predictions about the role of the factor *age of acquisition*, Ferré et al., in the same way as other researchers who studied early bilinguals (Kotz, Elston-Güttler, 2004) predicted that early bilinguals (i.e., because of their high proficiencies) access concepts directly from their L2, without having to activate first the L1 translation equivalent. Ferré et al. (2006) found that the two groups of proficient bilinguals (i.e., early and late) showed interference effects both in words related in form and in meaning. Contrary to the predictions of the RHM, interference effects had a similar magnitude in both groups. As mentioned earlier, the RHM suggests that proficient bilinguals can have direct access to the conceptual system when translating from L2 to L1. If this prediction is right, then bilinguals like the ones who participated in the Ferré et al.'s (2006) study, should show more semantic than form interference. In another study, Guasch et al. (2008) examined a group of highly proficient bilinguals and found a pattern of results very similar to the one reported by Ferré et al. (2006). The findings of these two studies are important since they suggest that highly proficient bilinguals access meaning directly. More importantly, the results also suggest that even when meaning is accessed directly, the L1 translation equivalent also becomes active, causing interference. What is not clear, then, is whether the L1 translation equivalent is activated before accessing the conceptual store (i.e., through the lexically mediated route), or if it is activated once the meaning of the L2 word has been accessed (i.e., the direct or conceptual route).

Reaction time measures are not sensitive enough to capture the temporal dynamics of the activation of translation equivalents with respect to meaning access. In order to address in depth this issue, one needs to find a measure sensitive enough to characterize the time course of language processing. Such a measure can be the recording of event-related potentials (ERPs), a technique that allows monitoring the on-line mechanisms underlying word processing. There have been some studies that have addressed these issues by combining behavioral and ERP measures (Guo et al., 2012; Thierry & Wu, 2007). For instance, Thierry and Wu (2007) used ERPs to compare the performance of Chinese (L1)-English (L2) proficient bilinguals with the performance of English monolinguals in a semantic relatedness task in English. In this task, participants were presented with semantically related word pairs (e.g., *post-mail*) as well as unrelated pairs (e.g., *train-ham*) and were asked to decide whether the two words were semantically related to one another. Unbeknownst to the participants, among the experimental pairs there were pairs in which the Chinese translations of the pairs had shared Chinese characters. The words *train* and *ham*, for instance, are not related in meaning but their Chinese translations ***Huo*** *Che* and ***Huo*** *Tui* have a Chinese character in common. By means of this experimental manipulation, Thierry and Wu aimed to examine to what extent the non-target language (i.e., Chinese) is active when Chinese-English proficient bilinguals perform the task in English (i.e., their L2). The authors found that whereas the hidden factor failed to affect behavioral performance, it significantly modulated brain potentials in the expected direction, establishing that English words were automatically and unconsciously translated into Chinese. Critically, the same modulation was absent in the English monolingual control group. The ERPs showed that the N400 was smaller for English word pairs with a shared character in their Chinese translations relative to word pairs without shared characters. Several ERPs studies focusing on semantics have reported modulations of the N400, a negative deflection in the EEG, peaking at around 400 ms post-stimulus onset, which has been used to examine semantic integration processes (e.g., Kutas & Federmeier, 2011; Kutas & Hillyard, 1980). The amplitude of the N400 increases in correlation with integration difficulties and is attenuated for items that are easier to integrate. The N400 attenuation for English word pairs that had common characters with their Chinese translation observed by Thierry and Wu (2007) was interpreted to reflect priming due to the similarity between the Chinese translations. Thierry and Wu (2007) concluded that although meaning access can be direct in proficient bilinguals when they process L2 words, the native language lexicon is also activated, and this fact could be attributed to a nonselective access in which both languages of the bilingual interact.

Guo et al. (2012) provided an alternative explanation for the findings that suggest that highly proficient bilinguals activate L1 translation equivalents. According to Guo et al. (2012) the studies that have reported activation of the L1 translation equivalent in proficient bilinguals have used a relatively long SOA (i.e., between 1000 ms and 1200 ms in Thierry & Wu, 2007). This long SOA might encourage bilinguals to activate the L1 translation equivalents after accessing the meaning of the L2 words due to the long interval to process the words. In order to test this proposal, Guo et al. (2012) tested highly proficient Chinese (L1)-English (L2) bilinguals immersed in their L2 by using behavioral and ERP measures, and by manipulating the SOA (i.e., 750 ms in Experiment 1, and 350 ms in Experiment 2). The experiments were conducted from L2 to L1 (i.e., from English to Chinese). The authors used the translation recognition task as in previous studies (e.g., Ferré et al., 2006; Talamas et. al., 1999). The critical pairs were the non-translation ones. There were (a) semantically related pairs, (b) form related pairs, in which the Chinese word resembled the L1 translation equivalent. The related pairs were compared to non related pairs. In Experiment 1, behavioral interference effects were observed for both the semantically and the form related word pairs. Interestingly, the ERP results showed a different pattern for the two conditions. The semantic condition elicited effects primarily on the N400, with a smaller N400 for related pairs relative to unrelated controls. In contrast, the translation form condition elicited a larger P200 component (sensitive to lexical processing; Liu, Perfetti, & Hart, 2003) than did unrelated controls. In Experiment 2, with a shorter SOA, the behavioral results also revealed interference for both types of relations. However, the ERP results showed a markedly different time course for the semantic and translation form interference effects. A significant semantic interference effect was observed in the time window for the N400, but a translation form interference effect was seen only at a later positive component (i.e., the LPC). The modulation of the LPC in Experiment 2 occurred approximately 800 ms after the presentation of the English word. According to Guo et al. (2012), the LPC effect in Experiment 2 is consistent with the P200 in Experiment 2, since both components were elicited about 850 ms after the onset of the English word. The results obtained by Guo et al. (2012) suggest that proficient bilinguals are able to access conceptual information directly from L2 words without relying on L1. This is supported by the fact that the semantic condition elicited an N400 in both experiments. Moreover, the results also showed that proficient bilinguals activate the L1 translation of the L2 word, and that it is likely that sensitivity to the translation equivalent in highly skilled bilinguals is related to the time afforded to perform the task. Thus, the results of Guo et al. (2012) give support to the proposal according to which the activation of L1 translation equivalents in proficient bilinguals occurs after having accessed the meaning of an L2 word. Moreover, these results are relevant since they highlight the importance of the SOA in the activation of L1 translation equivalents. Nevertheless, it might be the case that other factors, such as factors related to the type of bilinguals or to the frequency of use of the two languages, could also contribute to this activation.

The first aim of the present dissertation was to study how highly proficient and balanced Catalan-Spanish bilinguals access meaning from their two languages, by addressing the issue of the activation of the translation equivalents during translation recognition. The bilinguals who participated in these studies were similar to the proficient groups examined by Ferré et al. (2006) and Guasch et al. (2008). Remember that both studies found evidence that L1 translation equivalents are activated even in highly proficient bilinguals. According to Guo et al. (2012), this result might be explained as a consequence of the long SOAs used (500 ms in Ferré et al. and 750 ms in Guasch et al.). In a series of five experiments (distributed in three studies: Study 1, Study 3 and Study 4), I recorded behavioral measures while participants performed a translation recognition task in which a short SOA was used (i.e., 250 ms). In one of these experiments (Study 4), ERP measures were also registered. The way to test whether translation equivalents (i.e., *ruc-burro*; Catalan-Spanish) were activated was the inclusion of translation neighbors (i.e., *ruc-berro*) among the critical conditions of the experiments. If the activation of the translation equivalents is produced after meaning access, it might be hard to observe interference effects when a short SOA is used. However, it might also be that in bilinguals so proficient as the ones examined in this work, access to meaning is so fast that there is enough time to activate translation equivalents after meaning access even with a SOA of 250 ms. If this is the case, the activation of translation equivalents would not constitute a problem for the RHM. I expected that ERP recordings would contribute to elucidate which is the temporal course of this activation. It is worth mentioning that there was only a single previous study that examined this issue by using both behavioral and ERP measures (Guo et al., 2012) and that the present work was the first one that used the same approach with highly proficient and balanced bilinguals.

A second aim of the thesis, in relation with this topic, was to study the role of the characteristics of the bilinguals in the pattern of cross-languages activation during translation recognition. In particular, the role of language dominance was investigated in Study 1, in which bilinguals of Catalan and Spanish who were dominant in either Catalan or Spanish participated. They performed the translation recognition task from the more dominant language to the less dominant one or the other way around. Previous research has usually tested unbalanced bilinguals, more or less proficient in L2 and has focused on the L2-L1 direction (i.e., the one that might be lexically mediated in non-proficient bilinguals), as it is the critical direction to test the predictions of the RHM. For instance, in the studies of Talamas et al. (1999) and Sunderman and Kroll (2006), participants were English-Spanish bilinguals who were dominant in English. In both cases, the dominant language was always the one in which the bilingual had a higher level of proficiency (i.e., English). In the studies of Ferré et al. (2006) and Guasch et al. (2008), the bilinguals were very proficient in both languages but were more dominant in Spanish. The question of interest in this thesis was to examine whether dominance affects the interference pattern when the level of proficiency of the bilingual was high and very similar in the two languages (i.e., balanced bilinguals). As the bilinguals are highly proficient and balanced, it might be predicted that the interference effects would be symmetric, that is, they would be of a similar magnitude independently of the language from which the participants had to perform the translation recognition task. However, it might also be that the dominant language interferes more than the non-dominant one, as it is more used and preferred by the participants.

1.3.2. On The Role of Languages Use

The influence of language use in meaning access is quite a new issue that has recently received more research attention (e.g., Baus, Costa, & Carreiras, 2013; Linck et al, 2009). As we have seen in this introductory part, researchers interested in the topics addressed here have focused on the effects of word properties (i.e., orthographic, phonological and semantic similarities across languages, Dijkstra, Miwa, Brummelhuis, Sappelli, & Baayen, 2010) as well as on the characteristics of bilinguals (i.e., more concretely on proficiency and age of acquisition of a second language, Van Hell & Dijkstra, 2002). Language use has not been clearly segregated from proficiency, since it has been assumed that proficiency and use have a strong correlation, that is, bilinguals who are more proficient in one language use this language more often than the language in which they are less proficient. However, it is worth noting that although use and proficiency are related (i.e., using a language improves proficiency), there are proficient bilinguals who regularly use the two languages, whereas other proficient bilinguals use two languages in an asymmetrical manner (i.e., one language is used much more often than the other). Then it is important to examine whether language use has a differential role in meaning access across these different types of bilinguals.

Among the few studies that have considered the possible role of language use, by examining different immersion contexts, is the study of Linck et al. (2009), which in its turn was inspired by the work of Sunderman and Kroll (2006). Sunderman and Kroll (2006) compared the performance of two groups of native English speakers, one more proficient and the other less proficient in Spanish, using a translation recognition task in the L2-L1 direction (i.e., Spanish-English). The authors aimed to contrast the predictions of the BIA model with the predictions of the RHM. By the time the study was conducted, the bilinguals were living in the USA, an L1 environment. However, the more proficient group had an abroad experience in an L2 (Spanish) environment. The authors employed the translation recognition task and used three different types of distractors: (a) lexical neighbors (e.g., *cara* [f*ace*]-*card*), which, according to the BIA model, are expected to produce interference in proficient bilinguals; (b) L1 translation neighbors (e.g., *cara*-*fact*), which, according to the RHM, are expected to produce interference effects in non-proficient bilinguals; and (c) semantically related words (e.g., *cara*-*head*), which, according to the RHM, are expected to produce interference effects in more proficient bilinguals. In performing the translation recognition task in the L2-L1 direction it is important to note that both models asked whether L1's lexical information is active when bilinguals process words in L2. However, they differ in that the BIA model holds a nonselective access, addressing this issue mostly in proficient bilinguals, while the RHM claims that L1 translation equivalents are active as a way to accessing the meaning of L2 words for bilinguals at the early stages of learning a second language. Therefore, Sunderman and Kroll (2006) by using two groups, one less proficient and one more proficient in L2 (Spanish) examined the degree to which lexical information in L1, (i.e., either with respect to lexical form (BIA model) or to the translation equivalent (RHM)) is active, and, thus, could interfere in the translation processes in the two groups. The results showed interference effects in both groups of bilinguals for lexical neighbors and for semantically related words. Translation neighbors produced interference effects only in the less proficient group. The results supported, on the one hand, the RHM in that the early learners had a mediated meaning access, whereas relatively proficient bilinguals directly accessed the meaning of L2 words. On the other hand, the nonselective access proposed by the BIA model was not only observed in proficient bilinguals but also in L2 learners.

Linck et al. (1999) used the experimental materials of Sunderman and Kroll (2006) with the aim of examining the role of the immersion context in meaning access by testing two groups of English native speakers (L1) with an intermediate level of proficiency in Spanish (L2). The two groups were matched in cognitive abilities and proficiency. The only difference between them was the immersion context, and, implicitly, the use of the second language. By the time of the study, one of the groups lived in USA, an L1 environment, whereas the other group was immersed in an L2 context following a study abroad program in Spain. The second group had an L2 immersion experience of three months. Therefore, there was a difference between the two groups concerning the use of both English and Spanish. The group that was living in the USA used more English than Spanish, whereas the group that was following a study abroad program used English less often, and used Spanish much more often than the first group. The experiments were performed from Spanish to English (i.e., L2-L1). The authors found semantic interference for both groups of participants. In contrast, interference with both lexical neighbors and translation neighbors was only observed in the group immersed in an L1 context, but not in the group immersed in an L2 context. The absence of interference effects in the group immersed in a Spanish context were interpreted by Linck et al. as follows: When bilinguals are immersed in an L2 context, they use their L1 less frequently, and this causes the L1 language to be inhibited. These results are important since they show that under specific circumstances, such as a low use of L1, this language might be temporarily inhibited and as a consequence this could affect across languages processing. More generally, the findings of Linck et al. revealed that lexical access in bilinguals is modulated not only by proficiency, but also by the immersion context or use of a particular language, an aspect that was less attended in past studies.

The studies of Sunderman and Kroll (2006) and Linck et al. (2009) showed that both lexical and translation neighbors become active during translation, as it was predicted from the BIA model and the RHM, respectively. Furthermore, they revealed that this activation can be modulated by language use. Clearly, the issue of under what circumstances L1 is activated or inhibited during L2 processing is highly relevant to the domain of bilingual word recognition. A further aim of the present dissertation was to place the predictions of the BIA model and the RHM in the same experimental context with respect to highly proficient and balanced bilinguals, who live immersed in both languages (i.e., Catalan and Spanish are the two official languages in Catalonia) and use them on a daily basis. We aimed to test the extent to which the lexical level of representation of the two languages becomes active and, thus, interfere, when participants are to judge if a word is the correct translation of a word in another language. It might be possible that a linguistic immersion context that requires both languages to be used actively and whereby bilinguals regularly change from one language to the other depending on a particular context, might call for a quick retrieval of word meaning and its lexical form in order for the bilingual be able to speak. It might be that this particular circumstance of a daily use of both languages could affect the semantic and lexical levels of representation, resulting in a rapid activation of the translation equivalent. In Study 3, we adopted the same task and experimental manipulations as Sunderman and Kroll (2006) and Linck et al. (2009), who tested unbalanced bilinguals that clearly used one language more than the other in the L2-L1 direction. The main contributions of this study were the type of bilinguals tested as well as the examination of the two translation directions. According to the BIA model, the subjective frequency of a word (related to its use), plays a role on its recognition. If the regular use of both languages by Catalan-Spanish bilinguals is taken into account (i.e., the daily use might imply that the subjective frequencies of both languages are quite similar), a symmetrical pattern of interference effects across directions should be expected for lexical neighbors. Concerning translation neighbors, if there are effects in this condition, they were expected to be also symmetrical, as stated in the previous section.

1.3.3. On The Influence of Meaning Similarity

The issue of to what extent the degree of meaning similarity could affect language processing is quite a new topic that has begun to receive attention in studies both in the monolingual and in the bilingual domain, and that given its relevance deserves some more attention (van Hell & Kroll, 2012). For instance, in monolinguals, a large body of research has addressed the topic of to what extent priming effects can be obtained both (1) with associative relations and (2) with semantic relations not involving association (see Hutchison, 2003; Lucas, 2000, for reviews). Although there are only a few monolingual studies that have addressed the issue of meaning similarity by using highly semantically (e.g., *donkey-horse*) and less semantically related words (e.g., *donkey-bear*) these studies show that the degree of semantic overlap between two words influences the magnitude of priming effects both in a semantic priming paradigm as well as in a picture-word interference (PWI) paradigm. For instance, when the prime and target are two words, words highly related in meaning produce more facilitation than words less related in meaning (Cree & McRae, 2003; McRae & Boisvert, 1998; Sánchez-Casas, Ferré, García-Albea, & Guasch, 2006; Vigliocco, Vinson, Lewis, & Garrett, 2004). In the PWI paradigm, in which, for example, the prime could be a word and the target a picture (i.e., or vice versa, or when having two pictures as the prime-target pair) the direction of the effects is not so clear since the studies show that highly related words can either produce more facilitation effects (e.g., Mahon, Costa, Peterson, Vargas, & Caramazza, 2007) or interference than less related words (e.g., Vieth, McMahon, & de Zubicaray, *in press*).

In the bilingual domain, there is some evidence in the priming literature showing that highly related words produce greater facilitation than less related words. This evidence has been observed when examining highly proficient balanced Spanish-Catalan bilinguals. Interestingly, the pattern of results is very similar across the two language directions (i.e., from Spanish to Catalan, and from Catalan to Spanish; Guasch et al., 2011). However the results with the translation recognition task are not consistent, since a series of studies found interference in both types of semantically related words, with greater interference effects in more than in less related words (Talamas et al., 1999; Sunderman & Kroll, 2006), while other studies found interference only in the more semantically related words (Ferré et al., 2006; Guasch et al., 2008). For instance, Talamas et al. (1999), in a *post-hoc* analysis used a semantic *similarity-rating task* to assess the meaning similarity of the semantically related pairs used in their study. Then based on the values obtained in the semantic similarity rating task, the authors divided the set of words into two subsets: the more and the less semantically related. Bear in mind that the study of Talamas et al. (1999) examined two groups of English native speakers, one more proficient and the other less proficient in L2 (i.e., Spanish). The results of the *post-hoc* analysis showed that proficient bilinguals presented interference effects with both more and less similar words, the effects being greater in the former than in the latter. In the less proficient group, interference was found only with the more related words. In the same way, Sunderman and Kroll (2006) also performed a *post-hoc* semantic *similarity-rating task* with the words they used in the semantic condition of their study. They observed that interference effects were modulated by semantic similarity, in that, the greater the meaning similarity between two words the greater the interference effects. Overall, the results of Talamas et al. (1999) and Sunderman and Kroll (2006) are important since they suggest, first, that, as assumed by the DRM, the effects of the degree of meaning similarity can be used as an index of the extent to which semantic representations are activated across the two languages. Secondly, they suggest that even for less proficient bilinguals, there are reliable semantic interference effects, at least when the two words are highly related in meaning, as in Sunderman and Kroll's (2006) study. Although the RHM holds that semantics are more engaged in the L1-L2 direction than in the L2-L1 direction, the model does not discard the possibility of observing semantic effects even in bilinguals with a relatively low level of proficiency in L2 (see Kroll et al., 2010, for more details).

There is a second series of studies, which were aimed to examine the role of meaning similarity in the performance of proficient and balanced Spanish(L1)-Catalan (L2) bilinguals when performing a translation recognition task from L2 to L1 (Ferré et al., 2006, Guasch et al., 2008 see above). These studies used the triplets developed by Sánchez-Casas et al. (2006). A triplet consists of a target and two semantically related words, one more similar and the other less similar in meaning (e.g., more similar: *ruc-caballo* [*donkey-horse*] and less similar: *ruc-oso* [*donkey-bear*]; Catalan-Spanish). According to the DRM, it was expected that both types of semantically related words would produce interference effects, and that the magnitude of these effects would be greater for more similar than for less similar pairs (i.e., due to a greater semantic overlap for the former with respect to the latter). The results obtained by both Ferré et al. (2006) and Guasch et al. (2008) were not consistent with those reported in previous studies. While Talamas et al. (1999) and Sunderman and Kroll (2006) found that both more and less related words produced interference effects, Ferré et al. (2006) and Guasch et al. (2008) found evidence of these effects only with more similar words (e.g., *ruc-caballo*) but not with the less similar ones (e.g., *ruc-oso*). These were striking results if we take into account that Guasch et al. (2011) obtained semantic priming with both types of words. A possible explanation of the inconsistent findings reported with the less semantically related words might be related with the long SOAs used in the studies of Ferré et al. (500 ms) and Guasch et al. (750 ms). Thus, it might be that the failure to find interference effects with these words had to do with the rapid decay of the level of activation of their corresponding semantic representations (what we call "the low level activation account"). According to "the low level activation account" when the word *donkey* is presented, the nodes representing the meaning of the Spanish words *caballo* [*horse*] (i.e., more similar) and *oso* [*bear*] (i.e., less similar), would be activated, as both *caballo* and *oso* share semantic features with *donkey*. However, the level of activation would be comparatively higher for *caballo* than for *oso*, as there is a greater semantic overlap between *donkey* and *caballo* than between *donkey* and *oso*. Assuming that the level of activation gradually declines in time and that it is lower in the case of *oso* than in the case of *caballo*, it is possible that by the time the translation decision has to be made, the level of activation for the word *oso* would be too low to compete with the correct translation, thus producing no interference effects. In other words, *oso* "would have already been ruled out as a possible translation". On the other hand, in the case of the word *caballo*, the level of activation would still be high enough by the time the decision has to be made, thus producing interference effects when a long (750 ms; Guasch et al., 2008) or a medium SOA (500 ms; Ferré et al.,2006) is used.

A further aim of the present thesis was to examine the modulation of semantic interference effects by the degree of meaning similarity between words as well as to test the "low level activation account" as an explanation for the lack of interference effects with the less semantically related words. In Study 1 and Study 4, a translation recognition task with a short SOA (i.e., 250 ms) was used and pairs of words more and less similar in meaning were included. Behavioral measures were recorded in both studies and ERPs were registered in Study 4. By taking into account the DRM assumption that the degree of semantic similarity modulates a word's level of activation in tasks in which pairs of words are involved, larger interference effects would be expected for words more related in meaning than for words less related in meaning. Furthermore, considering the assumption of *"the low level activation account*", if 250 ms is a period of time short enough to capture the level of activation of less semantically related words, interference effects might be obtained with these words. If these effects are not observed in behavioral measures, they might be evident in the ERP waveforms, as a modulation of the N400 component. It is worth mentioning that this was the first study to date examining the effects of the degree of meaning similarity across languages on ERP signatures during a translation recognition task.

An additional aim of this dissertation was to obtain a large set of stimuli consisting of pairs of semantically related words that were non-associated.

One important aspect to highlight from the translation recognition studies is regarding the semantic relationship that they used. While in some cases were used only semantically coordinated words (Ferré et al., 2006; Guasch et al., 2008) in the other cases the authors did not control to distinguee semantic similar words from associated; thus is, the pairs were took from an English associative database (Nelson, McEvoy & Schreiber,

2004) mostly of them being only associated, but some of them additionally to be associated were also semantically related (Guo et al., 2012; Linck et al., 2009; Sunderman & Kroll, 2006; Talamas et al., 1999). For instance, Sunderman and Kroll (2006) used associatively pairs such as *mirror-reflection* mixed with pairs that were both associated and semantically coordinated, such as *table-chair*. In order to further examine whether semantically non-associativelly related words are able to produce interference on translation recognition, we extended the set of triplets of Sánchez-Casas et al. (2006) study by collecting semantic similarity ratings for 185 triplets of words. Given that in Spanish there is only one published database with associative norms (NIPE, Fernández, Díez, Alonso, & Beato, 2004), but none with semantically (and non-associatively) related pairs of words, this database is highly relevant, since it provides stimulus for researchers aimed to study the role of semantics in monolingual and bilingual language processing.

A final aim of this thesis in relation with the present topic concerns the comparison of the two translation directions. In Study 1 and in Study 3, semantically related pairs were included in the critical conditions and the two translation directions were tested. Furthermore, in Study 1, the effects of the degree of meaning similarity between non-translation pairs in translation recognition were examined. According to the DRM, and to the proposal of Schoonbaert et al. (2009) reviewed in the section devoted to that model, balanced bilinguals such as those examined in the present studies would activate the same number of nodes at the semantic level when processing words in L1 and in L2. Thus, a symmetrical pattern of modulation effects by semantic similarity would be expected between the two translation directions, in agreement with the priming literature showing a similar pattern of facilitation regardless of the language direction in balanced bilinguals (Guasch et al., 2011; Davis, Sánchez-Casas, García-Albea, Guasch, Molero & Ferré, 2010; Duñabeitia, et al., 2009; Perea, et. al., 2008)

II. Experimental Section

Presentation

The present dissertation includes four studies: a published paper, an accepted paper and two manuscripts that are in preparation. Three of these studies approach the issue of lexical and semantic processing during translation recognition in highly proficient and balanced bilinguals who live immersed in the two languages and use them on a regular basis. The other study provides normative ratings for a set of semantically related words. These normative data were used to select the experimental materials for some of the other three studies. In addition, they provide researchers in the field with a valuable tool as it is the first database with these characteristics in Spanish.

Past research in bilingual word processing has mainly focused on non-proficient bilinguals or on bilinguals that, in spite of being proficient, were unbalanced and lived immersed in a L1 environment and used their first language more than the second one. The specific characteristics of Catalan-Spanish bilinguals tested in this dissertation allows us to pursue a series of questions in relation with cross-languages lexical and semantic processing, with special emphasis either on the characteristics of the bilinguals (i.e., use or dominance) and the effects of the different types of words' relations.

The task used was the same in the three studies focused on bilingual lexical and semantic processing: A translation recognition task with the interference paradigm, in which pairs of words in Catalan and Spanish were presented and participants had to decide whether the second word in the pair is the translation of the first one. The critical conditions were the non-translation pairs (distractors). Depending on the particular aims of each study, these non-translation pairs could be words similar in form or in meaning across languages. With respect to similarity in form, we manipulated two types of relations: lexical neighbors (e.g., for a Catalan-Spanish pair, we presented as a distractor a Spanish word orthographically similar to the Catalan word) and translation neighbors (e.g., for a Catalan-Spanish pair, we presented as a distractor a Spanish word orthographically similar to the correct Spanish translation). Concerning meaning similarity, we manipulated the degree of semantic relationship, by comparing highly semantically related pairs with pairs with a low degree of semantic relationship.

In the three studies we used a SOA of 250 ms. (SOA, the interval from the onset of the first word to the onset of the second word of the pair to be recognized as translations). This is a very short SOA that, on the one hand, allows us to examine the variables of interest in relation with the particular aims and hypothesis tested in each study, and on the other hand, it reduces the strategies of the participants produced by their expectancies. Since these bilinguals are highly proficient, longer SOAs could be problematic because the extra time given to the participants to process the pairs could generate expectancies that would affect the processing of the second word in the pair. Furthermore, in the three studies we used behavioral measures (reaction times and percentage of errors) and in one of the studies we included event-related potentials (ERPs). This last measure allows us to obtain a very detailed recording of the time-course processing of form and semantic relations in proficient bilinguals.

The manipulation of semantic and formal relationships across languages obtained after a careful process of selection as well as the use of behavioral and electrophysiological measures can provide us with a detailed picture of the processes involved in translation recognition. Moreover, the idiosyncratic characteristics of Catalan-Spanish bilinguals provides us with the opportunity of studying the modulation of such processes even in highly proficient bilinguals by variables related with the characteristics of the words or the bilinguals themselves. In this way, the findings obtained might be relevant for the most influential models of bilingual memory.

Study 1

Moldovan, C. D., Sánchez-Casas, R., Demestre, J., & Ferré, P. (2012).

Interference effects as a function of semantic similarity in the translation recognition task in bilinguals of Catalan and Spanish.

Psicológica, 33, 77-110.

Psicológica (2012), 33, 77-110.

Interference effects as a function of semantic similarity in the translation recognition task in bilinguals of Catalan and Spanish

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Previous evidence has shown that word pairs that are either related in form (e.g., *ruc-berro*; donkey-watercress) or very closely semantically related (e.g., *ruc-caballo*, donkey-horse) produce interference effects in a translation recognition task (Ferré et al., 2006; Guasch et al., 2008). However, these effects are not observed when the words have a less close semantic relation (e.g., *ruc-oso*, donkey-bear). The lack of interference in less similar words could be due to the low level of activation of the corresponding semantic representations by the time the translation decision has to be made. The present experiments tested this possibility using the same materials as the previous studies but decreasing from 500 ms to 250 ms the presentation time of the word to be translated. Performance of highly proficient bilinguals of Spanish and Catalan was examined in two experiments. Catalan-Spanish translation direction was tested in Experiment 1 and Spanish-Catalan direction in Experiment 2. The results showed significant effects only with form and very close semantic relations, but not in the case of less closely semantically related words. The pattern of results was the same, regardless of translation direction and language dominance.

The representation and access to meaning is a central issue in current studies of bilingual memory, not only for a speaker who has learnt a second language but also for the bilingual speaker who has achieved a high level of proficiency in his/her two languages. There is a consensus among the various theoretical models of bilingual memory regarding the two levels of

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representation to be posited: a lexical level, containing information of the orthographic and phonological form of the word, and a semantic-conceptual level that represents its meaning. All these models agree that the level of semantic/conceptual representation is shared (to a greater or lesser extent) between the two languages, but while some postulate local representations (e.g. the Revised Hierarchical Model of Kroll & Stewart, 1994, or the BIA+ interactive activation model of Dijkstra & van Heuven, 2002), others propose distributed representations (e.g. the distributed representational model proposed by de Groot 1992a, 1992b). Many studies have been carried out over the last two decades in an attempt to determine the type of connections between the lexical forms of words between the two languages of the bilingual, including how these forms are linked to the corresponding, shared semantic representations within the common conceptual system (e.g. Altarriba & Matis, 1997; Ferré, Sánchez-Casas, García-Albea & Guasch, 2006; Guasch, Sánchez-Casas, Ferré, & García-Albea, 2008; Kroll, Michael & Sankaranaraanan, 1998; Linck, Kroll & Sunderman, 2009; Sunderman & Kroll, 2006; Talamas, Kroll & Dofour, 1999). However, the available evidence is not always consistent and the answers to some of these questions are still subject to controversy. This work follows the same line of research of the aforementioned studies, focusing, in particular, on how meaning is accessed from the words in the two languages by examining highly proficient bilinguals of Catalan and Spanish (with dominance in either language).

One of the proposed bilingual models that has been very influential in recent years in the study on word meaning access is the Revised Hierarchical Model (RHM, Kroll & Stewart, 1994). The RHM proposes two separate lexicons, one for each language (L1 and L2), in addition to a shared integrated conceptual system that is connected to both lexicons. This model also assumes that L1 has connections and direct access to the conceptual system, and that the strength of the connections between L2 and the conceptual system varies according to the level of proficiency. This latter assumption is based on the fact that many words in L2 are learned by lexical associations with their equivalents in L1. The model, therefore, suggests that the connections between the words in L2 and its corresponding concepts are reinforced as proficiency in L2 increases while lexical dependence on L1 decreases. As a consequence, proficient bilinguals could access the conceptual system directly from both their L1 and their L2, while second-language learners would access the system using L1 only.

Translation from L2 into L1 has received greater attention in studies that test the RHM, as differences between learners and proficient bilinguals concerning how the conceptual system is accessed are only predicted by the model in this direction. These studies have mostly used the translation recognition task and an interference paradigm (e.g. Ferré et al., 2006; Guasch et al., 2008; Linck et al., 2009; Sunderman & Kroll, 2006). In this task, participants are presented with a word in one language followed by a second word in the other language, and have to decide whether the second word is a translation of the first (de Groot, 1992). As well as the word pairs that are translations, the task also includes critical items consisting of pairs of words that are not translations but may be related in form *(*e.g. *ruc-berro* [donkey-watercress], where *berro* [watercress] is similar to *burro* [donkey]*),* in meaning *(*e.g. *ruc–caballo* [donkey-horse]), or may not be related at all (e.g. *ruc-domingo* [donkey-Sunday]). The difference between the time taken to recognise the pairs of related words (in form or in meaning) as non-translations and the time used in this recognition for unrelated word pairs is known as the interference effect.

The first study to investigate how meaning is accessed from words in the two languages using the interference effect in the translation recognition task was performed by Talamas et al. (1999). Participants were native English (L1) speakers with varying levels of proficiency in Spanish (L2). The RHM predictions were tested by manipulating the relationship between the words in the pairs that were not translations (relationship of form: e.g. *cielo-blind (cielo=heaven, ciego =blind)*; semantically related: e.g. *sordo-blind (sordo=deaf)*; unrelated: e.g. *dueño-blind (dueño=owner)*). The results of the bilingual speakers with the highest level of L2 proficiency supported the RHM's predictions. Talamas et al. (1999) found that proficient bilinguals were slower when they had to reject as non-translations those pairs that were related in meaning (e.g. *sordo-blind*) than when the pairs were related in form (e.g. *cielo-blind*), which confirms that they access the conceptual system directly from their second language.

More recently, Sunderman and Kroll (2006) and Linck et al. (2009) also used the translation recognition task and obtained a similar pattern of results with proficient bilinguals of English (L1) and Spanish (L2). In both studies, the most proficient bilinguals showed a greater interference effect with semantically related words than with words related in form when the translation was from L2 to L1, which once again confirmed the predictions of the RHM.

Talamas et al. (1999) and Sunderman and Kroll (2006) found an additional result which was not related to the assumptions on which the RHM is based. In a post-hoc analysis, these authors compared the interference effect in the initial set of meaning-related words, dividing them into two groups according to their similarities (either more or less similar), using a judgement task. The results of this analysis showed that proficient bilinguals presented interference effects with both the more and the less similar words, but these effects were greater in the former than in the latter; in other words, the greater the similarity in meaning, the greater the interference effect. This pattern of results is important, as it suggests that the degree of meaning similarity can be used as an index of the extent to which semantic representations are activated across the two languages. However, it should be noted that these results were obtained in an *a posteriori* analysis in both studies, and any conclusion must therefore be considered with caution.

To the best of our knowledge, the only bilingual study which has experimentally manipulated the degree of similarity using the interference paradigm is that of Ferré et al. (2006). These authors carried out a study with native, bilingual speakers of Spanish (L1) and Catalan (L2) in the critical translation direction (i.e., from L2 to L1) in order to more rigorously analyse the influence of the degree of semantic similarity on interference effects in the translation recognition task. As well as using the similarity judgement task to establish proximity in meaning, as did Talamas et al. (1999) and Sunderman and Kroll (2006), Ferré et al. (2006) also employed a feature generation task, used to calculate the semantic distance between the words in non-translation pairs according to the number of common features (see Sánchez-Casas, Ferré, García-Albea & Guasch, 2006, for a detailed description of the procedure). Based on these two measures, the words that were semantically related were categorised either as words with a very close semantic relationship, or as having a less close relationship. The words with a very close relationship shared a larger number of semantic features (e.g. *ruc-caballo* [donkey-horse]) than those that were less close (e.g. *ruc-oso* [donkey-bear]). As well as specifying the variable "degree of semantic similarity" between words more precisely, these authors also manipulated it as a factor in the experiment.

Likewise, as in the previous studies (Talamas et al., 1999; Sunderman & Kroll, 2006), they included pairs of non-translations related in form (e.g. *ruc-berro* [donkey-watercress], where *berro* [watercress] is similar to *burro* [donkey]). Finally, the authors selected three groups of bilinguals of Spanish and Catalan: early and late highly proficient bilinguals, depending on the age of acquisition of the second language (before and after puberty), and a group of late non-proficient bilinguals.

The results obtained by Ferré et al. (2006) confirmed partially the predictions of the RHM. As predicted, non-proficient bilinguals only showed form interference effects supporting a lexically mediated access to the conceptual system with lower level of proficiency in L2. The two groups of proficient bilinguals (early and late) also showed the expected interference effects both in words related in form and in meaning. However, against the model´s predictions, these effects were of a similar magnitude in both groups. As mentioned earlier, the RHM proposes that proficient bilinguals can have direct access to the conceptual system when translating from L2 to L1; so bilinguals as the ones who participated in Ferre et al.´s study, should have shown more semantic than form interference effects.

Importantly, the pattern of interference effects reported by Ferré et al. with semantically related words also contrasts with previous studies (Talamas et al. (1999) and Sunderman & Kroll, 2006). While these studies found both very close and less close semantically related words to produce interference effects, Ferré et al. only found evidence of these effects in the very close semantic relationship (e.g. with *ruc-caballo* [donkey-horse] but not with *ruc-oso* [donkey-bear]). The same results were recently replicated by Guasch et al. (2008), who also examined proficient bilinguals of Spanish and Catalan by using the same materials. The present study was designed with the general aim of further exploring the pattern of interference effects with very close and less close semantically related words, testing also highly proficient bilinguals of Spanish and Catalan.

In its current formulation, the RHM does not explain how the degree of similarity could modulate the effect of semantic interference. Moreover, we have just reviewed some translation recognition data that are not always consistent with the model´s predictions (see Brysbaert & Duyk, 2010 for other limitations of the RHM and Kroll, van Hell, Tokowicz, & Green, 2010 for a reply). A model that could suggest a possible answer to the question under examination here, as well as to provide an alternative explanation of the different performance between non-proficient and proficient bilinguals, is the distributed representational model (DRM) (de Groot, 1992a., 1992b; van Hell & De Groot, 1998a, 1998b). The DRM represents the semantic/conceptual word level as a set of nodes which correspond to semantic features and which are connected to the corresponding lexical forms in the two languages. The model also assumes that the greater the similarity in meaning between two words, the larger the number of nodes shared by their semantic representations (e.g., Schoonbaert et al., 2009). Thus, two words which are very closely related in meaning across the two languages would be expected to activate more shared nodes than words with less close semantic relationships, and consequently, to produce greater interference effects than less close words.

Moreover, a recent version of the DRM could also explain why non-proficient bilinguals would not show evidence of semantic interference effects when translating form L2 to L1. In particular, it has been recently suggested that semantic representations would be richer for L1 than for L2 for unbalanced (proficient) bilinguals, what implies that an L1 word would activate more conceptual nodes than an L2 word (e.g., Duyck & Brysbaert, 2004; Schoonbaert et al., 2009). Based on this proposal, it seems reasonable to expect that non-proficient bilinguals will show less or no semantic interference effects. This explanation differs from that offered by the RHM since this model suggests that low proficient bilinguals will access the conceptual system via the L1 word (i.e., an interpretation in qualitative terms), while the DRM puts forward a quantitative interpretation by suggesting that the word in L2 does not activate all the nodes corresponding to the shared semantic representation.

Given that the DRM provides testable explanations regarding the influence of semantic relations across languages in translation recognition, and the role of meaning similarity in determining the magnitude of semantic interference effects, this model was adopted as the main theoretical framework in the present study.

Focusing now in the issue of very close and less close semantic relations, the majority of studies that have explored these relations both within-one-language (e.g. MacRae & Boisvert, 1998; Sánchez-Casas, et al., 2006; Vigliocco, Vinson, Lewis & Garrett, 2004), and between-languages (Guasch, Sánchez-Casas, Ferré & García-Albea, in press), used the priming paradigm. The evidence from these studies suggests that the magnitude of the priming effect is sensitive to the degree of semantic similarity (defined in terms of the number of shared semantic features). These studies found that recognition of a word (the target) was facilitated by the prior presentation of a semantically related word (the prime) in comparison with an unrelated control, and that this facilitation increases as the similarity in meaning increases. In particular, Guasch et al. (in press) obtained facilitation effects in the two types of semantic relations (very close and less close), which were greater when the semantic overlap was greater. These effects were found in proficient bilinguals of Spanish (L1) and Catalan (L2) in both directions (L1-L2 *vs*. L2-L1) in two different tasks: the lexical decision task (which involves deciding whether a sequence of letters constitutes a word or not) and the semantic decision task (where subjects must decide whether a word is concrete or abstract).

If we assume, as some data (Sunderman & Kroll, 2006; Talamas et al. 1999) appear to suggest, that the interference effect is sensitive to the degree of similarity (defined in terms of the number of shared features), as it is the case in the facilitation effect, the DRM would make the same predictions with respect to both types of effects. If the most similar word pairs (e.g. *ruc-caballo* [donkey-horse]) have more overlapping semantic features than those that are less similar (e.g. *ruc-oso* [donkey-bear]), then more semantic nodes would be activated in the former than in the latter. This greater number of activated nodes would be reflected in an increased facilitation effect in the priming paradigm (a shorter response time and fewer errors in the most similar words), and a greater interference effect in the translation recognition task (a longer response time and more errors in the most similar words). Regardless of the paradigm, the DRM therefore predicts that the more the number of shared features, the greater the activation at the conceptual/semantic level (see Figure 1).

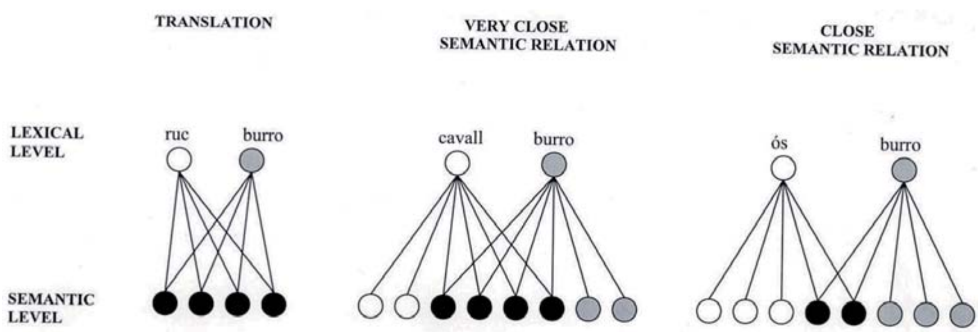

Figure 1: Explanation of the interference effects according to the DRM. The nodes activated by the two words in the pair in the semantic level are shown in black.

In the case of the interference effects, the predictions of the DRM regarding the influence of the degree of similarity (e.g. the greater the semantic similarity, the greater the interference effect) are only partially confirmed as we have seen that only the most similar words consistently produce interference effects. In the pairs with less semantic similarity, and despite sharing semantic features, the interference effects were not observed in all studies. One difference between these studies that can be important to take into account in order to explain the inconsistent results regarding the pattern of semantic interference effects, relates to the materials used. Specifically, in the studies of Talamas et al. (1999) and Sunderman & Kroll (2006), the selected word pairs had a semantic as well as an associative relationship (e.g. *ratón-queso*) [mouse-cheese]), while in Ferré et al. (2006) and Guasch et al. (2008) the relationship was purely semantic (e.g. *burro–caballo* [donkey–horse]). In the case of the priming paradigm, some data suggest that the words which have an associative as well as a semantic relationship lead to greater facilitation that those that are only related semantically (e.g. Perea & Rosa, 2002), so such a difference might also be relevant when the interference paradigm is used (see Ferré et al, 2006 for the discussion of this possibility).

Another factor that could contribute to explain the absence of effects in less similar words could be that their degree of similarity is not sufficient to cause interference. However, there are some data that question this explanation. Firstly, the semantic similarity of less similar words in the Ferré et al.´s (2006) study is similar to that of previous studies that did find some interference in post-hoc analyses (e.g. Sunderman & Kroll 2006; Talamas et al., 1998). Secondly, and as mentioned above, these same words show effects of priming both within (Sánchez-Casas et al., 2006) and between languages (Guasch et al., in press).

A different sort of explanation for the failure to find an interference effect in less similar words could be related to the decline of the level of activation in the semantic/conceptual level of representation (hereinafter *the low activation account*). The interpretation of interference effects in the DRM suggests that when two words that are related semantically are presented, the nodes at the semantic level are activated (shared and not shared), but the level of activation is modulated by the degree of similarity in meaning. For example, when the word *ruc* [donkey] is presented, the nodes for the semantic representation of the word *caballo* [horse] (very closely related), and *oso* [bear] (less closely related), would be activated, as both *caballo* and *oso* share semantic features with *ruc.* However, the attained activation level would be comparatively higher for *caballo* than for *oso,* as there is a greater semantic overlap between *ruc* and *caballo* than between *ruc* and *oso*. Assuming that the activation level gradually declines and that it is lower in the case of the word *oso*, it is possible that by the time the decision has to be made regarding whether or not *oso* is a translation of *ruc*, the activation level for the word *oso* is already too low to compete with the correct translation. In other words, *oso* "would have already been ruled out as a possible translation". On the other hand, in the case of the word *caballo* [horse], the level of activation would still be high at the time of the decision and it would, consequently, be able to produce an interference effect. If this interpretation is correct, the question to be answered is why priming effects are observed regardless of the degree of semantic similarity, albeit of lower magnitude in words that are less closely related. In this respect, it is noteworthy that in the priming experiments, the presentation time of the first word (the prime) was 250 ms (Guasch et al., in press), while in the translation recognition experiments, which included the same words, the presentation time was 500 ms (Ferré et al., 2006) and 750 ms

(Guasch et al., 2008). It is therefore possible that these presentation times were too long and, as a result, no interference effects were observed in words that were less closely related.

The first and main aim of the present study was to test the *low activation account* as a possible explanation of the absence of interference by reducing the presentation time of the first word to 250 ms; this time of presentation was chosen because it was the same as the one used in the priming experiments. If the *low activation account* is correct, we would predict that 250 ms of exposure would lead to interference effects in both types of semantic relations, with these effects being greater when the similarity of meaning is greater.

A second aim of this study was to ascertain whether the direction of the translation recognition task affects the pattern of the interference effects. As mentioned earlier, most translation recognition studies have examined translation from L2 to L1, as that was the critical direction for testing the predictions of the RHM (e.g. Ferré, et al., 2006; Guasch, et al., 2008; Linck et al., 2009; Sunderman & Kroll, 2006). However, to examine translation direction as an experimental factor is important since it has been found to be relevant in determining different findings. For instance, in priming studies, facilitation effects tend to be of a lesser magnitude or even nonexistent when the prime is in L2 than when it is in L1 (see Schoonbaert et al, 2009, for a review). More importantly, recent studies have shown that in the case of very proficient balanced bilinguals in the two languages, as the ones who participated in the present study, facilitation is the same regardless of the language of the prime (e.g. Guasch et al., in press; Davis et al., 2010; Duñabeitia, et al., 2009; Perea, Carreiras & Duñabeitia, 2008;). According to the DRM, highly balanced proficient bilinguals, as the ones tested in the current study, would not be expected to present differences in the magnitude of the interference effect as a function of translation direction (L1-L2 *vs.* L2-L1), since in this case the model proposes that both L1 and L2 lexical forms would activate the same number of nodes at the semantic/conceptual level.

A final variable object of investigation in this study, related to the previous one, is the dominance of the bilingual speaker (Spanish or Catalan). This variable has not been considered in previous studies where unbalanced bilinguals, more or less proficient in L2, have been examined. For instance, in the studies of Talamas et al. (1999) and Sunderman & Kroll (2006), the participants were English-Spanish bilinguals that were dominant in English. In both cases, the dominant language was always the one where the bilingual had a higher level of proficiency (i.e., subjects were clearly more proficient in English than in Spanish). In the studies by Ferré et al.

(2006) and Guasch et al. (2008), the bilinguals were very proficient in both languages but were dominant in Spanish (with the exception of Perea et al, 2008, and Guasch et al., in press) this has been also the case in the priming studies). The question of interest here is to examine whether dominance affects the interference pattern when the proficiency of the bilingual speakers is high and very similar in the two languages (i.e, balanced bilinguals); that is, to test separately the effects of the two variables. As can be seen in the description of the participants (see the Method section), the bilinguals we tested are highly proficient in both Spanish and Catalan, although they have a dominant language established primarily on language use. Therefore, in our view, they provide a good opportunity to determine if these two variables have a differential effect. If the determining factor is proficiency rather than dominance, as the DRM assumes, we would expect to find the same interference pattern regardless of the dominant language. On the other hand, if dominance is the critical variable, we could observe greater interference when the translation is from a more dominant language, as this is the first language.

In sum, the aims of the present study were as follows: 1) to determine whether with a presentation time of 250 ms for the first word, there are interference effects in the close semantic relationship, by using the same words and tasks used in previous studies; 2) to ascertain whether the interference effects are observed in both translation directions (L1-L2 *vs.* L2-L1); and 3) to establish the influence of language dominance (Spanish or Catalan) on the pattern of semantic interference effect. In order to fulfil these objectives, two translation recognition experiments were undertaken, from Catalan to Spanish (Experiment 1) and from Spanish to Catalan (Experiment 2). Two groups of highly proficient Catalan and Spanish bilinguals participated in each experiment: one group was dominant in Catalan and the other was dominant in Spanish; both groups came from a similar population. In Experiment 1, the group that was dominant in Catalan had to translate from their L1 (Catalan) to their L2 (Spanish) and the group dominant in Spanish from their L2 (Catalan) to their L1 (Spanish). Experiment 2 reversed the process, with the group dominant in Catalan translating from L2 (Spanish) to L1 (Catalan) and the group dominant in Spanish from their L1 (Spanish) to their L2 (Catalan). The materials and procedure were the same in both experiments.

EXPERIMENTS

General description of the participants. Before presenting the experiments, it is necessary to describe the bilingual speakers who participated in the study. In the two experiments carried out, the participants were bilinguals in Catalan and Spanish, and had learned both languages in a context of immersion since a young age (Catalan and Spanish are both official languages in Catalonia). In order to establish the bilingual speakers' background, all participants answered a questionnaire. In the questionnaire, they were asked about their experience with the two languages (L1, age of L2 acquisition, language spoken at home, at school, etc.) and to estimate their perceived proficiency in listening, speaking, reading and writing, as well as the frequency of use and preference in each of these four linguistic abilities. The level of Catalan and Spanish proficiency acquired in the two languages was evaluated using a scale from 1 to 7 (1= low level, 7= high level). The participants rated frequency and preference on a scale from 1 to 7, where the scores from 1 to 3 meant they used and prefer more Catalan than Spanish and 5 to 7, more Spanish than Catalan. The middle scores (4) represented that participants used and preferred both languages to an equal extent.

On the basis of the information from the questionnaire, two groups of participants were selected, one group of dominant Catalan bilinguals and the other dominant Spanish bilinguals. The main criteria to establish language dominance were: L1, proficiency, frequency of use, and preferred language. The Catalan dominant group had Catalan as their L1, and they used and preferred this language in the four abilities, while Spanish was the selected language for the Spanish dominant group. Regarding proficiency, both groups evaluated themselves as highly proficient in their two languages, although the non-dominant language received slightly lower rates than the dominant one. The data from the questionnaires obtained in each group are shown in Table 1.

EXPERIMENT 1: CATALAN – SPANISH DIRECTION

METHOD

Participants. A total of 85 third year Psychology students at Universitat Rovira i Virgili (Tarragona) participated in the experiment. The mean age of the participants was 20.3 (SD = 4.4). All had normal or corrected vision. Table 1 shows the scores (mean and standard deviation) in proficiency, frequency of use and preference in the four linguistic skills (listening, speaking, reading and writing) in two bilingual dominant groups.

Table 1: Data from the language questionnaire for the participants in Experiment1 (Catalan-Spanish direction) and in Experiment 2 (Spanish-Catalan direction). Mean and standard deviation of the proficiency, frequency of use and preference scores, in the four linguistic skills (listening, speaking, reading and writing).

	Experiment 1 (Catalan-Spanish direction)				Experiment 2 (Spanish-Catalan direction)			
	Dominant Catalan		Dominant Spanish		Dominant Catalan		Dominant Spanish	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Catalan proficiency								
Listening	7.0	0.2	6.8	0.5	7.0	0.2	6.4	0.7
Speaking	6.8	0.4	5.9	1.0	7.0	0.3	5.8	1.3
Reading	6.8	0.4	6.6	0.7	7.0	0.3	6.3	0.7
Writing	6.4	0.7	6.0	1.1	6.6	0.6	5.7	0.8
Spanish proficiency								
Listening	6.8	0.5	7.0	0.2	6.9	0.2	6.8	0.4
Speaking	6.3	0.9	6.8	0.4	6.4	0.8	6.7	0.5
Reading	6.7	0.6	6.9	0.3	6.9	0.4	6.7	0.5
Writing	6.3	0.8	6.6	0.6	6.6	0.6	5.9	1.6
Frequency of use								
Listening	3.1	0.9	4.8	0.9	2.8	1.0	4.4	1.2
Speaking	4.0	1.4	5.3	1.4	2.3	1.2	5.0	1.5
Reading	2.5	0.9	5.5	1.0	3.7	1.5	4.8	1.3
Writing	2.8	1.3	5.3	1.2	2.7	1.5	4.4	1.2
Preference								
Listening	3.0	1.3	4.7	1.0	3.1	1.2	4.2	0.6
Speaking	2.1	1.2	5.7	1.0	2.3	1.2	5.2	1.0
Reading	3.3	1.4	5.2	1.3	3.4	1.4	4.8	1.0
Writing	3.0	1.6	5.4	1.3	3.0	1.3	4.6	1.5

Catalan dominant group: The forty-eight participants in the Catalan dominant group had been born in Catalonia, where they acquired the two languages in childhood (age of acquisition of Spanish, $\overline{X}$ = 2.2, SD = 2.3). The statistical comparisons made between the measures of level of proficiency in Catalan and Spanish show that there are significant differences between Catalan and Spanish, in favour of Catalan in "listening" [$t(42)=2.47$, $p<.05$], "reading" [$t(42)=2.35$, $p<.05$] and "speaking" [$t(42)=4.79$, $p<.05$]. However, no significant differences were observed in the level of proficiency in "writing" [$t(42)=1.00$, $p>.05$]. The Catalan dominant participants considered themselves equally proficient when writing in both languages.

Spanish dominant group: Of the thirty-seven participants in the Spanish dominant group, thirty-three had been born in Catalonia, and four had arrived in Catalonia at a mean age of 2.2 (SD = 1.3) and had learned Catalan during their childhood (age of acquisition $\overline{X}$ = 2.2, SD = 1.6). The Spanish dominant participants assessed themselves as more proficient in Spanish than Catalan in "listening" [$t\ (30)=1.98$, $p=.05$], "reading" [$t\ (30)=2.75$, $p<.05$], "speaking" [$t\ (30)=5.33$, $p<.05$] and "writing" [$t\ (30)=2.82$, $p<.05$].

As regards the frequency of use, each group was found to use its first language more often than its second language. The differences between each group's scores are significant in each of the skills measured: "listening" [$t\ (72)=7.62$, $p<.05$], "speaking" [$t\ (72)=3.96$, $p<.05$], "reading" [$t\ (72)=13.19$, $p<.05$] and "writing" [$t\ (72)=7.97$; $p.<.05$] The same pattern of results was observed in the case of preference of use: "listening" [$t\ (72)=5.90$, $p<.05$], "speaking" [$t\ (72)=13.44$, $p<.05$], "reading" [$t\ (72)=5.81$, $p<.05$] and "writing" [$t\ (72)=6.68$; $p.<.05$]

Materials. The set of words previously used by Ferré et al. (2006) and Guasch et al. (2008) was used. A total of 70 sets of seven words each were selected as critical material for the experiment. All the words were specific nouns and belonged to various semantic categories. (e.g. appliances, living things, etc.). (See the Appendix for the list of materials).

The words were presented in pairs. In Experiment 1, the first word in the pair was always presented in Catalan and the second in Spanish, so that for the Catalan dominant group the first word was in its L1, while for the Spanish dominant group it was in its L2. The word in Catalan could be presented in one of the following seven experimental conditions:

1. *Translation*: the word in Catalan was followed by its Spanish translation (e.g. *ruc-BURRO*) [donkey-DONKEY].

2. *Very close semantic relationship*: the word in Catalan was presented followed by a word in Spanish that was very closely related in meaning with its correct translation (e.g. *ruc-CABALLO*) [donkey-HORSE].
3. *Control for the very close semantic relationship*: the word in Catalan was presented, and followed by a word in Spanish that was neither related in form nor in meaning (e.g. *ruc- DOMINGO*) [donkey-SUNDAY]
4. *Less close semantic relationship*: the word in Catalan was followed by a word in Spanish that was less closely related semantically (e.g. *ruc-OSO*) [donkey-BEAR].
5. *Control for the less close semantic relationship*: the word in Catalan was presented followed by a word in Spanish presented that was neither related in form nor in meaning (e.g. *ruc- SED*) [donkey-THIRST].
6. *Form*: the word in Catalan was presented followed by a word in Spanish that was orthographically similar to the translation (e.g. *ruc-BERRO*) [donkey-WATERCRESS].
7. *Control of form*: the word in Catalan was followed by a word in Spanish that was neither related in form nor in meaning (e.g. *ruc-LEJÍA*) [donkey-BLEACH].

The words in the control conditions (3, 5 and 7) were comparable in length and frequency to the words in the matching related condition (2, 4 and 6 respectively). (The data for frequency data of Spanish are taken from BPal, Davis and Perea, 2005, and those for Catalan from the IEC Dictionary). (See Table 2). None of the comparisons between these variables was significant (ts<1).

The level of similarity and semantic distance in the words of the semantic conditions (condition 2 and 4) were taken from the study by Sánchez-Casas, et al. (2006). The similarity was obtained using the same procedure as Talamas. et. al, (1999) and Sunderman & Kroll (2006), and the semantic distance from the data obtained in a feature generation task (see Sánchez-Casas et al., 2006, for details of the procedure). The data showed that the words in the very close relationship were closer to each other semantically than those in the less close relationship and were rated as significantly more similar to each other (see Table 3).

Table 2: Mean length (number of letters) and frequency of use of the words included in the experimental and control conditions in Experiment 1 (Catalan- Spanish direction).

	Relationship		Control	
Condition	Length	Frequency	Length	Frequency
Very close semantic	6.5	16.2	6.4	15.8
Less close semantic	6.3	13.2	6.3	13.3
Form	6.2	38.4	6.2	31.3

Table 3: Means (and standard deviation) of similarity ratings between words with very close and less close relationship, used in Experiment 1 and 2.

	Very close	Less close
Similarity ratings	6.19 (0.82)	4.07 (0.71)
Semantic distance	0.73 (0.21)	1.03 (0.15)

As well as the sets of critical words, there were 50 other pairs of translations, which acted as filler pairs. These translations belonged to the same semantic categories as the pairs of non-translations. The seven experimental conditions were counterbalanced, leading to seven different lists, so that each participant only saw one item in a given experimental condition, but each item appeared in each experimental condition on all the lists. All the lists consisted of 120 items: 60 translations and 60 false translations. Each list was administered to two groups of participants (dominant in Catalan *vs*. dominant in Spanish). The 50 pairs of filler translations were the same in the seven lists.

Procedure. The participants participated in the experiment individually. Each one was randomly administered one of the seven versions of the experiment. A translation recognition task was used, in which the participants were asked to decide whether the second word in a pair was a correct translation of the first. They had to answer by pushing one of two buttons: the "YES" button, with their preferred hand, if the second word in the translation was a correct translation, or the "NO" button, with the other hand, if it was not the correct translation. The computer generated a pseudo-random order of presentation for each participant, thereby avoiding the consecutive appearance of more than two stimuli in the same condition. The stimuli were presented on a video monitor controlled by a PC, using the DMDX program (Forster & Forster, 2003). This programme enables the on-screen display time for each stimulus to be synchronised with the monitor's screen reload rate. The presentation sequence was as follows: first, a fixation point ("#") appeared for 500 ms; immediately afterwards, the first word of the pair (in Catalan) was presented for 250 ms, and immediately afterwards, the second word (in Spanish) was presented in capital letters for 1,500 ms in one of the seven experimental conditions. The participants self-administered the tests by pressing a pedal with their foot. After each test, they were given a feedback about the answer they had given. If the answer was correct, the word "*Correcto*" or "*Correcte*" [Correct] appeared on the screen, depending on the translation direction (i.e., Catalan-Spanish or Spanish-Catalan, respectively), with the reaction time in milliseconds; if the answer was incorrect, only the word "*Error*" [Error] appeared on the screen. If there was no response to the stimulus, the phrase "*No respuesta*" or "*No resposta*" [No response] was displayed.

Before starting the experiment, the participants received written instructions in their dominant language. These instructions explained the task, and emphasised that they had to answer as accurately and as quickly as possible, but not quickly enough to lead to a high percentage of errors. The experiment began with 11 practice stimuli that represented the different conditions in the experiment. The experiment lasted approximately 25 minutes.

RESULTS AND DISCUSSION

Reaction times (RTs) for the trials in which the participants made an error were not included in the analysis. Likewise, the RTs with values of more or less than two standard deviations from the participant's mean were adjusted to the values of 200 ms (minimum) and 2000 ms (maximum) established beforehand as cut-off points, to moderate the influence of extreme responses. This led to the exclusion of 4.7% of the data. Data from five participants who made more than 15% of errors were excluded from the analysis.

Data from non-translation tests: Table 4 shows the RTs and the percentage of errors (%E) in each of the three types of related words (very close semantic, less close semantic and form) in the two relationship conditions (relationship *vs.* control).

ANOVAs based on participant and item response latencies and error percentages were conducted based on a factorial design of three factors (3x2x2). The “type of relationship” factor had three levels (very close, less close and form). The “relationship” factor had two levels (related *vs.* control). Finally, the “group of participants” factor had two levels (Catalan dominance and Spanish dominance). The first two factors were repeated measures both in the analysis by participants and in the analysis by items. The third factor was between-subjects in the analysis by participants, and within-subjects in the analysis by items.

ANOVAs on the reaction times revealed a main effect of type of relationship both in the analysis by participants [F_1 (2, 166)=15.60, p<.05, η^2=0.16] and in the analysis by items [F_2 (2, 264)=7.51, p<.05, η^2=0.05]. The relationship factor was also significant in the analysis by participants [F_1 (1, 83)=79.76, p<.05, η^2=0.49] and in the analysis by items [F_2 (1, 132)=44.64, p<.05, η^2=0.25]. The dominance factor was not significant in the analysis by participants [F_1(1, 83)=2.24, p>.05], but was significant in the analysis by items [F_2 (1, 132)=18.71, p<.05, η^2=0.12]. The interaction between type of relationship and relationship was significant in both analyses [F_1 (2, 166)=6.48, p<.05, η^2=.07; F_2 (2, 264)=5.70 p<.05, η^2=0.04]. The interaction between type of relationship and dominance, and the threefold interaction between type of relationship, relationship and dominance, were not significant (Fs <1).

Table 4: Mean reaction time (RT, in ms) and percentage of errors (%E) in the different experimental conditions together with the corresponding interference effects in Experiment 1 and 2, after collapsing dominance.

	Experiment 1 Catalan- Spanish direction		Experiment 2 Spanish – Catalan direction	
Condition	Mean	%E	Mean	%E
Very close (e.g. *ruc-caballo) [donkey-horse]*	775	30.0	768	27.8
Control (e.g. *ruc-domingo) [donkey-Sunday]*	721	2.4	717	2.2
Interference effect	**54***	**28.6***	**51***	**25.6***
Less close (e.g. *ruc-oso) [donkey-bear].*	721	4.0	728	4.2
Control (e.g. *ruc-beso) [donkey-kiss]*	701	1.8	712	3.3
Interference effect	**20**	**2.2**	**16**	**0.9**
Form (e.g. *ruc-berro) [donkey-watercress]*	778	14.7	784	15.8
Control (e.g. *ruc-lejía) [donkey-bleach].*	711	2.0	713	2.9
Interference effect	**67***	**12.7***	**71***	**12.9***

*p.<.05. *The examples of the items in condition (very close, less close and form) are from Experiment 1.*

Due to the lack of interaction between dominance and the factors type of relationship and relationship, the data for the two dominance groups (Catalan and Spanish) were collapsed. Planned comparisons were performed with the RTs between each of the conditions of the type of relationship factor (very close, less close and form) and the specific control condition for each one. The comparisons revealed a significant interference effect on the very close semantic condition (54ms) [t_1 (84)=5.00, $p<.05$; t_2 (64)=4.67, $p<.05$], on the form condition (67ms) [t_1 (84)=8.45, $p< 0.5$; t_2 (68)=5.04, $p<.05$], and on the less close semantic condition (20ms) in the analysis by participants [t_1 (84)=2.53, $p<.05$] but not in the analysis by items [t_2 (69)=1.67, $p=.10$].

The pattern of ANOVA results for the errors is similar to that obtained in the RT analysis. The type of relationship factor was significant [F_1 (2, 166)=97.30, $p<.05$, $\eta^2=0.54$; F_2 (2, 276)=50.17, $p<.05$, $\eta^2=0.27$]. The relationship factor was also significant [F_1 (1, 83)=239.96, $p<.05$ $\eta_1{}^2=0.74$; F_2 (1, 138)=169.76, $p<.05$, $\eta_2{}^2=0.55$] as was the interaction between type of relationship and relationship [F_1 (2, 166)=91.09, $p<.05$, $\eta^2=.52$; F_2 (2, 276)=43.72, $p<.05$, $\eta^2=0.24$]. The dominance factor was neither significant in the analysis by participants [F_1(1, 83)=0.14, $p>.05$] nor in the analysis by items [(F_2(1, 138)=0.37, $p>.05$.]. As in the analysis of the RTs, the interactions between type of relationship and dominance [F_1 (2, 166)=0.64, $p>.05$; F_2(2, 276)=0.16, $p>.05$], between relationship and dominance [F_1 (1, 83)=0.05, $p>.05$; F_2(1, 138)=0.00, $p>.05$] and between type of relationship, relationship and dominance [F_1 (2, 166)=0.62, $p>.05$; F_2 (2, 276)=0.09, $p>.05$] were not significant.

After collapsing the dominance factor, the results of the planned comparisons with the error data showed a significant interference effect in the very close semantic relationship [t_1 (84)=15.40, $p<.05$; t_2 (69)=8.77, $p<.05$], and in the form relationship [t_1 (84)=8.92, $p<.05$; t_2 (69)=5.92, $p<.05$]. In the case of the less close semantic relationship, the interference effect was significant only in the analysis by participants [t_1 (84)=2.68, $p<.05$; t_2 (69)=1.43, $p=0.16$]. The pattern of results is consistent with that obtained with the RTs. The participants made more errors in the related conditions than in the control conditions.

Figure 2 shows the magnitude of the interference effect in the three experimental conditions: very close and less close semantic relationships, and relationship of form.

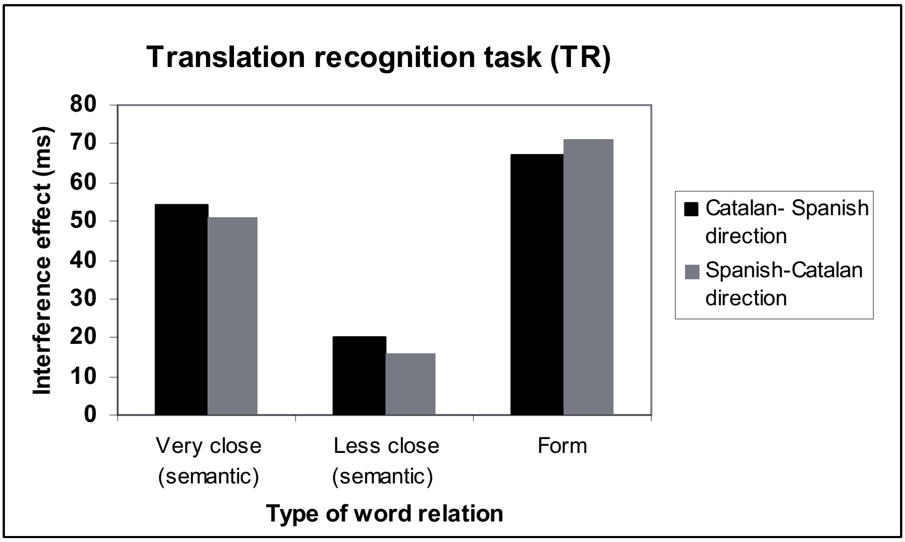

Figure 2: Magnitude of the interference effect (ms) in the three types of word relations (very close, less close, and form) and in the two translation directions (Catalan-Spanish *vs.* Spanish-Catalan)

Similarly to Ferré et al. (2006) with early highly proficient bilinguals, words with a very close semantic relationship and words related in form were found to produce interference effects. Moreover, planned comparisons between the magnitude of these effects revealed that they were of a similar magnitude in response times (54 *vs.* 67 ms, see Figure 2) [$t_1(84)=1.00$, $p>.05$; $t_2(63)=0.75$, $p>.05$], with less errors being observed with form related words [$t_1(84)=7.49$, $p<.05$; $t_2(69)=3.38$, $p<.05$]. However, unlike these authors, it is important to notice that in the present experiment less close semantic relations did produce some interference effect (20 ms significant by participants), while this was not the case in Ferré et al.´s study (a non-significant 7 ms). More relevant, the correlation between the similarity ratings[1] and the magnitude of the semantic interference was significant [$r=0.239$, $p<.05$], as well as the difference in magnitude (34 ms) between very close (54 ms) and less close semantic relationships (20 ms) [$t_1(84)=2.50$, $p<.05$; $t_2(64)=2.60$, $p<.05$ and $t_1(84)p.<.05$; $t_2(69)=8.15$,

[1] Semantic similarity ratings were used instead of semantic distances as only the former were distributed within a continuum (from 1 to 7). The classification of the very close and less close semantically related words was established dichotomically. However, the correlations between both measures is significant measures (r = -0.59, p < .001, see Sánchez-Casas, Ferré, García-Albea, & Guasch, 2006).

$p<.05$ for RT and errors respectively]. These findings can be interpreted as supporting the DRM since they showed that the greater the degree of meaning similarity between two words, the more number of shared nodes will became activated, and consequently, greater interference effects will be observed when the semantic relation is very close.

In the following experiment, we examined the interference effects in the same type of relationships but in this case, the first word was presented in Spanish and the second in Catalan.

EXPERIMENT 2: SPANISH – CATALAN DIRECTION

METHOD

Participants. A total of 71 first year Psychology students at Universitat Rovira i Virgili (Tarragona) participated in the experiment. The mean age of the participants was 19.6 (SD = 2.6). They all had normal or corrected vision and none had participated in the previous experiment (see Table 1).

*Spanish dominant group***:** The 21 participants in the Spanish dominant group had been born in Catalonia and had learned Catalan in childhood (age of acquisition $\overline{X}$ = 1.7, SD = 1.5). The Spanish dominant group assessed itself as more proficient in Spanish than in Catalan at “listening” [t (16)=2.74, p<.05], “reading” [t (16)=3.34, p<.05] and “speaking” [t (16)=2.89, p<.05]; while for "writing", it assessed itself as equally proficient in both languages [t (16)=0.53, p>.05].

Catalan dominant group: The 50 participants in the Catalan dominant group were born in Catalonia and had acquired both languages during their childhood (age of acquisition of Spanish $\overline{X}$ = 2.3, SD = 2.2). No significant differences were observed between Catalan and Spanish in “listening” [t(33)=1.00, p>.05], “reading” [t (33)=1.00, p>.05] and “writing” [t (33)=0.68, p>.05]. The only significant difference observed was in “speaking” [t(33)=4.37, p<.05].

As for the comparison of frequency and preference of use, the pattern found is identical to the bilingual speakers in Experiment 1. The first language is used more often (“listening” [t (49)=4.78, p<.05]; “speaking” [t (49)=7.17, p<.05]; “reading” [t (49)=2.80., p.<.05] “writing” [t (49)=4.09; p.<.05]); likewise, the first language obtained higher scores in preferences for use (“listening” [t (49)=3.57, p<.05]; “speaking” [t (49)=8.54, p<.05]; “reading” [t (49)=3.66, p<.05]; “writing” [t (49)=4.30; p.<.05]).

Material. In this experiment, the first word was presented in Spanish and the second one in Catalan (e.g. *burro –CAVALL, close semantic relation)* [donkey-HORSE]. The critical words were the same as those used in Experiment 1 (see Appendix). The only difference here concerns the words in the control conditions, since in this case the controls for each condition were selected so that they were matched in frequency and length to the words in Catalan. For instance, in the word pair *burro – CAVALL*, the control word *PASSAT* was the same frequency and length as the Catalan word *CAVALL*. For the Spanish dominant group, the first word was in its L1 and for the Catalan dominant group it was in its L2.

Table 5 shows the data for length and frequencies of the various types of relations in the relationship and control condition. None of the comparisons between the related condition and the control were significant (all ts < 1).

Procedure. The procedure and equipment used were the same as those used in Experiment 1.

Table 5: Mean length (number of letters) and frequency of use of the words included in the experimental and control conditions in Experiment 2 (Spanish- Catalan direction).

	Relationship		Control	
Condition	Length	Frequency	Length	Frequency
Very close semantic	6.4	31.6	6.4	30.5
Less close semantic	5.9	35.4	5.9	35.0
Form	5.9	165.4	5.9	180.2

RESULTS AND DISCUSSION

Reaction times (RTs) of the trials in which the participants made an error were not included in the analysis. Likewise, RTs with values of more or less than two standard deviations from the participant's mean were adjusted to the values of 200 ms (minimum) and 2,000 ms (maximum) established beforehand as cut-off points, to moderate the influence of extreme responses. This led to the exclusion of 4.8% of the data. Data from eight participants who made more than 15% of errors were excluded from the analysis.

Data from non-translation tests: Table 3 shows the mean reaction times (RTs) and the percentage of errors (%E) when the first word appeared in Spanish and the second in Catalan.

The results were similar to those obtained in the previous experiment. In the analysis of the RTs, both type of relationship [F_1 (2, 138)=7.58, p<.05, η^2=0.10; F_2 (2, 238)=7.63, p<.05, η^2=0.06] and relationship [F_1 (1, 69)=58.90, p<.05, η^2=0.46; F_2 (1, 119)=39.70, p<.05, η^2=0.25] were significant. The dominance factor was not significant in the analysis by participants but was significant in the analysis by items [F_1(1, 69)=0.34, p>.05; F_2(1, 119)=7.08, p<.05]. The same was observed in the interaction between the factors type of relationship and relationship [F_1 (2, 138)=4.26, p<.05, η^2=0.06; F_2 (2, 238)=5.80 p<.05, η^2=0.05]. On the other hand, neither the interaction between type of relationship and dominance [F_1 (2, 138)=0.24, p>.05; F_2 (2, 238)=0.74, p>.05], nor between relationship and dominance [F_1 (1, 69)=0.27, p>.05; F_2 (1, 119)=0.72, p>.05] nor the triple interaction [F_1 (2, 138)=0.27, p>.05; F_2 (2, 238)=0.03, p>.05] were significant.

After collapsing the dominance factor, planned comparisons showed a significant interference effect in the RTs in the very close semantic relationship (51 ms) [t_1 (70)=4.19, p<.05; t_2 (57)=4.12, p<.05]. In the less close semantic relationship, this effect was less marked (16 ms) and was marginal in the analysis by participants, and significant in the analysis by items [t_1(70)=1.77, p=.08; t_2 (67)=2.20, p<.05]. In the form relationship, the interference effect was significant in both analyses [t_1 (70)=6.78, p<.05; t_2 (62)=5.73, p<.05].

The pattern of ANOVA results for the error data revealed a main effects of type of relationship [F_1 (2, 138)=42.50, p<.05, η^2=.38; F_2 (2, 276)=29.89, p<.05, η^2=0.18], and of relationship [F_1 (1, 69)=170.32, p<.05, η^2=0.71; F_2 (1, 138)=102.10, p<.05, η^2=0.43]). The interaction between type of relationship and relationship was also significant [F_1 (2, 138)=48.93, p<.05, η^2=.42; F_2 (2, 276)=29.66, p<.05, η^2=0.18]. The dominance factor presented no significant differences [F_1(1, 69)=2.70, p>.05; F_2(1, 138)=1.56, p>.05]. Neither the interaction between type of relationship and dominance [F_1 (2, 138)=1.09, p>.05; F_2(2, 276)=0.80, p>.05], nor the interaction between relationship and dominance [F_1 (1, 69)=1.00, p>.05; F_2 (1, 138)=0.58, p>.05], nor the triple interaction [F_1 (2, 138)=0.70, p>.05; F_2 (2, 276)=0.81, p>.05] were significant. ANOVA on the percentage of errors were generally similar to those obtained with the RTs, with the only difference being that the dominance factor was not significant in the analysis by items.

Planned comparisons of the %E showed a significant interference effect in the very close semantic relationship [t_1 (70)=11.99, p<.05; t_2 (69)=7.15, p<.05], and in the form relationship [t_1 (70)=9.27, p<.05; t_2 (69)=5.70, p<.05]. Unlike the results obtained in the RTs analysis, the differences in the less close relationship were not significant [t_1(70)=0.73, p>.05; t_2 (69)=0.66, p>0.5].

The results obtained in the Spanish to Catalan direction were very similar to those observed in the Catalan to Spanish direction examined in the previous experiment. Interference effects in both very close semantic and form relationships were obtained and they were not reliable with less closely semantically related words. As in Experiment 1, planned comparisons were performed to compare the magnitude of the interference effects across the relevant conditions (see Figure 2). The results of these comparisons in the RTs once again revealed that the effects when words were very close related in meaning were not significantly different that when words were related in form in the [t_1(70)=1.14, p>.05; t_2(51)=1.03, p>.05], and they reached significance in the case of errors [t_1(70)=4.90, p<.05; t_2(69)=2.90, p<.05].

As predicted by the DRM, the results of this experiment also showed that the interference effects are modulated by the degree of meaning similarity. Once again, the semantic interference was greater in the very close semantic relationships (51 ms.) than in the less close ones (16), both in the RT [t_1(70)=2.21, p<.05; t_2(57)=2.44, p<.05 and in the errors [t_1(70)=10.64, p<.05; t_2(69)=6.80, p<.05]. Similarly, the correlation between the semantic similarity ratings and the size of the interference effect was significant.[r=0.335, p<.05].

GENERAL DISCUSSION

The main aim of this study was to examine the effect of the degree of semantic similarity between L1 and L2 words in order to determine how words from the two languages are connected at the semantic/conceptual representation level, and to what extent meaning is activated across languages during the translation processes. In order to achieve this aim, we carried out two experiments with proficient bilinguals of Spanish and Catalan who were dominant in one of the two languages by using the translation recognition task and by manipulating the degree of similarity in meaning between the words from both languages (very close relationship and less close relationship), as well as their relationship in form.

Based on previous studies, and taking the distributed representational model (DRM) as theoretical framework, our specific objectives were as follows. First, we aimed to determine whether interference effects could be observed in the less close semantic relationship with an exposure time of 250 ms for the first word of the pair, as these effects had not been previously observed on a systematic basis with longer exposure times. Secondly, we tested, for the first time, whether the interference effects were observed in highly proficient bilinguals in both directions of translation (L1-L2 *vs*. L2-L1). Finally, we attempted to examine, also for the first time, whether the pattern of interference effects is influenced by the bilingual speaker's dominance (Spanish or Catalan) or what is relevant is to have a high level of proficiency in the two languages.

With regard to the first objective, our hypothesis, the *low activation account*, was that a presentation time of 250 ms would enable detection of the activation of the semantic representation of the less similar words, which would be apparent in the presence of interference effects. This hypothesis was not clearly confirmed by the reported findings. As predicted by the DRM and similarly to previous studies with bilinguals of Spanish and Catalan, a reliable interference effect was observed in the very close semantic relationships. Moreover, this effect (52 ms.) was of a similar magnitude to that reported in those studies (47 and 40 ms in (Ferré et al., 2006; Guasch et al., 2008, respectively).

However, the effects observed in the less close semantic relationship (e.g. *ruc-oso*) [donkey-bear], although in the expected direction, did not reach significance, contrasting with Talamas et al. (1999) and Sunderman & Kroll´s (2006) *ad hoc* analyses which revealed semantic interference effects with words both very closely and less closely related. Nevertheless, it is important to notice that in the present experiments close semantic relations did not produce null interference effects (20 and 16 ms. in the Catalan-

Spanish and Spanish-Catalan direction respectively); and the correlations between the similarity judgments and the magnitude of the semantic interference were in both cases significant. These data could be interpreted as evidence that the degree of semantic similarity may also modulate semantic activation across languages in the interference paradigm, in line with the DRM predictions.

One question that needs to be addressed before further exploring such an interpretation is why the same manipulation with the same non-associative semantic relations produced a clear modulation of the facilitation effects with Spanish-Catalan bilinguals (Guasch et al., in press). One possible explanation is that the paradigm and the demands of the tasks (translation recognition, lexical decision, or semantic categorization) used in all these studies partially determine whether interference and facilitation effects are observed in words with a less close semantic relationship. Although it is obvious that in all the tasks used the meaning of words is processed, as semantic facilitation and interference effects can be observed in all of them, the participants have to decide whether the two words have the same meaning only in the translation recognition task. This decision could require greater demands for semantic processing than either lexical decisions or concreteness judgements in the semantic categorisation task. Complementary to this explanation, it is also possible that the exposure time of 250 ms is not short enough for clear interference effects to emerge in the reaction times, as the activation level declines very quickly. One measure that has proven to be very sensitive to the time-course of processing from very early stages, and which could detect the activation caused by less similar words, is the recording of event-related brain potentials (ERPs). Various studies provide evidence that the N400 component is sensitive to semantic processing when the priming paradigm is used (e.g. Holcomb & Grainger, 2006; Kiyonaga, Grainger, Midgley & Holcomb, 2007). It would be necessary to determine whether this component is elicited in the translation recognition task, using the same type of related words as those included in our study. If less similar words lead to activation through languages, we would expect to find an N400, although perhaps one smaller than that produced by words with more similarity in meaning.

Our second aim was to test for the first time in highly proficient (balanced) bilinguals, whether the interference effects could be observed in both directions of translation (L1-L2 *vs*. L2-L1). Our data clearly show that the pattern of results is very similar, not only in terms of the pattern of interference effects, but also with respect to the magnitude of these effects. These data are consistent with those obtained in priming studies with very proficient bilinguals, where the magnitude of the semantic facilitation effects is the same in both translation directions (e.g. Guasch et al., in press; Perea, et al., 2008). They also confirm the prediction of the DRM that proficient bilingual speakers would present no differences in the magnitude of interference effects regardless of the language they are translating from (L1 or L2), supporting the view that semantic representations are shared across languages and are activated during access from either language.

Finally, the third aim of this study was to examine, also for the first time, the possible role of dominance (Catalan or Spanish) of the bilinguals when proficiency is very high and similar in both languages. Our hypothesis was that if dominance is the critical variable in determining the pattern of interference effects, it would be possible to observe an asymmetry in the pattern of interference so that greater effects would be observed when translating from the more dominant language to the less dominant (in our case L1 to L2) than in the opposite direction (L2-L1). On the other hand, if proficiency is the determinant factor, we would expect to find the same interference pattern in the two groups of bilinguals (those dominant in Spanish and those dominant in Catalan). The results showed the same pattern of interference effects regardless of the participants´ dominant language. As well as being a new result, the absence of effects of dominance suggests that proficiency is the critical factor in determining the connections established between the lexical level and the conceptual level, as well as the extent to which meaning is activated across languages.

To conclude, this study was designed to contribute to a greater understanding of how words from L1 and L2 are connected at the semantic level of representation, and to what extent their meanings can be accessed directly from both languages. The results obtained provide evidence that confirms that there is semantic activation between languages in very proficient bilinguals, regardless of their dominance and the direction of translation. Likewise, the results have confirmed that the amount of semantic activation can vary depending on the degree of proximity in meaning, as the DRM predicts. In addition, the data also enable us to identify some factors that would be interesting to examine in future research, such as the type of semantic relationship, the demands of the task and the type of measure used to record the time course of the activation.

RESUMEN

Efectos de interferencia en función del grado de semejanza en la tarea de reconocimiento de traducciones en bilingües de catalán y castellano. Estudios previos han mostrado que pares de palabras relacionadas en forma (*ej., ruc-berro*) o con una relación semántica muy próxima (*ej., ruc-caballo*) producen efectos de interferencia en una tarea de reconocimiento de traducciones (Ferré et al., 2006; Guasch et al., 2008). Sin embargo, dichos efectos no se observan en palabras de relación semántica próxima (*ej., ruc-oso*). La ausencia de efecto de interferencia en las palabras menos semejante en el significado podría ser atribuida al bajo nivel de activation de las representaciones semánticas correspondientes en el momento de determinar si son o no traducciones. El presente estudio pone a prueba dicha posibilidad utilizando el mismo material que los estudios previos, pero disminuyendo el tiempo de presentación de la palabra a traducir de 500 ms. a 250 ms. En concreto, se examina el rendimiento de bilingües muy competentes en castellano y catalán en dos experimentos, manipulando la dirección de la traducción: catalán - castellano (Exp.1) y castellano- catalán (Exp.2). Los resultados revelan efectos de interferencia significativos únicamente en las palabras relacionadas en forma y muy próximas en el significado, pero no en aquellas con una relación semántica menos próxima. El patrón de los resultados fue similar en las dos direcciones de traducción, independientemente de la lengua dominante de los participantes.

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APPENDIX

List of critical words used, in alphabetical order, in the various relationship conditions (translation, very close semantic, less close semantic and form), both in Spanish (first word) and in Catalan (second word). The translations into English are in brackets.

Translation	Very close semantic	Less close semantic	Form
acelgas bledes (chard)	espinacas espinacs (spinach)	calabaza carbassa (pumpkin)	acacias fredes (acacias /cold)
alfombra catifa (carpet)	esterilla estora (mat)	parqué parquet (parquet)	almendra califa (almond /caliph)
atún tonyina (tuna)	lubina llobarro (sea bass)	foca foca (seal)	azul teranyina (blue /cobweb)
azúcar sucre (sugar)	canela canyella (cinnamon)	harina farina (flour)	azahar sogre (orange blossom /noose)
barco vaixell (ship)	canoa canoa (canoe)	avión avió (aeroplane)	basto vaixella (coarse /crockery)
barro fang (mud)	tierra terra (earth)	césped gespa (lawn)	tarro sang (jar /blood)
botella ampolla (bottle)	jarra gerra (jug)	plato plat (dish)	bocina amplària (megaphone /width)
búho mussol (owl)	águila àliga (eagle)	avestruz estruç (ostrich)	buzo múscul (diver /muscle)
burro ruc (donkey)	caballo cavall (horse)	oso ós (bear)	berro rec (watercress /donkey)
calabacín carabassó (courgette)	pepino cogombre (cucumber)	limón llimona (lemon)	balancín carboner (seesaw /collier)
calcetines mitges (socks)	medias mitges (tights)	bañador banyador (swimsuit)	maletines mitjans (briefcases /means)
calle carrer (street)	camino camí (path)	túnel túnel (tunnel)	valle cirerer (valley /cherry tree)
cama llit (bed)	sofá sofa (sofá)	mesa taula (table)	caña llet (reed /milk)
cerdo porc (pig)	jabalí senglar (boar)	cebra zebra (zebra)	nardo parc (nard /park)
cerilla llumí (match)	mechero encenedor (lighter)	vela espelma (sail)	cepillo lluna (brush /moon)

Appendix (continued)

Translation	Very close semantic	Less close semantic	Form
colchón matalàs (mattress)	cojín coixí (cushion)	cortina cortina (curtain)	chichón catalans (lump /Catalans)
cordero xai (lamb)	cabra cabra (goat)	ciervo cérvol (stag)	cartero mai (postman /never)
cubo galleda (bucket)	barreño cossi (basin)	escoba escombra (broom)	cabo gallec (cape /Galician)
cuchillo ganivet (knife)	espada espasa (sword)	pistola pistola (pistol)	carrillo ganyota (cheek /grimace)
ensalada amanida (salad)	escalivada escalivada (escalivada)	potaje potatge (stew)	ensaimada ensorrada (pastry /sunken
fresa maduixa (strawberry)	cereza cirera (cherry)	nuez nou (nut)	freno madeixa (brake /hank)
garbanzo cigró (chickpeas)	lentejas llenties (lentils)	fideos fideus (noodles)	garganta mugró (throat /nipple)
gorrión pardal (sparrow)	golondrina orejeta (swallow)	ardilla esquirol (squirrel)	gorrón parlar (pebble /speak)
guisante pèsol (pea)	judía mongeta (bean)	patata patata potato	galante pesat (gallant /heavy)
gusano cuc (worm)	anguila anguila (eel)	abeja abella (wasp)	paisano cua (peasant /queue)
hielo gel (ice)	granizo calamarsa (hail)	niebla boira (fog)	cielo cel (sky/sky)
hilo fil (thread)	lana llana (wool)	cadena cadena (chain)	higo fill (fig /son)
jamón pernil (ham)	salchichón llonganissa (sausage)	tortilla truita (omelette)	jarrón peril (vase /danger)
lagartija sargantana (small lizard)	lagarto llangardaix (lizard)	ratón ratolí (mouse)	baratija tramontana (trinket /northerly)
lata llauna (tin)	bote pot (jar)	bandeja safata (tray)	lado llarga (side /long)
lavadora rentadora (washing machine)	lavaplatos rentaplats (dishwasher)	horno forn (oven)	leñadora montadora (woodcutter /fitter)
lechuga enciam (lettuce)	col col (cabbage)	champiñón xampinyó (mushroom)	lechuza encant (barn owl /charm)
lluvia pluja (rain)	nieve neu (snow)	tornado tornado (tornado)	novia truja (girlfriend /sow)
madera fusta (wood)	corcho suro (cork)	cemento ciment (cement)	madeja fosca (bundle /dark)

Appendix (continued)

Translation	Very close semantic	Less close semantic	Form
manzana poma (apple)	naranja taronja (orange tree)	coliflor coliflor (cauliflower)	manteca pota (lard /leg)
mariposa papallona (butterfly)	polilla arna (moth)	pavo titot (turkey)	marinera paperina (seafaring /cone)
mejillón muscle (mussel)	almeja cloïssa (clam)	ballena balena (whale)	mejilla mascle (cheek /male)
melocotón préssec (peach)	ciruela pruna (plum)	nabo nap (turnip)	malecón préstec (pier /loan)
merluza lluç (hake)	lenguado llenguado (sole)	sapo gripau (toad)	maleza llaç (weeds /knot)
mono mico (monkey)	gorila gorilla (gorilla)	vaca vaca (cow)	mano maco (hand /nice)
muela queixal (molar)	colmillo ullal (tusk)	cuerno banya (horn)	mueca queixar (grimace /complain)
muñeca nina (doll)	marioneta titella (puppet)	puzzle puzzle (puzzle)	muleta eina (crutch /tool)
naranjo taronger (orange tree)	limonero llimoner (lemon tree)	rosal roser (rosebush)	narciso taverner (narcissist /bartender)
paloma colom (dove)	gaviota gavina (seagull)	delfín dofí (dolphin)	pelota color (ball /color)
pañuelo mocador(handkerchief)	bufanda bufanda (scarf)	guantes guants (gloves)	señuelo mirador (bait /viewpoint)
pato ànec (duck)	ganso oca (goose)	tortuga tortuga (tortoise)	palo anar (stick /go)
peca piga (freckle)	verruga berruga (wart)	grano gra (spot)	poco figa (little /fig)
pendiente aracada (slope)	anillo anell (ring)	reloj rellotge (clock)	pariente arribada arrival (relative)
perejil julivert (parsley)	tomillo farigola (thyme)	vainilla vainilla (vanilla)	peregrino jurament (pilgrim /oath)
perro gos (dog)	hiena hiena (hyena)	buey bou (ox)	puerro cós (leek /body)
pimiento pebrot (pepper)	berenjena albergínia (aubergine)	níspero nespra (medlar)	cimiento rebrot (cement /shoot)
pulpo pop (octopus)	calamar calamar (squid)	salmón salmó (salmon)	pulso pou (pulse /well)
queso formatge (cheese)	cuajada quallada (curd)	flan flam (crème caramel)	hueso fullatge (bone / foliage)

Appendix (continued)

Translation	Very close semantic	Less close semantic	Form
rana granota (frog)	salamandra salamandra (salamander)	serpiente serp (snake)	rana granger (branch /farmer)
rodilla genol (knee)	codo colze (elbow)	ojo ull (eye)	colilla gendre (cigarette end /son-in-law)
sábana llençol (sheet)	colcha cobrellit (bedspread)	tapete tapet (tablecloth)	semana llençar (week / throw away)
servilleta tovalló (napkin)	mantel tovalles (tablecloth)	manta manta (blanket)	sirvienta medalló (maid / medallion)
silla cadira (chair)	butaca butaca (armchair)	estantería prestageria (shelf)	villa cadena (town / chain)
sombrero barret (hat)	gorra gorra (cap)	pantalón pantaló (trousers)	bombero barres (fireman / bars)
techo sostre (roof)	tejado teulada (roof)	pasillo passadís (corridor)	hecho rostre (fact / face)
tiburón tiburó (shark)	orca orca (killer whale)	cangrejo cranc (crab)	tirabuzón tauló (curl / plank)
tijeras estisoras (scissors)	alicates alicates (pliers)	destornilla tornavís (screwdriver)	literas estirades (bunks / stretched)
tormenta tempesta (storm)	hurcán huracà (hurricane)	terremoto terratrèmol (earthquake)	torpeza tempor (clumsiness /temporary)
trigo blat (wheat)	centeno civada (rye)	avellana avellana (hazelnut)	trago blau (drink /blue)
uva raïm (grape)	pasas panses (raisins)	remolacha remolatxa (beetroot)	uña raig (nail / ray)
vaso got (glass)	taza tassa (cup)	fuente font (fountain)	paso tot (step / whole)
ventana finestra (window)	puerta porta (door)	armario armari (cupboard)	ventaja sinistra (advantage /left)
yegua egua (mare)	mula mula (mule)	elefante elefant (elephant)	legua fugida (league / leak)
zanahoria pastanaga (carrot)	rábano rave (radish)	albaricoque albercoc (apricot)	zapatería pastoreta (shoe shop/shepherdess)
zumo suc (juice)	batido batut (milkshake)	aceite oli (oil)	grumo sac (lump/ bag)

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Study 2

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Semantic similarity: normative ratings for 185 Spanish noun triplets

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Abstract The present study introduces the first Spanish database with normative ratings of semantic similarity for 185 word triplets. Each word triplet is constituted by a target word (e.g., *guisante* [pea]) and two semantically related and nonassociatively related words: a word highly related in meaning to the target (e.g., *judía* [bean]), and a word less related in meaning to the target (e.g., *patata* [potato]). The degree of meaning similarity was assessed by 332 participants by using a *semantic similarity rating task* on a 9-point scale. Pairs having a value of semantic similarity ranging from 5 to 9 were classified as being more semantically related, whereas those with values ranging from 2 to 4.99 were considered as being less semantically related. The relative distance between the two pairs for the same target ranged from 0.48 to 5.07 points. Mean comparisons revealed that participants rated the more similar words as being significantly more similar in meaning to the target word than were the less similar words. In addition to the semantic similarity norms, values of concreteness and familiarity of each word in a triplet are provided. The present database can be a very useful tool for scientists interested in designing experiments to examine the role of semantics in language processing. Since the variable of semantic similarity includes a wide range of values, it can be used as either a continuous or a dichotomous variable. The full database is available in the supplementary materials.

Keywords Semantic similarity · Semantic norms · Normative ratings · Concreteness · Familiarity

One of the central topics in the study of semantic memory has been the question of how meaning is represented in the human mind/brain. Theories of semantic memory can be divided into two broad classes: Whereas some authors consider that word meaning is represented in a holistic manner (Anderson, 1983; Collins & Loftus, 1975; McNamara, 1992), other authors propose that word meaning is represented in a distributed manner (Minsky, 1975; Moss, Hare, Day, & Tyler, 1994; Norman & Rumelhart, 1975; Plaut, 1995; Rosch & Mervis, 1975; Smith, Shoben, & Rips, 1974).

According to the holistic, nondecompositional view of Collins and Loftus (1975), concepts have holistic representations, since they are represented by single nodes in a semantic network. For instance, in a semantic network, the concept *apple* would be represented by a single node, which, in turn, would be connected to other related concepts (i.e., nodes), such as *green*. The concepts *apple* and *green* would be connected, since the second is a property of the first. In its turn, *green* would also be connected to other concepts, such as *bean*, since *green* is a property of the concept *bean*. In such a semantic network, *apple* and *bean* may become indirectly connected via this common property (i.e., *green*). The more properties that two concepts share, the more connections will be established between them.

Contrary to the holistic view, distributed models of semantic memory assume that word meaning is represented not by a single node, but by a set of nodes, each representing a feature (or a micro-feature) of a concept. In other words, meaning is decomposable into many different features, and each of these

Rosa Sánchez-Casas is deceased.

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features can be part of the meaning of multiple concepts. For instance, *apple* and *bean* are similar in meaning because their representations share common features (e.g., both are foods, can be green, etc.). Although the holistic and distributed views differ in the ways in which they conceptualize meaning, both approaches assume that the critical components of concepts are properties or features and that the similarity between concepts depends on the features that they have in common. In fact, the semantic similarity between lexical concepts has become one of the most central theoretical issues in the study of meaning representation. During the last decades, a great effort has been devoted to obtaining empirical measures of semantic similarity, with the aim of using such measures in the experimental study of semantic memory (McRae & Boisvert, 1998; Sánchez-Casas, Ferré, García-Albea, & Guasch, 2006; Vigliocco, Vinson, Lewis, & Garrett, 2004). In accordance with this previous work, the main aim of the present study is to provide a normative database for a set of 185 triplets of semantically related Spanish words. Each triplet is constituted by a target word, which is paired with two semantically related words (i.e., one highly related and the other less related in meaning). Such a database can be very useful for researchers who aim to design experiments to study semantic memory and to examine how meaning is represented in the human mind/brain.

One of the most commonly used paradigms for the study of semantic memory is the *semantic-priming paradigm* (Meyer & Schvaneveldt, 1971). In this paradigm, participants are typically presented a first word (i.e., the prime) followed by a second word (i.e., the target), and they are asked to make a decision about the target. The semantic-priming effect refers to the robust finding that participants respond faster to the target word (e.g., *eagle*) when it is preceded by a semantically related prime (e.g., *owl*) than when it is preceded by a semantically unrelated prime (e.g., *doctor*). This effect has been observed with tasks such as the lexical decision task (LDT), in which participants have to decide whether or not the target is an existing word. Given that semantic relatedness exerts a clear influence even in nonsemantic tasks such as the LDT, which requires little access to meaning, it has been suggested that semantic priming reflects the underlying organization of concepts in semantic memory (Meyer, Schvaneveldt, & Ruddy, 1975). In fact, both of the theoretical views about semantic memory organization can account for semantic-priming effects. For the holistic point of view, reading a prime word (e.g., *owl*) leads to automatic spreading of activation to the associated or related concepts (e.g., *eagle*; Anderson, 1983; Collins & Loftus, 1975; Neely, 1977). Alternatively, according to distributed models, when the target and the prime are semantically related (i.e., share a subset of features), the presentation of the prime activates part of the target's representation. That is, the features shared by the prime and the target are activated, thus leading to faster responses in comparison to when the prime and the target are semantically unrelated (Fischler, 1977).

In a wide sense, primes and targets can be considered to be semantically related if they are members of the same category (e.g., *whale–dolphin*; Frenck-Mestre & Bueno, 1999; Lupker, 1984; Neely, Keefe, & Ross, 1989), if they are synonyms (e.g., *country–nation*; Perea & Rosa, 2002), if they have a functional relation (e.g., *hammer–nail*; Moss, Ostrin, Tyler, & Marslen-Wilson, 1995), or if they have a part–whole relation (e.g., *stem–flower*; Thompson-Schill, Kurtz, & Gabrieli, 1998). A different type of relationship that has been widely examined in the semantic-priming literature is *associations* between prime and target (e.g., *mouse–cheese*; for reviews, see Hutchison, 2003, and Lucas, 2000). Whereas semantic relatedness reflects the similarity in meaning between two concepts, associative relations between pairs of words are mainly based on co-occurrence and are thought to reflect word use rather than meaning overlap (McNamara, 1992; Plaut, 1995). A hotly debated topic in the study of semantic memory has been the extent to which similar experimental effects can be obtained with associative relations and with semantic relations not involving association (see Hutchison, 2003, and Lucas, 2000 for overviews). This question has been addressed in the field of word comprehension, as well as in word production. Concerning visual word recognition, it has been repeatedly demonstrated that both semantic and associative relations are able to produce semantic priming (Perea & Rosa, 2002; Sánchez-Casas, Ferré, Demestre, García-Chico, & García-Albea, 2012). Conversely, auditory word recognition studies that have used the visual-world paradigm (in which the pattern of eye movements is recorded) reveal that participants' performance is sensitive to semantic relations, but not to associative relations (Yee, Overton, & Thompson-Schill, 2009). With respect to production studies, a commonly used tool is the picture–word interference task, in which participants are presented successively with a word and a target picture to be named, and the type of relation between the two stimuli is manipulated. Several studies in the field have revealed that whereas semantically related words produce an interference effect in picture naming, associatively related words produce a facilitatory effect (Alario, Segui, & Ferrand, 2000; La Heij, Dirkx, & Kramer, 1990).

In order to dissociate associative and semantic relations, it is necessary to have pairs of semantically related words that are not associated, as well as pairs of associatively related words that are not semantically similar. Several studies have been conducted to provide normative measures for both types of relations. The procedure used to obtain the associative strength between two words consists of presenting participants with a *cue* word (e.g., *mouse*) and asking them to produce the first word that comes to mind (e.g., *cheese*). Whereas in some cases, as in the *mouse–cheese* example, the two words do not share semantic features, in other cases, the first word that comes to mind after being presented with the cue word does share semantic features with the eliciting word (e.g., *table–chair*; for a detailed list of different kinds of associative relationships, see Hutchison, 2003). The *associative strength* between two words is the proportion of participants who responded with a particular word after being presented with a cue word. During the last few years, several databases have been published for associative norms in different languages, such as Dutch (De Deyne & Storms, 2008), English (Nelson, McEvoy, & Schreiber, 2004), European Portuguese (Comesaña, Fraga, Moreira, Frade, & Soares, 2014; Marques, 2002), French (Thérouanne & Denhière, 2004), Hebrew (Kenett, Kenett, Ben-Jacob, & Faust, 2011), Japanese (Joyce, 2005), and Spanish (NIPE; Díez, Fernández, & Alonso, 2006; Fernandez, Diez, Alonso, & Beato, 2004). These databases are helpful tools in the selection of the experimental materials for studies examining the role of associative strength in word recognition and production. For instance, Sánchez-Casas et al. (2012) examined the pattern of semantic-priming effects in an LDT by manipulating associative strength and having semantically related pairs that were and were not associatively related. Therefore, using the NIPE database (Díez et al., 2006; Fernandez et al., 2004), Sánchez-Casas et al. (2012) selected semantically related pairs that were strongly associated (e.g., *mesa* [table]–*silla* [chair]) and semantically related pairs that were weakly associated (*sapo* [toad]–*rana* [frog]). The study also included pairs that were only semantically related (*codo* [elbow]–*rodilla* [knee]). The authors found that, when primes were briefly presented (50 ms), associative strength modulated the effects, since significant priming was only obtained with strongly associated pairs, but not with weakly associated or nonassociated pairs.

Regarding the empirical procedures used to obtain semantic similarity measures, one of the most commonly used tasks is *feature generation*. In this task, participants are presented with a set of words and are asked to list features that they consider relevant to describing and defining the meaning of each word (McRae, Cree, Seidenberg, & McNorgan, 2005; McRae, de Sa, & Seidenberg, 1997; Sánchez-Casas et al., 2006, Vigliocco et al., 2004; Vinson & Vigliocco, 2008). With the features given by the participants, it is possible to obtain a measure of semantic relatedness or similarity between any pair of words by calculating the number of features that the two words share (McRae et al., 1997; Sánchez-Casas et al., 2006). During the last several years, several databases have been published using this (or a similar) approach in different languages, such as Dutch (De Deyne et al., 2008), English (McRae et al., 2005; Vinson & Vigliocco, 2008), Italian (Kremer & Baroni, 2011), and German (Kremer & Baroni, 2011). Concerning Spanish, although no normative database has been published to date, Sánchez-Casas et al. (2006) used the feature generation task to obtain a set of 72 semantically related pairs of words that were tested in a series of semantic-priming experiments (see below). This study, along with others in the field, has shown that the degree of semantic overlap between two words (in terms of the number of features that they share) can influence the magnitude of the experimental effects obtained. For instance, highly semantically related words produced more facilitation effects than did words less semantically related in a semantic-priming paradigm (Cree & McRae, 2003; Sánchez-Casas et al., 2006; Vigliocco et al., 2004). Other tasks, such as the picture–word interference task, have also revealed a modulation of effects by semantic overlap, although the pattern of results has not been consistent. In one study, picture-naming latencies were faster in the context of more semantically related words, relative to less semantically related words (Mahon, Costa, Peterson, Vargas, & Caramazza, 2007). However, a recent picture-naming study failed to replicate the facilitation effect, showing larger interference effects for more than for less semantically related words (Vieth, McMahon, & de Zubicaray, 2014).

Although during the last decade the use of feature norms has been one of the most widely used empirical approach for measuring semantic overlap, this method is time-consuming and has several limitations (see McRae et al., 2005, for a detailed discussion of the limits of feature norms). These limitations have led some authors to explore alternative methods. One such method is the collection of similarity judgments by means of the *semantic similarity-rating task* (Ferrand & New, 2003; Perea & Rosa, 2002). In this task, participants are presented with pairs of words (e.g., *owl–eagle*) and are asked to rate the similarity in meaning between the two words by using a Likert-like scale (Ferrand & New, 2003; Sánchez-Casas et al., 2006). Pairs selected from the similarity-rating task have been shown to produce priming effects. For instance, Ferrand and New, in an attempt to dissociate semantic relatedness from association, selected a set of nonassociated French word pairs and asked participants to rate on a 7-point scale (1 = *not at all similar*, 7 = *highly similar*) the meaning similarity between the two words of a pair. By selecting only the pairs that were judged as being more similar (mean: 5.0), the authors conducted a series of experiments that showed reliable semantic-priming effects (see Perea & Rosa, 2002, for a similar pattern of results).

It is worth mentioning here that some studies have used both the feature generation task and the semantic similarity-rating task. The most relevant finding of these studies is that a highly significant correlation exists between the measures of semantic similarity obtained by the two different procedures (McRae et al., 1997; Sánchez-Casas et al., 2006). For instance, Sánchez-Casas et al. (2006) selected, on the basis of their intuition, a set of 72 Spanish semantically related word triplets. The first word in each triplet (e.g., *burro* [donkey], hereafter the *target* word) was paired with two semantically (and nonassociatively) related words, one being more similar (e.g., *caballo* [horse]) and another being less similar (e.g., *oso* [bear]) in meaning. Then, the authors used both the semantic similarity-rating task and the feature generation task to assess the degrees of meaning similarity for the 72 word triplets. Thus, they obtained two different values of semantic similarity, one from the semantic similarity-rating task and the other from the feature generation task (the Euclidean distance between the target words and both the more and less similar words was calculated from the features provided by participants). The authors calculated the correlation between the measures provided by the two tasks and found this correlation to be highly significant (see Bueno & Frenck-Mestre, 2008; McRae et al., 1997, for similar results); that is, the higher the rating of similarity between two words, the smaller the semantic distance between them. Finally, the authors conducted a semantic-priming study with this set of words. They observed that the magnitude of the semantic-priming effect was dependent on the degree of semantic similarity, because more semantically related words produced stronger effects than did less semantically related ones. Subsequently, using the same materials in a bilingual version of the original experiment (i.e., the first word was presented in one language and the second in another language), a series of priming experiments (Guasch, Sánchez-Casas, Ferré, & García-Albea, 2011) and a series of translation recognition experiments (Ferré, Sánchez-Casas, & Guasch, 2006; Moldovan, Sánchez-Casas, Demestre, & Ferré, 2012) were conducted. The main finding of this set of bilingual studies was that the degree of semantic similarity also affects cross-language processing, since more semantically related words produced greater facilitation effects in priming and more interference with translation recognition than did less semantically related words. What can be concluded from the above-mentioned studies are two important points: Firstly, semantic similarity ratings provide a measure that can predict the magnitude of semantic priming, and, secondly, the values of semantic similarity obtained from semantic similarity ratings and from feature norms are highly correlated. These findings support the validity of the semantic similarity-rating task as a good approach to obtaining measures of semantic similarity between two words. Moreover, the semantic similarity-rating task has a clear advantage over the feature generation task, since it is less time-consuming.

In the present study, we aimed to provide a normative database of semantic similarity for a set of 185 nonassociatively related Spanish word triplets (a target word and two words semantically related to the target: a highly related word and a less related word), obtained by means of the semantic similarity-rating task. This database would be useful in investigating different issues regarding the role of semantics in visual and auditory word recognition as well as in word production, because it provides researchers with a set of semantically related words that are not associatively related. Considering that in Spanish there are normative free association data (NIPE; Díez et al., 2006; Fernandez et al., 2004), but no published database includes semantically related words that are not associatively related, the present database could fill this gap. Moreover, this set of semantically related words could also be used in studies examining language processing in bilinguals. In fact, the use of semantically related words across languages has been a common strategy in testing the predictions of some of the most influential models of bilingual memory organization, such as the revised hierarchical model (Kroll & Stewart, 1994) and the distributed representational model (De Groot, 1992a, 1992b) (e.g., Altarriba & Mathis, 1997; Ferré et al., 2006; Sunderman & Kroll, 2006; Talamas, Kroll, & Dufour, 1999). It is worth mentioning that because the variable of semantic similarity in the present database includes a wide range of values, it can be used as a continuous variable to select semantically related pairs. Alternatively, researchers interested in examining the role of the degree of meaning similarity in lexical processing can use our classification of pairs as being either more or less semantically related. The issue of how the degree of meaning similarity might affect lexical processing has begun to receive attention in studies in both the monolingual (Cree & McRae, 2003; Mahon et al., 2007; Sánchez-Casas et al., 2006; Vieth et al., 2014) and the bilingual (Guasch et al., 2011; Moldovan et al., 2012) domains, and given its relevance, deserves some more attention (van Hell & Kroll, 2012). Finally, the present database could also be used not only in reaction time studies, but also in research using other measures, such as electrophysiological recordings. For instance, in a recent study conducted with Chinese–English bilinguals, Guo, Misra, Tam, and Kroll (2012) demonstrated that semantic relatedness across languages affected the pattern of neural responses, as revealed by event-related potentials.

To sum up, we present a database that could be a useful tool for studies aiming to further investigate semantic processing. It is important to note that it can be used in both the monolingual and bilingual domains, as well as with different experimental paradigms and types of measures. In order to facilitate stimulus selection, the database provides for each word values of concreteness and familiarity, two important variables known to affect word processing (Balota, Cortese, Sergent-Marshall, Spieler, & Yap, 2004).

Method

Overview of the procedure and criteria used to develop the present database

The first step in the development of the present database was the selection of 278 sets of triplets. Each triplet contained a target word that was paired with two semantically related words, one more similar in meaning and the other less similar in meaning to the target (see the Materials section below). Since we aimed to develop a database of words that were semantically related only, a series of controls were applied in order to minimize the influence of nonsemantic factors. For instance, to avoid any influence of form similarity on the ratings, we calculated the orthographic similarity between each related word and the target (i.e., the more related word with respect to the target, and the less related word with respect to the target). The reason was to assure that this similarity was low for each pair, in order to avoid any bias produced by formal similarity when participants performed the semantic similarity rating task (see the Controlling for Orthographic Similarity section below). To avoid pairs that were associatively related, we checked the associative strength between the two members of each pair in the free association norms for Spanish words (NIPE; Díez et al., 2006; Fernandez et al., 2004). In addition, we conducted a free association study with the words of the database that were not included in the Spanish association norms (see the Excluding Associates section for further details). Once we had obtained the associative strength (i.e., the proportion of participants who provided a given word as an associate in response to another word, ranging from 0 to 1) between the members of our pairs, we excluded from our initial selection those pairs whose members had an associative strength higher than .10. This criterion was used because pairs of words with values lower than .10 are usually considered not to be associatively related (Nelson, McEvoy, & Schreiber, 1998). As a consequence, 28 triplets were excluded. We obtained the values of semantic similarity for the remaining 250 triplets through a series of questionnaires that were administered in two rounds (see the First and Second Round Questionnaires below). In the first round, we obtained 18 responses for each pair and calculated the average semantic similarity for pairs considered as being more and less semantically related in our initial classification. In the second round, we aimed to reach a minimum of 28–30 responses per pair. After having reached 28 to 30 responses per pair, we calculated the mean (4.91), the standard deviation (1.42), and the standard error of the mean (*SEM* = 0.26). The obtained *SEM* value was considered to be rather small and precise enough for a 9-point scale; the *SEM* of 0.26 indicated that the size of the sample was appropriate. In order to classify the pairs into the more and less semantically related items, we relied on the criteria used in some previous studies, in which participants' performance was affected by the degree of similarity in meaning (McRae & Boisvert, 1998; Sánchez-Casas et al., 2006). Thus, we considered pairs having a value of semantic similarity ranging from 5 to 9 as being more semantically related, and pairs with values ranging from 2 to 4.99 as being less semantically related. Furthermore, the statistical comparison between the more and less similar pairs should reveal a significant difference. The initially selected triplets in which either the more or the less similar word did not fall in the established interval were removed from the database. This resulted in the exclusion of 65 triplets, reducing the set of word triplets to 185. Finally, subjective ratings of concreteness and familiarity were obtained for all of the words in the database. In what follows, we will describe in detail the procedure, as well as the analyses conducted, to obtain the present database.

Participants

A total of 570 students participated in the present study: 332 participated in the similarity rating task (mean age = 22.0 years, *SD* = 4.05; 48 males and 284 females), 80 participated in the concreteness rating task (means age = 20.6 years, *SD* = 3.20; 11 males and 69 females); 80 participated in the familiarity rating task (means age = 20.3 years, *SD* = 2.45; 68 females and 12 males); and 78 participated in the free association task (mean age = 20.3 years, *SD* = 2.15; 65 females and 13 males). They were undergraduate students from the Universitat Rovira i Virgili and participated voluntarily in the study. Importantly, no participant took part in more than one task.

Materials

A set of 278 Spanish nouns were initially selected (e.g., *guisante* [pea]; hereafter, the *target* word). Each target word was paired with two words that were semantically related, but one was more similar in meaning to the target (e.g., *guisante–judía* [bean]; hereafter, the *more similar* word) than the other (e.g., guisante–*patata* [potato]); hereafter, the *less similar* word), resulting in 278 word triplets. The initial classification of the pairs into more and less similar was based on our own intuition. Concerning the type of relations included, the two members of the pair belonged to a given semantic category (such as animals, vegetables, articles of furniture, parts of the body, articles of clothing, tools, weather phenomena, professions, etc.). However, we did not include superordinate category names, synonyms, antonyms, or part–whole relations.

Procedure and data analysis

Controlling for orthographic similarity

In developing the present database, we wanted to be sure that semantic similarity ratings would not be affected by orthographic similarity. Thus, we looked for values of orthographic similarity between the two members of the 556 pairs (278 triplets) in the NIM database (Guasch, Boada, Ferré, & Sánchez-Casas, 2013). NIM provides different indexes of orthographic similarity. The index that we used was obtained from the application of the Van Orden's (1987) algorithm, on a scale that ranged from 0 (*not similar at all*) to 1 (*exactly the same thing*). Table 1 shows the mean values of orthographic similarity for the more and less semantically related words with respect to the target. We found no significant difference between these means, $t(184) = 1.89$, $p > .05$.

Excluding associates

Since our aim was to provide a database of semantically related words that were not associatively related, we ensured that the two members of the pairs were neither forward nor backward associatively related according to word association norms. To check the associative strength of our pairs, we used the Spanish association norms (NIPE; Díez et al. 2006; Fernandez et al., 2004). This database provides associates for 5,819 cue words produced by people in free association tasks. We checked the forward association to be sure that any given target word (e.g., *guisante*) did not produce as associates either the more similar (e.g., *judía*) or the less similar (e.g., *patata*) semantically related word. Moreover, the backward association strengths of the more and less similar words with the corresponding target words were also checked. That is, we ensured that neither the more similar nor the less similar word was associatively related to the target. Given that words from some of the pairs were not in the NIPE database, a free association task was conducted with these words (i.e., 177 words: 40 targets, 73 more similar words, and 64 less similar words). These words were randomized and grouped in three different lists, with 59 words each. Seventy-eight participants (26 for each list) were asked to perform the task, following the same instructions as in NIPE database. Thus, participants were instructed to write, for each word in the list, the first word that came to their minds. We removed all triplets in which the associative strength (either forward or backward) between the target and the more similar word or between the target and the less similar word was higher than .10. By applying this criterion, 28 word triplets were excluded from the set, resulting in a set of 250 word triplets that were only semantically related. Table 1 shows the average forward and backward associative strength values for the more and the less semantically related pairs.

Table 1 Mean and standard deviations (in parentheses) of semantic similarity, forward association, backward association, and orthographic similarity between target words and the more and less similar words

	More Similar Word	Less Similar Word
Semantic similarity	6.13 (0.70)	3.69 (0.73)
Forward association	.01 (.02)	.00 (.00)
Backward association	.02 (.02)	.00 (.00)
Orthographic similarity	.19 (.16)	.17 (.14)

Ratings of semantic similarity

Once we were sure that the selected pairs had no (or low) orthographic overlap and were not associatively related, we collected the semantic similarity ratings, which was the main aim of the present study. The semantic similarity ratings were obtained through a series of questionnaires administered in two different rounds.

First round of questionnaires We constructed 10 questionnaires with the 250 triplets. Each questionnaire contained 75 word pairs: 25 pairs in which the target word was paired with a more similar word (e.g., *guisante–judía*), 25 pairs in which the target word was paired with a less similar word (e.g., *fresa–nuez* [strawberry–walnut], and finally, 25 unrelated pairs that were included as fillers (e.g., *piedra–violín* [stone–violin]). We took care that a target word (e.g., *guisante*) that was paired with a more similar word in a given questionnaire was presented with a less similar word in another questionnaire. That is, any participant saw a target only once in a given condition (with either a more or a less similar pair). The 25 fillers were the same across the ten questionnaires. The different pairs were randomly distributed within each questionnaire.

To obtain the degrees of semantic similarity between the 500 pairs, we used a *semantic similarity rating task* following the same procedure as in previous studies (Ferrand & New, 2003; Markman & Gentner, 1993; Moss et al., 1995; Puerta-Melguizo, Bajo, & Gómez-Ariza, 1998; Sánchez-Casas et al., 2006). In particular, we used the same instructions as Sánchez-Casas et al. (2006). That is, participants were instructed to rate the similarity in meaning of the things to which the two words in the pairs referred, on a scale from 1 (*not all similar*) to 9 (*exactly the same thing*) (see the Instructions in English in Appendix 1 and the original Instructions in Spanish in Appendix 2). Two examples were provided. A total of 180 participants completed the task, with each questionnaire being evaluated by 18 participants. The average duration of the task was 15 min. We stopped at 18 participants per questionnaire to make a preliminary analysis, in order to examine whether the selected pairs fulfilled the above-mentioned criterion to be considered more or less semantically related (i.e., semantic similarity ratings from 5 to 9 for more similar pairs and from 2 to 4.99 for less similar pairs, respectively). With this aim, we computed a value of semantic similarity for each pair by averaging the ratings of the 18 participants who had rated a pair. From the initial 250 triplets, 184 triplets met the criterion. Concerning the remaining 66 triplets, in 21 cases the more similar word paired with the target had a good value of semantic similarity (e.g., *alcantarilla–desagüe*, [sewer–drain]: mean = 6.33), but the less similar word had a score above 5 (e.g., *alcantarilla–tubería*, [sewer–pipe]: mean = 6.18). Another 45 triplets showed the opposite pattern (i.e., they had a good value for the less similar word but not for the more similar one). Those 66 triplets were removed and substituted with new semantically unassociated words (as checked in NIPE; Díez et al., 2006; Fernandez et al., 2004). For example, *pozo* [well] was substituted for *tubería* as a word less similar to the original target (i.e., *alcantarilla*).

Second round of questionnaires The task and procedure were the same as in the first round. The aim was to achieve at least between 28 and 30 evaluations for each pair of the 250 triplets. Thus, for the pairs that fulfilled the criterion in the first round, more ratings had to be obtained in order to have the desired number of evaluations. In addition, similarity ratings for the new pairs (i.e., those in which one member was substituted for not meeting the above-mentioned criterion) had to be obtained. With all of these pairs, we constructed 14 different questionnaires. As in the first round, we avoided the repetition of any target word in the same questionnaire. The questionnaires that included the pairs that had met the criterion in the first round were completed by 10 to 12 new participants, and those that included the new pairs of words were responded by 28 to 30 new participants, resulting in a total of 152 participants (mean age = 21.8 years, *SD* = 3.83; 19 males and 133 females).

The value of semantic similarity for every pair was computed by averaging the scores of the 28–30 participants who had rated it. After applying the aforementioned criterion to classify the pairs as more or less semantically related, 65 triplets were excluded, leading to a final set of 185 triplets. If we consider the overall database (see the supplementary materials), our pairs included a wide range of semantic similarity values, with the highest value being 8.20 and the lowest value 2.07. Concerning the difference between the more and less similar pairs in each triplet, the minimum difference was 0.48 points, and the maximum difference was 5.07 points. The distribution of this variable was as follows: 12 triplets had a difference ranging from 0 to 0.99 points, 48 triplets had a difference ranging from 1 to 1.99, 79 triplets had a difference ranging from 2 to 2.99, 34 triplets had a difference ranging from 3 to 3.99, and 12 triplets had a difference value greater than 4. Table 1 shows the means and standard deviations of the semantic similarity ratings for the more and less semantically related words. An analysis conducted to compare the average values of semantic similarity for the more and less similar pairs (with respect to the same target) revealed that the difference of 2.44 points was significant [$t(184) = 36.471$, $p < .000$, $d = 2.68$]. Thus, participants rated the more similar words (e.g., *judía*) as being significantly more similar in meaning to the target word (e.g., *guisante*) than were the less similar words (e.g., *patata*). On the basis of this result, we can conclude that our semantically nonassociatively related word pairs differ in their degrees of semantic similarity.

Values of concreteness and familiarity

In the present database, we also provide values of concreteness and familiarity for the 555 words contained in the 185 triplets. We looked for these variables in a published Spanish database (EsPal; Duchon, Perea, Sebastián-Gallés, Martí, & Carreiras, 2013), which contained values for 335 of our 555 words. To obtain the values for the remaining 220 words, we conducted a rating study, using the same instructions and scale as had been in EsPal (see the Appendices). Because most of those 220 words were concrete (names of animals, vegetables, tools, objects, etc.), we included 152 fillers that in our intuition were more abstract (e.g., *capacity*). With those 372 words, we created four different questionnaires, each one containing 93 words. Furthermore, two forms of each of the four questionnaires were created, one for concreteness and the other for familiarity. Eighty participants (20 per version) evaluated concreteness and 80 more participants rated the words' familiarity. The scales for both concreteness and familiarity ranged from 1 to 7. Concerning concreteness, 1 represented the *minimum level* of concreteness, and 7 the *maximum level*. Regarding familiarity, 1 meant *not familiar at all*, and 7 *very familiar*. Table 2 shows the mean values of concreteness and familiarity for the words included in the database.

In order to examine whether concreteness and/or familiarity have an influence on semantic similarity ratings, we calculated the Pearson correlations between semantic similarity values and the two aforementioned variables. We failed to find any significant correlation. Thus, the values of semantic similarity for the more similar words were not related to either concreteness ($r = .06$, $p > .05$) or familiarity ($r = .03$, $p > .05$). Similarly, semantic similarity for less similar pairs did not correlate with either concreteness ($r = .04$, $p > .05$) or familiarity ($r = .09$, $p > .05$).

Relation between the values of the present database and those of the study of Sánchez-Casas et al. (2006)

Since several of the triplets of Sánchez-Casas et al.'s study (2006) were included in the present database, we decided to examine the consistency of the semantic similarity ratings across different participants. Thus, we examined whether there was a relationship between our values of semantic

Table 2 Mean values of concreteness and familiarity for the words included in the database

	Target Word	More Similar Word	Less Similar Word
Concreteness	5.90	5.72	5.88
Familiarity	5.66	5.54	5.64

Standard deviations are not reported because the EsPal (Duchon et al., 2013) database does not provide these values similarity and those reported by Sánchez-Casas et al. (2006). Fifty-one out of the original 72 triplets used by Sánchez-Casas et al. (2006) were included in the present database. The 21 remaining triplets were excluded, given that they did not meet the criteria we have followed in the present study (see the Procedure and Data Analysis section). New semantic similarity ratings had been collected for these 51 triplets. A highly significant correlation between the new ratings and the values reported by Sánchez-Casas et al. (2006) was obtained for these triplets (r = .849, p < .001). Furthermore, the new similarity ratings were also highly correlated with the values of Euclidean semantic distance obtained by Sánchez-Casas et al. (2006) with the feature generation task (r = –.684, p < .001), suggesting that, as semantic distance increases, semantic similarity decreases.

Conclusion

The present study aimed to provide a Spanish database containing norms for semantically related and nonassociatively related word pairs with different degrees of meaning similarity. The database is organized in triplets including a target and two words, one of which is more semantically related, and the other less semantically related, to the target. We used the value of 5 as a cutoff point to classify pairs into those that were more and less semantically related. We did not exclude pairs in which the difference in semantic similarity between the more and the less similar words was small; we considered that the best option was to provide researchers with a database from which they could select pairs according to their particular interests and needs (e.g., to select only triplets whose pairs had a difference of three or more points in semantic similarity values). Furthermore, semantic similarity can be used as a continuous variable (i.e., by selecting a large set of pairs differing in semantic similarity) or as a dichotomous one (i.e., by selecting for each target the more and the less semantically related words).

To the best of our knowledge, this is the first Spanish database with these characteristics. Several published databases in different languages have provided values of semantic relatedness between words obtained through feature generation tasks (e.g., Kremer & Baroni, 2011; McRae et al., 2005; Vinson & Vigliocco, 2008). It is important that researchers interested in the effects of semantic similarity on word processing be able to select their stimuli from databases conducted in the language under study, and not from databases conducted in a different language. This allows researchers to rule out the effects of variables such as orthographic similarity or associative strength, which can vary across languages. It is worth mentioning that although the values of semantic similarity provided in the present database were not derived from a feature generation task, a high correlation between our similarity ratings and semantic distance (calculated from values obtained from a feature generation task) was obtained for those pairs used both in the present study and in Sánchez-Casas et al.'s (2006) study. This result shows that the similarity rating task can be a reliable measure of semantic similarity, and that such a task can be used instead of having to collect semantic features, which is a highly time-consuming procedure.

The present database was developed with rigorous controls of orthographic similarity and associative strength. In addition, subjective ratings of concreteness and familiarity are provided. It could be argued that the visual similarity between the objects to which the two words in the pairs referred should have also been controlled, since there seems to be a correlation between semantic distance and visual similarity (Vitkovitch, Humphreys, & Lloyd-Jones, 1993). We cannot rule out the possibility that our ratings of semantic similarity were affected by visual similarity. Nevertheless, if we take into account that most of the words in the database are concrete, we can assume that this possible influence would be constant across pairs. On the other hand, visual similarity might be especially relevant for studies involving pictures, in tasks such as the picture–word interference task (but see Damian, Vigliocco, & Levelt, 2001, for results showing that even when visual similarity is controlled for, there is an effect of semantic relatedness). Its relevance is probably smaller in tasks and paradigms such as semantic priming, which only use words.

Overall, we consider that the present database can be very useful for selecting stimuli in research aimed to study the role of semantics in language processing. The semantic similarity values can be used in different experimental paradigms and tasks (e.g., the semantic priming paradigm, the picture–word interference task, the visual-world paradigm, or the translation recognition paradigm) that use both behavioral (e.g., reaction times and eye movement recordings) and electrophysiological measures.

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Appendices

Appendix 1

Instructions for the similarity rating

In accordance with Sánchez-Casas et al. (2006), the specific instructions for the familiarity rating task were as follows (translated):

You will be presented with a list of pairs of words. Think about the meaning of the two words of the pair and indicate, on a scale from 1 to 9, how much you think that the two words in the pair refer to similar things. If you consider that the two words refer to very similar things, please choose 9. If you consider that the two words refer to very different things (they are nothing alike), please choose 1. You could mark any value on the scale. If you do not know the meaning of some word of the pairs, please, cross out this word and do not evaluate this pair.

Example:
If the pair is *professor–teacher*, you could mark 8:

Not Similar **Very Similar**

1	2	3	4	5	6	7	8	9
							X	

If the pair is *moon–track*, you could mark 1:

Not Similar **Very Similar**

1	2	3	4	5	6	7	8	9
X								

Instructions for the concreteness rating

In accordance with EsPal (Duchon et al., 2013), the specific instructions for the concreteness ratings were as follows (translated):

You will participate in a language research. Your task is to rate the following words in terms of their *concreteness*. The level of concreteness of a word can be defined as the extent to which it has a specific content. For example, the word "object" has a low level of concreteness because its content can include a varied set of different objects. The word "object" can be applied either to a ball, to a lamp, to a chair, to a car, etc. Conversely, the word "hanger" has a high level of concreteness because its content can be applied to a very restricted set of objects. Most of the words can be located at any intermediate point between the two extremes of the scale. You have to do your ratings by using a 1 to 7 scale. A score of 1 indicates a minimum level of concreteness (very abstract words). Conversely, a score of 7 indicates a maximum level of concreteness (very concrete words). You can use any of the intermediate values of the scale.

Instructions for the familiarity rating

In accordance with EsPal (Duchon et al., 2013), the specific instructions for the familiarity ratings were as follows (translated):

You will participate in a language research. Your task is to rate the following words in terms of their familiarity. You have to rate how often the word occurs in everyday language, both in the spoken and in the written form. For example, you may hear the word on conversations, at the radio, on movies, at TV, or you may find it in a written form in magazines, books, Internet, etc. You have to do your ratings by using a 1 to 7 scale. A score of 1 indicates that you rarely find the word in everyday language. Conversely, a score of 7 indicates that you find the word almost always in everyday language. You can use any of the intermediate values of the scale.

Instructions for the free association task

In accordance with NIPE (Díez et al., 2006; Fernandez et al., 2004), the specific instructions for word association were as follows (translated):

You will be presented with a list of words. Read, one by one, each word and write the first Spanish word which comes to your mind after reading the printed word. That is, write the first word that comes to your mind. Do it as fast as you can. There are no right or wrong answers.

Appendix 2

Original instructions for the similarity rating (Spanish)

A continuación se te presenta una lista con pares de palabras. Piensa a qué se refiere cada una de las palabras del par e indica, en una escala de 1 a 9, hasta qué punto crees que las dos palabras del par se refieren a cosas semejantes. Si consideras que las dos palabras se refieren a cosas muy semejantes, deberás marcar un 9. Si consideras que las dos palabras del par se refieren a cosas muy distintas (nada semejantes), deberás marcar un 1. Puedes utilizar todos los valores de la escala.

Original instructions for the concreteness rating (Spanish)

Vas a participar en una investigación sobre lenguaje. Tu tarea consiste en evaluar el nivel de concreción de las palabras que se presentan a continuación, es decir, evaluar si te parecen abstractas o concretas. El nivel de concreción de una palabra se puede entender como el grado de especificidad de su contenido. Por ejemplo, la palabra *objeto* es poco concreta porque su contenido es compatible con una familia muy amplia y variada de objetos diferentes. La palabra *objeto* se puede aplicar a una pelota, a una lámpara, a una silla, a un coche, etc. A diferencia de la anterior, la palabra *percha* es bastante concreta porque su contenido sólo es compatible con una gama muy restringida de objetos. Probablemente, la mayor parte de las palabras se pueden situar en algún punto entre los extremos de muy bajo nivel y muy alto nivel de concreción. Para efectuar tu juicio sobre cada palabra te aparecerá una escala que contiene 7 casillas dispuestas horizontalmente. Debes seleccionar el número de aquella casilla de la escala que mejor represente tu estimación sobre el nivel de concreción de la palabra que estés evaluando. El extremo derecho de la escala indica un nivel máximo de concreción (7 = *palabras muy concretas*), mientras que el extremo izquierdo de la escala indica un nivel mínimo de concreción (1 = *palabras muy abstractas*). Puedes utilizar todos los valores de la escala. Por último, queremos manifestar nuestro agradecimiento por tu participación en esta prueba.

Original instructions for the familiarity rating (Spanish)

Vas a participar en una investigación sobre el lenguaje. Tu tarea consiste en evaluar el grado de *familiaridad* de una serie de palabras, es decir, evaluar si las palabras de la siguiente hoja te resultan familiares o desconocidas. Si tienes un buen conocimiento del significado de una palabra determinada o si la usas con bastante frecuencia, entonces dicha palabra resulta muy familiar para ti. Un ejemplo podría ser la palabra "*mano*". Por el contrario, si el significado de una palabra te resulta en gran medida desconocido y las usas con muy poca frecuencia o nunca, entonces dicha palabra te resulta muy poco o nada familiar. Posiblemente, la palabra "*quarks*" te resultará muy poco familiar.

Para efectuar tu juicio sobre cada palabra te aparecerá una escala que contiene 7 casillas dispuestas horizontalmente. Debes seleccionar el número de aquella casilla de la escala que mejor represente tu estimación sobre el nivel de familiaridad de la palabra que estés evaluando. El extremo derecho de la escala indica un nivel máximo de familiaridad (7 = *palabra muy familiar*), mientras que el extremo izquierdo de la escala indica un nivel mínimo de familiaridad (1 = *palabra nada familiar*). Puedes utilizar todos los valores de la escala. Por último, queremos manifestar nuestro agradecimiento por tu participación en esta prueba.

Original instructions for the free association task (Spanish)

A continuación se te presenta una lista de palabras. Lee, una por una, cada una de las palabras y escribe al lado la primera palabra en castellano en la que pienses después de leer la palabra impresa. Esto es, escribe la primera palabra que te venga a la cabeza.

Hazlo lo más rápido que puedas. No hay respuestas correctas ni incorrectas.

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	Target Word	Concreteness (Mean)	Familiarity (Mean)	More Similar Word	Similarity (Mean)	Similarity (SD)	Concreteness (Mean)	Familiarity (Mean)	Less Similar Word	Similarity (Mean)	Similarity (SD)	Concreteness (Mean)	Familiarity (Mean)
1	**abuela**	6,29	6,73	**madre**	5,40	2,13	6,21	6,95	**suegro**	3,87	2,27	6,50	6,20
2	**aguacate**	6,65	5,35	**papaya**	6,87	1,50	6,60	4,30	**sandía**	4,48	2,28	6,90	6,30
3	**ajo**	5,77	5,61	**apio**	5,47	2,36	6,50	5,05	**alcachofa**	4,21	1,91	6,45	6,15
4	**alambre**	6,05	5,05	**filamento**	5,83	2,17	4,10	3,75	**caucho**	2,60	1,85	5,65	4,80
5	**albóndiga**	5,70	6,45	**buñuelo**	5,14	2,03	6,00	5,60	**tortilla**	3,70	2,29	5,84	6,18
6	**albornoz**	6,50	6,05	**toalla**	6,90	1,61	6,40	6,60	**mantilla**	3,03	1,80	5,65	3,65
7	**alcantarilla**	6,35	5,55	**desagüe**	6,33	2,23	5,30	5,65	**pozo**	4,07	1,84	6,00	5,27
8	**alfarero**	4,88	2,80	**artesano**	5,79	2,33	4,36	3,96	**ingeniero**	3,30	1,99	5,40	6,25
9	**alfombra**	6,20	6,22	**esterilla**	7,13	1,83	6,20	5,50	**parqué**	4,43	2,01	5,40	5,75
10	**algodón**	6,09	5,57	**lino**	5,30	1,86	5,28	4,05	**terciopelo**	4,33	2,32	5,77	5,23
11	**almacén**	4,90	5,91	**depósito**	5,53	2,54	3,65	4,86	**granero**	4,57	2,51	6,08	3,76
12	**alpargata**	6,45	4,45	**chancleta**	6,31	1,95	6,30	6,60	**bolso**	3,03	2,16	5,35	6,31
13	**amapola**	6,65	5,25	**tulipán**	5,90	2,20	6,35	5,60	**seta**	2,80	1,90	5,80	6,05
14	**apeadero**	5,11	2,80	**andén**	5,43	2,20	5,88	4,90	**aeropuerto**	2,79	1,88	6,12	5,72
15	**arena**	5,79	5,52	**tierra**	7,90	1,42	5,68	6,36	**mármol**	2,83	1,98	6,38	5,37
16	**arroyo**	5,71	4,60	**pantano**	5,47	2,27	5,71	5,00	**estanque**	4,73	2,07	5,67	5,38
17	**astillero**	5,55	3,80	**puerto**	5,30	2,09	5,70	6,20	**aduana**	2,07	1,57	5,99	3,98
18	**atún**	6,15	5,93	**lubina**	6,55	1,84	6,10	4,90	**foca**	3,90	2,32	6,14	5,85
19	**avena**	6,15	5,45	**mazorca**	5,71	2,48	5,75	4,35	**nabo**	2,77	1,65	5,80	4,40
20	**azafata**	6,05	5,85	**camarera**	5,40	2,31	5,89	6,23	**peluquera**	3,34	1,86	6,30	6,45
21	**azulejo**	5,65	5,20	**mosaico**	6,77	1,68	5,51	4,88	**zócalo**	4,27	2,20	4,78	3,55
22	**barro**	5,79	6,10	**tierra**	7,13	2,08	5,68	6,36	**césped**	4,30	1,97	6,07	5,62
23	**bebé**	6,26	6,10	**infante**	7,07	1,68	4,42	3,43	**joven**	3,90	2,01	4,92	6,69
24	**bellota**	6,15	5,60	**castaña**	5,87	1,59	5,65	6,10	**pistacho**	4,38	1,93	6,60	6,05
25	**berberecho**	6,50	5,40	**almeja**	6,73	1,87	5,75	5,90	**rape**	4,36	1,95	6,40	5,40
26	**bocadillo**	5,56	6,55	**sándwich**	6,80	1,86	5,35	6,05	**canelones**	3,80	1,83	5,75	6,35
27	**bodega**	5,74	6,04	**sótano**	5,28	2,43	6,49	5,74	**trastero**	4,50	2,11	5,50	6,05
28	**botella**	6,03	6,42	**jarra**	6,77	1,36	6,26	5,87	**plato**	4,67	2,01	5,85	6,80
29	**buhardilla**	5,62	3,98	**ático**	6,82	2,09	5,70	6,00	**terraza**	3,41	2,32	6,03	6,13
30	**buitre**	5,80	5,60	**cuervo**	6,10	1,81	6,50	5,15	**canario**	4,50	1,81	5,78	6,61
31	**burro**	4,94	6,24	**caballo**	6,87	1,22	6,23	5,60	**oso**	4,70	2,26	6,38	5,52
32	**cadera**	6,29	6,48	**costilla**	5,93	1,61	6,30	6,20	**vértebras**	4,00	2,10	5,95	4,80
33	**calabacín**	6,85	5,55	**pepino**	6,53	1,87	6,15	6,30	**limón**	4,27	2,07	6,50	6,50
34	**calcetines**	6,51	6,34	**medias**	7,00	1,51	4,67	6,07	**bañador**	4,50	1,78	6,26	6,51
35	**caldo**	4,89	5,65	**infusión**	5,17	1,75	5,25	6,00	**mayonesa**	2,55	1,76	6,35	6,35
36	**calle**	5,05	6,85	**camino**	7,30	1,70	4,75	5,97	**túnel**	3,97	2,09	6,03	6,50
37	**cama**	6,12	6,52	**sofá**	6,40	1,94	6,71	6,53	**mesa**	4,33	1,99	6,40	6,58
38	**camiseta**	6,37	6,60	**blusa**	7,07	1,56	6,40	5,68	**delantal**	3,63	1,87	6,01	6,06
39	**campesino**	6,33	6,01	**ganadero**	5,63	1,69	4,75	4,20	**vendedor**	2,93	1,87	4,54	6,41
40	**cangrejo**	6,15	5,85	**langostino**	5,77	1,91	6,45	5,60	**salmón**	3,89	1,99	6,00	6,40
41	**cárcel**	5,83	5,67	**reformatorio**	5,47	1,72	6,15	4,15	**asilo**	3,67	2,17	5,96	4,54
42	**carpintero**	6,47	5,01	**albañil**	5,53	2,53	6,39	4,81	**profesor**	2,53	1,72	5,47	6,88

43	cencerro	5,25	3,95	campanilla	5,93	2,68	5,03	4,34	silbato	2,50	2,06	5,55	5,85
44	cepillo	5,50	6,87	escobilla	5,17	2,41	5,95	5,80	pincel	4,20	1,52	6,35	5,30
45	cerilla	6,28	5,87	mechero	6,40	2,21	6,65	6,44	vela	4,87	2,24	5,10	5,82
46	chaleco	5,99	6,16	cazadora	5,77	1,83	6,02	6,01	gabardina	4,96	1,69	6,07	5,70
47	charco	5,44	5,99	laguna	5,83	2,02	4,73	4,04	océano	3,60	2,16	5,50	5,40
48	chica	5,76	6,53	niña	7,57	1,50	6,25	6,90	viuda	3,00	1,93	5,96	5,44
49	chichón	5,95	4,45	bulto	5,83	2,18	3,91	4,80	joroba	3,23	2,21	4,90	4,95
50	codorniz	6,70	5,10	perdiz	6,40	1,99	6,50	4,85	liebre	3,70	2,31	6,20	3,68
51	colchón	6,21	6,22	cojín	5,37	2,04	6,02	6,27	cortinas	4,17	1,95	6,20	5,66
52	colmena	5,40	4,50	hormiguero	5,75	2,24	5,89	5,22	acuario	2,87	1,96	5,97	5,77
53	comadrona	6,45	6,45	ginecóloga	6,50	1,70	6,25	5,90	maestra	3,46	2,16	5,85	5,98
54	comedor	6,23	6,12	restaurante	6,07	1,76	6,03	6,19	despacho	3,70	1,97	5,42	6,14
55	concha	6,10	4,95	cáscara	5,48	2,28	5,89	5,44	escamas	2,83	1,29	5,48	3,82
56	cordillera	5,72	4,76	sierra	6,40	2,36	5,47	5,68	valle	4,75	2,50	5,64	5,48
57	corteza	4,77	4,91	envoltura	5,34	2,18	3,00	4,05	forro	2,60	1,94	4,98	5,34
58	cristal	5,88	6,64	lente	5,63	2,14	5,25	4,85	diamante	4,43	2,10	6,20	5,60
59	cuchara	6,65	6,90	cazo	5,43	1,91	5,45	5,35	cacerola	3,86	2,07	5,90	5,40
60	cuchillo	6,51	6,34	espada	6,77	1,38	6,46	5,30	pistola	4,97	2,14	5,76	4,78
61	cuero	5,10	5,38	piel	5,66	2,35	5,30	6,23	caucho	4,33	1,88	5,65	4,80
62	cuna	5,86	4,72	litera	5,45	1,76	6,45	5,50	taburete	2,10	1,35	6,14	4,91
63	desayuno	5,81	5,99	almuerzo	6,57	2,10	5,70	5,47	banquete	4,27	2,10	5,51	5,77
64	dueño	4,81	5,28	patrón	6,40	2,06	4,31	5,34	cliente	3,33	1,77	5,05	6,34
65	eco	5,17	5,01	ruido	5,13	1,59	4,04	6,39	susurro	3,89	1,99	5,12	6,02
66	enchufe	5,85	6,45	cargador	5,43	2,36	5,50	6,90	bombilla	4,00	2,14	6,36	6,84
67	encina	5,20	3,90	roble	6,87	1,20	6,47	4,17	cerezo	4,40	2,18	6,60	5,85
68	estiércol	6,41	4,39	abono	7,54	1,71	4,45	5,50	vómito	4,04	2,40	6,10	6,35
69	farol	4,86	4,73	linterna	5,50	2,08	6,37	6,03	fuego	2,41	1,74	5,82	6,76
70	flequillo	5,65	6,29	mechas	5,96	1,29	5,20	5,85	vello	3,48	2,10	4,98	4,34
71	frambuesa	6,15	5,70	mora	5,55	1,97	4,84	4,75	aceituna	2,63	1,81	6,15	6,45
72	fregadero	6,28	5,31	lavadero	7,60	1,22	5,37	5,22	bañera	4,00	2,02	6,32	6,64
73	fresa	5,88	6,69	cereza	6,40	1,94	6,50	6,70	nuez	3,50	2,08	5,72	5,06
74	garbanzos	6,75	6,15	lentejas	6,97	1,35	6,44	5,59	fideos	4,72	2,28	6,06	5,69
75	gasolina	6,22	6,47	petróleo	6,73	2,00	6,27	5,36	agua	2,47	1,36	6,11	6,87
76	golosina	4,55	5,95	chocolate	5,62	2,03	6,13	6,68	pan	3,03	1,85	6,25	6,80
77	gorrión	6,20	4,05	golondrina	6,47	1,85	6,18	4,43	ardilla	4,27	2,05	6,39	5,80
78	guisante	6,40	5,90	judía	6,57	1,76	5,15	5,28	patata	4,47	1,98	6,19	6,78
79	habas	5,95	4,05	judías	7,43	1,70	5,15	5,28	cacahuetes	2,90	1,95	6,35	6,39
80	hacha	6,35	3,95	martillo	5,38	2,04	5,90	5,63	destornillador	2,79	1,92	6,60	5,65
81	hijo	5,68	6,10	nieto	5,43	1,53	6,23	5,63	yerno	4,63	2,06	6,30	5,35
82	hilo	5,83	6,61	lana	6,23	2,03	5,64	6,38	cadena	4,50	2,32	4,14	6,56
83	hinojo	5,22	3,10	tomillo	5,89	2,50	6,37	5,05	almendro	2,86	1,94	6,70	5,30
84	hogar	4,89	6,60	apartamento	6,87	1,07	5,80	5,23	guarida	4,83	1,95	4,69	4,22
85	hoja	5,26	6,18	pétalo	5,07	2,08	5,75	6,15	pradera	2,97	2,20	6,05	5,41
86	hombro	6,41	6,35	antebrazo	5,43	2,08	6,85	5,52	útero	2,77	2,03	6,50	5,18
87	hoz	5,21	3,37	martillo	5,14	2,22	5,90	5,63	puñal	3,00	1,76	5,65	4,90

88	**hucha**	5,55	6,65	**monedero**	6,03	1,87	6,10	6,25	**baúl**	3,67	2,11	6,33	6,16
89	**hueso**	5,67	6,42	**médula**	5,27	2,27	5,92	5,22	**estómago**	2,77	1,81	6,38	5,66
90	**huésped**	5,72	4,89	**inquilino**	6,59	2,44	5,15	5,05	**amigo**	3,89	2,13	5,85	6,78
91	**jamón**	6,25	5,92	**salchichón**	5,90	2,11	6,50	6,50	**tortilla**	3,93	2,15	6,69	6,29
92	**jarrón**	6,25	5,38	**cántaro**	5,83	2,22	5,65	2,95	**bidón**	3,70	2,14	5,80	5,40
93	**jaula**	6,07	6,47	**caja**	5,00	1,98	4,58	6,53	**tumba**	2,40	1,90	5,60	4,88
94	**jazmín**	6,45	3,09	**lirio**	5,52	1,88	6,33	3,54	**helecho**	3,70	2,02	4,75	2,55
95	**jilguero**	5,60	3,05	**ruiseñor**	6,37	2,08	5,80	4,30	**cisne**	3,63	2,20	6,55	5,56
96	**ladrillo**	6,16	4,85	**piedra**	5,17	2,28	6,30	6,42	**granito**	3,37	2,19	5,80	4,22
97	**lagartija**	6,75	5,55	**lagarto**	8,20	0,76	5,90	5,47	**ratón**	4,17	2,18	5,95	5,96
98	**lámpara**	6,11	6,15	**candil**	6,93	1,53	4,84	4,01	**proyector**	4,03	2,10	6,15	6,15
99	**lata**	5,70	6,07	**bote**	5,97	2,71	4,72	5,24	**bandeja**	2,87	2,13	5,66	6,29
100	**laurel**	6,23	4,37	**orégano**	6,40	1,83	6,55	6,10	**mostaza**	2,11	1,62	6,65	5,55
101	**lavavajillas**	6,70	6,15	**secadora**	6,36	1,47	6,20	5,80	**televisión**	3,31	2,04	6,24	6,42
102	**leche**	5,69	6,59	**horchata**	5,57	2,11	6,30	6,05	**cerveza**	3,97	2,09	6,03	6,53
103	**lechuga**	6,15	6,68	**col**	7,10	1,71	6,20	6,00	**champiñón**	4,40	2,06	6,20	6,40
104	**lluvia**	6,02	5,79	**nieve**	6,50	1,98	6,30	5,44	**tornado**	4,83	2,07	5,75	5,25
105	**madera**	6,04	6,34	**corcho**	5,00	2,02	5,90	6,20	**cemento**	4,17	1,97	5,57	5,65
106	**manguera**	5,95	5,90	**tubería**	5,27	1,76	5,85	5,25	**acueducto**	2,69	1,91	6,40	5,00
107	**manzana**	6,13	6,54	**naranja**	5,93	2,03	5,64	6,44	**coliflor**	3,77	1,81	6,40	4,07
108	**mariposa**	6,24	5,96	**polilla**	5,00	2,41	6,35	4,45	**pavo**	3,50	2,33	6,13	4,71
109	**médico**	5,78	6,54	**enfermera**	6,67	1,54	6,60	6,40	**abogado**	3,43	1,99	5,54	5,50
110	**mejilla**	6,57	5,44	**pómulo**	7,80	1,61	6,60	4,55	**ingle**	2,97	1,81	6,40	5,70
111	**melocotón**	6,70	6,20	**ciruela**	5,47	2,15	6,32	6,05	**nabo**	4,30	1,95	5,80	4,40
112	**merluza**	5,94	5,73	**lenguado**	7,17	1,14	6,25	6,05	**sapo**	3,43	2,30	6,10	5,05
113	**muela**	6,25	6,15	**colmillo**	6,73	2,23	6,13	5,75	**cuerno**	2,40	1,71	5,47	5,85
114	**muleta**	5,70	5,75	**bastón**	5,79	1,88	6,20	5,35	**caña**	2,36	1,31	4,51	5,97
115	**muñeca**	5,60	6,50	**marioneta**	6,23	2,13	5,35	5,60	**puzzle**	3,67	2,41	5,80	6,25
116	**murciélago**	6,58	5,92	**ratón**	5,55	2,06	5,95	5,96	**erizo**	3,83	2,21	5,85	6,25
117	**musgo**	6,22	5,45	**moho**	6,43	2,49	5,80	4,25	**arbusto**	4,77	1,99	5,65	5,50
118	**muslo**	5,49	5,43	**pantorrilla**	5,83	2,17	5,95	5,20	**riñón**	3,07	1,86	6,19	6,00
119	**naranjo**	6,45	6,00	**limonero**	6,27	2,05	6,55	6,20	**rosal**	4,80	2,22	6,53	6,12
120	**nariz**	6,65	6,50	**barbilla**	5,79	2,13	5,61	6,22	**pulmón**	3,83	1,86	6,25	5,74
121	**nido**	5,40	6,01	**madriguera**	6,23	1,99	5,05	4,40	**cueva**	3,53	2,22	6,00	4,45
122	**niño**	6,18	6,51	**adolescente**	5,40	1,69	5,45	6,42	**viejo**	3,60	2,25	5,14	6,26
123	**nutria**	6,20	4,60	**ardilla**	6,20	1,56	6,39	5,80	**antílope**	3,52	2,25	5,15	4,05
124	**ombligo**	6,01	5,92	**pezón**	5,93	1,64	6,40	6,30	**axila**	3,67	2,17	6,45	5,65
125	**orilla**	5,41	5,95	**borde**	5,53	2,37	4,13	6,08	**esquina**	2,79	2,02	5,45	6,14
126	**paloma**	6,42	6,18	**gaviota**	6,03	2,13	6,28	6,56	**delfín**	3,93	2,05	6,60	6,05
127	**palomitas**	6,15	6,55	**pistachos**	5,57	1,79	6,60	6,05	**pasas**	3,33	1,81	5,13	5,53
128	**panadería**	6,54	5,46	**pastelería**	7,30	1,39	5,95	6,35	**papelería**	3,80	1,90	5,90	6,35
129	**panadero**	6,54	5,46	**pastelero**	7,00	1,64	5,75	6,10	**zapatero**	3,90	2,51	6,25	6,25
130	**panal**	5,26	4,30	**avispero**	5,69	3,22	6,10	4,10	**gallinero**	2,83	1,58	5,54	4,99
131	**paño**	5,35	6,28	**bayeta**	6,45	2,11	5,78	5,56	**papel**	4,50	2,40	5,80	6,67
132	**pañuelo**	6,08	6,29	**bufanda**	6,17	2,07	6,71	6,08	**guantes**	3,97	1,87	6,57	4,27

133	parrilla	5,80	5,90	plancha	6,40	2,11	5,46	6,62	chimenea	4,47	2,08	6,17	5,70
134	peatón	5,65	5,55	caminante	7,75	1,04	4,95	5,15	vagabundo	3,27	1,78	5,67	6,10
135	peca	5,85	5,75	verruga	6,30	1,62	5,94	5,15	grano	4,73	2,24	4,95	6,16
136	pecho	6,09	6,13	corazón	5,79	1,87	6,01	6,76	nalgas	3,80	2,09	5,97	4,83
137	pelo	6,72	6,60	pestaña	5,53	1,91	5,55	6,50	cuello	3,33	2,22	5,77	6,02
138	pendiente	3,68	5,81	anillo	6,00	1,74	5,95	6,12	reloj	3,93	2,30	6,52	6,77
139	perejil	6,70	6,30	tomillo	6,20	2,12	6,37	5,05	vainilla	3,23	2,28	6,80	6,10
140	pimiento	6,25	6,55	berenjena	5,53	2,11	6,25	6,30	níspero	2,93	1,98	6,75	4,00
141	piojo	6,45	5,85	pulga	5,67	2,40	6,40	6,00	oruga	4,47	1,70	6,20	6,20
142	queso	5,99	5,93	cuajada	5,97	1,81	5,60	5,35	flan	4,27	2,20	6,15	6,15
143	raíz	5,24	6,43	tubérculo	5,25	2,19	4,80	4,25	semilla	4,43	2,22	5,55	4,63
144	rama	4,72	6,12	tronco	6,07	1,72	5,00	5,43	tubérculo	2,79	1,73	4,80	4,25
145	rana	6,37	5,76	salamandra	5,73	1,84	6,05	4,16	serpiente	4,77	2,30	6,05	4,16
146	rastrillo	5,90	4,95	escoba	6,30	1,58	6,33	6,09	navaja	2,28	1,67	6,69	5,40
147	rayo	5,60	5,90	descarga	6,87	1,80	4,55	4,63	ráfaga	3,93	2,28	4,15	4,65
148	rebanada	5,15	5,45	rodaja	6,83	2,68	5,05	6,10	galleta	4,82	2,07	6,05	6,80
149	rebaño	5,41	4,58	ganado	7,00	1,87	4,14	3,84	gentío	3,79	2,69	4,13	5,18
150	relámpago	6,22	4,65	centelleo	5,73	2,13	4,13	3,57	volcán	2,93	1,82	6,20	3,88
151	rodilla	6,56	5,95	codo	5,90	2,02	5,50	5,64	ojo	3,90	2,40	5,94	6,81
152	roscón	5,80	5,70	bollo	6,00	2,08	4,85	6,05	sorbete	2,68	1,63	5,20	5,65
153	sábana	5,90	6,26	colcha	6,70	1,91	6,43	5,96	tapete	4,03	1,92	5,38	4,46
154	sacacorchos	6,55	5,40	abrelatas	5,60	2,14	6,40	5,20	exprimidor	2,93	1,62	5,75	6,20
155	saltamontes	6,40	5,90	grillo	6,87	1,25	6,85	5,65	bogavante	2,24	1,57	6,75	5,10
156	servilleta	6,68	6,45	mantel	6,07	2,10	6,38	6,31	manta	3,13	1,59	6,09	6,70
157	sobrina	6,05	5,36	prima	5,93	2,40	4,54	5,20	padre	3,80	2,02	6,08	6,57
158	sobrino	6,20	6,80	primo	5,28	2,36	5,43	6,71	cuñado	4,80	2,27	5,44	5,84
159	sombrero	5,93	3,24	gorra	7,03	1,75	5,63	6,53	pantalón	3,97	1,94	6,34	6,27
160	sujetador	5,39	6,10	falda	5,20	1,77	5,44	6,34	chándal	3,50	2,11	6,50	6,70
161	tarro	4,70	5,10	frasco	7,20	2,37	5,22	5,36	bolsa	2,27	1,68	4,72	6,42
162	tarta	6,36	6,24	bizcocho	6,80	2,01	5,95	6,55	tostada	3,52	1,70	5,85	6,75
163	techo	5,68	6,52	tejado	7,00	1,97	5,58	5,70	pasillo	3,17	2,00	5,52	6,72
164	ternera	6,05	6,20	toro	5,60	2,11	6,26	5,52	tigre	2,83	2,11	6,49	5,54
165	tiburón	6,00	5,85	orca	6,23	1,33	6,00	4,75	cangrejo	4,27	2,43	6,15	5,85
166	tienda	4,81	6,61	supermercado	6,63	1,79	5,52	6,50	feria	3,47	1,94	4,93	5,66
167	tijeras	6,46	6,59	alicates	5,73	1,96	6,25	6,05	destornillador	4,63	2,11	6,60	5,65
168	tobillo	6,60	6,60	pierna	5,03	1,90	6,29	6,48	costilla	4,07	1,62	6,30	6,20
169	toldo	5,94	5,45	porche	5,71	2,00	5,18	3,86	telón	3,93	1,78	5,62	4,64
170	tormenta	5,33	6,59	huracán	6,10	2,19	5,69	4,14	terremoto	4,53	2,06	5,70	5,25
171	trigo	6,41	4,07	centeno	5,69	2,73	5,95	4,55	avellana	3,93	2,39	6,55	6,05
172	uña	6,33	6,34	zarpa	6,53	1,98	5,90	4,15	diente	3,77	2,01	6,24	6,31
173	uva	6,30	6,70	pasas	5,77	2,84	5,13	5,53	remolacha	3,93	1,72	6,30	4,90
174	valla	5,90	5,21	reja	7,83	1,21	6,12	5,77	pared	4,90	1,79	6,25	6,27
175	vecino	5,83	6,80	residente	5,14	1,81	4,00	6,25	arrendatario	3,20	2,12	4,95	3,85
176	vendaje	2,90	5,45	tirita	6,75	1,32	6,25	6,15	faja	3,79	2,18	6,15	4,65
177	veneno	4,48	5,08	pócima	5,36	2,72	3,20	4,00	fármaco	4,20	2,44	4,80	5,77

178	**ventanal**	6,08	5,93	**balcón**	6,61	1,66	6,03	5,71	**baranda**	3,14	2,39	5,33	4,95
179	**vertedero**	5,65	4,65	**contenedor**	6,70	2,10	5,90	6,45	**descampado**	3,79	2,29	4,57	4,87
180	**vivienda**	5,45	4,85	**piso**	7,53	1,33	4,62	6,66	**campamento**	4,86	2,00	5,42	5,33
181	**yegua**	6,19	5,10	**mula**	5,87	2,16	6,17	4,77	**elefante**	4,00	1,97	6,41	5,82
182	**yeso**	5,61	4,05	**arcilla**	5,24	2,39	4,95	6,24	**carbón**	2,57	1,92	6,04	5,31
183	**zanahoria**	6,67	5,58	**rábano**	6,00	1,64	6,40	5,45	**albaricoque**	4,31	2,39	6,85	5,40
184	**zorro**	6,05	5,83	**lobo**	5,80	1,92	5,97	6,13	**gallo**	4,76	2,28	5,94	6,24
185	**zumo**	5,23	5,55	**batido**	6,30	2,07	3,95	6,10	**aceite**	4,00	2,44	5,80	6,27

Study 3

Moldovan, C., Ferré, P., Demestre, J., & Sánchez-Casas, R. (in preparation).

Lexical and semantic activation during the translation process in highly proficient and immersed Catalan-Spanish bilinguals.

Lexical and semantic activation in the translation process in highly balanced and immersed Catalan-Spanish bilinguals

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Abstract

In order to examine the pattern of cross-language lexical and semantic activation during translation recognition, the present study places the predictions of the BIA model (Dijkstra & Van Heuven, 1998) and the RHM (Kroll & Stewart, 1994) in the same experimental context. It focused on highly proficient and balanced bilinguals of Catalan and Spanish who live immersed in a bilingual context and who use both languages regularly. Two experiments were conducted in the two directions of translation (Catalan-Spanish and Spanish-Catalan). Critical distractors were words related either in form or in meaning to the correct translation. For instance, for the Catalan-Spanish translation pair *mussol-búho* (*owl*), critical conditions included: lexical neighbors: *mussol-muslo* (*tight*); translation neighbors: *mussol-buzo* (*diver*) and semantically related words: *mussol-águila* (*eagle*). There were interference effects for the three types of relations, although they were larger for the semantically related pairs than for the form related pairs. Furthermore, the pattern of effects was the same across directions. These findings are discussed in relation to languages' use and context of immersion.

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Over the last decades, many studies have been carried out in an attempt to determine how words are represented and accessed in the bilingual mental lexicon. An important issue in bilingualism research concerns the question of whether reading a word activates lexical representations in both languages, or in only the contextually relevant (target) language. Many findings, in the literature, about word processing seem to suggest that both languages are active to some degree when a bilingual uses one of them and even when the communicative context demands only one language (Kroll & De Groot, 2005). The non-selective activation of the two languages has been observed across a wide variety of paradigms and tasks when bilinguals process words in their first language (L1) as well as in their second language (L2) (see Kroll, Dussias, Bogulski & Valdes-Kroff, 2012; Schwartz & Van Hell, 2012; van Assche, Duyck, & Hartsuiker, 2012; van Hell & Tanner, 2012; for recent reviews). Cross-languages interactions have been observed not only in languages that share the same script (e.g., Dijkstra, Miwa, Brummelhuis, Sappelli, & Baayen, 2010), but also in languages with different script (e.g., Thierry & Wu, 2007; Wu & Thierry, 2010). Moreover, there is evidence that deaf readers of English activate the translations of English words in the American Sign Language (ASL), thus demonstrating that ASL signs are active during print word recognition in deaf bilinguals who are highly proficient in both ASL and English (Morford, Wilkinson, Villwock, Piñar, & Kroll, 2011).

From the abovementioned studies, it can be concluded that the parallel co-activation of lexical entries of the two languages has been extensively demonstrated. Researchers in this field have studied the modulation of such activation by words' properties (i.e., orthographic, phonological and semantic similarities across languages, Dijkstra, et al., 2010) and by the characteristics of bilinguals (i.e., proficiency and age of second language acquisition, Van Hell & Dijkstra, 2002). However, there are still important issues that need to be addressed such as, for instance, the extent to which languages' use could affect cross-language interactions. The role of languages' use has scarcely been addressed in the literature (e.g., Baus, Costa, & Carreiras, 2013; Linck, Kroll, & Sunderman, 2009) and it has often been mixed with proficiency (i.e., bilinguals who are more proficient in one language than in the other also use one more than the other). However, it is worth noting that although use and proficiency are related (i.e., using a language improves proficiency), there are proficient bilinguals who regularly use the two languages whereas other proficient bilinguals use the two languages in an asymmetrical manner (i.e., one language is used more often than the other). Since bilingualism is a very complex phenomenon, the field would benefit from more studies aimed to elucidate the effects of variables such as proficiency, dominance, language use and immersion on bilingual word processing. In the present work we will study the pattern of cross-languages activation during the translation process in highly proficient and balanced bilinguals of Catalan and Spanish who use their two languages in a regular basis and who are immersed in a context in which both languages are present. We address this issue through the framework of two of the most influential models of bilingual memory: The Bilingual Interactive Activation (BIA) model (Grainger & Dijkstra 1992; van Heuven, Dijkstra & Grainger 1998) and its revised version, the BIA+ (Dijkstra & Van Heuven, 2002) and the Revised Hierarchical Model (RHM, Kroll & Stewart, 1994; Kroll, Van Hell, Tokowicz & Green, 2010). In what follows we will briefly review the main characteristics of the two models and then we will consider their predictions in proficient bilinguals, focusing on how proficiency and language use might affect bilingual word processing.

The BIA model (Dijkstra & Van Heuven, 1998) is an extension to the bilingual domain of the Interactive Activation (IA) model that McClelland and Rumelhart (1981) proposed for visual word recognition in monolinguals. BIA (see Figure 1) consists of four layers of nodes. The first layer contains the features of letters, the second individual letters, and the third entire words in each of the two languages in an integrated lexicon (in our example, Spanish and English). Furthermore, in the fourth layer the model implements a language node for each language, which acts as a mechanism for coding the language to which a word belongs (i.e., Spanish or English). Arrows with triangular heads represent excitatory connections and those with circular heads represent inhibitory connections. According to BIA, word recognition proceeds in different steps (or cycles), beginning with a bottom-up, language non-selective activation in response to an input word/non-word (e.g., *cara [face]*; Spanish). Thus, when the word "*cara*" is presented, features of the individual letters will be activated, followed by the activation (and inhibition) of letters that match (and do not match) those specific features. The activated letters will, in turn, activate words in both languages that have that letter in the same position and will inhibit those words that do not share the orthographic properties of the input. Thus, at the word level, "*cara*" will activate a series of orthographically similar words in both languages as a function of their orthographic similarity (e.g., Spanish: *cara* [*face*], *caro* [*expensive*]; English: *care, cars,* etc.). These words will compete with each other during the word recognition process. The model postulates a lateral inhibition mechanism at the word level, which regulates the competition and inhibition of the words of the two languages. That is, the words of the two languages can mutually inhibit each other (i.e., inhibit the activation of those words that do not match the orthographic characteristics of the input pattern), thus reducing their level of activation. Additionally, the two language nodes of the fourth layer receive activation from the words represented at the third layer, and their function is to reduce the activation of the words that do not belong to the language represented by the node. In our example the level of activation of the English words will be reduced and the processing system will effectively recognize "*cara*" as a Spanish word. As can be seen in Fig. 1, letters and words are influenced by both bottom-up and top-down processes, since letters receive activation from features (i.e., a bottom-up process) and language node inhibits the non-target language (i.e., a top-down process).

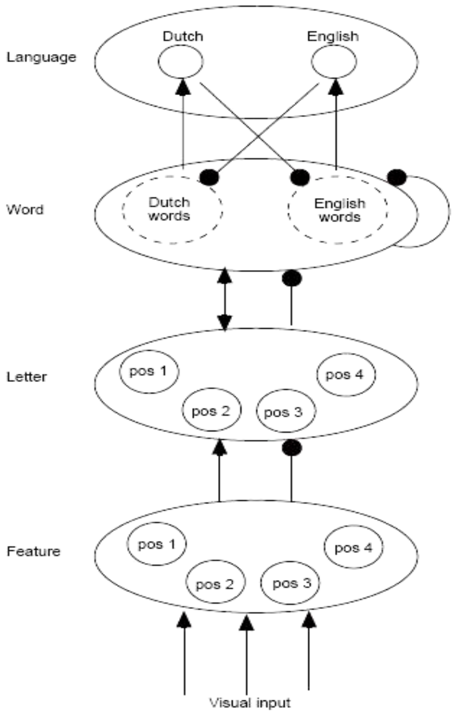


Figure 1. The Bilingual Interactive Activation model (Dijkstra & Van Heuven, 1998). Arrowheads indicate excitatory connections; black filled circles indicate inhibitory connections. In our example, Dutch is substituted by Spanish.

BIA has successfully simulated empirical findings such as frequency effects and formal similarity effects with different types of words that share orthography across languages (see Dijkstra & Van Heuven, 1998, 2002). The frequency effect means that words frequently used are recognized faster than words with a lower frequency of usage, because they have a higher resting activation level (Dijkstra, 2006). Concerning the effects of formal similarity across languages, studies on word recognition have addressed the issue of selective vs non-selective access by testing: a) *interlexical homographs,* which are words with the same written form across two languages but with a different meaning in each language (e.g., the Spanish-English interlexical homograph *pan*, which means *bread* in Spanish, Dijkstra, Van Jaarsveld & Ten Brinke, 1998; Kerkhofs, Dijkstra, Chwilla, & de Bruijn, 2006); b) *orthographic/phonological neighbors*, which are words differing by only one letter/phoneme across languages and which have a distinct meaning (e.g., Spanish-English: *cara [face]-card*, Brysbaert, Van Dyuck & Van de Poel, 1999; Grainger & Dijkstra 1992; Jared & Kroll, 2001; Van Heuven, et al., 1998) and c) *cognate words*, which are translation equivalents with full or partial form and meaning overlap across-languages (e.g., Spanish-English *tomate-tomato*, De Groot & Nass, 1991; Sánchez-Casas, Davis & García-Albea, 1992; Van Hell & De Groot, 1998; Van Hell & Dijkstra, 2002). Across a variety of tasks and languages, the aforementioned studies show that these three types of words affect the performance of bilinguals in different directions, as cognates usually produce facilitation whereas the effects of homographs and orthographically neighbors are commonly inhibitory. The interference in homographs (i.e., *pan [bread]-pan*) is thought to arise because there are two representations for them, one in each language. These representations compete with words of both languages, slowing word recognition in comparison with two words that do not share lexical form (i.e., Spanish-English: *pan-sun*, see also Dijkstra, Grainger, & Van Heuven, 1999). Further, findings with homographs show that words' frequency modulates these effects, being their magnitude larger for low-frequent homographs than for high-frequent ones (De Groot, Delmar and Lupker, 2000). With respect to cross-language orthographic/ phonological neighbors (i.e., *cara-card*), the inhibitory effect in comparison with lexically unrelated words (i.e., *cara-seat*) is attributed to the excitatory input of the shared letters (e.g., three in *cara-card)* that produces word competition during recognition. Also, high frequent neighbors are stronger competitors than low frequent ones (Brysbaert & Dijkstra, 2006). Finally, facilitative effects for cognates (i.e., *tomate-tomato*) are thought to arise as a consequence of their orthographic/ phonological and semantic overlap that produces an increase in activation in comparison with non-cognate words (i.e., *mesa-table*, see Dijkstra et al., 2010 for a review of several accounts of the cognate effect).

Overall, the above reviewed studies support the non-selective lexical access assumption of the BIA. Moreover, they highlight that it is not only orthographic similarity that influences cross-languages processing, but also phonological similarity, semantics and task demands. By considering these influences, Dijkstra and Van Heuven (2002) updated the BIA to BIA+. As can be seen from the above, BIA and BIA+ were designed to explain bilingual word recognition with the emphasis mostly placed on the process of lexical access in proficient bilinguals. Therefore they are static models that do not incorporate changes in their structure as language proficiency increases (but see Grainger, Midley, & Holcomb, 2010, for an attempt to include a developmental perspective in BIA). In further reviews about word recognition during lexical access, Dijkstra (2005) and Thomas and Van Heuven (2005) provided a way in which BIA could account for the effects of language proficiency. They introduced the subjective frequency of use (i.e., the number of times that a speaker/ hearer encounters or uses a particular word) as well as the recency of use as relevant factors. According to this view, high frequency and more recently used words would have a higher resting level of activation, being recognized faster and more accurately than less frequently used words that have not been used for a while. Thomas and

Van Heuven (2005) did not assume that the effects of proficiency are exclusively explained in terms of subjective frequency of use. However, they reasoned that for bilinguals who acquired their second language (L2) late in life and who are unbalanced (i.e., being more proficient in their first language, L1, than in L2), the subjective frequency of L2 words is lower than that of L1 words, as they are exposed to the later much more often than to the former. As a consequence, there would be an asymmetry in the processing of L1 and L2 words (see Dimitropoulou, Duñabeitia, & Carreiras, 2011; Schoonbaert, Duyck, Brysbaert, & Hartsuiker, 2009 for reviews). In support of this proposal, several studies testing L1 words have revealed a nonselective lexical access, either when words were presented in isolation (e.g., Lemhöfer & Dijkstra, 2004) or embedded in sentences (e.g., Van Hell & De Groot, 2008). With respect to L2 words, the effects are less reliable and, when obtained, a minimal proficiency in the non-dominant language seems necessary to obtain cross-linguistic activation effects (see Van Assche et al., 2012).

The first aim of the present work was to study the pattern of cross-languages activation during translation recognition in a group of highly proficient bilinguals, by testing the effect of lexical neighbors (i.e., words similar in form, but not in meaning, across languages, *cara[face]-card;* Spanish-English). These bilinguals learned both languages during early childhood and have been immersed in a Catalan-Spanish bilingual context for a period of 18 or more years. Furthermore, they use both languages on a daily basis. By considering BIA predictions, a symmetrical pattern of effects across directions should be expected in bilinguals with such characteristics.

In another relevant line of research about translation processes, other types of words related across-languages have been used, the so-called translation neighbors (i.e., *cara-fact*, with *fact* being similar to the correct translation, *face*). This research has been inspired in the Revised Hierarchical Model (RHM, Kroll & Stewart, 1994; Kroll et al., 2010), a very influential model in the field of bilingual language processing, able to accommodate the developmental changes that occur during the initial stages of L2 acquisition. The RHM (see Figure 2) assumes two separate, interconnected lexicons, one for each language (L1 and L2). In addition, it posits a shared integrated conceptual system that is connected to both lexicons. The model also assumes that L1 has strong connections and a direct access to the conceptual system, and that the strength of the connections between L2 and the conceptual system varies according to the level of L2 proficiency. At the initial stages of L2 acquisition, L2 words would automatically activate their L1 translation equivalent via lexical links as a means to access meaning. As proficiency in L2 increases, the connections between L2 words and their corresponding concepts would be reinforced while lexical dependence on L1 would decrease. As a consequence, bilinguals highly proficient in L2 and relatively balanced could reach a level of lexical-to-conceptual mappings that are equivalent to those in L1.

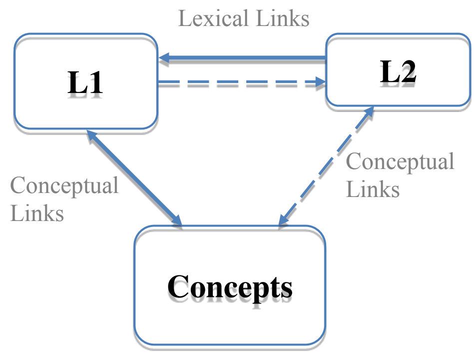


Figure 2: The Revised Hierarchical Model (adapted from Kroll & Stewart, 1994). Words in the two languages (L1 and L2) are connected via lexical and conceptual links. Solid lines represent stronger connections and dotted lines represent weaker connections.

Empirical research, mainly focused on translation recognition, examined the asymmetry proposed by the RHM by comparing the performance of L2 learners and proficient bilinguals. In the translation recognition task (De Groot, 1992), participants are presented with a first word in one language followed by a second word in another language and they have to decide whether the second word is the correct translation of the first one. For instance, a correct translation pair between Spanish (L2) and English (L1) could be *cara-face*. Then, to test the degree to which conceptual access from L2 is direct and/or L1 mediated, an interference paradigm is commonly used (e.g., Talamas, Kroll, & Dufour, 1999). In this paradigm, in addition to the correct translations pairs, critical non-translation (or distractor) pairs are used, which can either be similar in form to the L1 translation equivalent (i.e., translation neighbors, TNs: *cara-fact*), or semantically related (e.g., *cara-hand*). Then, if TNs and semantically related words become active during the translation process, they would compete with the correct candidate and cause interference (when compared to unrelated pairs such as *cara-room*) when the participants have to reject them as non-correct translations. The difference in reaction times (TRs) and accuracy between the related and unrelated pairs is the so-called "interference effect". According to the asymmetry proposed by the RHM, L2 learners would exhibit more interference with TNs than with semantically related pairs, as they would be mainly using the lexical route to access meaning. Conversely, a reversed pattern is expected for proficient bilinguals, namely, stronger semantic than TNs interference effects, as they can access meaning directly from L2. Using the translation recognition task, a series of studies found that relatively proficient bilinguals showed a negligible interference effect with TNs, which was always smaller than the interference for semantically, related pairs. In less proficient bilinguals, the reverse pattern was observed. These results revealed that sensitivity to form and meaning manipulations is a function of proficiency, as the RHM predicted (Linck et al., 2009; Sunderman & Kroll, 2006; Talamas, et al., 1999). However, another series of studies conducted with highly proficient bilinguals found a robust effect of the formal manipulation (i.e., the interference produced by TNs), which in some cases was of the same magnitude as the semantic interference effect (Ferré, Sánchez-Casas & Guasch, 2006; Guasch, Sánchez-Casas, Ferré, & García-Albea, 2008; Guo, Misra, Tam, & Kroll, 2012; Moldovan, Sánchez-Casas, Demestre, & Ferré, 2012). These last results might suggest that L1 translation equivalents are active even in highly proficient bilinguals when they translate from L2, contrary to the predictions of the RHM.

The issue of the activation of L1 translation equivalents in highly proficient bilinguals when accessing meaning from the L2 has become a hotly debated topic during the last years. Given that according to the

RHM, highly proficient bilinguals are able to access meaning directly from their two languages, the question to be addressed is which factors, other than proficiency, might contribute to activate L1 translation equivalents. Several studies that have used behavioral measures as well as event-related potentials (ERPs), a very sensitive technique to monitor the on-line word processing, have begun to address this issue (Guo et al., 2012; Thierry & Wu, 2007). For instance, Thierry and Wu (2007) used ERPs to compare Chinese (L1)-English (L2) proficient bilinguals with English monolinguals in a semantic relatedness task in English. In this task, participants were presented with semantically related pairs (e.g., *post-mail*) as well as unrelated pairs (e.g., *train-ham*) and were asked to decide whether the two words were semantically related. Unbeknownst to the participants, among the experimental items there were pairs where the Chinese translations of the two English words in the pair shared Chinese characters. For instance, the words *train* and *ham* are not related in meaning but their Chinese translations (Huo Che and Huo Tui) have a Chinese character in common. With this experimental manipulation, Thierry and Wu aimed to examine to what extent the non-target language (i.e., Chinese) is active when Chinese-English proficient bilinguals perform the task in English (i.e., their L2). The authors found that whereas the hidden factor failed to affect behavioral performance, it significantly modulated brain potentials in the expected direction, suggesting that English words were automatically and unconsciously translated into Chinese. The ERPs showed that the N400, a component indexing semantic integration processes (Kutas & Hillyard, 1980, 1984), was smaller for English pairs with a shared character in their Chinese translations relative to word pairs without shared characters. Critically, there was no such modulation in the English monolinguals control group (see also Wu & Thierry, 2010, for a demonstration of unconscious access also to the phonology of Chinese words). Thierry and Wu concluded that although meaning access can be direct when L2 words are processed, the native language lexicon is also activated, as a result of language non-selective access.

Guo et al., (2012) proposed an alternative explanation. According to these authors, the studies that have reported an activation of L1 translation equivalents in proficient bilinguals (e.g., Guasch et al., 2008; Thierry & Wu, 2007) have used relatively long stimulus onset asynchronies (SOAs, the interval from the onset of the first word to the onset of the second word). These long SOAs might encourage bilinguals to activate the L1 translation equivalent after accessing the L2 word meaning. In order to test this proposal, Guo et al. tested highly proficient Chinese (L1)-English (L2) bilinguals immersed in their L2. They used a translation recognition task which in addition to correct translations included also different types of critical non-translation pairs: semantically related, translation neighbors and unrelated pairs. While participants performed the task from L2 to L1 (i.e., English-Chinese), both behavioral and electrophysiological measures were recorded. The authors manipulated the SOA, having a long SOA condition (750, Experiment 1) and a short SOA condition (350, Experiment 2). In Experiment 1, behavioral interference was obtained for both relations under study, but ERPs revealed a different time course for the two conditions. The semantic condition elicited effects primarily on the N400, with a smaller N400 relative to unrelated controls. In contrast, the translation neighbors condition elicited a larger P200 component (sensitive to lexical processing; Liu, Perfetti, & Hart, 2003) than did unrelated controls. In Experiment 2, with a shorter SOA, the behavioral results revealed again interference for both types of relations. However, the ERP results showed a markedly different time course for the semantic and translation form interference effects. A significant semantic interference effect was observed in the time windows of the N400, but a translation form interference effect was seen only at a later positive component (i.e., the LPC). These results supported the claim that proficient bilinguals are able to access conceptual information directly from L2 words. Moreover, they showed that these bilinguals activated the L1 translation of the L2 word, and that this activation is related to the time course of processing afforded by the task. The results of Guo et al. give support to their proposal concerning the activation of L1 translation equivalents in proficient bilinguals after having accessed the meaning of an L2 word. However, the results of a series of studies conducted with highly proficient and balanced bilinguals of Catalan and Spanish have reported a robust interference effect with TNs, by using long (SOA of 750 ms, Guasch et al., 2008), middle (SOA of 500 ms, Ferré et al., 2006) and short SOAs (SOA of 250 ms, Moldovan et al., 2012). A relevant characteristic of these bilinguals is that they are highly proficient and that they live in a linguistic context of immersion in both languages, in which both Catalan and Spanish are used on a daily basis. Thus, it might be that in such conditions of immersion, with an active use of both languages, the lexical representations of the two languages are "functionally" active and that this might be the reason why TNs produce such a robust and strong interference effect (Moldovan et al., 2012). This possibility would be also in line with the assumption of BIA concerning the high resting level of activation (and its influence on lexical access) of high-frequently and recently used words.

A relevant study dealing with the topic of the effects of language use in the translation recognition task in proficient bilinguals is that conducted by Linck et al., (2009). Those authors compared the performance of two groups of English (L1)-Spanish (L2) bilinguals immersed in two distinct language contexts in a translation recognition experiment: one of the groups (G1) lived in USA (i.e., an L1 environment) and the other group (G2) was enrolled in a study abroad program for 3 months in Spain and thus immersed in an L2-speaking context. The two groups were matched in cognitive ability and L2 language proficiency, the only difference between them being the degree of L1 and L2 use as a consequence of the language immersion context (i.e., G1 used more L1 than L2 and G2 more L2 than L1). Linck et al. tested the performance of those bilinguals in a translation recognition task conducted from Spanish (L2) to English (L1), by using different types of distractors: (a) lexical neighbors (e.g., *cara [face]-card*), (b) translation neighbors (e.g., *cara-fact*), and (c) semantic distractors (e.g., *cara- head*). On the one hand, according to BIA, lexical neighbors would produce interference. On the other hand, RHM would predict interference effects mainly with semantic distractors (as participants were proficient bilinguals), whereas the interference produced by translation neighbors would be smaller. The results revealed interference effects in all conditions for the G1 immersed in English. With respect to the G2 immersed in Spanish, there were interference effects only for the semantic distractors. Since both lexical neighbors and translation neighbors require L1 activation, this lack of interference was interpreted by Linck et al. as produced by the inhibition of L1 when bilinguals are immersed in L2, given that in such a context the L1 is scarcely used (but see the study of Baus, et al., 2013 for an alternative account of the effects of second language immersion on first language production in terms of a decreased frequency of use of L1 words). These results are important since they show, firstly, that under some specific circumstances such as a limited use, it might be possible to inhibit L1, and the pattern of cross-language interactions would be affected by this reason. Secondly, these findings suggest that lexical access is modulated not only by the level of proficiency but also by specific circumstances of the bilinguals, such as how often a particular language is used. In this line of reasoning, the study of Sunderman and Priya (2012) is also relevant. It tested the interference produced by translation neighbors and lexical neighbors in highly proficient Hindi-English bilinguals immersed in English in a translation recognition task conducted in the two translation directions. The authors observed that the interference produced by translation neighbors was larger in the Hindi-English direction (L1-L2) than in the English-Hindi direction (L2-L1). As these participants were immersed in an English environment, what these findings suggest is that the activation of the translation equivalent is affected by specific characteristics of the bilinguals, such as the language of immersion, which can became the most dominant one (regardless of the language native status).

Clearly the issue of under what circumstances L1 is activated or inhibited during L2 processing is highly relevant to the domain of bilingual word processing. Past research in translation recognition has focused extensively on the effects of bilinguals' proficiency (e.g., Ferré et al., 2006; Guasch et al., 2008; Sunderman & Kroll, 2006), whereas the role of language use has scarcely been addressed. As stated before, in this study we tested highly proficient early Catalan-Spanish bilinguals, immersed in the two languages and who use both languages on a regular basis. The second aim of the present work (apart from testing the interference effects of lexical neighbors) was to study the activation of L1 translation equivalents by testing the interference effects produced by translation neighbors during a translation recognition task conducted in both translation directions. Similarly as in previous studies (Linck et al., 2009; Sunderman & Kroll, 2006), we also included lexical neighbors as well as semantically related words as non-translation pairs.

To our knowledge this is the first study that places the predictions of BIA (Dijkstra & Van Heuven, 1998) and RHM (Kroll & Stewart, 1994) in the same context in highly proficient bilinguals who live immersed in both languages and use them on a daily basis, and by testing the two directions of translation (i.e., Catalan-Spanish and Spanish-Catalan). According with RHM, and in line with previous findings, we expect a reliable semantic interference effect in the two translation directions, since highly proficient bilinguals can access meaning directly from their two languages (Ferré et al., 2006; Guasch et al., 2009; Guo et al., 2012; Moldovan et al., 2012). With respect to TNs, and also in line with past research conducted with similar bilinguals (e.g., Moldovan et al., 2012), we expect to find a robust interference effect. Concerning lexical neighbors, and according to BIA and BIA+, and in line with previous results (Linck et al., 2012; Sunderman et al., 2006), we expect an interference effect as a result of the language non-selective access. Furthermore, if we consider that our bilinguals use the two languages on a regular basis, we might expect symmetrical effects between the two translation directions with the formally related distractors (lexical and translation neighbors), since the BIA suggests that the subjective frequency of a word plays a role on its recognition. Two experiments were conducted to test these predictions. The translation recognition task was performed from Catalan to Spanish in Experiment 1 and from Spanish to Catalan in Experiment 2.

Method

Participants

A total of 123 participants took part in the two experiments reported in the present study. Sixty-four participated in Experiment 1 (mean age: 19.5; SD=2.3; 11 males and 53 females) and 59 participated in Experiment 2 (mean age= 20.1; SD=3.1; 7 males and 52 females). All the participants had normal or corrected to normal vision. All participants were born in Catalonia, a region of Spain where there are two official languages: Catalan and Spanish. They were undergraduate students of Psychology, Communication Sciences, and Education, at the Rovira i Virgili University, Tarragona, and they received course credit for their participation. None of the participants took part in more than one experiment.

Participants' proficiency

All participants completed a questionnaire to assess their use and proficiency of Catalan and Spanish. This questionnaire included questions regarding the age of acquisition, the language spoken at home and in society. There also were questions regarding their proficiency in the two languages in listening, speaking, reading and writing. Participants were also asked to rate their frequency of use and preference for each language in the four aforementioned linguistic skills. The proficiency levels of Catalan and Spanish were assessed by using a 1-to-7 Likert scale (1= low proficiency, 7= high proficiency). The participants' level of proficiency in listening, speaking, reading and writing in the two languages is presented in Table 1.

Participants also rated the frequency and preference of use of the two languages on a scale from 1 to 7, where the values from 1 to 3 indicated that respondents use more Catalan than Spanish and prefer Catalan over Spanish, and from 5 to 7 indicated that respondents use more Spanish than Catalan, and prefer Spanish over Catalan. The middle score (i.e., 4) on the scale indicated that respondents use both languages to the same extent, and do not prefer one language over the other.

Table 1. Mean (SD in parentheses) of the level of proficiency in listening, reading, speaking and writing in Catalan and Spanish.

	Experiment 1		Experiment 2	
Proficiency	Catalan	Spanish	Catalan	Spanish
Listening	6.4 (1.7)	6.4 (1.5)	6.8 (0.4)	6.8 (0.6)
Reading	6.4 (1.7)	6.3 (1.5)	6.7 (0.6)	6.6 (1.1)
Speaking	6.2 (1.7)	5.9 (1.6)	6.5 (0.7)	6.6 (0.7)
Writing	6.0 (1.7)	6.0 (1.6)	6.3 (0.8)	6.5 (0.8)

The questionnaire showed that the 64 participants of Experiment 1 had acquired both languages in their early childhood (mean age of acquisition of Catalan: 2.48; SD = 2.23; mean age of acquisition of Spanish: 4.19; SD = 3.76). As can be seen in Table 1, participants rated themselves as highly proficient in both languages. Planned comparisons showed no differences in proficiency between Catalan and Spanish, listening [$t(126) = 0.05$; $p > .05$], reading [$t(126) = 0.16$; $p > .05$], speaking [t (126) = 1.05; p > .05] and writing [t (126) = 0.11; p > .05]. However, the questionnaire revealed that participants used relatively more Catalan than Spanish and also that they show a slight preference for Catalan over Spanish in each of the four aforementioned skills: *use* (listening: 3.4 (SD=1.5); speaking: 3.1 (SD=1.9); reading: 3.4 (SD=1.5); writing: 2.6 (SD=1.4)); *preference* (listening: 3.2 (SD=1.5); speaking: 3.0 (SD=2.0); reading: 3.3 (SD=1.6); writing: 3.1 (SD=1.7)).

The questionnaire showed that the 59 participants of Experiment 2 had acquired both languages in their early childhood (mean age of acquisition of Catalan: 3.22; SD= 3.08; mean age of acquisition of Spanish: 3.34; SD= 3.61). As seen in Table 1, the participants of Experiment 2 rated themselves as being highly proficient in both languages. Planned comparisons failed to show any difference in proficiency between Catalan and Spanish: listening [t (116) = 0.70; p > .05]; reading [t (116) =0.18; p > .05]; speaking [t (116) = 0.18; p > .05]; writing [t (116) = 1.32; p > .05]. As in Experiment 1, the questionnaire revealed that participants used and preferred slightly more Catalan than Spanish in each of the four aforementioned skills: *use* (listening: 3.5 (SD = 1.4); speaking: 3.6 (SD = 1.9); reading: 3.7 (SD = 1.7); writing: 3.2 (SD = 1.6); *preference* (listening: 3.7 (SD = 1.6); speaking: 3.8 (SD = 2.1); reading: 3.9 (SD = 1.7); writing: 3.8 (SD = 1.8)).

Experiment 1: Translating from Catalan to Spanish

Materials

Seventy-two semantically related pairs (e.g., *mussol-águila [owl-eagle]*; Catalan-Spanish) were initially selected from a Spanish database (Moldovan, Ferré, Demestre, & Sánchez-Casas, in press) and from Sánchez-Casas, Ferré, García-Albea, and Guasch (2006). It is important to note that according to the Spanish free association norms (NIPE, Fernández, Díez, Alonso, & Beato, 2004) the pairs were not associatively related. The mean semantic similarity (in a Likert-like scale ranging from 1(nothing similar) to 9 (exactly the same thing)) of the 72 pairs was 5.74 (SD = 0.75).

Besides the semantically related word, each Catalan word was also paired with two types of orthographically similar words in Spanish. On the one hand, there were lexical neighbors. In the present work, we considered as a lexical neighbor for a given word in one language, an orthographically similar word in the other language. For example, a lexical neighbor for the Catalan word "*mussol*" (*owl*) is the Spanish word "*muslo*" (*thigh*), given that they are orthographically similar and share no meaning. On the other hand, there were translation neighbors. A translation neighbor for a particular word in one language is a word in a different language that is orthographically similar to the correct translation of the original word. For example, a translation neighbor for the Catalan word "*mussol*" is the Spanish word "*buzo*" (*diver*), given that "*buzo*" is orthographically similar to "*búho*", the correct translation of the Catalan word "*mussol*". The NIM database (Guasch, Boada, Ferré, & Sánchez-Casas 2013) was used to obtain the orthographic similarity between each Catalan word and its lexical and translation neighbors in Spanish. The orthographic similarity between two words was obtained by applying Van Orden's (1987) algorithm, that uses a scale from 0 (not similar at all) to 1 (exactly the same lexical string). Lexical neighbors had a mean orthographic similarity of 0.65 (SD = 0.14) and translation neighbors of 0.69 (SD = 0.11).

The two orthographically related conditions, as well as the semantically related condition, were paired with their corresponding control conditions, that is, Spanish words neither related in form nor in meaning to the Catalan word. The words in the control conditions had the same length and frequency (all ts < 1) as the words in the related conditions. Table 2 provides frequency and length information for each experimental condition.

Table 2: Mean length (number of letters) and frequency of use of the materials of experiments 1 and 2.

	Experiment 1				Experiment 2			
	Frequency		Length		Frequency		Length	
Condition	Related	Unrelated	Related	Unrelated	Related	Unrelated	Related	Unrelated
Lexical Neighbors	25.2	25.7	6.1	6.1	28.7	28.5	6.3	6.3
Semantically related	14.6	14.7	7.0	7.1	18.6	18.2	6.6	6.6
Translation Neighbors	16.6	16.5	6.4	6.5	34.2	35.5	6.2	6.1

Note: The Catalan and Spanish word frequency counts were obtained from NIM (Guasch, et al., 2013).

The experiment had six experimental conditions that resulted from crossing the factors type of relationship (semantic, lexical neighbors, translation neighbors) and relatedness (related vs. unrelated). Six experimental lists were constructed in order for each Catalan word to appear only once in each list, but each time in a different experimental condition. Apart from the critical 72 non-translation pairs, seventy-two filler translation pairs were created. Thus, all lists had 144 word pairs, 72 translation pairs and 72 non-translations pairs. The 72 translation pairs were the same in the six experimental lists.

Procedure

We used a translation recognition task, in which participants were asked to decide whether the second word in a pair was a correct translation of the first one. Participants had to answer by pushing one of two buttons: the "YES" button, with their preferred hand, if the second word of the pair was the correct translation, or the "NO" button, with the other hand, if the second word was not the correct translation. For each participant the computer generated a pseudo-random order of the 144 pairs, thereby avoiding the consecutive appearance of more than two stimuli of the same condition.

Participants were tested individually in a quiet room. Presentation of the stimuli and recording of response times were controlled by PC compatible computers. The experiment was run using DMDX (Forster & Forster, 2003). The presentation sequence was as follows: first, a fixation point ("#") appeared for 500 ms; immediately afterwards, the first word of the pair was presented for 250 ms, and then this word was replaced by the second word of the pair. The second word remained on the screen until the participant responded or 2000 ms had elapsed.

Participants were given written and oral instructions in the language of the first word of the pair (i.e., Catalan). Both speed and accuracy were stressed in the instructions. Twelve practice trials preceded the experimental trials. The experiment lasted approximately 15 minutes.

Results and Discussion

Reaction times (RTs) with values below 200 ms and above 2000 ms, established beforehand as cut-off points, were removed from the analysis and were treated as outliers. Values that were 2.0 standard deviations below or above the participant's mean were discarded. Further, trials with 100 % of errors were excluded. This data-trimming led to the exclusion of 7.1 % of the original data. In addition, data from 4 participants were removed from the analysis because they made more than 15% errors.

The data for the critical non-translation pairs are shown in Table 3. Separate ANOVAs were performed on the RTs and error rates (%E) following a 3x2 factorial design, including the factors: “type of relationship” and “relatedness”. The “type of relationship” factor had three levels (lexical neighbors, semantically related and translation neighbors), and the “relatedness” factor had two levels (related *vs*. unrelated). For participant analyses, the two factors were within-subjects. For item analyses, “relatedness” was a within-items factor, whereas “type of relationship” was a between-items factor.

Table 3: Mean RTs and error rates (%E) in the different experimental conditions and interference effects in Experiments 1 and 2. Interference effects are computed as the difference between related and unrelated conditions. The examples come from Experiment 1 (translation from Catalan to Spanish).

	Experiment 1 (Catalan-Spanish)		**Experiment 2 (Spanish-Catalan)**	
Condition	**Mean**	**% E**	**Mean**	**% E**
Lexical Neighbors *(e.g., mussol-muslo [owl-tight])*	867	7.4	868	8.7
Unrelated *(e.g., mussol-telón [owl-curtain])*	792	2.4	767	1.2
Interference Effect	**75**	**5.0**	**101**	**7.5**
Semantically related *(e.g., mussol-áquila [owl-eagle])*	923	31.7	937	27.5
Unrelated *(e.g., mussol-encaje [owl-lace])*	799	1.4	777	2.2
Interference Effect	**124**	**30.3**	**160**	**25.3**
Translation Neighbors *(e.g., mussol-buzo [owl-diver])*	875	12.7	858	9.4
Unrelated *(e.g., mussol-caño) [owl-spout])*	801	2.4	777	2.1

Interference Effect	**74**	**10.3**	**81**	**7.3**

RT analysis:

The ANOVA revealed main effects of type of relationship [$F_1(2,118) =7.02$, $p<.001$, $\eta^2 =.106$; $F_2(2,140) =2.91$, $p=.58$, $\eta^2 =.040$] and relatedness [$F_1(1,59) =159.81$, $p<.001$, $\eta^2 =.730$; $F_2(1,70) =49.16$, $p<.001$, $\eta^2 =.413$]. The interaction between both factors also reached significance in both analyses [$F_1(2,118) =4.17$, $p<.05$, $\eta^2 =.066$; $F_2(2,140) =2.75$, $p =.67$, $\eta^2 =.038$].

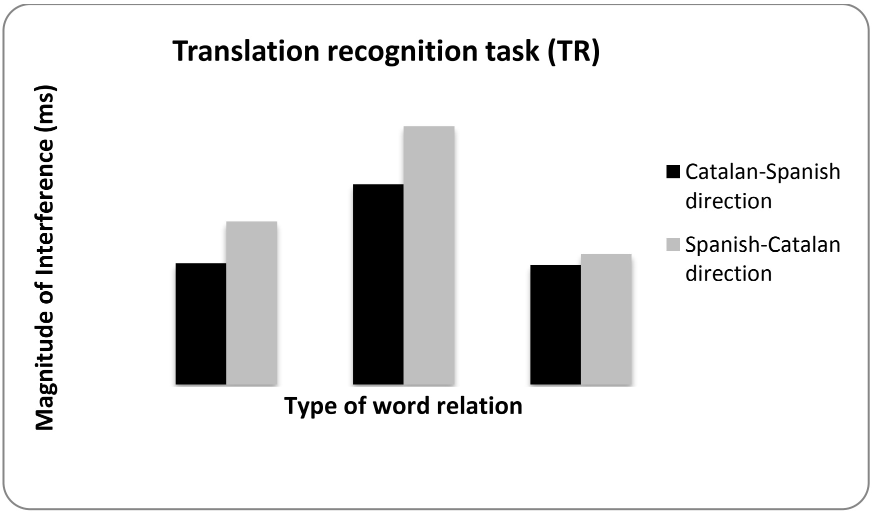
Planned comparisons showed a significant interference effect for the three types of relationships: lexical neighbors [t_1 (59) =7.62, $p<.001$; t_2 (70) =5.17, $p<.001$], semantically related words [t_1 (59) =8.42, $p<.001$; t_2 (70) =5.20, $p<.001$] and translation neighbors [t_1 (59) =4.82, $p<.001$; t_2 (70) =4.64, $p<.001$]. We also analyzed whether the magnitude of the interference effect was different across conditions (see Figure 3). The results of the analyses revealed that semantically related words produced a larger interference effect than both translation neighbors (50 ms difference) [t_1 (59) =2.31, $p<.05$; t_2 (70) =1.85, $p=.06$] and lexical neighbors (49 ms difference) [t_1 (59) =2.62, $p<.05$; t_2 (70) =1.85, $p=.06$]. Conversely, there were not differences between lexical and translation neighbors (1 ms difference) [t_1 (59) =0.05, $p>.05$; t_2 (70) =0.17, $p>.05$].

%E analysis:

The ANOVA revealed main effects of type of relationship [F1 (2,118) =57.45, $p<.001$, $\eta^2 =.493$; F2 (2,140) =37.72, $p<.001$, $\eta^2 =.350$] and relatedness [F1 (1,59) =276.48, $p<.001$, $\eta^2 =.824$; F2 (1,70) =90.23,

$p<.001$, $\eta^2=.563$], as well as an interaction between both factors [F1 (2,118) =63.76, $p<.001$, $\eta^2=.519$; F2 (2,140) =40.53, $p<.001$, $\eta^2=.367$]. Planned comparisons showed a significant interference effect for the three types of relationships. Participants were less accurate in rejecting pairs that were lexical neighbors [t_1 (59) =4.47, $p<.001$; t_2 (70) =3.66, $p<.001$], semantically related [t_1 (59) =14.81, $p<.001$; t_2 (70) =9.21, $p<.001$] and translation neighbors [t_1 (59) =6.30, $p<.001$; t_2 (70) =5.62, $p<.001$] than in rejecting non-related pairs. The comparison of the magnitude of effects across conditions (see Figure 3) revealed that semantically related words produced a larger interference effect than translation neighbors (20 % difference) [t_1 (59) =7.51, $p<.001$; t_2 (70) =6.23, $p<.001$]. A similar pattern was observed when comparing semantically related words with lexical neighbors (25% difference) [t_1 (59) =10.36, $p<.001$; t_2 (70) =7.31, $p<.001$]. Furthermore, the magnitude of interference was higher for translation neighbors than for lexical neighbors (5.3 % difference) [t_1 (59) =2.78 $p<.05$; t_2 (70) =2.56, $p<.05$].

Figure 3: Magnitude of the interference effect (ms) in Experiment 1 and 2 for the three types of word relations (lexical neighbors, semantically similar pairs and translation neighbors) in the two languages direction of translation (Catalan-Spanish and Spanish-Catalan)



As it was predicted, Experiment 1 showed that the three types of word relationships interfered when bilinguals translated from Catalan to Spanish, although the magnitude of the interference was higher for semantically related words than for the two lexically related conditions. In addition, both types of lexically related pairs interfered to the same extent. If we consider the results of the semantic and the translation neighbors condition, they are in agreement with previous findings obtained with the same population of bilinguals (Ferré et al., 2006; Guasch et al., 2008; Moldovan et al., 2012). The present results, obtained with a short SOA, do not seem to support the account of Guo et al., (2012) concerning the activation of translation equivalents in proficient bilinguals only with long SOAs. Instead, they suggest that variables such as the use and exposure to Catalan and Spanish might contribute to maintain a high activation level for both languages, as the strong interference effect obtained with lexical neighbors also indicates. As an additional aim of our study was to test whether the effects are symmetrical across directions, in the following experiment we examined the interference pattern for the same types of relationships in the other direction of translation (i.e., from Spanish to Catalan).

Experiment 2: Translating from Spanish to Catalan

Materials

The 72 semantically similar pairs were the same as in Experiment 1. The only difference being that for the initial word (i.e., the Spanish word that was presented as the first word of the pair to be translated), we selected new lexical and translation neighbors, by using the same database as in the previous experiment. The mean of orthographic similarity for the lexical neighbors was 0.64 (SD =0.12) and for translation neighbors 0.69 (SD =0.12). New control words for the six experimental conditions were also selected. The characteristics of the words of Experiment 2 are presented in Table 2. The 72 correct translation pairs that acted as fillers were the same as in Experiment 1, the only difference being that in Experiment 2 the first word of the pairs was presented in Spanish and the second one in Catalan.

As in the previous experiment, the six experimental conditions were counterbalanced, leading to six different lists of 144 pairs: 72 non-translation and 72 translation pairs. All the words appeared in each of the six lists that were created, but each time in a different condition.

Procedure

The procedure and equipment were the same as in Experiment1.

Results and discussion

The same data trimming as in Experiment 1 was applied to the data of this experiment. It led to the exclusion of 6.5 % of the original data. Moreover, data from 7 participants were removed from the analysis because they made more than 15% errors.

The data for the critical non-translation pairs are shown in Table 3. As in Experiment 1, separate ANOVAs were performed on the RTs and %E following a 3x2 factorial design, including the factors: "type of relationship" and "relatedness".

RT analysis:
The ANOVA revealed a main effect of type of relationship [F1 (2,102) =8.69, p<.001, η^2=.146; F2 (2,132) =7.02, p<.001, η^2=.096] and relatedness [F1 (1,51) =172.56, p<.001, η^2=.772; F2 (1,66) =143.15, p<.001, η^2=.684]. The interaction between both factors was also significant [F1 (2,102) =9.80, p<.001, η^2=.161; F2 (2,132) =5.23, p< .05, η^2=.07].
Planned comparisons showed a significant interference effect for the three types of relationships: lexical neighbors [t_1 (51) =8.36, p<.001; t_2 (66) =7.49, p<.001], semantically related words [t_1 (51) =9.75, p<.001; t_2 (66) =8.04, p<.001] and translation neighbors [t_1 (51) =6.57, p<.001; t_2 (66) =5.56, p<.001]. The comparison of the magnitude of effects (see Figure 3) revealed that semantically related words produced a larger interference effect than either translation neighbors (51 ms difference) [t_1 (51) =3.82, p<.001; t_2 (66) =2.78, p<.05] or lexical neighbors (59 ms difference) [t_1 (51) =3.08, p<.05; t_2 (66) =2.30, p<.05]. Conversely, the difference in the magnitude of interference produced by lexical and translation neighbors

(20 ms difference) was not reliable [t_1 (51) =1.31, p>.05; t_2 (66) =0.91, p>.05].

%E analysis:

The ANOVA revealed main effects of type of relationship [F1 (2,102)=51.70, p<.001, η^2=.503; F2 (2,132)=26.19, p<.001, η^2=.284] and relatedness [F1 (1,51)=146.13, p<.001, η^2=.741; F2 (1,66)=92.64, p<.001, η^2=.584], as well as an interaction between both factors [F1 (2,102)=39.67, p<.001, η^2=.437; F2 (2,132)=22.46, p<.001, η^2=.25].

Planned comparisons showed a significant interference effect for the three types of relationships. Participants were less accurate in rejecting pairs that were lexical neighbors [t_1 (51) =5.60, p<.001; t_2 (66) =4.2, p<.001], semantically related [t_1 (51) =11.70, p<.001; t_2 (66) =8.35, p<.001] and translation neighbors [t_1 (51) =4.55, p<.001; t_2 (66) =4.10, p<.001], than in responding to non-related pairs. The comparison of magnitudes (see Figure 3) showed that the amount of interference produced by semantically related words was higher than the interference obtained with either translation neighbors (18 % difference) [t_1 (51) =6.91, p<.001; t_2 (66) =5.32, p<.05] or lexical neighbors (18 % difference) [t_1 (51) =7.66, p<.001; t_2 (66) =4.99, p<.05]. As in reaction times, there was not a reliable difference between translation neighbors and lexical neighbors in the amount of interference produced (0.2 % difference) [t_1 (51) =0.11 p>.05; t_2 (66) =0.29, p>.05].

The pattern of results of Experiment 2 is exactly the same as those obtained in Experiment 1: strong interference effects in the three experimental conditions that had a greater magnitude in semantically related pairs. In order to test whether translation direction has affected the magnitude of effects, we conducted a conjoint analysis of both experiments.

Analyzing Translation Direction:

Data from translation pairs: In order to see whether there was any difference in translation speed when participants translated from Catalan to Spanish (Experiment 1) and from Spanish to Catalan (Experiment 2), we also compared the reaction time (RTs) and percentage of errors (%E) to the correct translations between the two translation directions. The mean RT in Experiment 1 was 745 ms (SD=154) and the %E was 10.2 (SD=3.5). In Experiment 2, the mean RT was 708 (SD=135) and %E 10.0 (SD=4.3). Planed comparisons between the two translation directions showed no significant difference neither in RTs (37 ms of difference), $t(110)=1.34$; $p>.05$ nor in %E (0.2 difference), $t(110)=0.24$; $p>0.5$.

Data from the critical non-translation pairs: We conducted two ANOVAs on RTs and %E in which , besides “type of relationship” and “relatedness”, the factor “direction” was included as a between-subjects factor in the analysis by participants and a between-items factor in the analysis by items.

Concerning RTs, the ANOVA revealed a significant effect of type of relationship [$F1\ (2,220) = 15.73$, $p<.001$, $\eta^2 = .12$; $F2\ (2,408) = 6.52$, $p<.05$, $\eta^2 = .03$] and relatedness [$F1\ (1,408) = 208.08$, $p<.001$, $\eta^2 = .75$; $F2\ (1,66) = 92.64$, $p<.05$, $\eta^2 = .58$], as well as an interaction between both factors [$F1\ (2,220) = 12.73$, $p<.001$, $\eta^2 = .10$; $F2\ (2,408) = 6.56$, $p<.005$,

η^2 =.25]. Importantly, although there was not any effect on the factor direction (M=842.9 ms and M=830.6 ms, for the Catalan-Spanish direction and the Spanish-Catalan direction, respectively), the interaction between relatedness and translation direction reached statistical significance [F1 (1,110) =4.36, $p<.05$, η^2=.04; F2 (1,408) =3.58, p =.06, η^2=.01]. This interaction revealed that, taking all the conditions together; interference effects were higher in the Spanish-Catalan direction (M=114.1, Experiment 2) than in the Catalan-Spanish direction (M=90.7, Experiment 1), [t_1 (110) =2.09, $p<.05$; t_2 (412) =1.87, p= .06].

The analysis of %E showed a significant effect of the type of relationship [F1 (2,220) =106.56, $p<.001$, η^2 =.49; F2 (2,408) =52.68, $p<.001$, η^2 =.28] and relatedness [F1 (1,110) = 403.29, $p < .001$, η^2 =.79; F2 (1, 408) = 232.56, $p < .001$, η^2=.58], as well as an interaction between both factors [F1 (2, 220) =99.78, $p<.001$, η^2=.48; F2 (2,408) =51.44, $p<.001$, η^2=.25]. There was neither an effect of the factor direction (M=9.61 and M=8.68 for Experiment 1 and Experiment 2, respectively) nor any reliable interaction with this factor.

The results of the joint analysis of both experiments reveal that, whereas there was not any difference between the two directions of translation in either response times or percentage of errors, as would be expected in highly proficient and balanced bilinguals, the amount of interference, when considering reaction times, was higher in the Spanish-Catalan direction than in the Catalan-Spanish direction. The implications of these results are addressed in the General Discussion.

General Discussion

The present study placed the predictions of the BIA model (Dijkstra & Van Heuven, 1998) and the RHM (Kroll & Stewart, 1994) in the same experimental context in order to examine the pattern of cross-language lexical and semantic activation during translation recognition. It focused on highly proficient bilinguals of Catalan and Spanish who live immersed in a context in which the two languages are actively used. We performed two experiments by using the translation recognition task with the interference paradigm and by testing two types of form related words (i.e., lexical and translation neighbors) as well as a semantically related condition. Experiment 1 was performed from Catalan to Spanish and Experiment 2 from Spanish to Catalan. We obtained strong and reliable interference effects with the three types of relations, which were larger for the semantically related pairs than for the form related pairs, whereas the magnitude of interference was the same for lexical neighbors as for translation neighbors. The pattern of effects was the same in the two directions of translations, although overall the magnitude of interference was larger in the Spanish-Catalan direction than in the Catalan-Spanish direction.

In line with previous evidence and with the predictions of the RHM, we found a strong semantic interference effect. This result is in agreement with all the past research conducted with the translation recognition task with proficient bilinguals (Ferré et al., 2006; Guasch et al., 2008; Guo et al., 2012; Linck et al., 2009; Moldovan et al., 2012; Sunderman et al., 2006; Talamas et al., 1999). Furthermore, semantic interference was observed in both translation directions, also in line with previous studies that have manipulated translation direction in this task (Moldovan et al., 2012). Another experimental approach commonly used in research aimed to test RHM predictions concerning semantic access in highly proficient bilinguals has been the use of semantic and translation priming across languages (see Basnight-Brown & Altarriba, 2007, for a review). Priming findings have usually revealed stronger effects in the L1-L2 direction than in the L2-L1 direction (in which many times there is no priming at all). However, in highly proficient and balanced bilinguals this asymmetry between directions is reduced (e.g., Duñabeitia, Perea, & Carreiras, 2010; Guasch, Sánchez-Casas, Ferré, & García-Albea, 2011; Perea, Duñabeitia, & Carreiras, 2008). As Catalan-Spanish bilinguals are highly proficient and use both languages on a regular basis, our results are in agreement with those obtained in priming in a similar type of bilinguals.

The regular use of both languages might also explain the robust interference effect observed with translation neighbors. In line with past research conducted with the same type of bilinguals (Guasch et al., 2008; Ferré et al., 2006; Moldovan et al., 2012), we obtained a reliable interference effect with this type of words related in form to the correct translation, although it was of a smaller magnitude than that produced by semantically related words. The strong interference effect obtained with translation neighbors contrasted with the RHM assumption with respect to proficient bilinguals. Given the increasing evidence suggesting that L1 translation equivalents may be activated not only when proficient bilinguals are translating but also when they are performing tasks exclusively in L2 (e.g., Thierry & Wu, 2007; Wu & Thierry, 2010), Guo et al., (2012) proposed that these bilinguals would activate translation equivalents after accessing the meaning of L2 words. According to these authors, most of the findings reported in translation recognition concerning this issue might be explained by the long SOAs used (Ferré et al., 2006; Guasch et al., 2008). In the present study we used a very short

SOA (250 ms, see also Moldovan et al., 2012), even shorter than that of Guo et al., (2012). Thus, it is unlikely that the interference obtained with translation neighbors is a consequence only of long SOAs that allow their activation once meaning is accessed. However, it might be possible that highly proficient and skilled bilinguals such as those tested in the present study are able to access meaning very quickly and that 250 ms is a period of time long enough to allow the subsequent activation of the translation equivalent. We cannot discard this possibility from behavioral measures. In order to properly test this account, we should use ERP recordings, which could reveal the temporal course of meaning access and activation of translation equivalents, as done by Guo et al., (2012). Another possible reason for the strong interference effects obtained with translation neighbors in Catalan-Spanish bilinguals is that they are in fact using the lexical route of translation because of the characteristics of the pair of languages. That is, Catalan and English have a very high percentage of cognates. Although in the present experiment the critical translations were non-cognates, the immersion of bilinguals in two languages with such a high amount of cognates might strengthen the use of the lexical route as a usual translation strategy, as it has been proposed that cognate words have stronger links at the lexical level than non-cognates (Kroll & Stewart, 1994). Nevertheless, the results of Guo et al., (2012) showing reliable behavioral interference effects with translation neighbors in bilinguals of two languages sharing a few number of cognates (i.e., Chinese and English) do not provide support to this possibility. In our opinion, the present and past results obtained in Catalan-Spanish bilinguals might be better explained by the regular and constant exposure to both languages in the immersion context. The idiosyncratic characteristics of such context, very difficult to find in other populations of bilinguals, might contribute to a high resting level of activation of the two languages that could support strong interference effects. Admittedly, we cannot conclude that it is the use/exposure of both languages the reason for this effect, as we did not manipulate it in our study. To pursue this issue, we should test two groups of Catalan-Spanish bilinguals, one immersed in the usual context (i.e., living in Catalonia), and another one that, being highly proficient, uses much more one language than the other (e.g., because they were living outside of Catalonia, in a Spanish-speaking environment). Further research should be conducted in this direction.

The last experimental condition included in our study (i.e., lexical neighbors) also produced a reliable interference effect, as predicted by BIA (Dijkstra & Van Heuven, 1998) and BIA+ (Dijkstra & Van Heuven, 2002) and in line with past research with the translation recognition task (Linck et al., 2009; Sunderman et al., 2007), thus giving support to the well-established language non-selective access (Schwartz & Van Hell, 2012; van Hell & Tanner, 2012; van Assche et al., 2012). Interestingly, the effects were of the same size as those obtained with translation neighbors, despite the path steps underlying the activation of theses two types of word relatedness are probably distinct. According to BIA, the interference of lexical neighbors is produced by the competition between words that share some letters, as a result of their activation. Thus, it is a "direct or automatic" cross-languages interference effect (i.e., the presentation of a word in one language, as in the Catalan-Spanish example "*mussol-muslo*" [*owl-tight*] directly/automatically activates words similar in form in the other language). Differently, the interference produced by translation neighbors (e.g., *mussol-buzo* [*owl-diver*]) cannot be explained directly. In fact, BIA and BIA+ would not predict such interference with pairs of non-cognate translations, as those used in the present study. That is, as the Spanish translation "*búho*" is not similar in form to the Catalan word "*mussol*", neither is the translation neighbor "*buzo*". Thus, the Spanish translation neighbor cannot be directly/automatically activated when the Catalan word is presented. Rather, such interference is better explained through a more indirect route; namely, the first word presented "*mussol*" would activate its translation equivalent "*búho*" which in turn would activate orthographically similar words in the same language (i.e., *buzo*, in Spanish). Therefore, in this case, the interference is necessarily mediated by the activation of the translation equivalent (i.e., indirect). If we consider the processes involved in translation recognition, the interference produced by lexical neighbors seems to be located at the beginning of the process (i.e., during nonselective lexical access produced by a visual string of letters), whereas the interference observed with translation neighbors might be more related with a competition at the end of this process, when bilinguals have to give their answer to the presented pair. Clearly, this possibility cannot be tested with behavioral measures. It would be very interesting in the future to use ERPs to study the on-line processing of these two types of word relationships in order to test whether the predicted differences in the time-course of their activation are confirmed.

There is a final relevant point to be mentioned, which concerns the effects of translation direction. Although we obtained the same pattern of interference in the two translation directions with the three types of relationships, considering all the experimental conditions together, the effects were greater in the Spanish-Catalan direction than in the Catalan-Spanish direction. As our bilinguals are balanced, we should expect the same magnitude of effects across directions. However, if we look at the description of the bilinguals obtained from their self ratings, we will realize that they use and prefer slightly more Catalan than Spanish. By taking this bilinguals' characteristic into account, our result might suggest that slight differences in use can modulate the asymmetries observed, since the interference produced by the most used language (Catalan) was stronger than that produced by the less used one (Spanish). This interpretation would be in agreement with past research demonstrating an effect of use/immersion on bilinguals' performance in the translation recognition task (Linck et al., 2009; Sunderman & Priyah, 2012) as well as in other tasks such as picture naming (Baus et al., 2013). The effects of language use may be accounted for BIA (Dijkstra, 2005; Thomas & Van Heuven, 2005), at least for lexical neighbors, as it proposes that the activation of a word is modulated by its subjective frequency of use. If Catalan words are slightly more used by these bilinguals than Spanish words, it is logical to expect more interference from the former than from the latter. Nevertheless, it is worth considering that the study conducted by Moldovan et al., (2012) with similar bilinguals failed to find any effect of bilinguals' dominance (defined in terms of language proficiency, use and preference), a result that is at odds with the present interpretation. Although we do not have at present a clear explanation for this discrepant pattern of findings, they should be interpreted with caution. It has to be considered that, in the present study (as well as in Moldovan et al., 2012), the data of the two translation directions were obtained from different groups of bilinguals, in a between-subjects design, which is clearly a limitation. Thus, it might be argued that the difference in magnitude is a result of differences between the participants of Experiment 1 and 2 with respect to their patterns of language proficiency/use or overall reaction times (i.e., there might be more room to observe interference effects with faster participants). There are several reasons that led us to think that this is not the cause of the difference between directions. On the one hand, the average values of proficiency and use/preference of the bilinguals of Experiment 1 and 2 are very similar and in both cases Catalan was the more used language. On the other, bilinguals of Experiment 1 were as fast as those of Experiment 2, as revealed by the lack of differences in overall reaction times. Nevertheless, in order to obtain more reliable conclusions, a further experiment should be conducted where translation direction is manipulated within-participants.

To conclude, the results of the present study provided evidence of cross-languages lexical and semantic activation in early and highly proficient bilinguals of Catalan and Spanish. They were immersed in the two languages and they used both of them on a regular basis. There were interference effects with the three types of related pairs: lexical and translation neighbors and semantically related words. There were interference effects in the two translation directions, which were greater from the more used language than for the lesser used one. Further research should be conducted by manipulating language use in a between-participants' design and by manipulating language direction in a within-participants' design. Additionally, it would be very informative to use electrophysiological measures, such as ERPs, to characterize the time-course of the lexical and semantic activation during translation recognition.

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Study 4

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The role of meaning and form similarity in translation recognition in highly proficient bilinguals: an ERP study

The role of meaning and form similarity in translation recognition in highly proficient balanced bilinguals: an ERP study

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Abstract

Previous behavioral findings have shown that pairs of words that are highly related in meaning across two languages and pairs of words in which the second word is related in lexical form to the correct translation of the first word produce interference effects when highly proficient balanced bilinguals perform a translation recognition task (Ferré et al., 2006; Moldovan et al., 2012). Likewise, interference effects were not observed when the two words were less related in meaning. The lack of interference effects with less related words could be explained by the fact that the level of activation of the corresponding semantic representations is too low and decreases rapidly so as to produce interference at the time the translation decision has to be made. Moreover, the lack of effects might also be due to the fact that behavioral measures are not sensitive enough to capture the activation of such representations. In the present study, a SOA of 250 ms was used while highly proficient balanced Catalan-Spanish bilinguals performed a translation recognition task. Both behavioral and electrophysiological measures were recorded. Three experimental conditions were used: pairs of words highly related in meaning, pairs of words less related in meaning, and pairs in which the second word was similar in lexical form to the correct translation of the first word of the pair. Behavioral results showed interference effects in all conditions. ERPs revealed modulations of the N400 for the two semantic conditions, and modulations of the LPC for the form condition. These results suggest that meaning is accessed before the translation equivalent becomes available, that is, highly proficient balanced bilinguals can directly access the conceptual system from both of their languages.

Keywords: bilingualism, lexicon, semantics, translation, ERPs

Introduction

Words can be more or less similar in (orthographic or phonological) form and in meaning. Form and meaning similarity can be observed both within and between languages. We will first focus on meaning similarity. Meaning similarity between two words can be explained in terms of the number of semantic features shared by these words (e.g., McRae, Cree, Seidenberg, & McNorgan, 2005; Sánchez-Casas, Ferré, García-Albea, & Guasch, 2006; Vigliocco, Vinson, Lewis, & Garrett, 2004). Studies that have explored the issue of semantic similarity suggest that it affects word processing both in monolinguals (McRae, de Sa, & Seidenberg, 1997) and in bilinguals (Guasch, Sánchez-Casas, Ferré, & García-Albea, 2011). Focusing on semantic similarity between words of a first (L1) and a second language (L2), the present study examines the time course of meaning activation across languages during the translation process in highly proficient balanced Catalan-Spanish bilinguals.

There are two models of bilingual memory that address how meaning is represented and accessed in the two languages of a bilingual. These are the Distributed Representational Model (DRM, de Groot, 1992a, 1992b) and the Revised Hierarchical Model (RHM, Kroll & Stewart, 1994). Both models assume that form and meaning are represented in two separate but interconnected levels. On the one side, there is a lexical level that represents the words' orthographic and phonological information. On the other side, there is the semantic-conceptual level that represents the words' meaning. The models differ in that the DRM is somehow more focused on the nature of semantic representations, and, thus, can address more directly issues related to the semantic relations among words of different languages, whereas the RHM is more focused on trying to explain how the meaning of a word is accessed differently (i.e., directly or via an indirect route through the translation equivalent of an L2 word) as a function of L2 proficiency, and, thus, is more suitable to address issues related to the connections between the lexical and the conceptual levels of representation. The two models are complementary in that taken together they offer a wider picture of how meaning is represented, and how meaning is accessed at different levels of L2 proficiency. In what follows, we will first address the issue of meaning similarity following the assumptions of the DRM, and, after that, we will address how meaning is accessed in highly proficient bilinguals according to the RHM.

According to the DRM, the meaning of a word is represented as a set of nodes, each node representing a semantic feature. The nodes are connected to the corresponding lexical forms in the two languages of a bilingual. For instance, translation equivalents (e.g., the Catalan-Spanish pair *ruc-burro* [donkey]) are represented at the lexical level by two nodes, each node representing a word in each of the two languages. These two individual nodes are then connected to a number of nodes at the semantic level of representation. In the cases, as in the example *ruc-burro,* in which there is a complete overlap in meaning between the two words, the nodes representing the meaning of the first word would be the same as the nodes representing the meaning of the second word. Furthermore, words that are related in meaning but do not have a complete meaning overlap, will share part of (but not all) the features at the conceptual level. The more similarity between the meaning of the two words the more nodes shared by the two featural representations. Thus, two words that are highly related in meaning across the two languages (e.g., the Catalan–Spanish pair *ruc–caballo* [donkey-horse]) would share (and activate) more nodes than pairs of word less related in meaning (e.g., the Catalan–Spanish pair *ruc–oso* [donkey-bear]).

A task that has been used to examine how bilinguals access the meaning of L2 words is the translation recognition task (de Groot, 1992b). In this task, participants are presented with a first word in one language followed by a second word in another language and they have to decide whether the second word is the correct translation of the first one (e.g. *ruc-burro* where "burro" is the correct Spanish translation of the Catalan word "ruc"). The critical pairs are those in which the two words are not correct translations. The critical pairs are expected to produce interference effects. Interference effects are the difference in reaction times (RTs) and in error rates between the responses given by participants to the related pairs and the responses given to the unrelated pairs. As the DRM assumes that the number of features shared by two words depends on their similarity in meaning, one would expect that pairs of words that are highly related in meaning (e.g. *ruc-caballo*; henceforth S1) would produce stronger interference effects than pairs of words that are less related in meaning (e.g. *ruc-oso*; henceforth S2). That is, if the second word of a pair shares a great number of features with the first word of the pair, processing the first word would activate part of the features representing the second word, and thus, after encountering the second word it would be harder for subjects to answer that the second word is not the translation of the first word.

The first bilingual study that experimentally manipulated the degree of semantic similarity between two words and that used the interference paradigm is that of Ferré, Sánchez-Casas, and Guasch (2006).

The authors examined highly proficient balanced Catalan-Spanish bilinguals and used a stimulus onset asynchrony (SOA, the time interval from the onset of the first word to the onset of the second word) of 500 ms. They observed interference effects with highly related word pairs (i.e., the S1 condition), but no effects were observed with less related word pairs (i.e., the S2 condition). According to Moldovan, Sánchez-Casas, Demestre, and Ferré (2012), a possible explanation for the absence of interference effects in S2 pairs might be that the level of activation of their semantic representations is two low (and decreases very rapidly) so as to produce interference by the time the translation decision has to be made (*the low level activation account)*. According to the DRM, when two semantically related words are presented, semantic nodes (both the nodes shared and the nodes not shared by the two words) are activated, and the level of activation is higher for those nodes that are shared as compared to the nodes that are not shared by the two words. In the translation recognition task, when the Catalan word *ruc* is presented, the nodes that represent its meaning will be activated. Some of the activated nodes will be part of the semantic representation of words such as *caballo* (S1) and *oso* (S2) that are related in meaning to the word *ruc*. However, the level of activation would be higher for *caballo* than for *oso,* since the number of features shared by *caballo* and *ruc* is greater than then number of features shared by *oso* and *ruc*. According to *the low level activation account* (Moldovan et al., 2012), if the level of activation is lower for S2 pairs (e.g., *ruc-oso*) than for S1 pairs (e.g., *ruc-caballo*), it is possible that by the time the translation decision has to be made, the activation level for the word *oso* is too low to compete with the correct translation. In other words, given its low level of activation, *oso* would have already been ruled out as a possible translation. Conversely, the level of activation of the word *caballo* would be high enough to compete with the correct translation, thus producing interference effects by the time the decision has to be made. This proposal takes into account the level of activation and the temporal dynamics of a word's semantic representation, and thus, could account for the absence of interference effects in S2 pairs when a long SOA and the translation recognition task were used: a 500 ms SOA in Ferré et al.'s (2006) study and a 750 ms SOA in Guasch, Sánchez-Casas, Ferré, and García-Albea's (2008) study. Results supporting "the low level activation account" were obtained in a recent study (Moldovan et al., 2012) that used a shorter SOA (250 ms). The behavioral findings showed that S2 pairs produced an interference effect (20 ms) that almost approached statistical significance. Similarly, facilitatory effects for S2 pairs were observed in a semantic priming study using the same SOA (Guasch et al., 2011). This evidence was obtained by using behavioral measures. As it is possible that the activation of an S2 word is too low and decreases very rapidly, RT measures might not be sensitive enough to reveal interference effects in a translation recognition task. The event-related potentials (ERPs) technique is a measure that has been proven to be very sensitive to the time course of word processing (Holcomb & Grainger, 2007). Given its high temporal resolution, it is an excellent technique to examine in greater detail the activation of S2 pairs.

One ERP component that is sensitive to semantic aspects of word processing is theN400 (Kutas & Hillyard, 1980). The N400 is a negative-going component peaking around 400 ms after stimulus onset and is characterized by a large distribution over posterior electrode sites (Kutas & Van Petten, 1994). The amplitude of the N400 is assumed to reflect how easily a word can be semantically integrated into the current context, whether the context is a single word, a sentence, or a discourse (Kutas & Federmeier, 2000; see also van Berkum, Hagoort, & Brown, 1999). The amplitude of the N400 increases in correlation with integration difficulties and is attenuated for items that are easy to integrate. For instance, several studies have demonstrated that the N400 is modulated by the semantic relation between pairs of words, its amplitude being attenuated by prior exposure to a semantically related word (Brown, Hagoort, & Chwilla, 2000). The N400 has also been demonstrated to be modulated by semantic similarity in the bilingual domain. Guo, Misra, Tam, and Kroll (2012) examined proficient unbalanced Chinese (L1)-English (L2) bilinguals immersed in an L2 environment. Participants had to judge whether a Chinese word was the correct translation of an English word. In one type of critical condition, there were Chinese words that were semantically (or associatively) related to the correct translation of the English word (e.g., the English word *needle* was paired with the Chinese word for *thread*). In Experiment 1, with a SOA of 750 ms, both ERP and behavioral data showed that the meaning of the L2 word was available to these bilinguals. Response times to reject Chinese words that were semantically related to the English words were longer than for unrelated controls. Furthermore, semantically related words elicited a smaller N400 relative to unrelated controls as well as a smaller late positive component (LPC) over the posterior scalp and a larger LPC over the anterior scalp. A second behavioral and ERP experiment with identical materials was carried out at a shorter SOA (i.e., 300 ms). The behavioral data in Experiment 2 replicated the findings of Experiment 1 in that there were significant interference effects for semantically related words in RTs and accuracy. A significant semantic interference effect was observed in the time windows for both the N400 and the LPC. These results provide robust evidence for a very rapid activation of the meaning of an L2 word.

The first aim of the present study was to examine how S1 and S2 words are processed in highly proficient balanced bilinguals who live immersed in both languages. Both behavioral and ERP measures were registered while participants performed a translation recognition task with the interference paradigm. Having in mind that the DRM assumes that the degree of semantic similarity modulates the level of activation of a word's semantic representation, and given the sensitivity of the N400 component to semantic manipulations, one would expect to find modulations of the N400 for both types of semantically related pairs. That is, the amplitude of the N400 would be smaller for semantically related words than for unrelated words. Moreover, the magnitude (i.e., the difference between the unrelated condition and the related condition) of the effect on the N400 would be greater for S1 pairs than for S2 pairs, as a consequence of the greater semantic overlap in the former than in the latter. That is, after having processed the first word of a semantically related pair, it would be easier to integrate the meaning of an S1 word than the meaning of an S2 word, and thus the former would elicit lower N400 amplitudes than the latter. These results could also be predicted by the RHM, since it assumes that highly proficient bilinguals can access the meaning of an L2 word directly, that is, without having to access first the equivalent translation in L1. The RHM assumes two separate, but interconnected lexicons, one for each language (L1 and L2); in addition it assumes a shared integrated conceptual system that is connected to both lexicons. L1 has direct access to the conceptual system, whereas L2 is connected to both the L1 translation equivalents and to the conceptual system, but the strength of these connections and the way meaning is accessed varies as proficiency increases. At the initial stages of L2 acquisition, given that the connections between L2 and the conceptual level are very weak, L2 words will access their meaning by an indirect route. That is, an L2 word will first activate (via lexical links) its translation equivalent in L1, and the translation equivalent will activate its semantic representations stored at the conceptual level. As proficiency in L2 increases, the connections between L2 and their corresponding concepts are reinforced while lexical dependence on L1 translation equivalents decreases. As a consequence, highly proficient bilinguals could directly access the conceptual system from both L1 and L2.

A second aim of the present study was to examine whether purely semantic (and not associative) relations would produce interference effects. The semantically related words used by Guo et al. (2012) varied in the nature of their relationship with the correct translation (i.e., some were categorically related, some were associatively related[3]). Whereas semantic relatedness reflects the similarity in meaning between two concepts, associative relations are mainly based on lexical co-occurrence and are thought to reflect word use rather than meaning overlap (McNamara, 1992; Plaut, 1995). If associative relations are mainly based on lexical connections, then the results of Guo et al. (2012) might be explained not in terms of relations at the conceptual level, but in terms of relations at the lexical level. Thus, it is important to examine whether semantic relations defined by semantic similarity and not by associative

[3] The authors do not provide the percentages of associatively related and semantically related pairs used in their study.

strength would produce behavioral and ERP interference effects. It is important to note that the materials for the two semantic conditions of the present study were not selected from a free association database but from a semantic similarity rating task.

Focusing now on the role form similarity might play in bilingual word recognition, several translation recognition studies have examined the claim of the RHM that reliance on the L1 translation to understand words in the L2 is a function of L2 proficiency (i.e., an indirect lexical route when the level of proficiency is low, and a direct conceptual route when the level of proficiency is high). Different studies have manipulated the form similarity between words in two different languages (Ferré et al., 2006; Guasch et al., 2008; Guo et al., 2012; Linck, Kroll, & Sunderman, 2009; Moldovan, Demestre, Ferré, & Sánchez-Casas, 2014; Moldovan et al., 2012; Sunderman & Kroll, 2006; Talamas, Kroll, & Dufour, 1999). These studies used incorrect translations that were related in lexical form to the correct translation (known as translation neighbors, TN). For example, in Spanish a translation distractor for the English word *man* might be the word *hambre*, meaning “hunger,” instead of *hombre* for “man”. By comparing the performance on these incorrect translations to the performance on controls matched on lexical properties but otherwise unrelated to the correct translation, it is possible to examine the relative sensitivity of learners at different levels of proficiency to the form of L1 words. If bilinguals must first access the translation equivalent in L1 to retrieve the meaning of an L2 word, then an L1 word related in form to the translation equivalent should produce interference. According to the RHM, when examining non-proficient bilinguals performing a translation recognition task, TNs should produce an interference effect whose magnitude should be greater than the interference produced by words being semantically related (i.e., S1 pairs); the reversed pattern should be expected in highly proficient bilinguals, namely stronger interference effects in the semantic condition than in the form condition. However, behavioral findings on translation recognition in highly proficient bilinguals revealed that the interference effects for S1 and TNs were of the same magnitude (Ferré et al., 2006; Guasch et al., 2008; Guo et al., 2012; Moldovan, Demestre, et al., 2014; Moldovan et al., 2012).

The evidence on translation recognition is largely based on behavioral findings alone. Other fine-grained measures, such as the ERP technique, have scarcely been used. To our knowledge, there are only three previous published studies of translation recognition using ERP measures (Guo et al., 2012; Palmer, van Hooff, & Havelka, 2010; Vigil-Colet, Pérez-Ollé, & García-Albea, 2000). Vigil-Colet et al. (2000) did not specifically investigate the activation of the L1 translation. Palmer et al. (2010) examined translation recognition in the two directions, from the L1 to the L2 and from the L2 to the L1, by comparing correct translation equivalents with incorrect translations. A larger N400 was observed for incorrect translations, and it was also larger for translations from the L2 to the L1 than for the reverse. According to Palmer et al. (2010), their results supported the claim of the RHM that the L1 translation equivalent is activated when processing the L2 for meaning. Guo et al. (2012) conducted two experiments to examine relatively proficient Chinese–English bilinguals who had to judge whether a Chinese word was the correct translation of an English word. In Experiment 1, by using a SOA of 750 ms, they observed that participants were sensitive to the lexical form of the translation equivalent in Chinese, with longer RTs to reject translation form distractors than controls. The ERP data showed that translation form distractors elicited a larger P200 (sensitive to lexical processing; Liu, Perfetti, & Hart, 2003) and a larger late positive component (LPC) than did controls, with only small, inconsistent effects on the N400. To test the hypothesis that the activation of the L1 translation equivalent in Experiment 1 was a consequence of the relatively long SOA (i.e., 750 ms), a second ERP experiment with identical materials was carried out at a short SOA of 300 ms. Behavioral results provided robust evidence for activation of L1 translation equivalent, but the ERP results showed that this activation occurred only in a late time window (i.e., from 500 ms to 700 ms). Taken together, the results of the two experiments suggest that for proficient bilinguals, access to the L1 translation equivalent follows the retrieval of the meaning of an L2 word.

To sum up, in the present study, a translation recognition task was used with a SOA of 250 ms (i.e., shorter than the SOA used by Guo et al. (2012) in Exp.2). Participants had to decide whether Spanish words were the correct translations of Catalan words. Critical trials were those on which incorrect translations were related in lexical form or meaning to the correct translation. The bilinguals tested in the present study differ from those tested by Guo et al. (2012) in that, in addition to being highly proficient in both languages as Guo et al.'s (2012) participants, they were balanced bilinguals who learned the two languages at childhood, and who use the two languages on a daily basis, since they live in a region of Spain (i.e., Catalonia) with two official language (i.e., Catalan and Spanish). Although in Catalonia the Catalan language is the vehicular language in education, all speakers have a perfect knowledge of Spanish We expected, as predicted by both the DRM and the RHM, behavioral and electrophysiological semantic interference effects for both S1 and S2. As suggested by the DRM, these effects would be grater in the S1 condition than in the S2 condition. This difference would be reflected in the ERPs in that S1 will elicit larger N400 amplitude modulations (i.e., the difference between the unrelated and the related conditions) than S2. Modulations of the N400 component could also be explained by the RHM, since it assumes that highly proficient bilinguals can access meaning directly from both L1 and L2. Furthermore, if highly proficient balanced bilinguals access meaning directly, and activate first translation equivalents of words in the second language after they have accessed the meaning of those words, one would expect the ERP component elicited by TNs to be a post-N400 component, that is, a late component such as the LPC. On the contrary, if access to the meaning of Catalan words requires mediation through the Spanish language, then the ERP response elicited by TNs should be evident at a time window previous to the classical time window for the N400 (i.e., from 300 to 500 ms).

Method

Participants

Twenty-four bilinguals of Catalan and Spanish (15 females and 9 males, mean age = 21.9, SD = 2.2) participated in the experiment. They were psychology students at the Universitat Rovira i Virgili (Tarragona, Spain). All had normal or corrected-to-normal vision and were right handed. They acquired both languages early in childhood (age of acquisition of Catalan = 0.7, SD = 1.6; age of acquisition of Spanish = 1.4, SD = 1.6). Although in the Catalan Autonomous Community the Catalan language is the vehicular language in education, all speakers have a perfect knowledge of Spanish; indeed, the most popular newspapers are written mostly in Spanish. We do not use the terms L1 and L2 to refer to Catalan and Spanish because the participants have been exposed to the two languages on a daily basis from birth. Participants were asked to rate several dimensions of Catalan and Spanish proficiency (i.e., listening, speaking, reading and writing) on a 7-point Likert scale that ranged from low level to high level. Proficiency values for Catalan and Spanish are reported in Table 1. Participants also rated their frequency and preference of use of the two languages on a scale from 1 to 7 (from 1 to 3 = use more Catalan than Spanish and prefer Catalan over Spanish; from 3 to 5 = use both languages to the same extent and do not prefer one language over the other; from 5 to 7 = use more Spanish than Catalan and prefer Spanish over Catalan). The average values of frequency of use (M = 3.72, SD = 1.61) and preference (M= 3.97, SD = 1.50) showed that participants were highly balanced.

Materials

Selection of the materials

Two-hundred and sixteen triplets of Spanish words (i.e., a target, and its S1 and S2 words) were selected as the materials of the present study. Each target had an S1 word (e.g., *burro-caballo*) and an S2 word (e.g., *burro-oso*). All the selected targets were non-cognates (i.e., translation equivalents without any similarity in form, e.g., "*libro*-book"). Given that we aimed to avoid associatively related pairs of words, all the selected pairs (i.e., target-S1 and target-S2) had a forward association strength lower than 0.10 (Fernandez, Diez, Alonso, & Beato, 2004). This criterion was used since pairs of words with values lower than 0.10 are usually considered as non-associatively related (Nelson, McEvoy, & Schreiber, 1998).

Table 1

Mean (SDs in parentheses) level of proficiency (in a 7-point Likert scale) in Catalan and Spanish.

	Catalan	Spanish
Listening	6.83 (0.39)	6.87 (0.35)
Speaking	6.57 (0.72)	6.39 (0.72)
Reading	6.78 (o.42)	6.71 (0.47)
Writing	6.57 (0.59)	6.26 (1.51)

One hundred and seventy-seven triplets were selected from a database (Moldovan, Ferré, Demestre, & Sánchez-Casas, 2014), which provides measures of semantic similarity for a set of Spanish words. In order to have the final set of 216 triplets, 39 new triplets were selected based on our intuition. With these 39 new triplets, two lists with 59 pairs each were constructed. List one had 19 target-S1 pairs, 20 target-S2 pairs, and 20 filler pairs, whereas list two had 20 target-S1 pairs, 19 target-S2 pairs, and the same 20 filler pairs. Each target appeared only once in each list (e.g., *burro-caballo* appeared in list 1, and *burro-oso* in list 2). By using a similarity-rating task we asked 60 participants (i.e., 30 in each list) to rate the meaning similarity between the two words of a pair by using a Likert-like scale ranging from 1 (nothing similar) to 9 (exactly the same thing). After having the ratings for the new 39 triplets, they were added to the triplets obtained from the database, thus achieving a final set of 216 triplets. A comparison between the semantic similarity values for S1 and S2 pairs showed that participants judged S1 pairs as more similar in meaning (mean = 6.86, SD = 0.79) than S2 pairs (mean = 3.63, SD = 0.75), $t(215) = 36.3$, $p < .000$.

Once the S1 and S2 pairs were obtained, the first word (i.e., the Spanish target) was translated into Catalan, since the experiment was conducted in the Catalan to Spanish direction. Then, for each pair, a Spanish word that was orthographically and phonologically similar to the original Spanish target was selected (i.e., the translation neighbor word). For example, the original Spanish target *burro* (whose translation to Catalan is *ruc*) was paired with the Spanish word *berro*, given that *burro* and *berro,* being not related in meaning, are phonologically and orthographically similar. Thus, the Catalan target *ruc* had the Spanish word *berro* as its translation neighbor. The orthographic similarity between each Catalan target and its translation neighbor in Spanish was computed by using the NIM database (Guasch, Boada, Ferré, & Sánchez-Casas, 2013). In this database, the orthographic similarity between two words is calculated by applying van Orden's (1987) algorithm in a scale from 0 (not similar at all) to 1 (exactly the same lexical string). The orthographic similarity between the original Spanish targets (i.e., *burro*) and the selected translation neighbors (i.e., *berro*) was computed. The values of orthographic similarity (M = 0.65, SD = 0.11) showed that the original Spanish targets and TNs were highly related in form. Moreover, the orthographic similarity between the Catalan targets (i.e., *ruc*) and the selected translation neighbors (i.e., *berro*) was also computed. The orthographic similarity between Catalan targets and TNs was quite low

(M= 0.20, SD = 0.15) thus avoiding any possible effects of orthographic similarity between the target and the critical word.

Experimental conditions

A total of 432 word sets were selected. The first item in each set was a Catalan word and the second one was a Spanish word. All words were nouns. Two hundred and sixteen pairs were translation pairs that acted as fillers (i.e., the YES trials). The remaining 216 sets of words were non-translations pairs (i.e., the NO trials), and were the six critical experimental conditions. In the 216 sets of non-translation pairs, three of them were related: S1 (e.g., *ruc-caballo*), S2 (e.g., *ruc-oso*) and TN (e.g., *ruc-berro*), while the other three were the controls for the related conditions: CS1 =control for S1 (e.g., *ruc-domingo* [*Sunday*]); CS2 =control for S2 (e.g., *ruc-beso* [*kiss*]) and CTN =control for TN *ruc-fresa* [*strawberry*]. The words in the control conditions were matched in length and frequency to the words in the related conditions. The characteristics of the words used in the experiment are presented in Table 2. Related and control words did not differ in length nor in frequency (all ts < 1).

Six experimental lists were constructed by counterbalancing the six critical conditions. Each list had 432 items: 216 translations and 216 non-translations (i.e., 36 pairs in each critical condition). The 216 translation pairs were the same in the six lists. Each participant was randomly assigned to a list. Each item appeared only in a given experimental condition in a particular list but it appeared in each experimental condition across the six lists.

Table 2: Means (and SDs) for characteristics of stimuli for critical NO responses.

Condition	Related		Control	
	Length	Frequency	Length	Frequency
S1	6.9 (1.8)	18.3 (52.4)	6.9 (1.8)	18.6 (53)
S2	6.7 (1.9)	19.7 (46.5)	6.7 (1.9)	19.7 (47.4)
TN	6.4 (1.7)	22.9 (75.2)	6.5 (1.7)	23.2 (78.5)

Procedure

A translation recognition task was used, in which the participants were asked to decide whether the second word of the pair was a correct translation of the first one. Participants had to answer by pushing the "YES" or the "NO" button. The EEG was monitored while participants performed the task. The stimuli were presented one at a time at the center of a screen in white font on a black background, using the DMDX program (Forster & Forster, 2003). The computer generated a pseudo-random order of presentation for each participant. Each trial started with an image of an eye displayed for 2000 ms, which indicated participants that they were allowed to blink the eyes, followed by a 500 ms fixation point ("#"). Just after the fixation point, a Catalan word was presented for 250 ms, followed by a Spanish word. The Spanish word remained on the screen until the participant responded or 2000 ms had elapsed. There was a 1000 ms ISI between the trails. The experiment began with 12 practice trials. There were brief breaks after every 72 pairs.

EEG recording

Participants were seated in a comfortable chair in a sound attenuated darkened and dimly illuminated room. The EEG was recorded continuously by means of 19 Ag/AgCl electrodes fixed at the scalp by means of an elastic cap (Electrocap International, Eaton, OH, USA.) that was positioned according to the 10-20 International system. In addition, electrodes were placed beneath the left eye to monitor blinking and vertical eye movements and at the outer canthus of the right eye to monitor horizontal eye movements. Recordings were referenced to the right earlobe, and the left earlobe was employed as an active recording channel. Subsequently ERPs were algebraically re-referenced to linked earlobes offline. Electrode impedances were kept below 5 kΩ. All EEG and EOG channels were amplified using a NuAmps Amplifier (Neuroscan Inc., North Carolina, USA) and recorded continuously with a bandpass from 0.01 to 30 Hz and digitized with 2 ms resolution. The EEG was refiltered off-line with a 25-Hz, low-pass, zerophase shift digital filter. Automatic and manual rejections were carried out to exclude periods containing movement or technical artifacts (the automatic EOG rejection criterion was +/- 50 μV).

ERP analysis

Data was processed using BrainVision Analyzer 2 (Brain Products, Gilching, Germany). Average ERPs were calculated per condition per participant from -100 to 700 ms relative to the onset of the critical word (i.e., the second word of each pair), before grand-averages were computed over all participants. A 100 ms pretarget period was used as the baseline. Only trials without muscle artifact or eye movement/blink activity were included in the averaging process. The nine relevant electrodes used in the analyses correspond to the International 10-20 Electrode System (Jasper, 1958) locations of Fz, Cz, and Pz along the midline; F3, C3, and P3 over the left hemisphere; and F4, C4, and P4 over the right hemisphere. We used this more restricted montage for two reasons. First to simplify the exposition of results (utilizing the entire montage requires multiple ANOVAs per epoch) and second, because the major effects reported were most clearly seen in these sites. Analysis involved repeated measures ANOVA with within-participants factors relatedness (related vs. unrelated), Location (anterior, central, posterior) and Laterality (left, middle, right). Based on visual inspection of the results and prior reports, the N400 was analyzed from 300 ms to 500 ms, and the LPC from 500 ms to 700 ms. The Greenhouse and Geisser (1959) correction was applied to all repeated measures having more than one degree of freedom in the numerator. In such cases, the corrected p-value is reported. To be brief, only the main effect of the relatedness factor and significant interaction effects between this factor and other factors are reported.

Results

Behavioral data

Trials with 100 % of errors were excluded from the analysis. This led to the exclusion of 5.6 % of the data. RTs with values bellow 200 ms and above 2000 ms were removed from the analysis and were treated as outliers. RTs that were more than two SDs above or below the mean for a given participant in all conditions were also excluded from the analysis. This led to the exclusion of 4.7% of the data. Moreover, data from one participant who made more than 15% of errors were excluded from the analysis. Table 3 shows the RTs and the error rates (%E) for the six experimental conditions.

Table 3: Mean reaction times (in ms) and error rates (in %) in the six experimental conditions. Interference effects are the differences between the related and the unrelated conditions.

Condition	Mean	Errors rate
S1	747	21.8
Control for S1	661	1.1
Interference	*86**	*20.7**
S2	697	3.0
Control for S2	661	1.3
Interference	*36**	*1.7**
TNs	728	8.4
Control for TNs	661	0.9
Interference	*67**	*7.5**

*Note: * p < .05*

Separate ANOVAs were conducted based on the participant and item response latencies and error percentage. The analyses was based on a 3 (Type of Relationship: S1, S2, TNs) × 2 (Relatedness: related, unrelated) design. The factor Type of Relationship was manipulated within-subjects and between-items, whereas the factor Relatedness was manipulated within-subjects and within-items.

The ANOVAs on the RTs revealed a main effect of type of relationship, F_1 (2,44) =5.2, p<.05, η^2 =.191; F_2 (2,406) =6.1, p<.05 η^2 =.029 as well as a main effect of relatedness, F_1 (1,22) =73.9, p<.001, η^2 =.771; F_2 (1,203) =83.1, p<.001. η^2 =.290. The interaction between these two factors was also significant, F_1 (2,44) =6.0, p<.05, η^2 =.213; F_2 (2,406) =3.0, p =.051, η^2 =.015.

Planned comparisons were conducted to compare the RTs in the related conditions to the RTs in their control conditions. The comparisons revealed significant interference effects for the three types of relationships: S1, t_1 (22) =5.7, p<.001; t_2 (203) =5.5, p<.001; S2, t_1 (22) =3.7, p<.001; t_2 (203) =3.5, p<.001, and TNs, t_1 (22) =8.4, p<.001; t_2 (203) =5.8, p<.001.

The pattern of results for error rates was similar to that obtained in the RTs analysis. The two main factors were significant: "type of relationship", F_1 (2,44) =45.0, p<.001, η^2 =.671; F_2 (2,406) =51.2, p<.001, η^2 =.201, and "relatedness", F_1 (1,22) =92.7, p<.001, η^2 =.808; F_2 (1,203) =168.9, p<.001, η^2 =.454. The interaction between these two factors was also significant, F_1 (2,44) =41.2, p<.001, η^2 =.652; F_2 (2,406) =53.6, p<.001. η^2 =.209.

As with RTs, the results of the planned comparisons with the error rates showed significant interference effects for the three types of relationship: S1, t_1 (22) =8.42, p<.001; t_2 (203) =10.96, p<.001; S2, t_1 (22) = 2.45, p<.05; t_2 (203) =2.59, p<.05, and TNs, t_1 (22) =6.63, p<.001; t_2 (203) =6.87, p<.001. Participants made more errors in the related conditions than in the control conditions.

The behavioral results showed interference effects for the two semantic conditions, as well as for the TN condition. In order to compare the magnitude of these interference effects in the three types of relationship, planned comparisons were conducted. As predicted by the DRM, the results showed larger interference effects for S1 pairs than for S2 pairs, both in RTs, t_1 (22) =3.3, p<.05; t_2 (203) =2.2, p<.05, and in error rates, t_1 (22) =7.5, p<.001; t_2 (203) =10.0, p<.001. Concerning TNs, there was no difference in the magnitude of the interference effects between TNs and S1 pairs in RTs, t_1 (22) =1.3, p>.05; t_2 (203) =0.6, p>.05; but there were significant differences in error rates, t_1 (22) =5.33, p<.001; t_2 (203) =5.65, p<.001. Participants made more errors in the S1 pairs than in the TNs pairs.

Electrophysiological results

Figures 1 (S1 condition) and 2 (S2 condition) depict brain potential variations in the linear derivation of a group of six electrodes (C3, Cz, C4, P3, Pz, P4) where the N400 component is typically maximal. As can be seen in Figures 1 and 2, relative to the unrelated conditions both the highly and the less related conditions exhibit a clear modulation of the N400 component, starting around 300 ms post-stimulus. Figures 3 (S1 condition) and 4 (S2 condition) illustrate the topographic distribution of the N400 effects (unrelated minus highly related, and unrelated minus less related difference waves) during the classic 300-500 ms N400 time window. As the topographic maps make clear, both the highly and the less related conditions elicited an N400 effect consistent with the previous literature (Kutas & Federmeier, 2011).

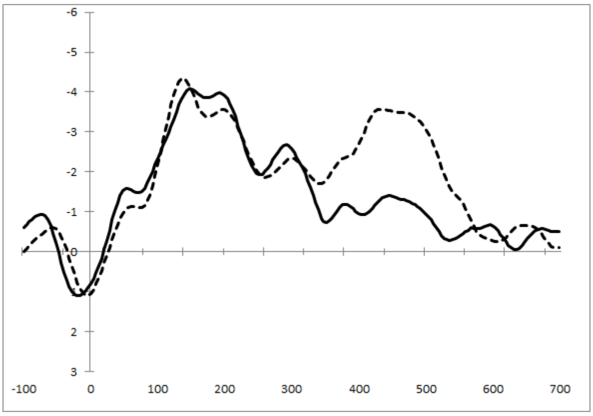

Figure 1. Brain potential variations in the linear derivation of a group of six electrodes (C3, Cz, C4, P3, Pz, P4) where the N400 component is typically maximal. The black line refers to S1 words and the dashed line refers to control words for S1. Negative values are plotted up.

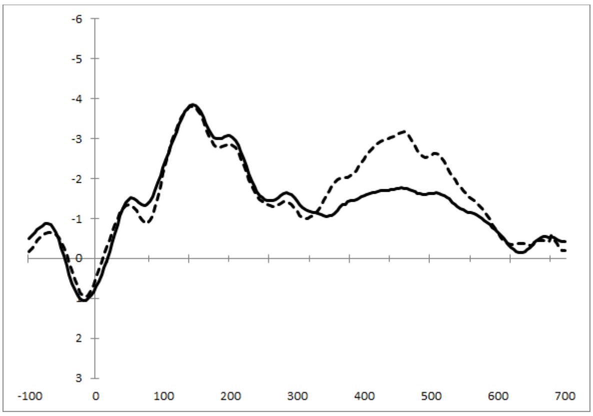

Figure 2. Brain potential variations in the linear derivation of a group of six electrodes (C3, Cz, C4, P3, Pz, P4) where the N400 component is typically maximal. The black line refers to S2 words and the dashed line refers to control words for S2. Negative values are plotted up.

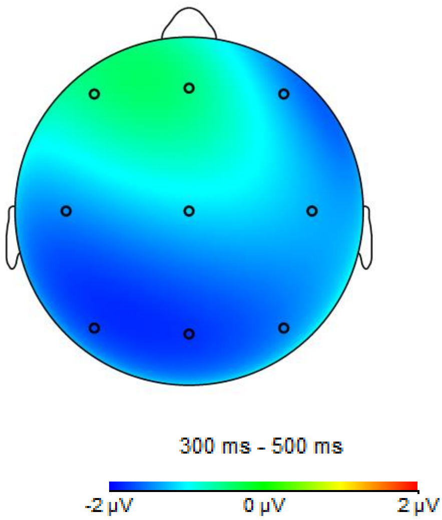

Figure 3. The voltage spline map illustrating the scalp distribution of the N400 effects (amplitude differences between related and unrelated words) during the classic 300-500 ms N400 time window for the S1 Condition.

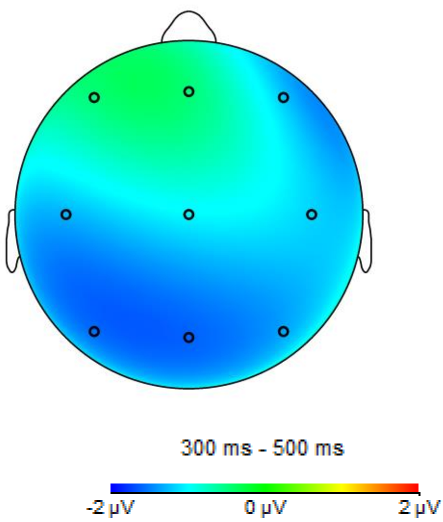

Figure 4. The voltage spline map illustrating the scalp distribution of the N400 effects (amplitude differences between related and unrelated words) during the classic 300-500 ms N400 time window for the S2 Condition.

Figure 5 (TN condition) depicts brain potential variations in the linear derivation of a group of six electrodes (C3, Cz, C4, P3, Pz, P4) where the LPC component is maximal. As can be seen in Figure 5, the unrelated condition exhibits a clear modulation of the LPC component, starting around 500 ms post-stimulus. Figure 6 (TN condition) illustrates the topographic distribution of the LPC effect (unrelated minus TN difference waves) during the 500-700 ms time window. As the topographic map makes clear, the unrelated condition elicited an LPC effect.

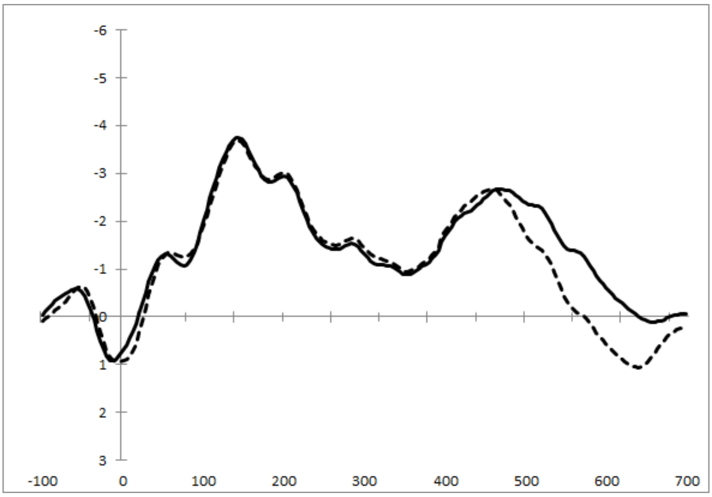

Figure 5. Brain potential variations in the linear derivation of a group of six electrodes (C3, Cz, C4, P3, Pz, P4) where the LPC component is maximal. The black line refers to TN words and the dashed line refers to control words for TNs. Negative values are plotted up.

Semantically related words

Highly related pairs (S1)

There was a main effect of relatedness, $F(1,23) = 21.67$, $p < .001$, $\eta^2_p = .485$, at the N400 time window (i.e., from 300 ms to 500 ms). This result reflects that the mean amplitude for the semantically unrelated control condition (M= -3.54 µV) was significantly more negative than that for the semantically related condition (M= -1.60 µV) during the N400 epoch. The interaction between the factors relatedness and location was significant, $F(2,46) = 11.77$, $p < .001$, $\eta^2_p = .33$, with N400 effects being more evident at central (M= -1.80 µV) and posterior (M= -2.84) regions than at the frontal region (M= -1.19 µV). Finally, there was a marginal interaction of relatedness, location and laterality, $F(4,92) = 2.47$, $p = .09$, $\eta^2_p = .09$. Whereas at central and posterior regions the relatedness factor was significant at left, middle and right sites (all ps<.002), at the frontal region this factor was only significant at the right hemisphere (p<.001).

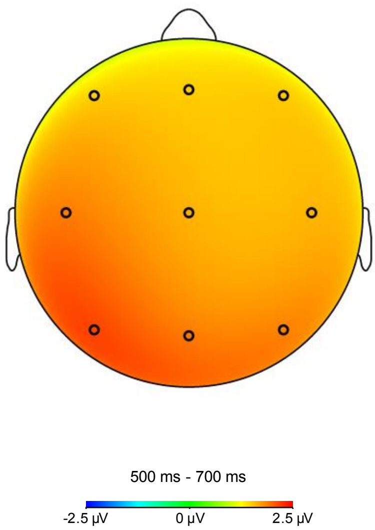

Figure 6. The voltage spline map illustrating the scalp distribution of the LPC effects (amplitude differences between related and unrelated words) during the 500-700 ms LPC time window for the TN Condition.

Less related pairs (S2)

There was a main effect of relatedness, F (1,23) =8.86, p=.006, η^2_p =.27, at the N400 time window (i.e., from 300 ms to 500 ms). This result reflects that the mean amplitude for the semantically unrelated control condition (M= -2.10 µV) was significantly more negative than that for the semantically related condition (M= -0.90 µV) during the N400 epoch. There was a significant interaction between relatedness, location and laterality, F (4,92) =4.04, p=.001, η^2_p =.14. Whereas at central and posterior regions the relatedness factor was significant at left, middle and right sites (all ps<.05), at the frontal region this factor was only significant at the right hemisphere (p=.047).

Comparing the magnitude of the N400 effect in S1 and S2

Figure 7 plots the differences waves (i.e., unrelated condition minus related condition) for S1 and S2 conditions. Visual inspection suggested that some differences may exist between S1 and S2 difference waveforms during the N400 epoch. The difference between S1 words and their controls was bigger than the difference between S2 words and their controls. In order to test whether such differences between S1 and S2 difference waveforms were significant, a post-hoc paired t-test on difference waveforms (unrelated minus related) was conducted. The t-test showed that the N400 modulations were significantly greater in the S1 condition (M= -1.94 µV) than in the S2 condition (M= -1.20 µV), t(23) =2.33, p=0.029.

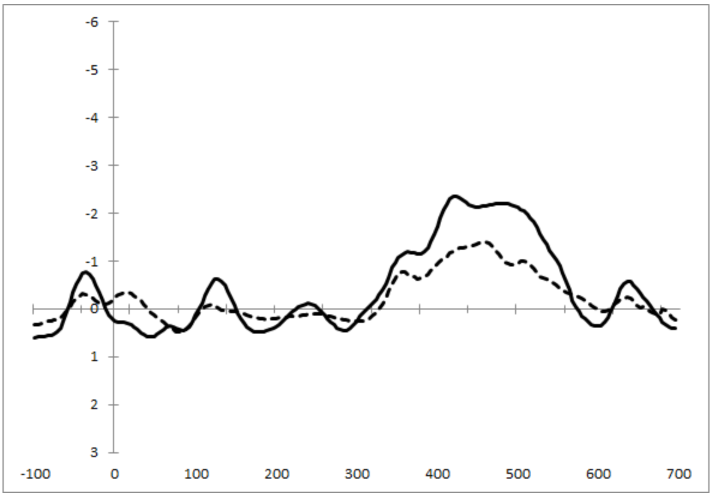

Figure 7. Comparison of the difference waves (amplitude differences between related and unrelated words) for the S1 and the S2 conditions. The black line refers to the difference wave in the S1 condition and the dashed line refers the difference wave in the S2 condition. Negative values are plotted up.

Translation Neighbors

There was a main effect of relatedness, $F(1,23) = 17.60$, $p < .001$, $\eta^2_p = .43$, at the LPC time window (i.e., from 500 ms to 700 ms). The amplitudes of brainwaves evoked by unrelated words (M= -0.31 μV) were significantly more positive than the amplitudes of brainwaves evoked by translation neighbors (M= -2.19 μV).

General Discussion

In the present study, highly proficient balanced Catalan-Spanish bilinguals judged whether a Spanish word was the correct translation of a Catalan word. The relationship between the Spanish and the Catalan words was manipulated such that the critical pairs were not correct translations but they were more or less related in meaning, or were related in form to the translation equivalent (i.e., they were related in form to the Spanish translation of the Catalan word). The performance on each of this type of word relationships was compared to controls matched on lexical proprieties but otherwise unrelated. The bilinguals who participated in the study acquired both Catalan and Spanish early in childhood (i.e., before they were 2 years old), and have since then been exposed to both languages on a daily bases. Thus, they can be considered to be highly proficient in both languages, and, more importantly, to be balanced bilinguals. In such bilinguals it is almost impossible to talk about L1 and L2, since both Catalan and Spanish can be considered L1s. In the present study, participants were asked to judge whether a Spanish word was the translation of a Catalan word. Behavioral as well as electrophysiological measures were registered as participants performed the task.

To test the hypothesis that the activation of the L1 translation equivalent in Guo et al.'s 2012 study was a consequence of the fact that their participants were unbalanced, having a clear preference for one language (i.e., Chinese) over the other (i.e., English), the present study was conducted with highly proficient balanced bilinguals who use the two languages on a daily basis, and who have a less clear preference for one language over the other. A short SOA (i.e., 250 ms) was used to examine the time course of meaning access, with the aim of exploring whether meaning is accessed directly or is accessed indirectly (i.e., after having accessed the translation equivalent). Previous studies that had combined behavioral and ERP measures used longer SOAs (i.e., 750 ms or 300 ms). Moreover, in the present study, instead of using associatively related words as in Guo et al.'s (2012) study, the semantically related words were selected from a semantic similarity rating task, and none of the pairs were associatively related. The fact of using non-associatively related words rules out a possible explanation of the effects in terms of lexical links. That is, semantic interference effects might only be explained in terms of semantic links at the conceptual level, and not in terms of lexical links between words.

Response times to reject Spanish words that were semantically related to the Catalan words were longer than for unrelated controls. Moreover, RTs to reject Spanish words that were highly related in meaning to the Catalan words were longer than for Spanish words that were less related in meaning to the Catalan words. These results are only partially consistent with previous behavioral findings, given that interference effects had only been observed for S1 pairs (Ferré et al., 2006; Guasch et al., 2008; Moldovan et al., 2012). Furthermore, semantically related words elicited a smaller N400 relative to unrelated controls. The N400 effect (i.e., the difference between the unrelated and the related conditions) for highly related words was larger than for less related words. This data could be interpreted as evidence that the degree of semantic similarity modulates semantic activation across languages in translation recognition, as predicted by the DRM. The same bilinguals were also sensitive to the lexical form of the translation equivalent in Spanish, with longer RTs to reject translation neighbors than controls. The behavioral results are consistent with the results of previous studies (Ferré et al., 2006; Guasch et al., 2008; Guo et al., 2012; Moldovan, Demestre, et al., 2014; Moldovan et al., 2012). Furthermore the magnitude of S1 effects was of the same size as that for TNs. However, the ERP data followed a different pattern for the translation neighbors than for the semantically related words. Translation neighbors elicited a smaller LPC than did unrelated words. Thus, behavioral results provided robust evidence for activation of L1 translation, but the ERP results showed that this activation occurred only in a late time window (i.e., from 500 ms to 700 ms). Guo et al. (2012) observed that translation neighbors elicited modulations on the LPC. They observed that the direction of the LPC varied as a function of the SOA used. When using a 750 ms SOA, translation neighbors elicited a larger LPC than did unrelated controls. The waveforms elicited by TNs were more positive at all electrode sites. When using a 300 ms SOA, the direction of the LPC effect differed by electrode site, such that at frontal sites there was a larger LPC for the TNs, while at the parietal and occipital sites, the LPC was larger for the controls. In the present study, we observed that controls elicited a more positive-going waveform than TNs, and that the direction of the LPC did not vary as a function of electrode site. It is not clear why the direction and the topographical distribution of the LPC observed in this study was different from that observed by Guo et al. (2012). Further research is needed to clarify what cognitive processes the LPC is indexing, and what factors and/or task demands modulate its amplitude, direction and topographical distribution.

Taken together, the results suggest that for highly proficient balanced Catalan-Spanish bilinguals, access to the Spanish translation equivalent follows the retrieval of the meaning of a Catalan word. The results of the present study support the claim that proficient bilinguals are able to access conceptual information directly from L2 words. In fact, pairs of words highly related in meaning generated the slowest, least accurate behavioral responses. That pattern suggests that the bilinguals in the present study were highly sensitive to the semantics of the Catalan word.

A number of recent studies have shown that proficient bilinguals appear to access the translation equivalent (e.g., Thierry & Wu, 2007). These results show that this type of bilinguals have already exceeded the stage of L2 learning when mediation via the translation equivalent is required. The experiments reported in the present article support the observation in the Thierry and Wu (2007) study in showing that relatively proficient bilinguals activate the L1 translation of the L2 word. However, the present results also go beyond the past studies in demonstrating that this is also true for highly proficient balanced bilinguals who have learnt the two languages at childhood and that are immersed in the two languages on a daily basis.

Results from the present ERP experiment show that the effects elicited by semantically related words and by form related words are quite different. The N400 effect for the semantically related words is similar to the type of semantic priming that might be observed where attenuated N400s are typically interpreted to reflect greater ease of lexical integration for related items (e.g., Holcomb et al., 2005). In our study, processing of the initial Catalan word may ease integration of the (more or less) semantically related Spanish word, providing evidence for conceptual access by the Catalan word. The fact that our behavioral results suggest inhibition, rather than facilitation, might be explained by the demands of the task. In the paradigms usually used for semantic priming experiments, such as lexical decision tasks, there is no need to make fine semantic distinctions between items. However, in the translation recognition task, these distinctions are critical and may adversely impact performance on measures of RTs and accuracy when words that are closely related semantically in two languages must be rejected as not being translation equivalents.

The present results have a number of important implications. First, ERP effects on the N400 for the two semantic conditions provide evidence that proficient bilinguals are sensitive to the conceptual, and not just lexical, information provided by Catalan words. In it is important to keep in mind that the two semantically related conditions excluded associatively related pairs, thus including only those relations that were conceptually and not lexically related. In addition, while there were significant ERP effects for the form related condition, they patterned differently from the semantic effects. The evidence suggests that highly proficient balanced Catalan-Spanish bilinguals first access the meaning of the Catalan word, and, when given sufficient time, they activate the Spanish translation of the Catalan word and then compare this translation to the subsequently presented Spanish word.

We would like to end by highlighting the importance of using both behavioral and electrophysiological measures to examine language processing. Behavioral measures have now a long history in the psycholinguistics literature, and have provided many valuable results. However, their nature has some important limitations concerning the study of the temporal dynamics of language processing. Thus, measures with a highest temporal resolution are needed, and ERPs are an excellent technique to provide these finer-grain measures that will allow the field to gain important information about the dynamics of language processing as it unfolds in time.

Acknowledgments:

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III. Discussion and conclusions

III. General discussion

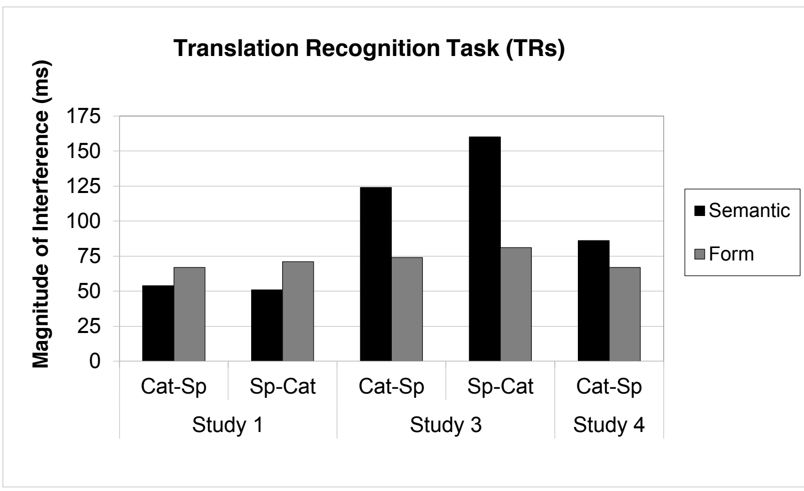
The main aim of the present dissertation was to examine how lexical and semantic factors influence the early stages of word recognition in bilinguals. By using behavioral and electrophysiological measures I have examined how these factors affect the performance of highly proficient balanced bilinguals when performing a translation recognition task. I have explored this issue by conducting a series of studies that included a total of five experiments. Additionally, given that I aimed to examine semantic relations that were not associative to avoid any influence of lexically driven relations, I have conducted a normative rating study for a set of semantically related words. This study provides a database from which part of the experimental materials used in some of the experiments were selected. The participants tested were highly proficient and balanced Catalan-Spanish bilinguals who had acquired both languages at childhood, and that use them on a daily basis. Thus, the kind of bilinguals I have explored have a long experience with both languages given that they have spent almost two decades in a language immersion context where both languages are used actively on a daily basis (i.e. Catalan and Spanish are both official languages in Catalonia). In all the experiments of the present dissertation I have used the translation recognition task with the interference paradigm. In this task pairs of words in Catalan and Spanish were presented and participants had to decide whether the second word in the pair was the translation of the first one. In such a task there are translations pairs and non-translation pairs. The critical conditions were the non-translation pairs. Depending on the particular aim of each study, the non-translation pairs were similar in form (i.e., lexical neighbors and/or translation neighbors) and in meaning (i.e., they were highly or less semantically related). In order to examine how lexical and semantic factors influence the early stages of bilingual word recognition and to avoid strategic factors, a short SOA of 250 ms was used in the five experiments. This SOA is shorter than that commonly used in translation recognition studies. The dependent variables in all of the studies were reaction times and error rates. In one study, besides registering behavioral measures, event-related potentials (ERPs) were recorded while participants performed the experimental task. The empirical results will be discussed in relation to the topics presented in the Introduction Section, and to the different theoretical models dealing with the organization of bilingual memory.

1.3.1. On The Issue of L1 Translation Equivalents

A first topic addressed in studies 1, 3 and 4 is the one related to whether translation equivalents are activated or not. We have explored its possible activation by examining the interference they might cause during a translation recognition task performed by highly proficient balanced bilinguals. The Revised Hierarchical Model (Kroll & Stewart, 1994) has provided some important theoretical insights concerning the time course of activation of translation equivalents. The RHM assumes that bilinguals access directly the meaning of L1 words. More importantly, it proposes that at the early stages of acquiring a second language the meaning of L2 words is accessed indirectly (i.e., lexically mediated) through the L1 translation equivalent. As the proficiency in L2 increase the dependency on L1 decreases and proficient bilinguals access the meaning of L2 words directly, without having to activate first the L1 translation equivalent. In order to examine whether proficient bilinguals access the meaning of L2 words directly, in Studies 1, 3 and 4, highly proficient balanced Catalan-Spanish bilinguals performed a translation recognition task in which the critical pairs included words related in form to the correct translation (i.e., translation neighbors) as well as semantically related words. The three studies were not identical, since in two of them (Study 1 and Study 4), two types of semantic relations were tested (i.e., pairs more and less semantically related), whereas in Study 3 a single semantic relation was included (i.e., pairs more semantically related), whereas an additional orthographic relation was tested (i.e., lexical neighbors). Furthermore, in Study 1 and Study 3 (but not in Study 4), the two translation directions were examined. Finally, it is worth mentioning that in Study 1, the effects of language dominance were investigated. This was the first time that such variable was considered in a translation recognition experiment involving highly proficient bilinguals. The criteria to establish language dominance relied on different factors: which language was acquired first, the level of proficiency in each language in four abilities (i.e., listening, speaking, reading and writing), as well as the frequency and preference of use of each language. The results of Moldovan et al. (2012) showed that the pattern of semantic and form interference effects was the same when participants translated from the dominant to the non-dominant language as when they translated in the reverse direction. This is an important finding since it shows that in bilinguals who had acquired both languages at childhood and simultaneously, and use both languages on a daily basis, dominance did not influence the pattern of interference effects. Given that dominance failed to show any effect in Study 1, it was not included as a factor in Studies 3 and 4.

The behavioral results of the three studies showed robust interference effects both in semantically related pairs as well as in translation neighbors. These findings are in accordance with the results reported in past research that examined proficient balanced bilinguals performing a translation recognition task (Ferré et al., 2006; Guasch et al., 2008; Guo et al., 2012). Figure 1 presents a summary of the results obtained in the three studies.

Figure 1: Magnitude of the interference effect (in ms) in the three studies performed in three studies in two types of word relationships (highly semantically related and form) and in the two translation directions (Catalan-Spanish and Spanish-Catalan)



Note: The magnitude of an interference effect is measured as the difference in TRs between the related and the unrelated conditions. "Cat" refers to Catalan and "Sp" to the Spanish. Translation neighbors are referred to as "Form".

As Figure 1 shows, both the semantic and the form manipulations produced interference effects. If we go into more detail about the magnitude of the effects, we can observe that effects in the form condition in Studies 1 and 3 are quite similar in the two translation directions. Moreover, the effects in the form condition are of a similar magnitude across the three studies. The effects in the semantic condition in Study 1 are similar in the two translation directions, and are somewhat smaller than the effects observed in Study 4. In Study 3 the interference effects in the semantic condition are more pronounced in the Spanish to Catalan direction than in the Catalan to Spanish direction. Moreover, the effects in the semantic condition are clearly greater in Study 3 than in the other two studies. Although there is not a clear explanation for the greater semantic interference effect in Study 3 than in the other two studies, a possible reason might be by the list composition. Although in all three studies there were semantic and form related conditions, their distribution was different. Whereas in studies 1 and 4 there were two semantically related conditions (i.e., more and less semantically related pairs) and one form related condition (i.e., translation neighbors), in study 3 there was only one semantically related condition (i.e., more semantically related pairs), and two form related conditions (i.e., translation neighbors and lexical neighbors). It might be that semantically related pairs were more distinctive in Experiment 3 (as there was a higher amount of form distractors than semantic distractors) than in the other two experiments and that they have captured participants' attention thus producing greater interference. On the other hand, it has to be considered that the participants, although being obtained from the same population, were different across studies. In order to know whether list composition has any effect on interference effects observed in translation recognition, the same participants should perform the task with different lists.

Statistical planned comparisons between semantic and form relations were conducted. Whereas in studies 1 and 4 there were not differences on the magnitude of the interference effects between the semantic and the form conditions, in study 3 the magnitude of the effects was larger in the semantic condition than in the form conditions.

Moreover, planned comparisons on errors rates showed that on all experiments participants made more errors in the semantic than in the form conditions. Overall, the results of the five experiments seem to show that when accessing the meaning of a word highly proficient balanced bilinguals, although being affected by both semantics and form manipulations, rely more on semantic than in form related factors.

The semantic interference effects observed in the experimental studies of this dissertation support the RHM, which assumes that highly proficient bilinguals access meaning directly. However, the fact of having observed robust interference effects in the translation neighbors condition contradicts the assumptions of the RHM, which assumes that the L1 translation equivalent does not impact L2 processing significantly unless the individual is at an early stage of acquisition. The results seem to indicate that even highly proficient balanced bilinguals access the translation equivalent of a word when they are reading to understand its meaning. A possible explanation for this pattern of results might be that Catalan-Spanish bilinguals are in fact using the lexical route as a result of the high percentage of cognates existing between the two languages. Although in the present work the translation pairs were non-cognates, the immersion of bilinguals in two languages with such a high amount of cognates might strengthen the lexical route as a usual translation strategy, as cognates have been proposed to have stronger lexical links than non-cognates (Kroll & Stewart, 1994). Nevertheless, Guo et al. (2012) obtained reliable interference effects with translation neighbors in bilinguals of Chinese and English, two languages that clearly have a very low amount of cognates. This last result suggests that the translation neighbors interference effect repeatedly reported in Catalan-Spanish bilinguals cannot be exclusively explained by the characteristics of these two languages concerning the number of cognates.

An alternative explanation for the robust interference effect obtained with translation neighbors in Catalan-Spanish bilinguals in the present work as well as in past studies (Guasch et al., 2008; Ferré et al., 2006) might be related to their constant exposure to Catalan and Spanish and their regular use of both languages. It is possible that this particular type of context in which bilinguals regularly change from one language to the other depending on the particular context, interlocutor, etc, might increase the level of activation of both languages and this would result in a rapid activation of the translation equivalents. It is not possible to conclude that it is the use/exposure of both languages the reason for the translation neighbors interference effect, as the comparison is being made between bilinguals (i.e., the English-Spanish bilinguals of the study of Sunderman and Kroll, 1994, vs Catalan-Spanish bilinguals) that differ in other characteristics apart from language use. Clearly, the way to address the role of use in cross-language processing is to compare two groups of bilinguals differing only in this variable. Thus, two groups of highly proficient Catalan-Spanish bilinguals might be tested, one immersed in the usual context (i.e., living in Catalonia) and the other living outside of Catalonia, in an Spanish-speaking context.

Whichever is the reason, what seems clear is that proficient balanced bilinguals activate the translation equivalent when performing a translation recognition task. The question then is when do these bilinguals activate the translation equivalent, after accessing meaning or at the same time, that is, they simultaneously activate the meaning of a word in one language and the translation equivalent in a second language? Although, behavioral measures have provided very valuable results in the scientific study of language processing in bilinguals, they are not sensitive enough to capture the temporal dynamics of the word recognition system. In order to answer the previous question one needs to use a measure sensitive to the time course of activation of representations at different levels of organization. A measure that has been proven to be sensitive to the time course of activation is the recording of ERPs. In study 4, we recorded both behavioral and electrophysiological measures to explore in more detail the temporal dynamics of word recognition processes. The ERP results showed that semantically related words elicited modulations on the N400. The N400 was attenuated for semantically related words as compared to their controls. Moreover, the attenuation of the N400 was more pronounced for highly related pairs than for less related pairs. These results are similar to the ones reported by Guo et al. (2012), and show that highly proficient bilinguals access meaning directly, as suggested by the RHM. There are some important differences between the semantic condition in the present study and the semantic condition in Guo et al. (2012). On the one hand, it is important to note that in the semantic condition of study 4 instead of using associatively related words as Guo et al. (2012), we used semantically related words being not associatively related. Thus the reported effects on the N400 might not be due to lexical relations. On the other hand, the present study manipulated the strength of the semantic relation between words, by including more and less semantically related words.

The ERP data followed a different pattern for the TNs condition from the two semantic conditions. The ERP modulations elicited by TNs began at about 500 ms after the onset of the Spanish word, on the time-window of the late positive component (LPC). Translation neighbors elicited a smaller LPC than did controls. Thus, behavioral results provided robust evidence for activation of L1 translation, but the ERP results showed that this activation occurred only in a late time window (i.e., from 500 ms to 700 ms). Guo et al. (2012) observed that translation neighbors elicited modulations on the LPC. They observed that the direction of the LPC varied as a function of the SOA used. When using a 750 ms SOA, translation neighbors elicited a larger LPC than did unrelated controls. The waveforms elicited by TNs were more positive at all electrode sites. When using a 300 ms SOA, the direction of the LPC effect differed by electrode site, such that at frontal sites there was a larger LPC for the TNs, while at the parietal and occipital sites, the LPC was larger for the controls. In the present study, we observed that controls elicited a more positive-going waveform than TNs, and that the direction of the LPC did not vary as a function of electrode site. It is not clear why the direction and the topographical distribution of the LPC observed in this study was different from that observed by Guo et al. (2012). Further research is needed to clarify what cognitive processes the LPC is indexing, and what factors and/or task demands modulate its amplitude, direction and topographical distribution.

Taken together, the results suggest that for highly proficient balanced Catalan-Spanish bilinguals, access to the Spanish translation equivalent follows the retrieval of the meaning of a Catalan word. The results of the present study support the claim that proficient bilinguals are able to access conceptual information directly from L2 words. A number of recent studies have shown that proficient bilinguals appear to access the translation equivalent (e.g., Thierry & Wu, 2007). These results show that this type of bilinguals have already exceeded the stage of L2 learning when mediation via the translation equivalent is required. The experiments reported in the present article support the observation in the

Thierry and Wu (2007) study in showing that relatively proficient bilinguals activate the L1 translation of the L2 word. It has to be considered that the present results go beyond the past studies in demonstrating that the activation of the translation equivalent in the non-target language is also true for highly proficient balanced bilinguals who have learnt the two languages at childhood and that are immersed in the two languages on a daily basis.

1.3.2. On The Role of Languages Use

One of the aims of the present research was to examine which type of information in one language is activated or inhibited while processing the other language. In Study 3, the predictions of the BIA model (Dijkstra & Van Heuven, 1998) and the RHM (Kroll & Stewart, 1994) were placed in the same experimental context with respect to the population under study (i.e., highly proficient and balanced bilinguals that use both languages regularly). Although the two models state that lexical L1 candidates are activated during L2 processing, they differ in the specific type of candidates proposed to be active. According to the RHM, there are the L1 translation equivalents as well as words similar in form to them (i.e., translation neighbors) those that are activated as a way to access meaning in the early stages of L2 acquisition (e.g., when processing the Catalan word *mussol* [*owl*], both their Spanish translation equivalent, *búho*, and other Spanish words similar in form, like *buzo* [*diver*] would be activated). In contrast, BIA proposed that it is not the translation equivalent itself that is active during visual word processing, but rather lexical form relatives, that is, words similar in form in the other language (i.e., lexical neighbors: *mussol-muslo [owl-thigh]*; Catalan-Spanish). Moreover, according to BIA, the asymmetrical effects observed between L1 and L2 processing in unbalanced bilinguals (i.e., nonselective access has been demonstrated more clearly with L2 words than with L1 words), would be a consequence of the lower subjective frequency of the former with respect to the later.

The two abovementioned proposals were tested in Study 3, in which participants performed a translation recognition task that included pairs of lexical neighbors as well as of translation neighbors (there were also semantically related pairs, *mussol-águila* [*owl-eagle*]) as critical conditions. In two past studies, the same manipulations and task were used with Spanish-English bilinguals (Linck et al., 2009; Sunderman & Kroll, 2006). The main contributions of Study 3 are that highly proficient bilinguals who use both languages regularly were tested and that the two translation directions (i.e. from Spanish to Catalan and from Catalan to Spanish) were examined. The results revealed strong interference effects with both types of form-related distractors, that is, translation neighbors and lexical neighbors. In addition, both types of lexically related pairs interfered to the same extent. Concerning translation direction, although the pattern of results was exactly the same in the two directions, the magnitude of effects was larger in the Spanish-Catalan direction than in the other way around.

If we compare lexical and translation neighbors, although the magnitude of the two effects is not different, it is clear that the processing steps involved cannot be the same. According to BIA, the interference of lexical neighbors is produced by their automatic activation as a result of the shared letters with the incoming word. Differently, the interference produced by translation neighbors, if we take into account that the translation pairs used in this work are non-cognates, cannot be produced by such automatic activation (i.e., because there are not shared letters between the word to be recognized and the translation neighbor). Rather, this interference seems to be the result of a more indirect route, that is, the incoming word would activate its translation equivalent and also words similar in form to the later. If this is the case, it is reasonable to think that the time needed for the activation of these two types of form relatedness might be different, in that it would be longer for translation neighbors than for lexical neighbors and that this would be evident in reaction times. However, if we look at the reaction times of Study 3, they were very similar between these two types of pairs. This lack of difference does not imply that the underlying mechanism is the same. It might be that the SOA used (250 msec), although being short, is long enough to allow the activation of both types of lexical candidates for the time the decision has to be made. In this case, no differences in reaction times should be expected. Clearly, the more suitable way to address the issue of a different time-course of activation for lexical neighbors and translation neighbors would be the use of ERPs to study the on-line processing of these two types of relationships.

Concerning the effects of translation direction, a symmetrical pattern of effects should be expected according to BIA (Dijkstra & Van Heuven, 1998). This is because participants are balanced bilinguals and presumably the subjective frequency of use should be the same for Catalan and Spanish words. However, if we look at the description of the bilinguals participating in Study 3, we will realize that they use and prefer Catalan slightly more than Spanish. Considering this information, it might be concluded that such a slight difference in use has consequences on across languages word processing. Thus, there would be a larger interference in the Spanish-Catalan direction because Catalan words might have a slight higher subjective frequency of use than Spanish words. Nevertheless, the results of Study 1 seem to contradict this conclusion. In that study, there was not any effect of participants' dominance (either in Catalan or in Spanish) on the magnitude of interference effects observed with translation neighbors. I do not have at present a clear explanation for what might seem a discrepant pattern of findings. However, it has to be considered that in both Studies 1 and 3, the data of the two translation directions were obtained from different participants, in a between-subjects design. In order to obtain more reliable conclusions, a further study should be conducted in which the same bilinguals perform the two translation directions. This is the only way to avoid the effects of individual differences in the pattern of findings here reported concerning translation direction.

The results of Study 3 are in agreement with those of Sunderman and Kroll (2006) concerning lexical neighbors but not translation neighbors. Sunderman and Kroll (2006) obtained interference effects with lexical neighbors regardless of bilinguals' proficiency whereas translation neighbors showed a reliable interference in the less proficient group, but not in the more proficient group, a result that was in line with the RHM predictions. However, the strong interference obtained in Study 3 with translation neighbors is completely consistent with previous results reported with bilinguals of the same characteristics (Guasch et al., 2008; Ferré et al., 2006). This finding suggests that, the strength of the excitatory lexical links between the two languages does not decrease as proficiency increases, in contrast to some proposals according to which these connections would became inhibitory with the increase in proficiency (Grainger et al., 2010). As discussed in the previous section (i.e., "On the issue of L1 translation equivalents"), the activation of the translation equivalents might be related to the constant exposure and use of both languages in Catalan-Spanish bilinguals. Furthermore, as demonstrated in the ERP experiment (Study 4), this activation does seem to be subsequent to meaning access, a result that would not contradict the RHM.

1.3.3. ON THE INFLUENCE OF MEANING SIMILARITY

Another aim of the present thesis was to examine the modulation of semantic interference effects in translation recognition by the degree of similarity in meaning between words of the two languages. According to the DRM (De Groot, 1992), the magnitude of cross-languages semantic effects obtained when testing a given pair of words would depend on the number of shared nodes between their meanings. In an update of the model, Schoonbaert et al. (2009) provided an explanation of the asymmetrical pattern of semantic priming effects usually obtained when comparing translation directions in unbalanced bilinguals. According to these authors, L1 words would activate a higher number of shared nodes than L2 words. Thus, in balanced bilinguals, a symmetric pattern of semantic effects across directions should be expected, as they would activate the same number of nodes when processing words in any of their two languages. The issue of the modulation of semantic interference effects by the degree of meaning similarity was addressed in Studies 1 and 4, by using both behavioral measures (Study 1 and 4) and ERPs recordings (Study 4). In Study 1 the effects of translation direction were also examined. The experimental materials of these studies were triplets of semantically related words (i.e., a high and a less semantically related word to a given target word), obtained from rating studies that also resulted in a normative database that is presented in Study 2. In the selection of those triplets, associative relations were avoided, as a way to assure that any semantic interference observed involves the conceptual level and is not based on lexical links. Since there were previous findings reporting that only the highly related pairs but not the less related ones produce interference in a translation recognition task in which long SOAs were used (Ferré et al., 2006; Guasch et al., 2008), whereas both types of pairs exhibited semantic priming with a shorter SOA (i.e., 250 ms, Guasch et al., 2011), the "low level activation account" was proposed as a possible explanation. According to this proposal, the less semantically related words would have a low activation level that would quickly decay and would not be observed at long SOAs. An additional aim of this work was to test this proposal.

In Studies 1 and 4, bilinguals performed a translation recognition task in which pairs of words more (e.g., *ruc-caballo* [*donkey-horse*]) or less semantically related (e.g., *ruc-oso* [*donkey-bear*]) across languages were included in the critical conditions. The behavioral results of the two studies showed reliable interference effects with the more semantically similar words which are in line with previous findings reported with both highly and relatively proficient bilinguals in past research that used longer SOAs (Ferré et al., 2006; Guasch et al., 2008; Talamas et al., 1999; Sunderman & Kroll, 2006). Concerning the less semantically related pairs, in Study 4 there were reliable interference effects whereas in Study 1 the magnitude of interference did not reach statistical significance. Nevertheless, it is important to notice that in Study 1 those pairs did not produce null interference effects (20 ms in the Catalan-Spanish direction and 16 ms in Spanish-Catalan direction respectively) and that the correlations between the similarity ratings and the magnitude of the semantic interference effects were significant in both directions. If we focus on the behavioral results of Study 4, the interference effects obtained with the less semantically similar words (36 ms) were larger than those observed in the same direction (i.e., Catalan-Spanish) of the Study 1. In fact, the effects were also more robust for the highly semantically related pairs in Study 4 (86 ms) than in Study 1 (54 ms). These stronger behavioral effects in Study 4 with respect to Study 1 might be related with the large number of stimuli used in the former, which might have contributed to a more stable effect. A relevant finding of both studies was also that the more semantically related words produced greater interference than the less semantically related pairs. These behavioral data provide evidence for the DRM (De Groot, 1992), suggesting that the degree of semantic similarity may modulate semantic activation across languages not only in the semantic priming paradigm (e.g., Guasch et al., 2011) but also in translation recognition. Further evidence for the DRM are the results of the Study 1 showing that the pattern of semantic effects was the same in the two translation directions, as it was expected for a population of balanced bilinguals which presumably are able to activate the same number of nodes when processing words in any of their two languages. This symmetrical pattern of effects is in agreement with past research conducted with balanced bilinguals with the semantic priming and translation priming paradigms (Duñabeitia, et al., 2010; Guasch, et al., 2011; Perea, et al., 2008) and also with the RHM predictions with respect to a direct access to meaning from their two languages in highly proficient bilinguals.

The ERP results obtained in Study 4 are in line with the behavioral ones. Both types of semantic relationships produced effects on the N400 component. Thus, the amplitude of the N400 was attenuated for semantically related words compared with their controls. Moreover, the magnitude of this effect was greater for the more semantically similar pairs than for the less semantically similar pairs, indicating an easier integration for the former than for the later probably due to a larger semantic overlap on their semantic representation. These data are relevant since, to the best of my knowledge, this is the first ERP study on translation recognition that has manipulated meaning similarity. Further, they provide strong support for the DRM as they show, with electrophysiological measures, that the degree of semantic similarity modulates cross-languages activation in translation recognition. Importantly, both behavioral and ERP data constitute solid evidence in favor of the "low level activation account": Not only highly semantically related words are activated during translation recognition, but also less semantically related words. This activation can be captured provided one uses measures sensitive enough (i.e., ERPs) and a short SOA that may enable researchers to observe the effects of this activation before it decays.

There is a last question to be considered. If we compare behavioral and ERP results, although in both cases there is a modulation of effects by the degree of semantic similarity, the direction is opposite, as there is behavioral interference with semantically related words while ERPs show an easier integration of these words, in the same line a that observed in semantic priming studies (Holcomb & Grainger, 2006;

Kiyonaga, Grainger, Midgley & Holcomb, 2007). In a related way, Guo et al., (2012), using the translation recognition task, found results similar to ours: interference effects in RTs and effects in the N400 component interpreted as an easier integration for semantically related words. This pattern of findings in studies using the translation recognition task is probably due to the characteristics of the task. Although there is an easier integration for semantically related words (as reflected by the ERPs), participants have to reject them as correct translations. This is the reason of the interference effect observed, because it would be hard to reject words that are activated and more easily integrated than non-related words, which would be less activated.

Conclusions

1. There is across languages lexical and semantic interference during translation recognition that confirms a nonselective access.

2. Highly proficient bilinguals are able to access meaning directly from their two languages as predicted by the RHM, since there is the same pattern of semantic interference effects in the two translation directions. This result is also in agreement with DRM predictions concerning the possibility that balanced bilinguals are able to activate the same number of nodes when processing words in any of their two languages.

3. The strength of the relationship between semantically non-associated words modulates the interference effects observed on translation recognition, both with behavioral and with ERP measures, confirming the predictions of the DRM. Furthermore, the results obtained with the less semantically related words provide evidence in favor of the "low level activation account". These words are activated during translation recognition, as revealed by the ERP data. This activation can produce behavioral effects when short SOAs are used, because in these conditions they would still be active when the decision about the second word has to be made.

4. Although highly proficient bilinguals are able to access meaning directly, regardless of the language in use, there are also influences of the non-target language, as revealed by the activation of lexical candidates. Translation equivalents seem to be activated when highly proficient bilinguals perform a translation recognition task. This activation might be explained by the characteristics of the bilinguals under examination. Namely, they are immersed in the two languages and use both of them in a regular basis. The activation of the translation equivalents is at odds with some past findings obtained with relatively proficient bilinguals. In addition, it would contrast with the RHM predictions. However, the ERP

results reveal that the activation of translation equivalents takes place after meaning access, suggesting that highly proficient bilinguals are not using the lexical links as a way to access meaning. In this way, these results would not constitute a problem for the RHM.

5. Apart from translation equivalents, words similar in form to the one to be translated (i.e., lexical neighbors) are also activated during translation recognition, as it is predicted from the BIA model. This interference has the same magnitude as that observed with translation neighbors. Although the size of effects is similar, probably the processing steps responsible for the interference produced by these two types of orthographically related words are not the same. Further ERPs studies should be conducted to characterize the time-course of the activation of these two types of lexical candidates in the non-target language.

6. The results concerning the effects of languages dominance/use on the performance of highly proficient bilinguals are not consistent. In the study in which dominance was manipulated, it was observed that the most dominant language (i.e., Catalan or Spanish) did not interfere differentially from the less dominant one during the translation process since the pattern of semantic and formal interference effects was the same regardless of the participants' dominant language. On the contrary, in the other study in which the two translation directions were examined, and in which bilinguals slightly used Catalan more than Spanish, larger interference effects were found from the most used language than from the less used language. It would be necessary to conduct further studies in which translation direction is manipulated within-participants to reach clearer conclusions.

7. The regular use and exposure to both languages (i.e., the immersion in both languages) might modulate the pattern of lexical and semantic cross-language activation during translation recognition. Further studies should be conducted with groups of highly proficient and balanced bilinguals living in different

immersion contexts (i.e., a bilingual immersion context vs a context of immersion in one of their two languages) in order to clarify which are the effects of language use on the pattern of findings observed in translation recognition when proficiency is very high.

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IV. References

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Lydia Cabau Parra

Design and Synthesis of Small Molecules for Organic and Grätzel Solar Cells

Doctoral Thesis

Supervised by Prof. Emilio Palomares
ICIQ-URV

UNIVERSITAT ROVIRA I VIRGILI

Tarragona-June 2014

Emilio Palomares Gil, Group Leader of the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona, and Research Professor of the Catalan Institution for research and Advanced Studies (ICREA) in Barcelona.

CERTIFIES:

That the present thesis, entitled “Design and Synthesis of Small Molecules for Organic and Grätzel Solar Cells” presented by **Lydia Cabau Parra** for the award of the degree of Doctor, has been carried out under my supervision at ICIQ.

Tarragona, June 2014

Prof. Dr. Emilio Palomares Gil

ICIQ Institut Català d'Investigació Química

Universitat Rovira i Virgili

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1.1 INTRODUCTION

The human population is growing up every year with the concomitant consumption of energy, In recent years, only 9% of the energy was provided by so-called renewable energies, 4% from nuclear source and the 87% from fossil fuels such as coal, oil or gas worldwide[1]. The last ones, oil and gas, being dominating the energy market. An observation of major concern is the difficulties to find novel oil reserves that can be exploited with the actual technology. As the new oil reserves are every day more difficult to access, the price increases and, thus, there is a real risk that most human population will not have access to energy[2].

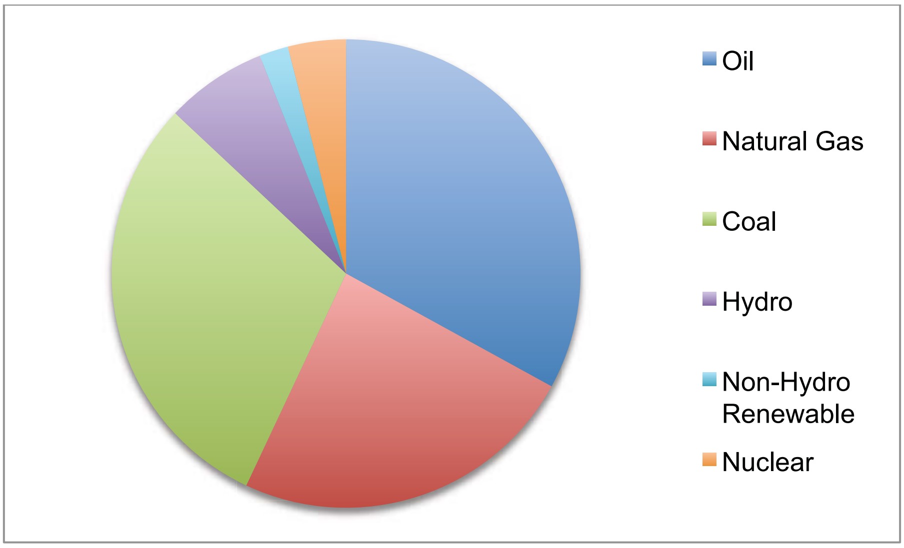


Figure 1.1: The world energy consumption by source in 2014

Solar energy is available for everyone and, for this reason, is a long-standing focus of research to make efficient and cheap light-to-energy (either electrical or chemical energy) conversion devices. The current solar PV (photovoltaic) market is mainly devoted to silicon solar cells (average efficiency 16%) and the best solar panels (triple junction solar cells made using Indium and Gallium) are just made available for space technology (average efficiency 40%) (ei:

communication satellites). The cost/energy conversion associated to this type of light-to-electrical conversion devices makes nowadays a dream to expand worldwide the use of solar energy and the reality is that only those countries that subsidise the use of solar panels have a flourished solar energy market. Thus the scientific and industrial community have developed efforts towards the research of new type of materials and devices to decrease the cost/efficiency value. In the next Figure NREL (National Renewable Energy Labs, USA) have illustrate all actual solar cell technologies[3].

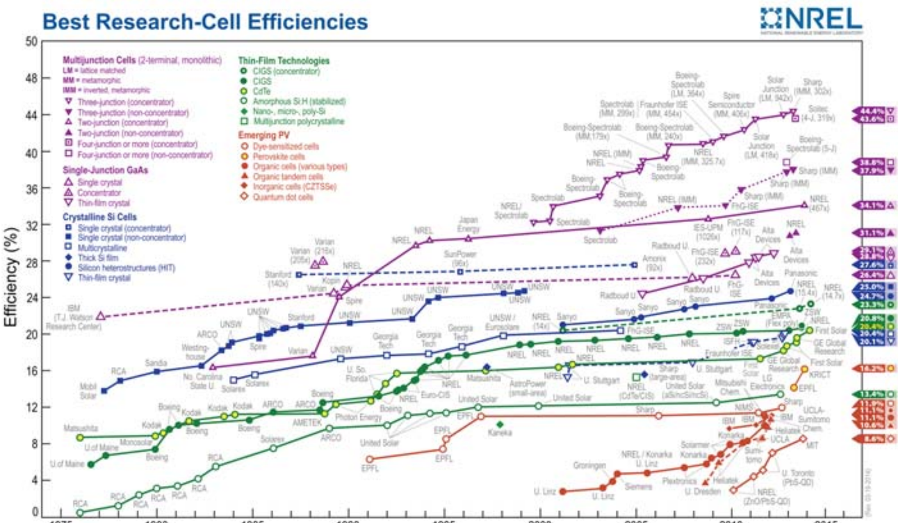


Figure 1.2: Progress on solar cells technologies. Copyright NREL

Two of these types of promising technologies are Dye Sensitized Solar Cells (DSSC) also known as Grätzel solar cells and Organic solar Cells (OPV).

1.2 DYE SENSITIZED SOLAR CELLS

The Dye Sensitized solar Cells (DSSC) are photoelectrochemical cells based on the use of a dye to sensitize a wide band-gap semiconductor metal oxide (generally TiO_2) supported in a transparent conducting glass (Fluorine-doped tin oxide, FTO) that works as a working electrode. The counter electrode consists of a layer of platinum coated on the FTO conducting glass. These two electrodes are sealed with a polymer and a redox electrolyte that serves to regenerate the dye ground state completes the solar cell.

1.2.1 Principles of DSSC

A typical DSSC basically contains 6 components: semiconductor photoanode or working electrode, the sensitizer, the electrolyte (redox pair), the spacer (usually Surilyn©) and the counter electrode.

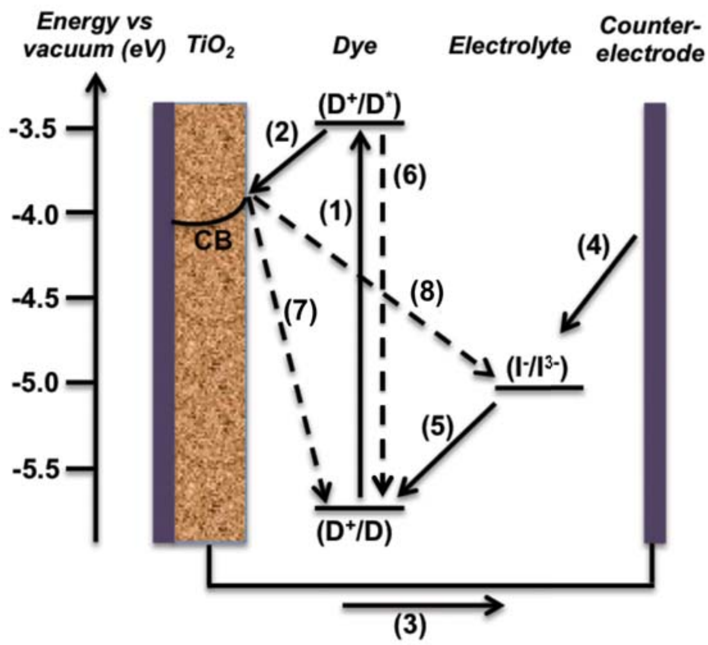


Figure 1.3 Scheme of a DSSC and the most relevant charge transfer events tacking place upon illumination.

First of all the incoming light is absorbed by the sensitizer promoting an electron from the ground state to the excited state (**1**).

$$TiO_2|D + hv \rightarrow TiO_2|D^* \quad (Eq. 1.1)$$

Thereafter, the electron is transferred to the semiconductor conduction band (**2**), and in an ideal case the electron will flow through an external circuit to the counter electrode (**3**).

$$TiO_2|D^* \rightarrow TiO_2|D^+ + e_{cb} \quad (Eq. 1.2)$$

From the counter electrode, the electron is transferred to the electrolyte (redox couple) (**4**) and the electron donating species at the electrolyte regenerates the oxidized dye (**5**).

$$2TiO_2|D^+ + 3I^- \rightarrow 2TiO_2|D + I_3^- \quad (Eq. 1.3)$$

The red/ox electrolyte (often iodine/iodide) is then regenerated at the counter electrode by reduction of triiodide.

$$I_3^- + 2e^-Pt \rightarrow 3I^- \quad (Eq. 1.4)$$

However, these devices have also undesirable charge recombination reactions, (Figure 1.3), which are responsible for the losses in the device efficiency. One of these reactions is the deactivation of the dye excited state (**6**). Nonetheless, this process occurs is nanosecond time scale (10^{-9}s) while the electron injection from the excited state into the semiconductor conduction band occurs at least one order of magnitude faster, making the electron injection more favourable than the deactivation of the dye excited state. Another undesired reaction is the recombination of the photoinjected electrons at the semiconductor with the oxidised sensitizer (**7**). This process as in the same case that for the first one loss mechanism is slower (10^{-6}-10^{-3} s) than the regeneration of the sensitizer (**5**)

(10^{-9}-10^{-6}s). In order to have a slow recombination we have to make sure that the regeneration of the dye is produced efficiently. To be sure of this, the HOMO (Highest Occupied Molecular Orbital) of the molecule has to be far from the surface of the semiconductor, and, moreover, its energy has to be lower in energy respect to the redox electrolyte potential to favour the regeneration driving force. The last recombination reaction is produced after the regeneration of the sensitizer, because the oxidized electrolyte is close to the surface of the semiconductor therefore, recombination of photoinjected electrons in the semiconductor with the oxidized electrolyte can occur and the lifetimes are in a range from 10^{-3}-10^{-1}s, making this mechanism one of the principal loss reactions[4].

1.2.2 Basic Solar Cell Parameters

When a solar cell is illuminated, a photocurrent and a voltage are generated which can be depicted as in figure 1.4

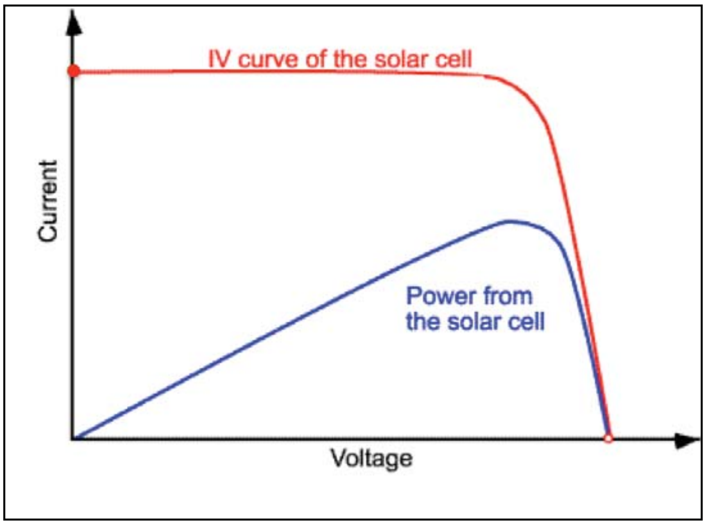


Figure 1.4: Typical IV-Curve of a solar cell

The overall energy conversion of a solar cell is defined as the ratio of the output power of the cell per incident irradiance (equation 1.7)

$$\eta = \frac{P_{max}}{P_{light}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{light}} \text{ (Eq. 1.7)}$$

Where J_{sc} (mA/cm^2) is the photocurrent density at short circuit, V_{oc} (V) the Voltage at open circuit, FF is the Fill Factor that measures the how squarer is the I-V curve (the higher Fill Factor the higher efficiency at a given Jsc and Voc), and the P_{light} the power of the incident light.

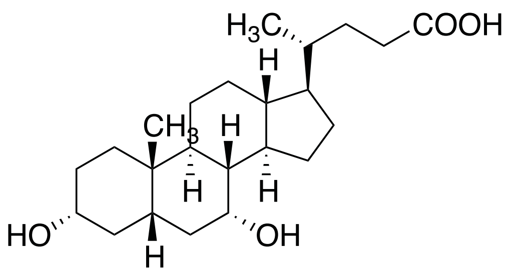
As one could imagine, the device efficiency and, thus, the IV curve is affected by the charge transfer reactions detailed above. Yet, in this Thesis we have focused on the sensitizers used mainly in DSSC and in an example of OPV.

1.2.3 Initial requisites for efficient sensitizers in DSSC

The sensitizer in a DSSC plays a very important role in order to achieve the maximum efficiency in devices. First of all, the sensitizer has to have the capability to capture the light, absorbing the incident photons from a wide range of wavelengths from the solar spectrum. Moreover, the sensitizer must have an anchoring group in order to bind strongly (covalently) to the semiconductor surface. Although several anchoring groups have described in the bibliography as, for example, phosphonates, catechols etc…[5,6]. The most common chemical group used is the carboxylic acid[7]. The hydroxyl group react with the TiO_2 surface forming a covalent bond in the best cases.

The HOMO and LUMO (Lowest Unoccupied Molecular Orbital) energy of the sensitizers is key in order to achieve good efficiency by decreasing unfavoured electron transfer reactions. As already mentioned above, the dye HOMO level has to be away from the semiconductor surface and with lower energy than the oxidation potential of the redox active electrolyte. On the other hand the LUMO of the sensitizer has to be close to the surface of the semiconductor in order to achieve an efficient electron injection. So called unidirectional electron transfer. Furthermore, it is paramount that the LUMO level is placed higher than the conduction band energy level of the TiO_2 to favour the electron injection from the dye excited state.

Secondly, the dye solubility in organic solvents preferably non-halogenated solvents is also of importance, as well as, the minimization of the presence of dye aggregates in the solution and in the semiconductor surface after sensitization. This last requisite can be partially solved with the addition of a co-sensitizer such as Chenodeoxycholic Acid[8] (CDCA) which decreases the formation of aggregates at the semiconductor surface (Figure).



CDCA

Figure 1.5: Molecular structure of CDCA

As an example of efficient dyes used in DSSC we will now detail the use of Ruthenium complexes.

1.2.4 Ruthenium Complexes

The first efficient dyes used for DSSC were Ru complexes (trinuclear Ruthenium dye), giving a light-to-photoelectrical conversion efficiency between 7.1 and 7.9%[9]. The trinuclear $RuL_2(\mu\text{-}(CN)Ru(CN)L'_2)_2$, where L is 2,2'bipyridine-4,4'-dicarboxylic acid and L' is 2,2'-bipyridine. One of the first reasons to use the Ruthenium complexes is due to broad absorbance from the visible region to the near-infrared[10]. The general structure of a Ruthenium dye for DSSC consist usually on a Ru(II) atom coordinated by polypyridyl ligands and thiocyanate moieties in an octahedral geometry. The carboxylic acids are used as anchoring groups and are attached to the bipyridyl moiety leading to easy injection of electrons in the semiconductor from the excited state. This complexes show an absorption band in the visible region of the sun spectra that can be tuned, which is due to the MLCT (metal to ligand charge transfer band) transition[11].

Since the seminal paper by Gratzel and O'Regan using ruthenium complexes many studies modifying these complexes have been published. Only in 2 years Professor Grätzel an co-workers increased the efficiency up to 10% (J_{sc}=18.2mA/cm^2, V_{oc}=720mV, FF= 0.73) with cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) most commonly known as **N3** (Figure 1.6) dye[12,13]. The following years many ruthenium complexes were reported as the tristhiocyanato-4,4',4''-tricarboxy-2,2':6,2''-terpyridine ruthenium(II) also called **Black dye** (Figure 1.6) with and efficiency of 10.4%[14] that was in 2012 updated to 11.4%[15]. Moreover, other Ru-complexes have been published with efficiencies close to the paradigm dye **N719** (Figure 1.6)[16] as , for example, the **Z907** (Figure 1.6) that presents long alkyl chains to increase the solubility and slows the recombination reaction between the photo-injected electrons and the oxidised electrolyte. Yet, a milestone was set in 2008 with the design of Ruthenium complexes bearing π-conjugated moieties as thiophene and other derivates at the bipyridyl ligands. The aim was to increase the absorption in the near-infrared region as well as to increase the molecular extinction coefficient of the dye. Needless to say that most of these novel dyes lead to higher efficiencies as in the case of the dye **C101**[17] that presents a 2-hexylthiophene in the bipyridyl ligand reaching an 11.0% (J_{sc}=17.9mA/cm^2, V_{oc}=778mV, FF= 0.78) (Figure 1.6) similar to the efficiency obtained with the dye **CYC-B1**[18] (Figure 1.6), the dye **CYC-B11**[19] (Figure 1.6) and the maximum performance achieved with Ruthenium dyes, with the moetiy 2-(hexylthio)-5-methylthiophene, the dye

C106[20] with an 11.7% (J_{sc}=19.8mA/cm^2, V_{oc}=758mV, FF= 0.78) of efficiency (Figure 1.6).

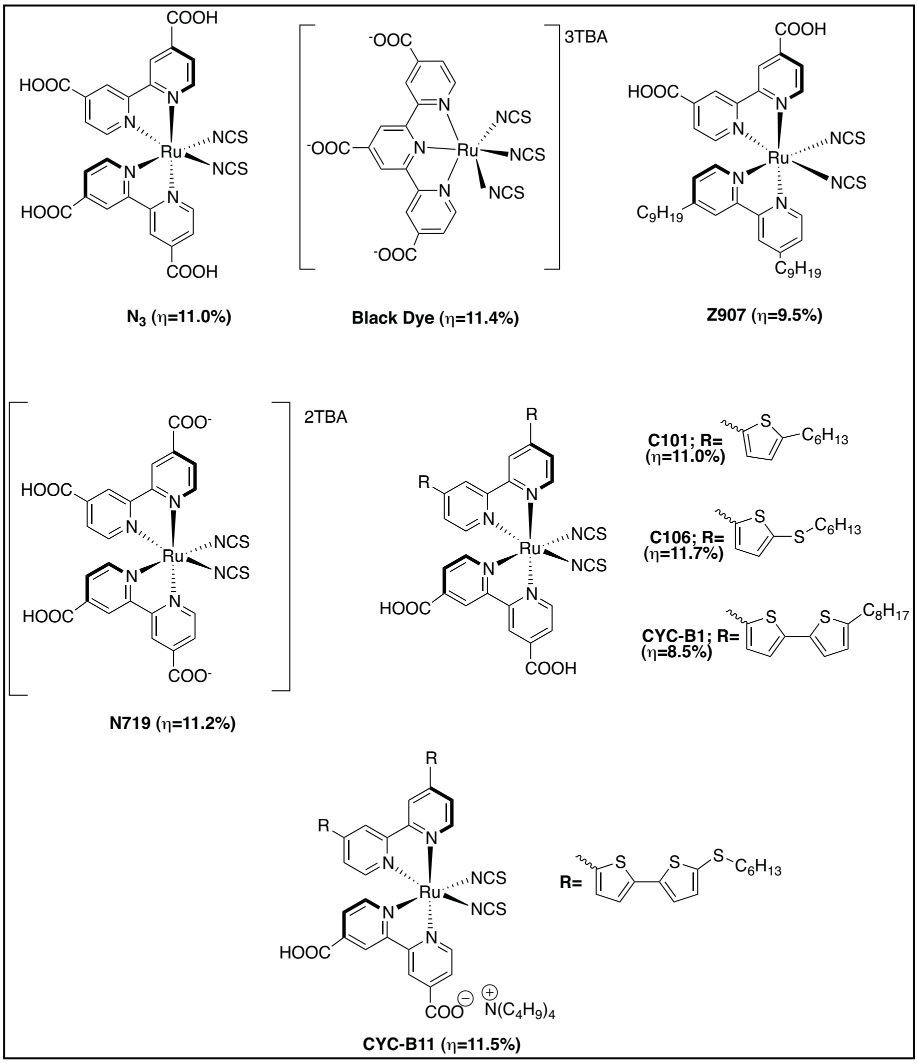


Figure 1.6: Efficient Ruthenium complexes used as sensitizers in DSSC

The Ruthenium complexes present high efficiency and also broad absorption; however, many drawbacks are associated to them. For example the cost; Ruthenium is considered a non-abundant earth metal and, moreover, there are increasing concerns on the environmental assessment of Ruthenium complexes. Last but not least, is also the moderate absorption coefficient. All these drawbacks make that many scientist make efforts in alternative sensitizers based on metal free organic dyes.

1.2.5 Metal free organic dyes. The Donor-π-Acceptor dyes

The donor-π-Acceptor dyes also known as push pull dyes consist in an electron donor and electron acceptor molecular unit linked covalently with a π conjugated spacer (Figure 1.7) The photophysical properties associated to these dyes are directly related to the intramolecular charge transfer (ICT) from the donor to the acceptor moiety. This ICT makes that the dyes present high molar extinction coefficients.

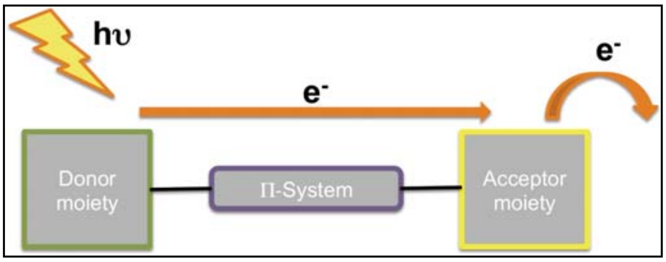


Figure 1.7: Structure of D-π-A dyes

These dyes with easy-to-tune absorption and high molecular extinction coefficients are a good alternative for Ruthenium complexes.

The design of these push-pull dyes is very important in order to achieve good results; otherwise organic dyes lie below the efficiency values obtained with Ruthenium complexes. For example, it is paramount to have a very good donor moiety, which remains stable when oxidised upon light irradiation. For example the use of oligoenes by Hara and co-workers, displayed efficiencies about 6% but the use of coumarin as donor moieties increased the efficiency up to 8.2[21-23].

In 2008 Professor Grätzel and co-workers published the **D205** dye (Figure 1.8) achieving an efficiency of 9.52% (J_{sc}=18.7mA/cm^2, V_{oc}=710mV, FF= 0.71). The structure of this dye shows an indoline group with an n-octyl moiety onto the rhodanine structure. The key issue, to include this long alkyl chain, was/is to decrease the dye aggregation and to make more soluble the molecule in organic solvents. The control over the formation of aggregates is an important issue for organic sensitizers in order to obtain excellent performances. In this particular work, they observed that the combination of a long alkyl chain and the use of CDCA lead to outstanding increase in efficiency[24].

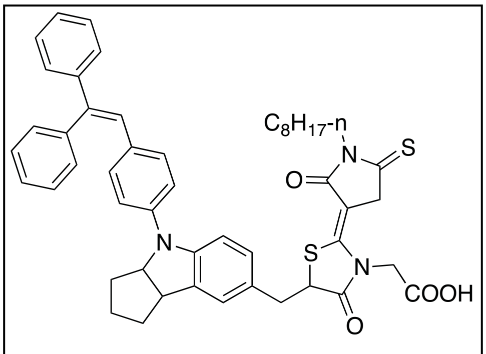


Figure 1.8: D205 molecular structure

Much recently, in 2010, Prof. Peng Wang and co-workers reported the **C219** dye (Figure 1.9) reaching, for the first time, efficiencies close or above 10%. The **C219** was reported to deliver an efficiency of 10.1% (J_{sc}=17.9mA/cm^2, V_{oc}=770mV, FF= 0.73). This novel dye consists in a binary π spacer: a 3,4-ethylenedioxythiophene unit (EDOT) connected to the donor moiety (alkoxy-substituted triphenylamine) to lift the HOMO and dihexyl-substituted dithienosilole (DTS) attached to the acceptor to achieve an appropriate LUMO[25].

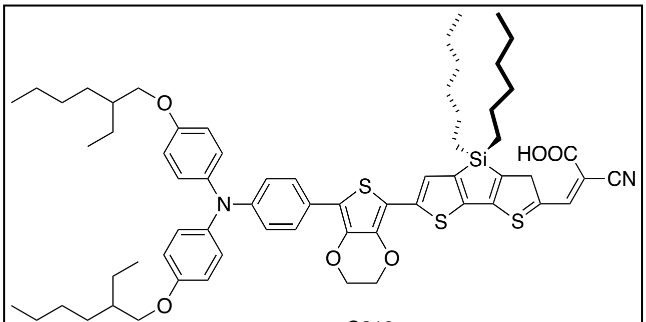


Figure 1.9: Molecular structures of C219

It is important to notice that until this year this moment all the best devices were fabricated using iodide/triiodide electrolyte. Yet, in 2010 a $Cobalt^{2+}/Cobalt^{3+}$ electrolyte was used for DSSC with a remarkable efficiency of 6.2% as reported by Hagfeldt, Sun and co-workers for the **D35** dye (Figure 1.10). In their work they synthesized two new sensitizers the **D35** and the **D29** with the same π–bridge and identical acceptor moiety but with a different donor group. For the **D29** dye the electron donating group was the group p-N,N-dimethylaminelinyl at the TPA moiety (triphenylamine) and for the **D35** it was the o,p-dibutoxylpheny grup at the TPA. These two dyes were investigated to compare the effect of bulky alkoxyl substituents in devices employing Cobalt electrolyte. For this, a series of cobalt electrolytes were synthesized to optimize the best one for use in the device and the election was done tacking into account the different oxidential potentials of the different cobalt complexes to achieve efficient dye regeneration and higher V_{oc}.[26]

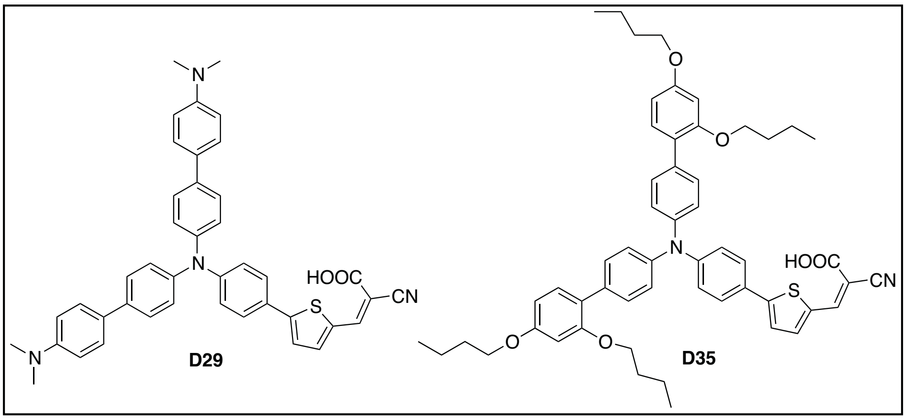


Figure 1.10: Molecular structures of C219

Professor Peng Wang and co-workers reported the sensitizer **C218** (Figure 1.11) which introduced the 4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) group, as a conjugated spacer to achieve a high molar absorption coefficient with an outstanding record efficiency of 8.95% (J_{sc}=15.8mA/cm^2, V_{oc}=768mV, FF= 0.74) using iodine electrolyte[27]. Thereafter, Professor Peng wang reported the same dye comparing their device performance in the same conditions with iodine/iodide and Cobalt electrolytes achieving 7.1% (J_{sc}=13.6mA/cm^2, V_{oc}=720mV, FF= 0.71) and 8.3% respectively (J_{sc}=14.1mA/cm^2, V_{oc}=820mV, FF= 0.73)[28]. Showing that using cobalt electrolyte make to increase to V_{oc} in 100mV. The dye efficiency was improved to 9.4% (J_{sc}=13.0mA/cm^2, V_{oc}=950mV, FF= 0.76)[29] just one year later, in 2012.

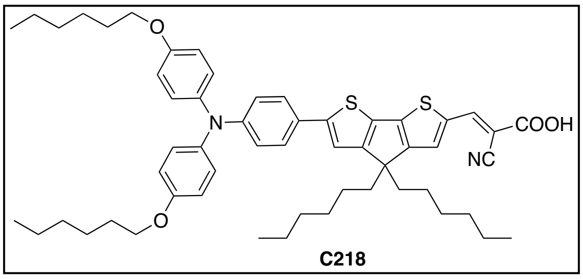


Figure 1.11: The C218 dye molecular structure.

Professor Peng Wang and his group focussed on the synthesis of organic dyes for DSSC in order to achieve record efficiencies by using Cobalt electrolytes and, in 2011, reported a new dye called the **C229** (Figure 1.12) with a similar structure as the C218 dye, however, in that work they decided to enlarge the π spacer introducing two thiophenes units and, thus, increasing the molar absorption coefficient owing a better delocalizability of π spacer. Meanwhile, the efficiency achieved using iodine/iodide electrolyte was just about 6.7% (J_{sc}=15.20mA/cm^2, V_{oc}=680mV, FF= 0.65). Nevertheless, in the same conditions with the cobalt electrolyte they reached 9.4% (J_{sc}=15.3mA/cm^2, V_{oc}=850mV, FF= 0.73)[30].

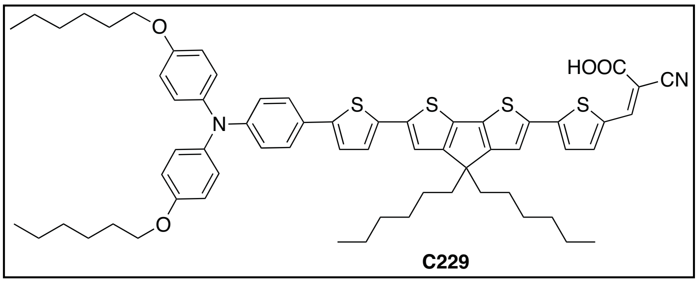


Figure 1.12: The dye C229 molecular structure.

Professor Michael Grätzel and co-workers reported also in 2011 the Y123 dye with the highest device performance using cobalt electrolyte reaching 9.6% in their champion cell[31] (Figure 1.13). Later in 2012 other study with this dye was reported for high open circuit Voltage with an impressive Voc of 1V just by using a Cobalt electrolyte[32].

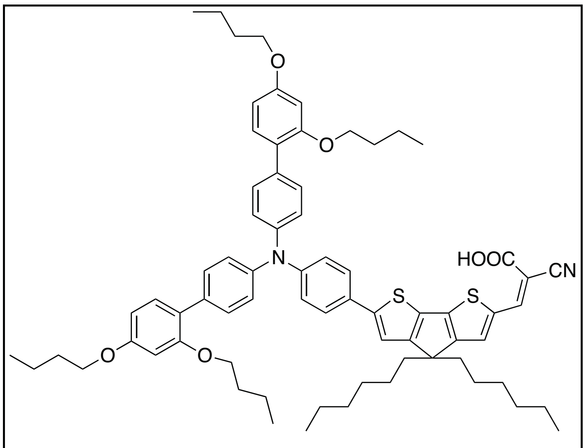


Figure 1.13: The dye Y123 molecular structure.

1.2.6 Porphyrins.

Porphyrins consist on a tetra pyrrole macrocycle composed of four modified pyrrole connected at carbon α by methine (Figure 1.14). Porphyrins follow Huckel's rule of aromaticity (possessing 4n+2 π electrons). This feature makes porphyrins outstanding dyes with a high molecular extinction coefficient and also is responsible for the nice colours that often porphyrin solutions have[33]. Porphyrins are present in nature in many biological systems as chlorophyll, hemoglobine, cytochromes, and many enzims too. Due to their excellent optical properties porphyrins are used in medicine[34-36], in electronic[37-39] devices and due to their role in photosynthesis these molecules have been a long-standing promise for efficient organic photovoltaic devices[40,41].

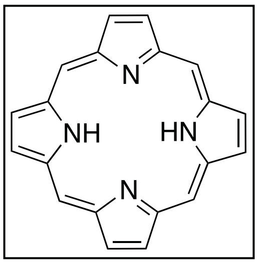


Figure 1.14: Basic core at the porphyrin molecules.

The typical absorption profile in porphyrins consists of an intense absorption band close to 400nm called Soret band and moderate absorption bands between 500 and 700nm[33]. In order to use these molecules for DSSC applications one point to take in account is that the molecule requires and anchoring group to attach in the semiconductor as in the case of the previous discussed organic dyes. The structure of porphyrins presents different positions to functionalize them. Four meso-positions and eight β-positions (figure 1.15) to attach the anchoring group, that in case of porphyrins the carboxylic acid is also considered the best [42,43].

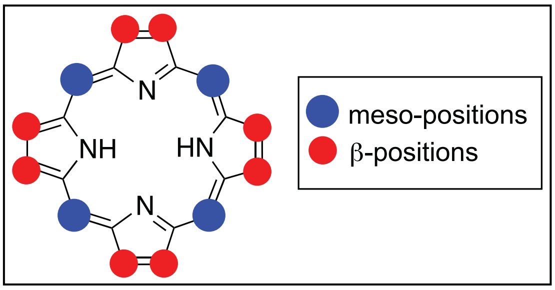


Figure 1.15: Available positions to functionalize porphyrins.

During the last decades many porphyrins have been synthesized for DSSC applications, with functionalization in the β and in meso-positions. The first remarkable example was the work by Professor Michael Grätzel and Professor Kay in 1993 with a modest efficiency of 2.6%[44]. Analogously, the first example for meso-position substituted porphyrin was published by Professor Cherian and Professor Wamser in 2000 with an efficiency of 3.5%[45].

During the last years several works with different porphyrins have been published in order to increase the efficiency, minimizing dye aggregation, and achieve good charge separation[46,47]. Nonetheless, it was not until the research groups of Professor Yeh and Professor Diau added a donor group in a porphyrin structure, as in the case of **YD1** and **YD2** (figure 1.16) when the efficiency increased by a factor of 5 or 6, adding a donor group at the porphyrin core did extend the absorption and improved the charge separation efficiency[48].

These groups tried to solve some aggregation problems too by adding different concentrations of chenodeoxycholic acid (CDCA) [49].

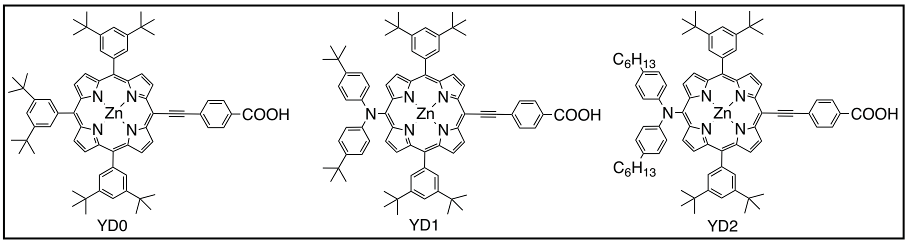


Figure 1.16: Dye molecular structures for YD1 and YD2.

In their work, it was synthesized the dye **YD0** (used as a reference) and the dyes **YD1** and **YD2**. The devices were made using different concentrations of CDCA. The dye **YD2** exhibited a cell performance close to 6.8% (J_{sc}=13.7mA/cm^2, V_{oc}=711mV, FF= 0.69). This efficiency is slightly smaller comparing the Ruthenium paradigm, **N719** 7.3% (J_{sc}=13.8mA/cm^2, V_{oc}=760mV, FF= 0.70). The high efficiencies were obtained with **YD2** and **YD1** compared with the **YD0** due to the slower recombination of the electrons with the oxidised electrolyte. In 2010 the device performance for **YD2** was improved by Professor Grätzel and co-workers exhibiting an overall efficiency of 10.9% (J_{sc}=18.6mA/cm^2, V_{oc}=770mV, FF= 0.76)[50].

During 2011, some porphyrins had been synthesised trying to achieve greater efficiencies than the dye **YD2**[51-57]. However, it was not possible until the end of 2011 when Dr. Aswani Yella and co-workers[58] published the new record porphyrin: The dye **YD2-0-C8** (figure 1.17).

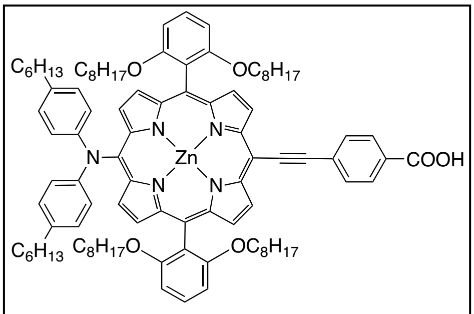


Figure 1.17: Molecular structure of YD2-o-C8

The structure of this porphyrin was similar to the **YD2** with the difference that new one incorporates two octyloxy groups in the ortho positions of each meso-phenyl ring increasing the electronic density on the porphyrin π-system compared to the **YD2** dye. This increase in electronic density is directly related to the LUMO level that now lies at higher energy. With this new dye, very promising results have been achieved using Cobalt electrolyte in D-π-A porphyrins making devices that achieved a record in efficiency of 11.9% (J_{sc}=17.3mA/cm^2, V_{oc}=965mV, FF= 0.71). This new value is higher than the previous record achieved with organic dyes[31]. In the same work, trying to increase the efficiency, the group added a co-sensitizer. The dye used for the "cocktail" was the **Y123**. They achieved a remarkable efficiency of 12.3% (J_{sc}=17.7mA/cm^2, V_{oc}=935mV, FF= 0.74).

The same group carried out further efforts to increase the efficiency achieved by using the dye **YD2-o-C8** and in 2014 they published two new porphyrins the **GY21** and **GY50** (Figure 1.18). In this work their strategy was the introduction of the benzothiadazole (BDT) unit as π-conjugated linker between the anchoring group and the porphyrin core to broaden the absorption spectra. Moreover, in this structure it was also introduced a phenyl group as a spacer between the BDT moiety and the carboxylic group.

The photovoltaic devices were made using Cobalt electrolyte due the high performance achieved for the **YD2-o-C8** dye. The results for **GY21** and **GY50** were 2.5% (J_{sc}=5.03mA/cm^2, V_{oc}=615mV, FF= 0.80) and 12.75% (J_{sc}=18.53mA/cm^2, V_{oc}=885mV, FF= 0.77) respectively.

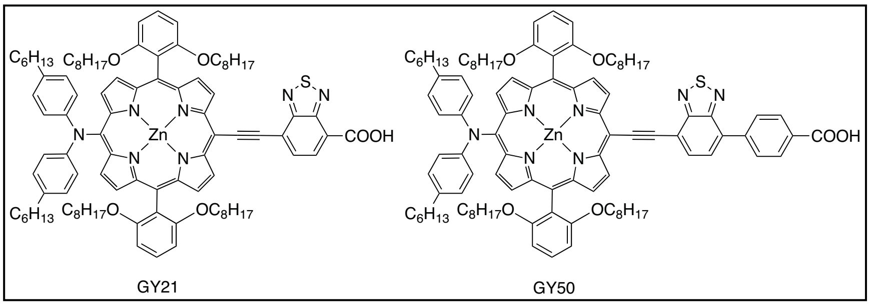


Figure 1.18: Molecular structure of GY21 and GY50

In one hand, the higher efficiency achieved with the **GY50** is due to the panchromatic absorption, which avoids the use of a secondary dye.

On the other hand, the lower conversion efficiency for **GY21** compared to **GY50** is due to the lack of directionality of the excited state and, thus, the observation of much less photocurrent[59].

During the same year different studies on porphyrins have been published too. For example the work presented by Professor Chin-Li Wang and co-workers where they synthesized a new porphyrin the, **LD31** and the **LD14**[60], inserting between the donor unit and the core porphyrin an ethynyl-antrhacenyl moiety to extend the π-conjugation in order to improve light-harvesting efficiency[51] (figure 1.19).

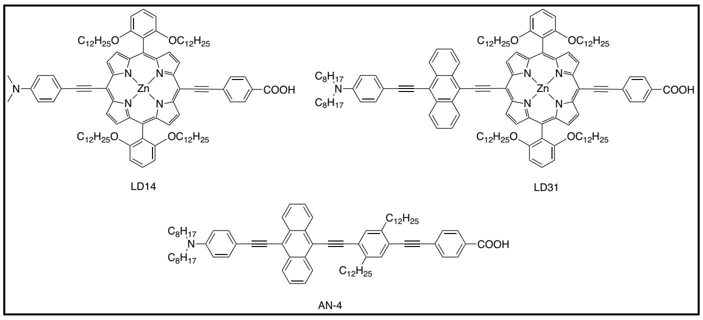


Figure 1.19: Molecular structures of LD14, LD31 and AN-4

The new porphyrins with and without the use of co-sensitization with the dye **AN-4** achieved 9.95% (J_{sc}=20.02mA/cm^2, V_{oc}=699mV, FF= 0.71) and 10.3% (J_{sc}=20.3mA/cm^2, V_{oc}=704mV, FF= 0.72) respectively.

Finally, this year, 2014, it was reported the champion molecule for DSSC achieving a power conversion of 13% by the group of Professor Michael Grätzel and co-workers. In that work they synthesized two new porphyrins called **SM371** and **SM315** (Figure 1.20)

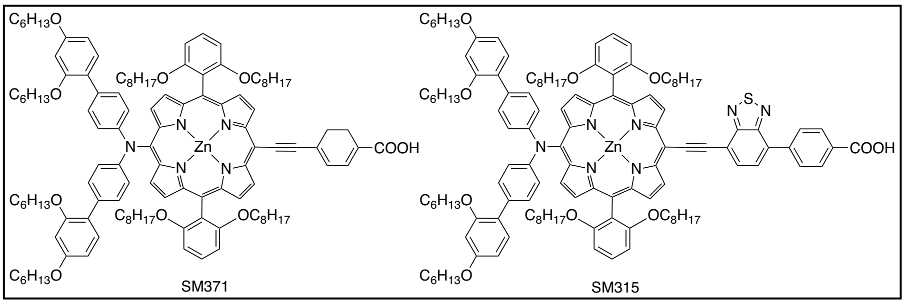


Figure 1.20: Molecular structures of SM371 and SM315

The structure of these porphyrins is similar to the previously reported Professor Grätzel and co-workers (**GY21** and **GY50**). However in that case, they uses as donor moiety the bis (2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine. This donor group has been using before in several organic dyes reporting good efficiencies in DSSC based on cobalt electrolyte[26,31]. The efficiencies achieved for **SM371** and **SM315** are 12% (J_{sc}=15.9mA/cm^2, V_{oc}=960mV, FF= 0.79) and 13.0% (J_{sc}=18.1mA/cm^2, V_{oc}=910mV, FF= 0.78) respectively using cobalt electrolyte. The higher J_{sc} obtained by SM315 is due to the dramatically improved absorption properties that lead to a high IPCE with an 80% across all visible wavelength (450nm-750nm). A small difference of just 50mV at the V_{oc} under standard irradiation conditions is observed between these two porphyrins presenting **SM371** higher voltage compared to the **SM315**. In their studies they observed that the electron lifetime is 6 times slower for the **SM371** dye. The slower recombination kinetics is likely to be produced by the BDT unit which improves the excited state directionality and prevents also back electron transfer to the oxidised electrolyte[61].

In the following figure (figure 1.21) we can observe how has been the evolution of photovoltaic performances of DSSC from 1991 to 2014 showing the most important family of dyes explained above.

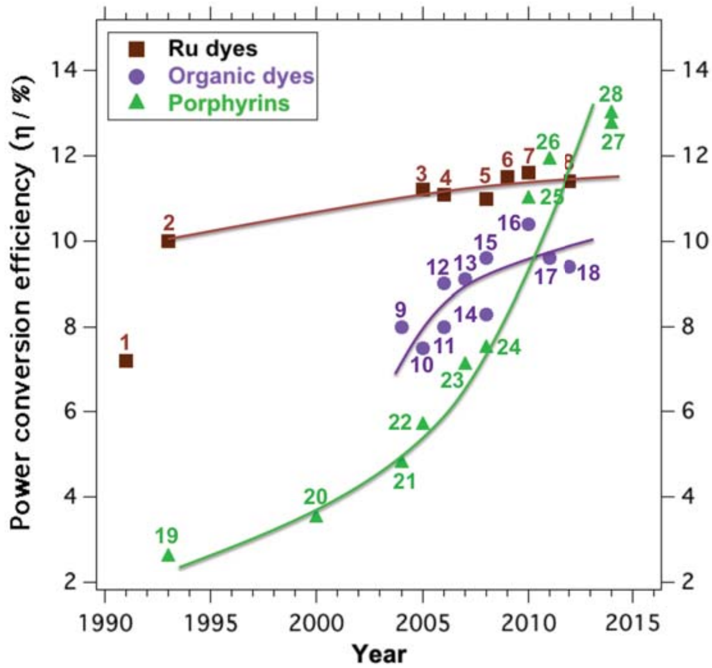


Figure 1.21: Progress on DSSC efficiency of the most relevant dyes involving Ruthenium complexes (**1-8**); organic dyes (**9-18**) and porphyrins (**19-28**). 1.-trinuclear

trinuclear $RuL_2(\mu\text{-}(CN)Ru(CN)L'_2)_2$[9]; **2**.-N3[13]; **3**.-N3[12]; **4**.-N719[16]; **5**.-C101[17]; **6**.-CYC-B11[19]; **7**.-C106[20]; **8**.-Black dye[15]; **9**.-Indoline dye[62]; **10**.-NKX-2677[63]; **11**.-JK2[64]; **12**.-D149[65]; **13**.-TA-St-CA[66]; **14**.-MK-2[67]; **15**.-D205[24]; **16**.-C219[25]; **17**.-Y123[31]; **18**.-C218[29]; **19**.-Cu-a-oxymesoisichlorin[44]; **20**.- TCPP[45]; **21**.-Zn-1a[68]; **22**.-Zn-3[69]; **23**.-GD2[70]; **24**.-tda-2b-bd-Zn[71]; **25**.-YD2[50]; **26**.-YD2oC8[58]; **27**.-GY50[59]; **28**.-SM371[61]

Another promising molecular solar cells studied in our group are the OSC (organic solar cells). In this Thesis the Chapter 5 shows my input to this field under Professor Palomares supervision.
Below is shown a short but detailed explanation about the fundamentals of OSC.

1.3 ORGANIC SOLAR CELLS (OSC)

OSC combine the use of two organic materials an electron donor or hole transport material (HTM) and an electron acceptor material or electron transport material (ETM), which are “sandwiched” between to metal electrodes with different work function (Figure 1.22). The photo-induced charges are separated at the interface between both type of organic materials and the free carriers are collected selectively at each electrode.

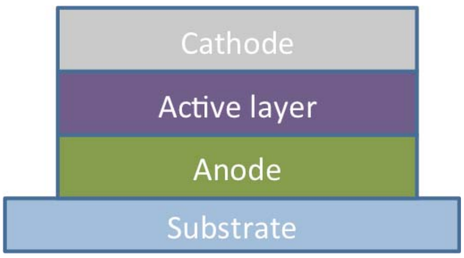


Figure 1.22: Schematic representation of the most simple OSC.

The electron-hole pairs (so called excitons) are generated upon irradiation of the solar cells and their lifetime is short being able to being transported a few nanometers (10-12nm) depending on the nature of the organic material. When the exciton arrives at the interface of both organic materials it separates in free carriers of different charge (so called polarons). The polarons must be transported before they can recombine to the contact electrodes (Figure 1.23).

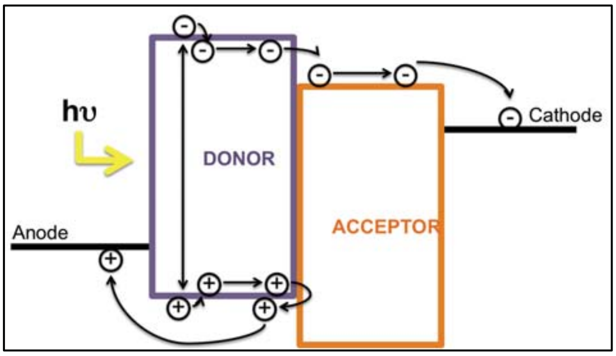


Figure 1.23: Schematic principle operation of OPV

Thus, the efficient formation of excitons as well as the optimization of the exciton separation and polaron collection is key to achieve excellent device performance. A first approach is to select the adequate donor and acceptor materials with sufficient energy onset to be able to separate efficiently the charges at the interface. For this reason, the study of new materials and the morphology at the nanoscale have attracted much attention in recent years. From the original device in the eighties by Professor Tang (Figura 1.24), with efficiencies as low as 1%[72] by using a bi-layer type device to the actual bulk-heterojunction solar cells, that mixes both type of organic materials, a great quantum leap in efficiency has been achieved to almost 10% for single junction solar cells.

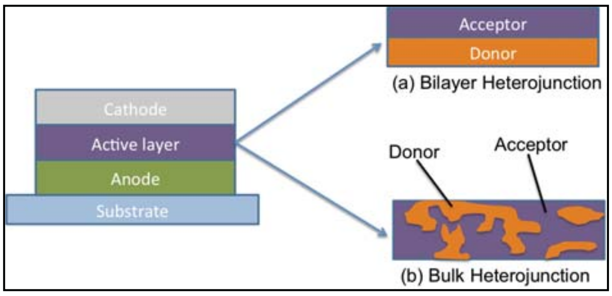


Figure 1.24: Architecture structure of a bilayer heterojunction (a) and a bulk heterojunction (b)

1.3.1 Donor and Acceptor Materials

Here, in this section, we describe briefly the most relevant materials used in OSC.

1.3.1.1 Electron Acceptor Materials:

The fullerenes and their derivates are the dominating molecules used as electron acceptor materials in OSC. The use of these type of molecules is justified due to their strong capability to accept electrons from donor materials and also their electron mobility[73]. The derivatives of C_{60} and C_{70} as $PC_{61}BM$ and $PC_{71}BM$ are the most used in solution processed OPVs (Figure 1.25).

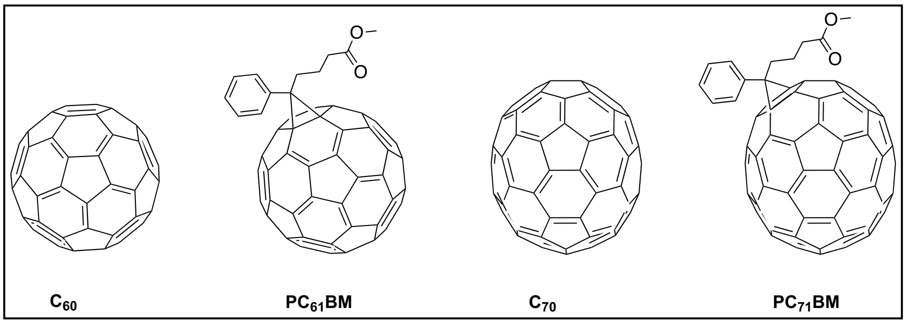


Figure 1.25: Principals fullerenes used as acceptor moieties

1.3.1.2 Electron Donor Materials:

The electron donor materials have been much more explored as they are used as the main light-harvesting moiety in the OSC. Several type of molecules have been designed and synthesized for their applications in solution processed OSC as squaraines (SQ)[74-78], diketo-pyrrolopyrroles (DPP)[79-81], BODIPY[82] and also D-π-A dyes bearing triphenylamine units as secondary electron donor[83-85] all of them with efficiencies ranging between 4% to 6% under standard illumination conditions of 1 sun (100mW/cm^2 of sun simulated light 1.5AM G spectrum)

Nowadays, the best reported OSC using small molecules for single junction devices is the work by C. Bazan and Alan J. Heeger at University of California (USA) that has achieved an impressive 8.9%(figure 1.26)[86].

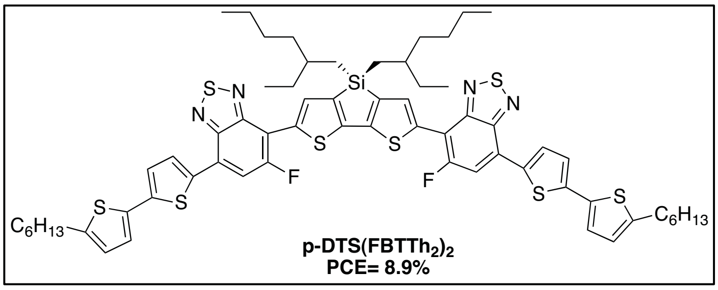


Figure 1.26: Molecular structure of p-DTS(FBTTh$_2$)$_2$

Alternatively, porphyrins (POR) have been also widely studied and used in many BHJ-OSC[87-91]. Professor Xiaobin Peng and co-workers have published in 2014 the best porphyrin for solution-processed BHJ OSC based in small molecule with an efficiency up to 7.23% (J_{sc}=16.0mA/cm^2, V_{oc}=710mV, FF= 0.63)[92].

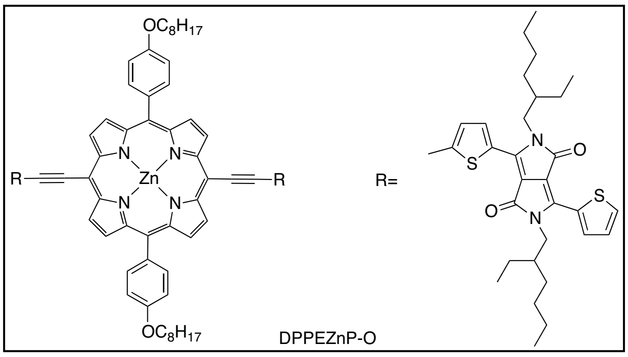


Figure1.27: Molecular structure of DPPEznP-O

1.4 AIM OF THIS THESIS

Dye Sensitized Solar Cells and Organic Solar Cells have great much attention during the last decades as molecular photovoltaic devices that hold the long-standing promise for inexpensive light-to-energy conversion devices. In both technologies the organic dyes play a very important role. The molecules structure and their physical properties determine the overall device efficiency.

In this Thesis a series of new sensitizers have been design and synthesized in order to study their applications in DSSC and OSC photovoltaics. Furthermore, the study about the relationship between the molecules structure, the film morphology in the case of OSC of these novel sensitizers and the device performance has been also studied.

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Chapter 2
Materials and Methods

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2.1 SYNTHETIC METHODS

The reagents, solvents and the main equipment used in this Ph. D. Thesis are described in this section.

2.1.1 General reagents and solvents

All of the chemical reagents were purchased from Sigma-Aldrich©, Frontier Scientific Ltd., Lumtec Ltd or Alfa Aesar© and they were used without further purification. The dry solvents used for solvent-sensitive reactions were purchased from Sigma-Aldrich© and Flucka© and common solvents from SdS.

2.1.2 General Instrumentation

The ^{1}H and ^{13}C NMR samples were measured on a Bruker Advance 400 (400mHz for ^{1}H and 100mHz for ^{13}C). The deuterated solvents are indicated when used in the respective chapters and the chemical shifts (d) are given in ppm, referenced to the solvent residual peak. Coupling constants (*J*) are given in Hz.

High resolution Mass Spectra (HR-MS) were carried out on a Waters LCT Premier liquid chromatograph coupled time-of-flight mass spectrometer (HPLC/MS-TOF), using electrospray ionization (ESI) as ionization mode. Matrix assisted laser desorption (MALDI) were recorded on a BRUKER Autoflex time-of-flight mass spectrometer.

Uv-Vis absorption spectra were measured in a 1 cm path-length quartz cell using a Shimadzu© model 1700 spectrophotometer. The steady state fluorescence spectra were recorded Spectrofluorimeter Fluorolog from Horiba Jobin Yvon Ltd. The system is composed by a continuum 450W Xenon lamp, double monochromator for excitation, a solid sample holder, and detection in Right Angle or Front Face mode and absorbance measurements. Two detectors PMT(UV-vis) and InGaAs (NIR) allow fluorescence measurements in the wavelengths range of the UV-Visible and NIR from 250 to 1600 nm.

The electrochemical measurements were carried out employing a conventional three-electrode cell connected to a CH instrument 660c potentiostat-galvanostat. The working electrode consisted of a platinum wire or a carbon electrode and the counter electrode was a platinum mesh. The reference electrode was a Ag/AgCl electrode (saturated KCl). All solutions were degassed with Argon prior the use. All the measurements were recorded in presence of 0.1M $TBAPF_6$ supporting electrolyte, using ferrocene as an internal reference.

2.2 DYE SENSITIZED SOLAR CELLS (DSSC)

2.2.1 Films used

In this Ph.D. Thesis we used 2 different cells depending on the measurement carried out. For Laser Transient Absorption Spectroscopy (L-TAS) experiments we need highly transparent thin film devices with an active area of $1cm^2$. These films were made screen-printing 4-6mm thick TiO_2 paste (Solaronix Ltd) and sensitized with the appropriated organic dye used in the studies. The other films we need are to optimize the device efficiency. For these films the active area is smaller ($0.16cm^2$) to decrease the losses by series resistance that affects the device fill factor. As the same way like other films these are also done by screen printing technique depositing a layer of 9 to 16mm of TiO_2 of 20nm TiO_2 nanoparticles (Dyesol, and Solaronix paste) and an additional layer of 4mm thick made of 400nm diameter particles of TiO_2 (so called the scatter layer) and sensitized with the appropriated dye See Figure 2.1.

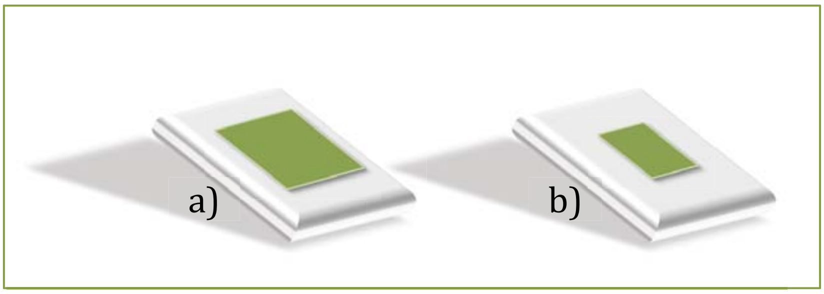

Figure 2.1: Scheme of different films used, a) Film for photophisical measurements and b) Film for device preparation

2.2.2 Device fabrication

The FTO (Fluorine doped tin oxide) glass (Hartford Glass inc. with 15 Ω/cm^2 resistance) was first cleaned three times; the first one in a detergent solution using an ultrasonic bath for 15 min, and then cleaned with ethanol two times. After, a treatment in a UV-O_3 system (PSD series UV-ozone cleaning, Novascan Technologies, Inc.) for 15 min is carried out. Then, the FTO glass plates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol.

A screen-printed double layer film of interconnected TiO_2 particles of 20nm (dyesol paste) and an additional layer of 400nm TiO_2 particles was used as the mesoporous negative electrode.

First a 8-14 **µ**m thick transparent layer of 20 nm sized TiO_2 particles were deposited on the FTO conducting glass electrode and further coated by a 4 **µ**m thick scattering layer of 400 nm sized TiO_2 particles with an active area of 0.16cm^2. The resulting electrodes were gradually heated under airflow at 325 ºC for 5 min., 375 ºC for 5 min., 450 ºC for 15 min., and 500 ºC for 15 min. Then, The electrodes are treated again with an aqueous solution of $TiCl_4$ 40mM at 70 ºC for 30min and then washed with ethanol. The electrodes were heated at 500ºC for 30 min and cooled at room temperature.

When the electrodes were cooled, they have been dipped in the dye solution in the optimal conditions in order to achieve the maximum efficiency possible (using a certain concentration, a good solvent a certain dipping time and if it is necessary a small quantity of Chenodeoxycholic acid to avoid aggregates).

The platinized counter electrode was made by adding a drop of $5 \cdot 10^{-3}$ M H_2 $PtCl_6$ in ethanol dry solution onto a conducting glass substrate (FTO) and heated under airflow at 390ºC for 15 min.

After the time required for the immersion of the electrodes into the dye solution, the electrodes were washed with the solvent used and dried under air. At the end the working and counter electrodes were assembled in a sandwich form using a thermoplastic (Surlyn) frame that melts at 100ºC.

The counter electrode has an internal space, which was filled with a liquid electrolyte using a vacuum backfilling system. After that this hole is sealed with a Bynel sheet and a thin glass cover by heating. The liquid electrolyte used consists in 2 pair redox coupling using iodine-iodide (I^-/I_3^-) or Co(II)/Co(III) with the presence of different additives in order to increase the performance of the devices and the characterization of them.

The composition of the different electrolyte solutions will be explained in more details in the respective chapters.

2.3 ORGANIC SOLAR CELLS (OSC)

2.3.1 Device fabrication

We used for OSC Indium Tin Oxide (ITO) 5 Ohm/square (PSiOTec, Ltd., UK) sodalime glass substrates. However, prior to use them we must remove the residual photoresist layer cleaned with acetone. The substrates were then placed in a holder and were sonicated first 10 min in acetone and two times more in isopropanol. After that, the substrates were dried under Nitrogen flow. Moreoverthe ITO substrates are ozone-treated in a UV-Ozone cleaner for 30 min in ambient atmosphere, and subsequently coated in air with a layer of filtered (0.45 μm, cellulose acetate) solution of Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC StarckBaytron P) (4500 rpm 30 seconds followed by 3500 rpm 30 seconds). The PEDOT:PSS film was dried at 120 ºC under inert atmosphere for 15 min. The blend or Active Layer consists in a solution of donor derivative and $PC_{70}BM$ as acceptor. The concentration used normally is 20mg/ml and the ratio between the donor and the acceptor is optimized for each device. Active layers were spin-coated in different conditions depending on the blend used.

The cathode layer was deposited by thermal evaporation in an ultra high vacuum chamber ($1 \cdot 10^{-6}$ mbar). Metals were evaporated through a shadow mask leading to devices with an area of 9 mm^2. LiF (0.6 nm) and Al (80 nm) were deposited at a rate of 0.1 Å/s and 0.5-1 Å/s respectively. Following fabrication, the films were maintained under a nitrogen atmosphere and stored in the dark until used. In the case of hole only and electron only devices the solar cells were prepared as expalined above but for hole only devices the structure was ITO/PEDOT:PSS/donor:$PC_{70}BM$/Au and for electron only devices the structure was ITO/ZnOnp/donor:$PC_{70}BM$/Al.

2.4 DEVICE CHARACTERIZATION

2.4.1 Charge Extraction (CE)

As the name indicates with this technique we extract and measure the charge accumulate in the system under determinate conditions. First of all, the cell is simultaneous putted in open circuit and illuminated with a series of LEDS and these conditions are applied until the cell reaches the steady state. Then, The cell is also simultaneously short-circuited and the light is switched off. In that situation all the charges accumulated in the open circuit conditions can be extracted, allowing the measurement of the charge density[1].

The Charge extraction system consists in 6 white light LEDS. These pulses are generated and controlled by the Trigger (TGP, from Thrurlby Thandar Instruments). The decay in voltage is measured using an oscilloscope TDS 2022 from Tektronix©. All the measurements are done in the dark to eliminate stray light that can increase the error.

The accumulate charge Q (C) can be calculated following equation (1).

$$Q = \frac{1}{R}\int_{t=0}^{t=t} V(t)dt \qquad (1)$$

Where R is the resistance in ohms (Ω) and V(t) is the voltage in volts (V) measured at each time.

To define the amount of charge accumulated in the semiconductor we use the charge density and it can be calculated from equation (2)

$$e^{-}_{density} = Q.\frac{1}{C_e}.\frac{1000}{d{\cdot}A{\cdot}(1-p)} \qquad (2)$$

Where Q is the accumulate charge (that it has been calculate before); C_e is the charge of the electron ($1.609.10^{19}$C/e^{-}), d is the film thickness in centimeters (cm), A is the area of the surface (cm^2) and p is the porosity of the film.

We can represent the different $e^{-}_{density}$ obtained at different voltages. The plot of these data can be fitted to an exponential curve defined by equation 3.

$$e^{-}_{density}(V) = A_0 + A_1 \cdot e^{V/m_c} \qquad (3)$$

2.4.2 Incident Photon to Current Efficiency (IPCE)

In this technique we irradiate the cell using a range of different wavelengths, at each wavelength the solar cells convert the incoming photons into electrical current.

The IPCE values can be calculated using equation 4.

$$IPCE = \frac{1240 \cdot J_{sc}}{\lambda \cdot P_{lamp}} \cdot 100 \qquad (4)$$

Where: J_{sc} is the short circuit photocurrent (mA/cm^2), λ is the wavelength for the incident light in nanometres (nm), P_{lamp} is the power of the incident light in Watts (W/m^2) and 1240 is the conversion factor of the energy of photons.

The instrument to measure the IPCE consists in a xenon lamp (Oriel 150 W) as the light source, a monochromator (PTIM-101) that automatically change the wavelength to promote homogeneous monochromatic light in all the exposed area of the cell, a 4 inch integrating sphere and a Keithley 2400 to measure the current generate.

2.4.3 Solar cell power conversion efficiency (η)

The overall efficiency of a solar cell is calculated using equation 5.

$$\eta_{eff} = \frac{J_{sc} \cdot V_{oc} \cdot ff}{P_{lamp}} \cdot 100 \qquad (5)$$

Where J_{sc} is the photocurrent at short circuit; V_{oc} is the open circuit photovoltage; ff, the fill factor of the cell and P_{lamp} the light intensity. The devices are measured under sun-simulated solar spectrum AM 1.5G (at 48.2º zenith angle)[2] conditions with an Abet solar simulator and a Keithley 2400 source meter to measure the current. A homemade software interface (Labview©) is used to register and record the I-V curves. To calibrate the light source intensity at 100mW/cm^2 (1 Sun) a calibrated silicone diode is used prior to each device measurement. When needed, a series of neutral filters are used to measure the efficiency of the cells at different intensities of light.

2.4.4 Transient Photovoltage (TPV)

The measurements of transient photovoltage provide us information about recombination dynamics in the devices between the charges accumulated at the semiconductor and the oxidized electrolyte[3]. The solar cell is illuminated with a set of white LEDS (in a similar way that the one used for charge extraction measurements) until the solar cell reaches steady state conditions. When the solar cell achieves the steady state condition a ultra short laser pulse with low intensity is applied to the device and a small perturbation in the equilibrium is created allowing an excess of charge to be generated producing a transient decay. The same laser pulse is used under different light intensities that lead to different device steady-state voltage and, thus, providing different transient decays.

The data obtained is fitted as an exponential equation (6)

$$V(t) = V_{oc} + V_1 \cdot e^{-(1/\tau)} \qquad (6)$$

Where V (V) is plotted as a function of time. V_{oc} (V) is the voltage at open circuit, V_1 (V) is the voltage generated by the pulse and τ (s) is the recombination lifetime.

2.4.5 Laser Transient Absorption Spectroscopy (L-TAS)

The measurements of Laser Transient Absorption Spectroscopy provide us with information about excited short living species[4,5]. Basically, a sample is irradiate constantly (probe light) at a determinate wavelength that corresponds to the maximum absorption of the sample excited state. At the same time, we excite the sample with a short light pulse producing a change in the sample optical density. The change in optical density is monitored during a short period of time to monitor the variations.

The data collected is treated in order to obtain units of optical density; the data can be fitted to an exponential function equation (7)

$$\Delta O.D.(t) = A_0 + A_1 e^{-(t/\tau)\beta} \quad (7)$$

Where A_0 (a.u.) is the baseline, A_1 (a.u.) is the signal amplitude, τ (s) is the lifetime of the transient and β (a.u) is the emprirical stretched factor whose value is between 0 and 1.

2.5 REFERENCES

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Chapter 3

Light soaking effects on Charge Recombination and Device Performance in DSSC based on indoline-Cyclopentadithiophene Chromophores

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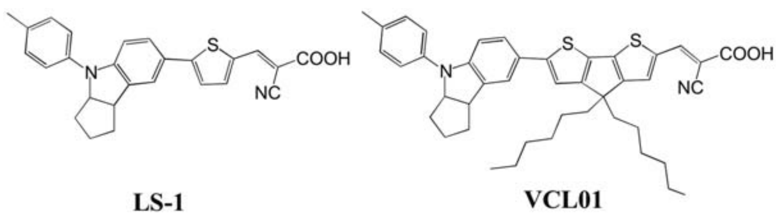
3.1 ABSTRACT

The synthesis, characterization, electrochemical and photophysical properties of a novel D-π-A indoline organic dye, **VCL01**, are described. Its performance characteristics in Dye Sensitized Solar Cell (DSC) devices under standard AM 1.5G illumination are also investigated. **VCL01** incorporates a cyclopentadithiophene unit as the π-bridge between the indoline donor and cyanoacetic acceptor units. In comparison to the reference dye **LS-1** containing only one thiophene unit in the π-bridge, **VCL01** shows a 40nm red shift in adsorption, an increase in molar absorptivity and a 0.13 V lower oxidation potential, all consistent with the more conjugated nature of this sensitizer. The efficiency of **VCL01** and **LS-1** DSC devices were 4.81% and 6.23% respectively, which upon >100 mins continuous light soaking under AM 1.5G illumination rose to 7.21% and 6.95%, representing an unprecedented 42% increase in efficiency for the **VCL01** device. This increase is overwhelmingly due to an increase in photocurrent but, remarkably, V_{oc} also increases by 50 mV upon illumination reflected in transient photovoltage data which indicate that electron lifetime increases considerably also. Time-Correlated Single Photon Counting data indicate that partly the light soaking effect can be attributed to improved TiO_2/dye interaction leading to enhanced electron injection.

3.2 INTRODUCTION

Development of dye Sensitised Solar Cells (DSCs) based on organic D-π-A sensitizers[1-3] is an active area of research as the properties of these sensitizers can be easily tailored by judicious selection of each individual unit and can be exploited commercially as efficient solar cells for indoor applications[4] and building integrated photovoltaics (BIPV).[5] Compared to those containing triphenylamine donor groups,[6-14] D-π-A sensitizers containing indolines[15-22] have been much less investigated despite the superior donating ability of these groups and the well-known stability they impart, which is a pre-requisite for long term device stability.

In this present work we perform a comprehensive study of the novel sensitizer **VCL01** (Scheme 1) using the dye **LS-1** reported by Li *et al.*[23] as a reference. **VCL01** consists of an indoline and cyanoacetic acid and, in addition, a cyclopentadithiophene unit is used in the π-bridge to increase conjugation and the light-harvesting dye properties. Moreover, the long alkyl chains are expected to block recombination loss reactions between TiO_2 electrons and the oxidised electrolyte. Cyclopentadithiophene is used in many efficient D-π-A dyes and for this reason it was coupled with an indoline donor group here for the first time. A dramatic 42% increase in efficiency is observed for **VCL01** devices upon continuous light soaking of over 100mins. We ascribe this increase to improved interaction between dyes and TiO_2 leading to an enhancement in electron injection



Scheme 3.1: Molecular structures of dyes **LS-1** and **VCL01**.

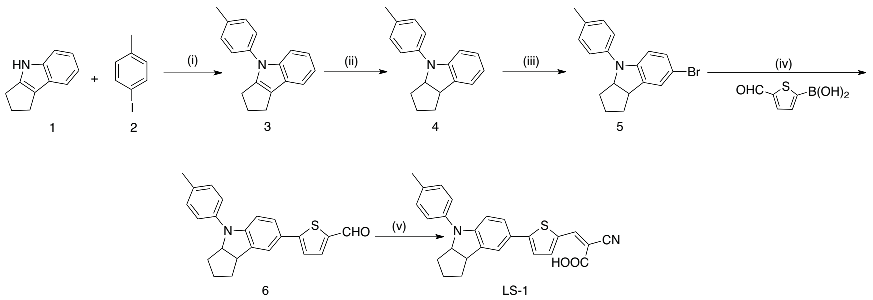
3.3 EXPERIMENTAL SECTION

3.3.1 Synthesis and characterization

LS-1 was synthesized according to the literature.[23]

3, **4** and **5** were synthesized according to the literature[24]

Synthesis of LS-1



Scheme 3.2: Synthetic route of **LS-1**. (*Reaction conditions:* (i) K_2CO_3, Cu, 1,2-dichlorobenzene, 48 h, 150ºC; (ii) $NaBH_4$, CH_3COOH, 4 h, 50ºC; (iii) NBS, CH_3COCH_3, 2 h, 0ºC; (iv) $Pd^{II}(dppf)Cl_2$, 2M K_2CO_3 aqueous solution, dimethoxyethane, 2 h, 90ºC; (v) cyanoacetic acid, piperidine, Chloroform, 12 h, reflux.)

Synthesis of 4-(*p*-tolyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**3**). In a round flask 3,4-dihydrocyclopenta[*b*]indole (9.4g, 0.06mol), 1-iodo-4-methylbenzene (16.8g, 0.07mol), Potassium carbonate (16g, 0.125g) and Cu (0.72g, 0.01mol) were added in 100mL of 1,2-dichlorobenzene. The solution was heated up at 150ºC for 48 hours. After that, de 1,2-dichlorobenzene was distilled. Then the mixture was extracted in CH_2Cl_2 and the organic layer was cleaned with brine. Then the organic layer was dried over Na_2SO_4 anhydrous. Then the crude is purified by column chromatographic using Hexane/Ethyl Acetate (9.5:0.5) as a solvent to obtain a yellow oil (4g, 27% of Yield). ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 7.46 (m, 1H): 7.38 (m, 1H); 7.29 (m, 4H); 7.09 (m, 2H); 2.87 (m, 4H); 2.53 (m, 2H); 2.41(s, 3H).

Synthesis of 4-(*p*-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (4): In a schlenk flask $NaBH_4$ (8.4g), 0.22mol) was added slowly to a solution of **3** (4g, 0.016mol) in acetic acid (120mL). Then the muxtire was heated up to reflux overnight. After that the mixture was stirred for 4 hours at 50ºC. Then, Na_2CO_3 was slowly added until pH 7. Then we extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. Then the crude is purified by column chromatographic using Hexane as a solvent to obtain a yellow oil (2.8g, 71% of

Yield). ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 7.18(m, 5H): 7.05(t, J=8.2Hz, 1H); 6.94 (d, J=8.2Hz, 1H); 6.73 (t, J=8.2Hz, 1H); 4.76 (m, 1H); 3.85 (m, 1H); 2.36 (m, 3H) 2.06 (m, 1H); 1.92 (m, 2H); 1.82 (m, 1H); 1.66 (m, 1H); 1.56 (m, 1H).

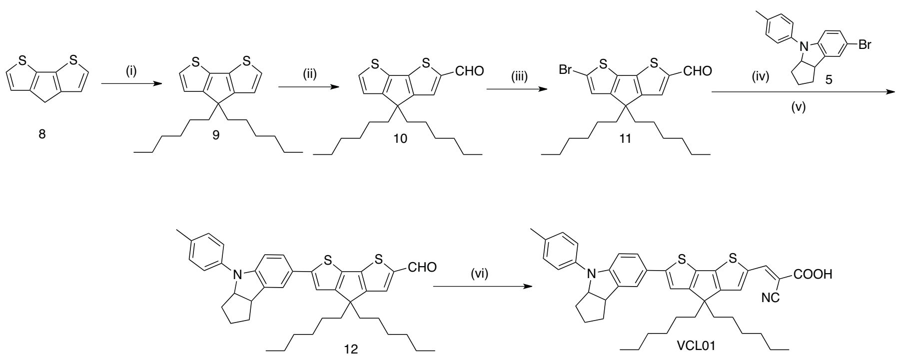
Synthesis of 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-6-ylium (5): in a schlenk flask a solution of **4** (2.14g, 8.62mmol) and Acetone (90mL) was cold at 0ºC. After that, N-bromosuccinimide (1.53g, 8.62mmol) was added and the mixture was stirred at 0ºC in the dark for 2h. Then water was added. The crude product was extracted into $CHCl_3$, and the organic layer was dried over Na_2SO_4. Finally the sample was recrystallized in Hexane to obtain a white solid. (2.4g, 96% of Yield) ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 7.14 (dd, J=2.2Hz, 1.2Hz, 1H); 7.11 (m, 4H); 7.06 (dd, J=8.6Hz, 1.2Hz, 1H); 6.70 (d, J=8.8Hz, 1H); 4.72 (m, 1H); 3.77 (m, 1H); 2.30 (s, 3H); 1.81 (m, 6H).

Synthesis of 5-(4-(*p*-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)thiophene-2-carbaldehyde (**6**): in a schlenk flask **5** (200mg. 0.61mmol), thiophen-2-ylboronic acid (135mg, 0.85mmol), $Pd^{II}(dppf)Cl_2$ (20.1mg, 0.027mmol) and 20ml of dimethoxyethane was added and the mixture was degassed. Then the solution was stirred at room temperature for 30 minutes. After this time 3mL of K_2CO_3 2M was added and the mixture was degassed again. Then the mixture was heated up to 90ªC for 2 hours. After cooling at room temperature water was added and the solution was extracted with Et_2O and washed with Brine. Then the crude is purified by column chromatographic using Hexane/Ethyl Acetate (8:2) as a solvent. (80mg, 36% of Yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 9.88 (s, 1H); 7.65 (d, J=4.0Hz, 1H); 7.39 (s, 1H); 7.35 (dd, J=8.2Hz, 2.0 Hz, 1H); 7.21 (d, J=4.0Hz, 1H); 7.16 (m, 4H); 6.81 (d, J=8.2Hz, 1H); 4.83 (m, 1H); 3.83 (m, 1H); 2.33 (s, 3H); 2.06 (m, 1H); 1.88 (m, 2H); 1.76 (m, 1H); 1.66 (m, 1H); 1.53 (m, 1H).

Synthesis of LS-1: In a schlenk flask **6** (0.08g, 0.22mmol), cyanoacetic acid (0.057g, 0.66mmol), piperidine (0.095g, 1.11mmol) and 15mL of dry chloroform was added and was refluxed overnight. Then the solution was acidified with

20% aqueous HCl and extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude was purified by column chromatography ($CHCl_3$/Methanol 9:1) on silica gel and the product was obtained as a violet solid (0.085g, 91% yield). ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 8.34 (s, 1H); 7.91 (d, J=4.0Hz, 1H); 7.54 (m, 2H); 7.45 (dd, 8.2Hz, 2.0Hz, 1H); 7.21 (m, 4H); 6.82 (d, J=8.2Hz, 1H); 4.92 (m, 1H); 3.85 (m, 1H); 2.27 (s, 3H); 2.05 (m, 1H); 1.77 (m, 3H); 1.62 (m, 1H); 1.37 (m, 1H).

Synthesis of VCL01



Scheme 3.3: Synthetic route of **VCL01**. (*Reaction conditions:* (i) KI, BrC_6H_{13}, KOH, RT overnight; (ii) $POCl_3$, DMF, 1,2-dichloroethane, 4h 0ºC; (iii) NBS, THF, 5h 0ºC; (iv) n-BuLi, THF, $B(OCH_3)_3$, -78ºC; (v) $Pd(PPh_3)_4$, 2 M K_2CO_3 aqueous solution, THF, 6 h, 80^0C; (vi) cyanoacetic acid, piperidine, chloroform, 12 h, reflux.)

9, **10** and **11** were synthesized according to the literature[25]

Synthesis of 4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (9):

A solution of 4H-cyclopenta[2,1-b:3,4-b']dithiophene (**8**) (0.7g, 3.92mmol), 1-bromohexane (1.27g, 7.84mmol), and KI(1.62mg, 0.013mmol) in DMSO (20mL) was cold at 0º. Then, KOH (0.44g, 7.84mmol) was added. The reaction was stirred overnight at room temperature under argon. Then water was added. The crude product was extracted into diethyl ether, and the organic layer was washed with saturated ammonium chloride and water, and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography using petroleum ether as a solvent to yield a colorless oil (0.9g, 66% yield) ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 7.12 (d, J=4.9Hz, 2H); 6.91 (d, J=4.9Hz, 2H); 1.82 (m, 4H); 1.13 (m, 12H); 0.79 (t, J= 6.8Hz, 6H).

Synthesis of 4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (10): A cold solution of **9** (0.90g, 2.6mmol) and DMF (0.22g, 3.12mmol)in 1,2-dichloroethane (20mL) at 0ºC was added phosphorus chloride oxide (0.48g, 3.12mmol) under argon. The reaction was stirred at same temperature for 4 hours and then saturated sodium acetate aqueous solution (10mL) was added. The mixture was stirred at room temperature for 2 hours. The crude was an extracted into dichloromethane, and the organic layer was washed with brine and water, and dried over sodium sulphate. After removing the solvent the residue was purified by column chromatography with petroleum ether and ethyl acetate (8:2) as a solvents to obtain a colourless oil (0.73g, 75% yield) ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 9.80 (s, 1H); 7.54 (s 1H); 7.37 (d, J=4.9Hz, 2H); 6.95 (d, J=4.9Hz, 2H); 1.84 (m, 4H); 1.13 (m, 12H); 0.78 (t, J= 6.8Hz, 6H).

Synthesis of 6-bromo-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehide[25] (11): A cold solution of **10** (0.70g, 1.86mmol) in tetrahydrofuran (20mL) was added N-bromosuccinimide (0.4g, 2.23mmol) at 0ºC under argon. The reaction mixture was warmed to room temperature and stirred for 5 hours and then water was added. The crude product was extracted into dichloromethane, and the organic layer was dried over sodium sulphate. The residue was purified by column chromatography (dichloromethane) to obtain yellow oil. (0.75g, 90% yield) ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 9.81 (s, 1H); 7.53 (s, 1H); 6.99 (s, 1H); 1.84 (m, 4H); 1.13 (m, 12H); 0.78 (t, J= 6.8Hz, 6H).

Synthesys of 4,4-dihexyl-6-(4-(*p*-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-2-carbaldehyde (12): **5** (0.240g, 0.735mmol) was added to a round flask with 30mL of THF and was stirred under nitrogen atmosphere at -78ºC. ^{n}BuLi 2M in hexane (0.33mL, 0.867mmol) was added and the mixture was stirred for 15 minutes at -78ºC. After that, $B(OMe)_3$ (0.12mLm, 1.10mmol) was added and the reaction was stirred overnight at -78ºC. The crude was warmed at room temperature. In another Schlenk, $Pd(PPh_3)_4$ (0.075g, 0.02mmol), **11** (0.3g, 0.66mmol), K_2CO_3 2M (3mL), the crude, and THF (20mL) was added and the reaction was stirred at 70ºC for 4 hours. Then water was added. The crude product was extracted into $CHCl_3$, and the organic layer was dried over $NaSO_4$. The residue was purified by column chromatography (Hexane/Dichloromethane 6:4) to obtain a red solid (0.270g, 60% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 9.78 (s, 1H); 7.56 (s, 1H); 7.35 (s, 1H); 7.30 (dd, J=8.4Hz, 2Hz, 1H); 7.20 (m, 4H); 7.02 (s, 1H); 6.85 (d, J=8.4Hz, 1H); 4.80 (m, 1H); 3.78 (m, 1H); 2.32 (s, 3H); 2.06 (m, 1H); 1.87 (m, 8H); 1.66 (m, 1H); 1.13 (m, 16H); 0.80 (t, J=6.8Hz, 6H). ^{13}CNMR (100MHZ, $CDCl_3$, ppm): δ 182.46; 164.05; 157.13; 151.43; 149.02; 148.54; 142.44; 140.17; 136.00; 132.60; 132.12; 130.07; 125.50; 124.90; 122.33; 120.55; 115.64; 107.77; 69.55; 54.20; 45.50; 38.04; 35.34; 33.90; 31.80; 29.67; 24.75; 24.62; 22.83; 21.03; 14.23. MS-ESI (*m/z*): $[M+Na]^+$ calculated for $C_{40}H_{47}NOS_2Na$: 644.2991; found: 644.2991.

Synthesis of VCL01

In a schlenk flask **12** (0.21g, 0.34mmol), cyanoacetic acid (0.086g, 1.02mmol), piperidine (0.144g, 1.7mmol) and 10mL of dry chloroform was added and was refluxed overnight. Then the solution was acidified with 20% aqueous HCl and extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude was purified by column chromatography ($CHCl_3$/Methanol 9:1) on silica gel and the product was obtained as a violet solid (0.140g, 67% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) d_H: 8.27 (s, 1H); 7.80 (s, 1H); 7.49 (s, 1H); 7.45 (s, 1H); 7.34 (dd, J=8.4Hz, 2Hz, 1H); 7.20 (m, 4H); 6.85 (d, J=8.4Hz, 1H); 4.88 (m, 1H); 3.84 (m, 1H); 2.28 (s, 3H); 2.05 (m, 1H); 1.89 (m, 4H); 1.76 (m, 3H); 1.63 (m, 1H); 1.39 (m, 1H); 1.11 (m, 12H); 0.90 (m, 4H); 0.77 (t, J=6.8Hz, 6H). ^{13}C NMR (100MHz, DMSO-d_6, ppm) δ 157.04; 150.80; 147.70; 139.50; 136.14; 135.96; 135.76; 131.82; 131.26; 130.48; 129.99; 125.27; 125.19; 124.41; 124.30; 121.93; 120.23; 119.94; 116.21; 107.26; 68.53; 53.57; 44.62; 37.11; 37.01; 34.97; 33.10; 31.09; 29.05; 24.15; 24.10; 22.13;

20.54; 13.97. MS-ESI (*m/z*): $[M-H]^-$ calculated for $C_{43}H_{47}N_2O_2S_2$: 687.3084; found: 687.3069.

3.3.2 Device preparation and characterization

As we have said in chapter 2 two different types of TiO_2 films were utilized depending on the measurements being conducted. Highly transparent thin films (8 μm) were utilized for L-TAS measurements. On the other hand, for efficient DSC devices were made using 9 μm thick films consisting of 20 nm TiO_2 nanoparticles (Dyesol© paste) and a scatter layer of 4 μm of 400 nm TiO_2 particles (CCIC, HPW-400).
All films were sensitized in dye solutions at concentrations of 0.125 mM in 1:1 acetonitrile:*tert*-butanol containing 1 mM chenoxydecholic acid were prepared and the film immersed overnight at room temperature. The sensitized electrodes were washed with 1:1 acetonitrile:*tert*-butanol and dried under air. The electrolyte used consisted of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M *tert*-butylpyridine in acetonitrile.

3.4 RESULTS AND DISCUSSION

The absorption and emission spectra in solution and the photophysical and electrochemical properties of **LS-1** and **VCL01** are collected in Table 3.1.

Table 3.1. Absorption, emission and electrochemical properties of **LS-1** and **VCL01**.

Dye	λ_{abs} (nm)[a]	λ_{em} (nm)[a]	E_{ox} (V v's Fc/Fc+)	E_{0-0} (eV)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
LS-1	527 (20200)	704	0.31	1.99	-5.19	-3.20
VCL01	567 (34500)	765	0.14	1.82	-5.02	-3.20

[a]Measured in dichloromethane. In parenthesis molar extinction efficient at λ_{abs} (in M^{-1} cm^{-1}). [c]E_{0-0} was determined from the intersection of absorption and emission spectra in dilute solutions. [d]E_{HOMO} was calculated using E_{HOMO}(vs vacuum) = -4.88-E_{ox}(vs Fc/Fc+). [e]E_{LUMO} was calculated using $E_{LUMO} = E_{HOMO} + E_{0-0}$.

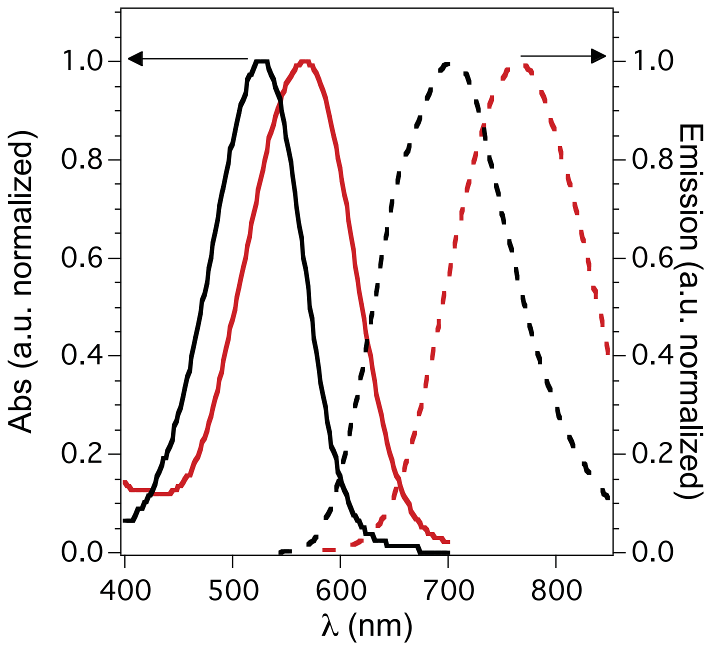


Figure 3.1: Absorption and emission spectra of **LS-1** and **VCL01** in dicholoromethane.

LS-1 and **VCL01** both show absorption bands in the UV-Vis region of the solar spectrum which are assigned to π-π* transitions. The increase in molar extinction coefficient and 40 nm red-shift in absorption maximum of **VCL01** with respect to **LS-1** is attributed to the increase in conjugation in this sensitizer afforded by the insertion of the cyclopentadithiophene unit. We note that the absorption maximum of **LS-1** at 527nm is different to that as reported as 483nm by Li *et al.*[23] This can be explained due to the dependence of the absorption spectra of D-π-A organic dyes on their degree of protonation in different acid/base media, as we have observed previously.[7] This can be demonstrated by adding triethylamine (TEA) and trifluroacetic acid (TFA) to a solution of **LS-1** which shows a blue shift and red shift respectively (Figure 3.2). A blue shifted spectrum corresponds to the deprontonated state and a red-shifted spectrum to the protonated state, therefore, **LS-1** as reported in the study by Li *et al.*[23] would appear to be in the deprotonated state. In any case, both studies show similar absorption maxima for **LS-1** immobilized onto TiO_2 film (≈ 450 nm). It is noted that the absorption spectrum of **VCL01** also changes when in its protonated or deprotonated state.

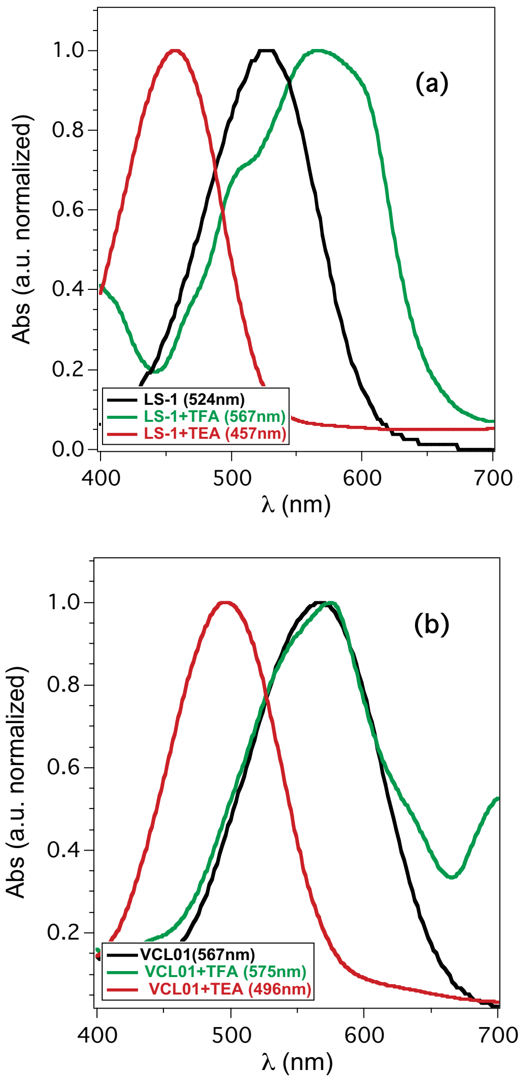


Figure 3.2: Absorption spectra of dichloromethane solutions of **LS-1 (a)** and **VCL01 (b)** in the presence of organic base (TEA, triethylamine) and organic acid (TFA, trifluoroacetic acid).

Cyclic voltammetry studies (Figure 3.3) indicate there is a significant difference of 0.13 V in ground state oxidation potential (E_{ox}) between **LS-1** and **VCL01** and again the effect of the cyclopentadithiophene unit is apparent reducing the E_{ox} of **VCL01**. The E_{HOMO} and E_{LUMO} in eV were calculated using the data in Table 1. E_{HOMO} and E_{LUMO} values indicate efficient dye regeneration by the iodide/tri-iodide redox electrolyte (E_{redox} = 4.75 eV) and also efficient electron injection into the TiO_2 conduction band (E_{TiO2} = 4.0 eV) is energetically possible for these sensitizers.

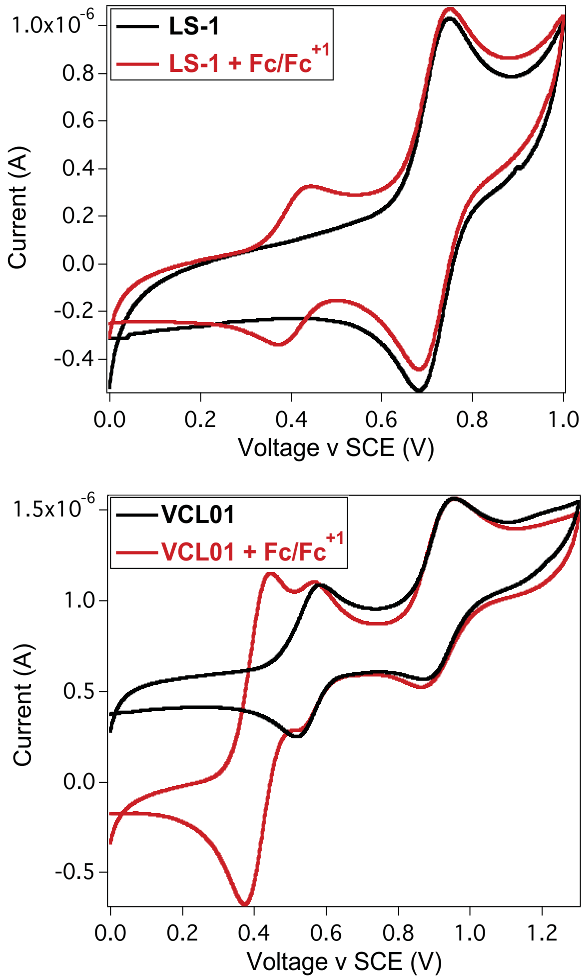


Figure 3.3: Cyclic voltammetry of **LS-1** (top) and **VCL01** (bottom) recorded in 0.1M

tetrabutylammonium hexafluorphosphate in 1:1 acetonitrile:*tert*-butanol at a scan rate of 10 mV s^{-1}. The working electrode consisted of a platinum wire and the counter electrode a platinum mesh. The reference electrode was the silver calomel electrode (saturated KCl). All solutions were degassed with argon for 5 mins prior to measurement. The red and black scans were recorded in the presence and absence of Ferrocene/Ferrocene+.

LS-1 and **VCL01** were used to fabricate DSC solar cells and the device properties are listed in Table 3.3. Devices were measured after periods of 0 and 120 mins of continuous illumination. The best efficiencies were found using 1mM chenoxydecholic acid as co-adsorbent. With higher concentrations of chenoxydecholic acid (10 mM), though **LS-1** devices increased somewhat in efficiency (also observed by Li *et. al*)[23], that of **VCL01** dropped sharply (see Table 3.2). For this reason a compromise was sought with a lower concentration of 1 mM of chenoxydecholic acid used (Table 3.3)

Table 3.2. Device optimization of **LS-1** and **VCL01** DSCs.

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	*η* (%)*
LS-1 (No chenoxydecholic acid)	0.66	8.44	67.41	3.79
LS-1 (10 mM chenoxydecholic acid)	0.73	14.06	66.20	6.83
VCL01 (No chenoxydecholic acid)	0.67	12.75	67.44	5.81
VCL01 (10 mM chenoxydecholic acid)	0.60	5.25	71.22	2.27

Table 3.3. Device properties of **LS-1** and **VCL01** DSCs.

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	*η* (%)*
LS-1 (0 mins)[a]	0.689	12.90	70	6.23 (7.84)
LS-1 (120 mins)[b]	0.704	13.81	71	6.95 (8.48)
VCL01 (0 mins)[a]	0.649	10.99	68	4.81 (6.52)
VCL01 (120 mins)[b]	0.699	14.69	70	7.21 (8.98)

[a]Recorded after 0 mins illumination. [b]Recorded after 120 mins continuous illumination. *Efficiencies recorded with mask. In parenthesis efficiencies without mask.

Following 0 mins illumination **LS-1** shows a superior power conversion efficiency of 6.23% compared to only 4.81% for **VCL01**. However, following a period of 120 mins continuous illumination the efficiency of the **VCL01** device manifests a dramatic increase in efficiency to 7.21% compared to **LS-1** which shows a smaller increase in efficiency to 6.95%. This phenomenon was always observed with, however, the time necessary for the efficiency maximum to be reached varying somewhat. This was probably due to small differences in the quantity of dye being adsorbed onto the TiO_2 films after sensitization and/or small differences in TiO_2 film thickness. The increase in efficiency is caused due to an increase in J_{sc} upon illumination. The nature of the increase in efficiency is discussed later. It should be noted that the efficiency of the **LS-1** device is higher than that reported by Li *et al.*,[23] however, the electrolyte used is different in both studies.

The I-V curves recorded under AM 1.5G radiation and IPCE spectra recorded for **LS-1** and **VCL01** devices are shown in Figure 3.4. IPCE spectra show broad absorption in the UV-vis and a notable spectral red-shift for **VCL01**. Following light soaking the increase in device IPCE is consistent with the J_{sc} data in Table 2. Moreover, integration of the IPCE data agrees with the J_{sc} data in Table 2 within an error of 5 %.

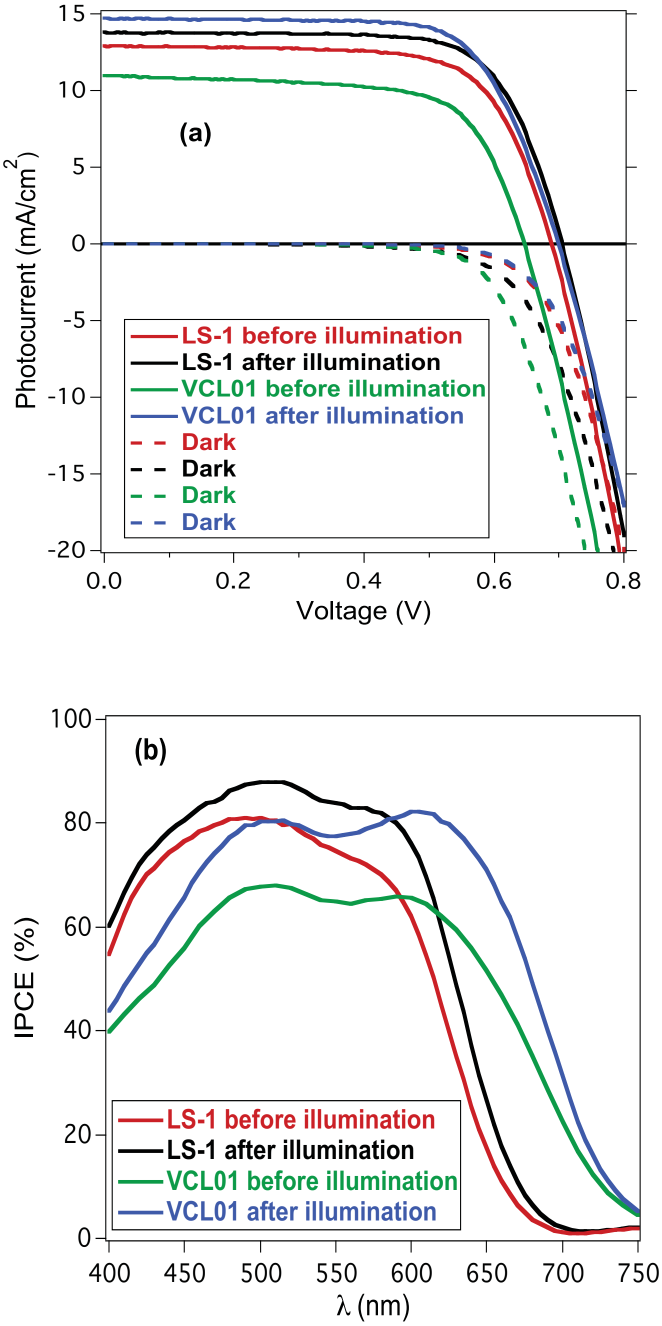
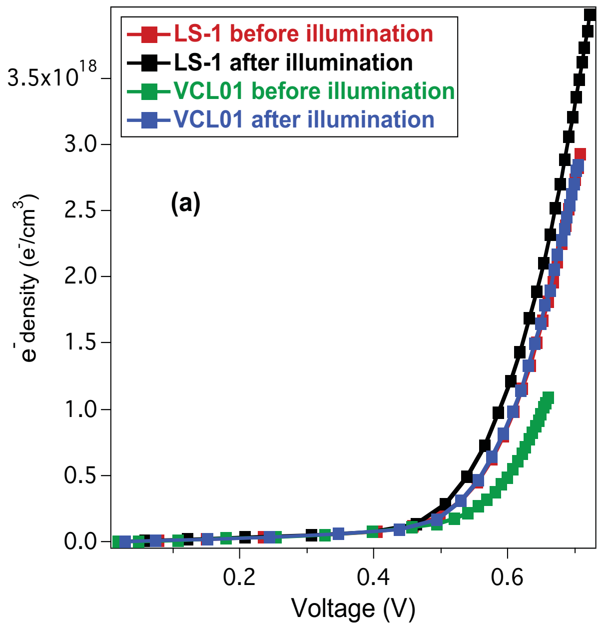


Figure 3.4: (a) I-V curves and (b) IPCE spectra for **LS-1** and **VCL01** DSC devices recorded under AM 1.5G radiation. Also shown are I-V dark curves.

Electron density and electron lifetime in these devices were probed using charge extraction and transient photovoltage measurements respectively (Figure 3.5). With 0 mins illumination the **LS-1** device shows a negligibly higher charge density than the **VCL01** device but almost an order of magnitude of difference longer electron lifetime under the same electron density. This explains the 40 mV higher V_{oc} for the **LS-1** device. Upon illumination for 120 mins, charge extraction data shows an increase in charge density for both devices suggesting a downward shift in the conduction band. Moreover charge density is now similar in both devices. Transient photovoltage data show that the effect of 120 mins light soaking on the devices is an increase in electron lifetime, with the increase notably more pronounced for the **VCL01** device (over 1 order of magnitude). The difference in lifetime between **LS-1** and **VCL01** is, however, narrowed significantly upon light soaking. This explains the very similar V_{oc} for the devices following illumination.

Transient absorption spectroscopy was then used to probe charge recombination and regeneration by the I_3^-/I^- redox couple in transparent DSC devices (Figure 3.6). The data recorded in the absence of red/ox active electrolyte (black) show long-lived decays assigned to the dye cation formed following photo-excitation and charge separation. These kinetics are similar to those which we have observed for D-π-A organic sensitizers previously.[7] In the presence of redox couple the kinetics become bi-phasic with the loss of the cation signal due to regeneration by I^- and the appearance of a long-lived signal assigned to TiO_2 injected electrons and/or $I_2^{\bullet-}$ (red decay). The $t_{50\%}$ (time taken for 50% of signal to disappear) for the regeneration reaction is estimated as 5 and 200 μs for **LS-1** and **VCL01** respectively. This difference can be explained by the difference in ground state oxidation (E_{ox}) potential for these dyes, with the more positive potential of **LS-1**



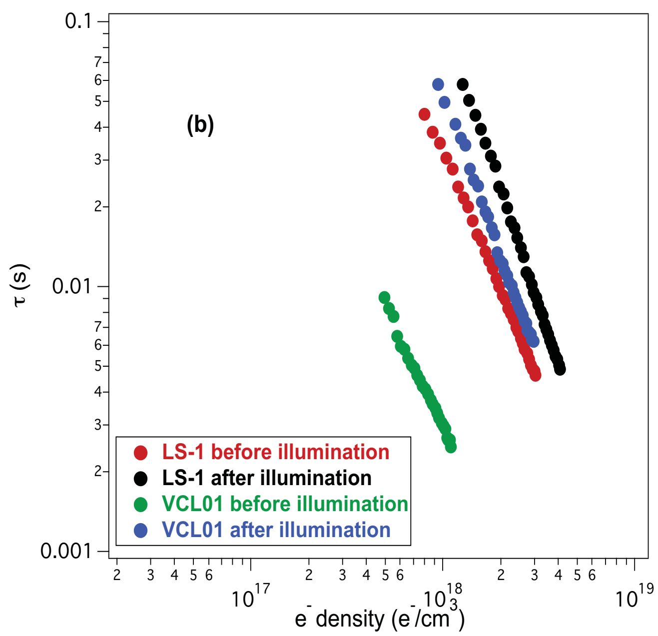


Figure 3.5: (a) Electron density as a function of cell voltage and (b) device electron lifetime τ as a function of charge density for **LS-1** and **VCL01** devices.

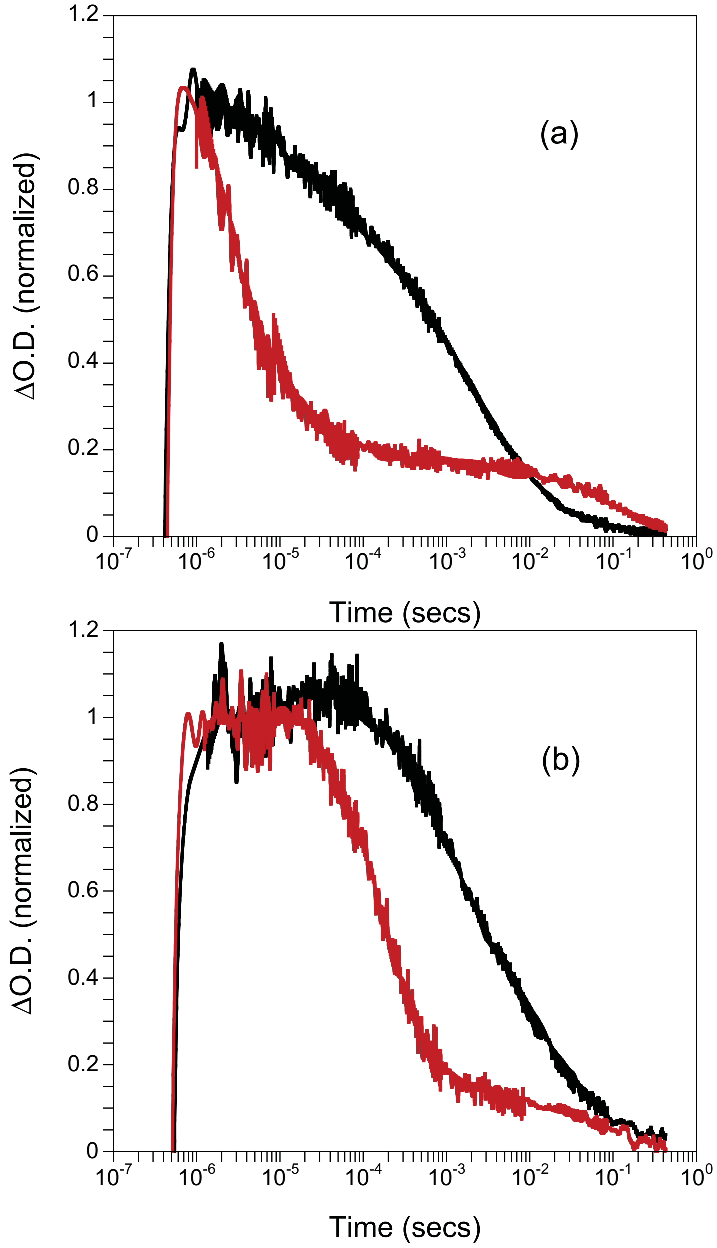


Figure 3.6: Transient absorption kinetics of (a) **LS-1** and (b) **VCL01** recorded for 1cm^2 area devices comprising 8 μm TiO_2 films in the presence of a blank electrolyte (black) and an iodide/tri-iodide red/ox electrolyte (red). Kinetics were recorded at 800nm following excitation at 490 nm.

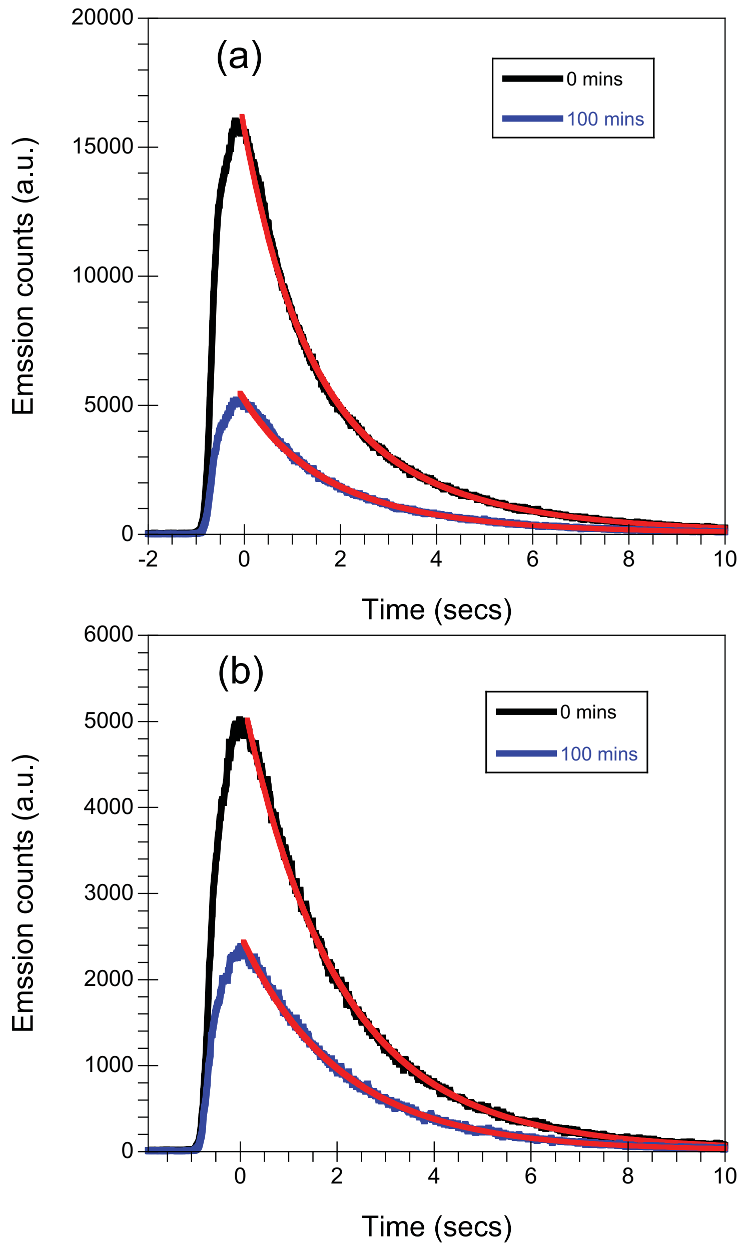


Figure 3.7 Emission lifetime decays for (a) **LS-1** and (b) **VCL01** devices after 0 and 100 mins AM 1.5G illumination light soaking measured at a 300 second acquisition time. Excitation wavelength was 470nm and emission wavelengths were 565 nm (**LS-1**) and 600 nm (**VCL01**).

Returning to the effect of light soaking on device efficiency, generally, for most DSCs regardless of the sensitizer employed, from our experience[26,27] and that of other groups[28-30] an increase in efficiency is observed. In an exhaustive study by Listorti *et al.*[31] involving DSC devices prepared with different materials (dyes, pastes, electrolytes etc.) in different laboratories the effect of light soaking on device parameters was investigated. In all cases an increase in both efficiency and J_{sc} was observed and explained as a downward shift in the TiO_2 conduction band resulting in lower V_{oc}. Luminescence lifetime studies indicated that this shift resulted in both faster electron injection and improved injection efficiency leading to higher J_{sc} and cell efficiency despite the lower V_{oc}.

Table 3.4. Emission lifetimes extracted from TC-SPC data of **LS-1** and **VCL01** DSC devices.

Dye	*Lifetime (ns)**
LS-1 (0 mins)	1.20 (42%); 2.96 (58%)
LS-1 (100 mins)	1.39 (41%); 2.99 (59%)
VCL01 (0 mins)	1.83 (75%); 3.37 (25%)
VCL01 (100 mins)	2.02 (92%); 4.79 (8%)

*Emission decays were fitted with 2 exponential parameters. The percentage in parenthesis is the contribution of each parameter.

LS-1 and **VCL01** devices also show an increase in efficiency and J_{sc} following light soaking coupled with a small downward shift in the TiO_2 conduction band and increase in device electron lifetime. Emission lifetime studies of **LS-1** and **VCL01** devices measured using Time-Correlated Single Photon Counting (Figure 3.7) before and after light soaking show negligible differences in lifetime (Table 3.4), however, a notable quenching of emission intensity is observed after light soaking. This indicates that light soaking improves TiO_2/dye interaction resulting in improved quenching of dye excited states by TiO_2 electron injection. This also helps to explain the increase in device electron lifetime following light soaking, as the improvement in TiO_2/dye interaction would improve the blocking of recombination of TiO_2 electrons with the electrolyte, with the much larger increase in electron lifetime for the **VCL01** device compared to the **LS-1** device due to the more bulky cyclopentadithiophene units. It is worth noting that no such affect was observed by leaving the cells in the dark indicating the positive effect of light soaking over device efficiency in these devices.

We therefore conclude that the improvement in device efficiency upon light soaking is less due to a change in the TiO_2 energetics and more to do with improved TiO_2/dye interaction resulting in a higher injection yield and larger J_{sc} on the one hand and improved blocking effect and larger V_{oc} on the other.

3.5 CONCLUSIONS

The synthesis and characterization of a novel indoline D-π-A sensitizer, **VCL01**, with a cyclopentadithiophene unit in the π-bridge was described and its performance determined in DSC devices. Though initially it showed an efficiency of 4.81%, this rose to 7.21% upon 120 mins light soaking under AM 1.5G illumination, representing an increase of 50%. This increase is mainly due to an increase in J_{sc} which is reflected in the improved IPCE spectra of devices following light soaking. Charge extraction data indicate a downward shift in the TiO_2 conduction band upon light soaking and transient photovoltage data show that device electron lifetime increases by over one order of magnitude. Time-correlated Single Photon Counting data explain partly the light soaking effect by an improvement in TiO_2/dye interaction leading to enhanced electron injection.

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Chapter 4

High Efficient Push-Pull Porphyrin dyes for Dye Sensitized Solar cells. The importance of molecular design

Table of contents

4.1 ABSTRACT

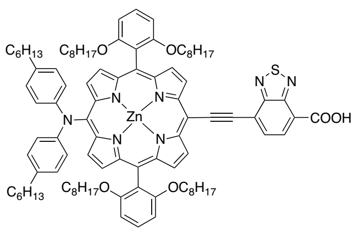
A new series of porphyrins have been synthesized in order to study their applicability in DSSC. The strategy followed to synthesize these porphyrins was the synthesis of a donor and acceptor zinc porphyrin introducing 2,1,3-bezothiadazole (BDT) group as a π-conjugated linker between the anchoring group and the porphyrin (**LCVC01**) and also the introduction of a thiophene (**LCVC02**) and a furan (**LCVC03**) between the BDT moiety and the anchoring group. These series of porphyrins were investigated for their application in DSSC devices. Devices of all of these dyes were characterized achieving a record cell of 10.4% for **LCVC02** but only a 3.84% and 2.55% were achieved for **LCVC01** and **LCVC03** respectively. The introduction of a thiophene shows us the importance to introduce a chemical group, such as thiophene, between of the BDT and the anchoring group. However the election of this group has to be accurate because, as we can see in this study, the change of one atom increases the recombination rate and decreases the device performance due to the interaction of oxygen atoms with iodine species.

4.2 INTRODUCTION

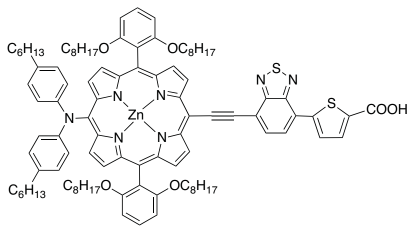
Dye Sensitized Solar Cells (DSSC) have attracted great much attention in recent years due to their potential low cost and the solar-energy conversion efficiency when compared to conventional photovoltaic devices[1,2]. A great number of sensitizers have been synthesized looking for the highest conversion efficiency as, for example, Ruthenium complexes that show high efficiencies due to the broad absorbance range from the UV-Visible and some of the complexes even expand their absorption to the near infrared (NIR)[3-7]. However, the moderate molar extinction coefficients of the Ruthenium complexes, their synthesis and the hard purification process have lead to new efforts towards the synthesis of novel Ruthenium-free dyes. Most of these new organic dyes have, as general molecular structure, the Donor-π-Acceptor (D-π-A) combination[8]. This configuration allows easy tunability of the absorption properties, as well as, higher molar extinction coefficient.

Since the seminal paper by Sun and collaborations, many organic dyes have been reported with high efficiencies not only in iodine electrolyte[9,10], but even better efficiencies when using cobalt electrolyte[11-15]. Moreover, recent studies on porphyrins have shown very promising results due to the high molar extinction coefficients of their Soret and Q band[16]. A landmark paper shows that the D-π-A structure consisting on the core of the porphyrin as π-moiety, leads to high efficiencies employing iodine as electrolyte[17-20]. Furthermore, the best efficiencies have been achieved using a cobalt electrolyte reaching an efficiency of 11.9% and 12.3%, for iodine/iodide and cobalt electrolytes respectively. However, these efficiencies can only be achieved with the use of co-sensitized semiconductor mesoporous TiO_2 films with the Y123 dye[21]. Recently, Aswani Yella et al. reported an efficiency close to13%, which is the highest reported efficiency ever for a DSSC[22,23]

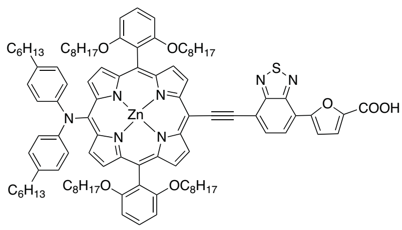
Based on the above mentioned results we synthesized a series of new porphyrins, namely **LCVC01** (GY21), **LCVC02** and **LCVC03**. We aim to study the effect of introducing a thiophene (LCVC02) and a furan group (LCVC03) between the benzothiadazole (BDT) and the anchoring group. The structures of these porphyrins are shown in Scheme 4.1.



LCVC01



LCVC02

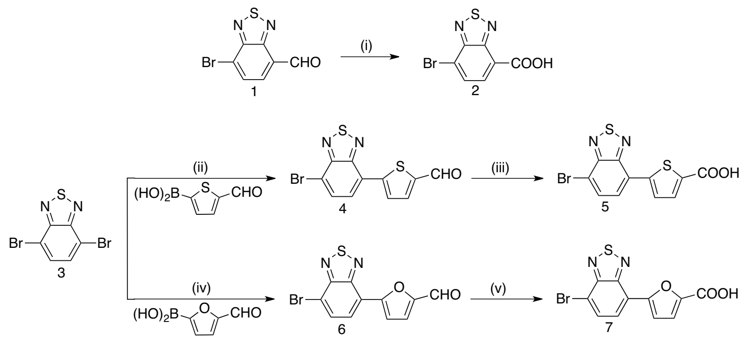


LCVC03

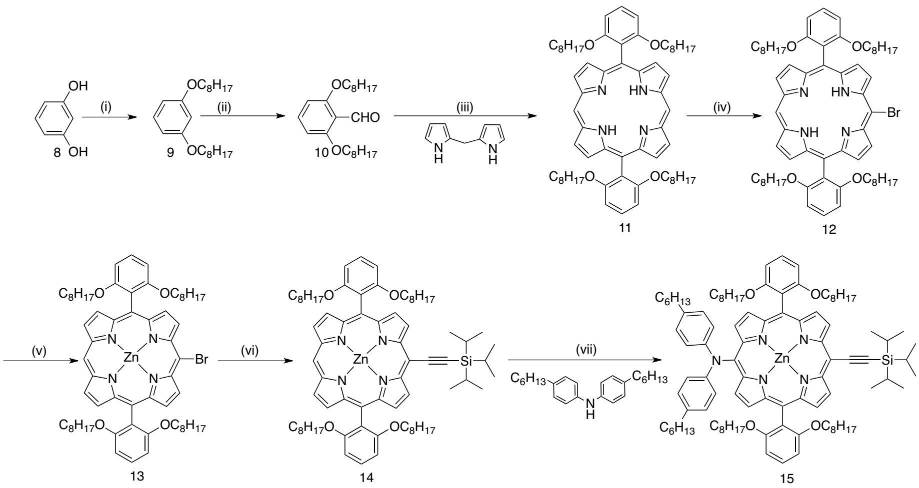
Scheme 4.1: Molecular structures of **LCVC01**, **LCVC02** and **LCVC03 dyes**.

4.3 EXPERIMETNAL SECTION

4.3.1 Synthesis and characterization

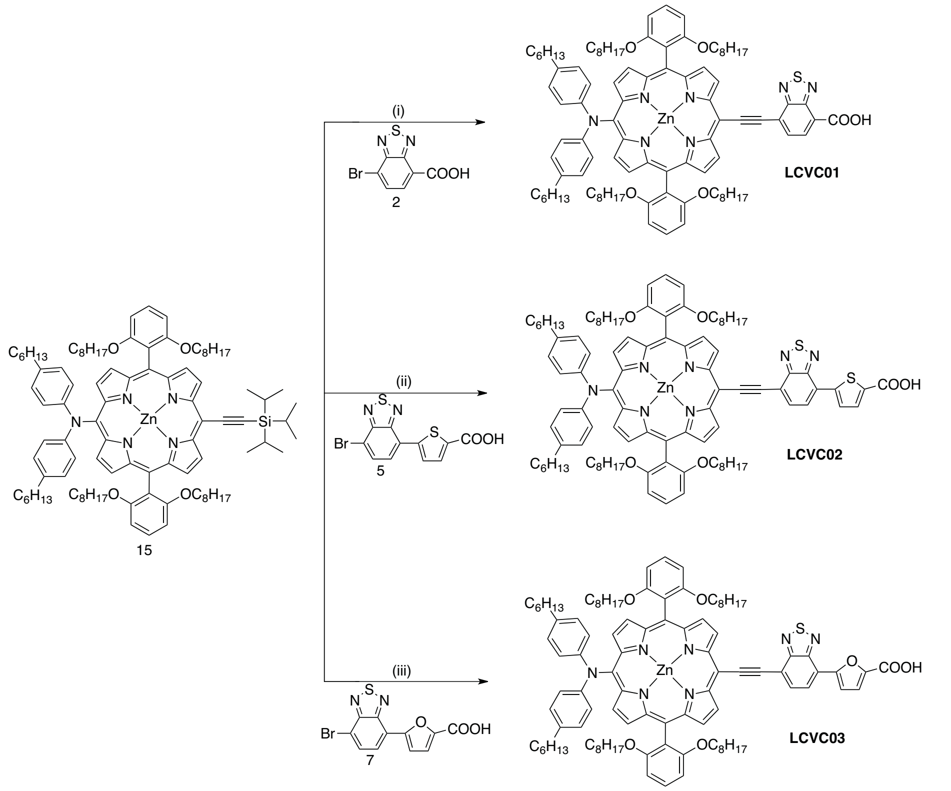


Scheme 4.2: Synthetic route for the **acceptor moieties**. (*Reaction conditions:* (i) $NaClO_2$, Sulfamic acid aqueous, Acetone, 4 h, RT; (ii) $Pd^{II}(dppf)Cl_2$, 2M K_2CO_3 aqueous solution,THF, 2 h, 76ºC; (iii) $NaClO_2$, Sulfamic acid aqueous, Acetone, 4 h, RT; (iv) $Pd^{II}(dppf)Cl_2$, 2M K_2CO_3 aqueous solution,THF, 2 h, 76ºC; (v) $NaClO_2$, Sulfamic acid aqueous, Acetone, 4 h, RT; $Pd^{II}(dppf)Cl_2$, 2M K_2CO_3 aqueous solution, dimethoxyethane, 2 h, 90ºC;



Scheme 4.3: Synthetic route for the **common part of porphyrins**. (*Reaction conditions:* (i) 1-Bromooctane, K_2CO_3, Acetone, reflux, 4 days; (ii) TMEDA, THF, 0ºC, ^nBuLi, 3 h, 0ºC, DMF, 2 h, RT; (iii) TFA, DCM, 4 h, 23ºC, DDQ, 1h; (iv) NBS, DCM, 6 h, 0ºC; (v) $Zn(OAc)_2{\cdot}2H_2O$, DCM/Methanol, 3 h, 23ºC; (vi) triisopropylsilylacetylene, $Pd(PPh_3)_2Cl_2$,

CuI, THF, Net$_3$, 4 h, reflux; (vii) Diphenylamine, iodobenzene diacetate, tetrachloroaurate dehydrate, DCM, 30 minutes, RT, Zn(OAc)$_2$·2H$_2$O, DCM/Methanol, 3 h, 23ºC;



Scheme 4.4: Synthetic route for the **LCVC01**, **LCVC02** and **LCVC03 dyes**. (*Reaction conditions:* (i) TBAF 1M in THF, THF, 30 minutes, 23ºC, **2**, NEt$_3$, Pd$_2$(dba)$_3$, ASPh$_3$, THF, 4 h, reflux; (ii) TBAF 1M in THF, THF, 30 minutes, 23ºC, **5**, NEt$_3$, Pd$_2$(dba)$_3$, ASPh$_3$, THF, 4 h, reflux; (iii) TBAF 1M in THF, THF, 30 minutes, 23ºC, **7**, NEt$_3$, Pd$_2$(dba)$_3$, ASPh$_3$, THF, 4 h, reflux;

Synthesis of 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carboxylic acid 2: A solution at 0ºC of 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.1g; 0.41mmol) in Acetone (70mL), NaClO$_2$ (0.109g, 1,21mmol), was added slowly. Then, a solution of sulfamic acid (0.117g; 1.21mmol) in Milli-Q-grade deionized water (8mL) was added and the solution was then stirred at room temperature for 4h. Then, the reaction was quenched with HCl (0.1M, 250mL) and the mixture was extracted with CHCl$_3$.The combined extracts were washed with water and dried over anhydrous MgSO$_4$**.** The solvent was removed under reduced pressure to give as the desired product (white solid). (0.093g, 88% Yield). ^1H NMR ($CDCl_3$, 400 MHZ) δ_H: 8.45 (d, J=7.7Hz, 1H); 8.05 (d, J=7.7Hz, 1H).

Synthesis of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (4): In a Schlenk flask **3** (0.5 g. 1.70mmol), (5-formylthiophen-2-yl) boronic acid (0.268 g, 1.70mmol), $Pd^{II}(dppf)Cl_2$ (0.056 g, 0.0765mmol) and 50ml of THF was added and the mixture was degassed. Then the solution was stirred at room temperature for 30 minutes. After this time 7 mL of K_2CO_3 2M was added and the mixture was degassed again. Then, the mixture was heated up to 76°C for 2 hours. After cooling,at room temperature, we added water and the solution was extracted with Et_2O and washed with brine. Then the crude is purified by column chromatography using Hexane/Ethyl Acetate (8:2) as a solvent to give us the desired product (yellow solid) (150mg, 27% Yield). ^1H NMR ($THF_{d\text{-}8}$, 400 MHZ) δ_H: 9.95 (s, 1H); 8.25 (d, J=4.0Hz, 1H); 8.06 (d, J=7.7Hz, 1H); 8.00 (d, J=7.7Hz, 1H); 7.93 (d, J=4.0Hz, 1H). ^{13}C NMR (100MHz, $THF_{d\text{-}8}$, ppm) δ 183.18; 162.87; 160.35; 153.92; 145.65; 136.99; 134.36; 132.99; 129.00; 128.05; 115.27 MS-ESI (*m/z*): [M-H] calculated for $C_{11}H_4N_2BrN_2OS_2$: 322.8954; found: 322.8958.

Synthesis of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)thiophene-2-carboxylic acid (5): $NaClO_2$ (0.124g, 1,38mmol), was added slowly to at 0ºc solution of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde, **4** (150mg; 0.46mmol) in acetone (100mL). Then, a solution of sulfamic acid (0.134g; 1.38mmol) in Milli-Q-grade deionized water (10mL) was added to proceed at room temperature for 4h. Then the reaction was quenched with HCl (0.1M, 250mL) and the mixture was extracted with $CHCl_3$. The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give as the desired product (white solid). (0.131g, 84% Yield). ^1H NMR ($CDCl_3$, 400 MHZ) δ_H: 8.12 (m, 3H); 7.82 (d, J=4.0Hz, 1H). ^{13}C NMR (100MHz, DMSO-d6, ppm) δ 162.85; 152.94; 150.82; 143.52; 135.81; 133.44; 132.49; 127.95; 127.18; 125.07; 113.22.

Synthesis of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde (6): In a Schlenk flask **3** (0.5 g. 1.70 mmol), (5-formylfuran-2-yl) boronic acid (0.237 g, 1.70mmol), $Pd^{II}(dppf)Cl_2$ (0.056 g, 0.0765mmol) and 50ml of THF was added and the mixture was degassed. Then, the solution was stirred at room temperature for 30 minutes. Thereafter, 7mL of K_2CO_3 2M were added and the mixture was degassed again. Then the mixture was heated up to 76^{o}C for 2 hours. After cooling at room temperature water was added and the solution was extracted with Et_2O and washed with brine. Then the crude was purified by column chromatography using Hexane/DCM (8:2) as a solvent to give us the desired product (yellow solid) (0.160g, 29% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 9.72(s, 1H); 8.14 (d, J=7.7Hz, 1H); 7.94 (d, J=7.7Hz, 1H); 7.87 (d, J=3.6Hz, 1H); 7.41 (d, J=3.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$, ppm) δ 177.71; 154.39; 154.017; 152.31; 150.92; 132.45; 126.50; 123.88; 121.50; 115.65; 114.89 MS-ESI (*m/z*): $[M+Na]^+$ calculated for $C_{11}H_5N_2BrN_2NaO_2S$: 330.9147; found: 330.9137.

Synthesis of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)furan-2-carboxylic acid (7): A solution at 0ºc of 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde **6** (0.160 g; 0.51mmol) in acetone (110mL), $NaClO_2$ (0.140 g, 1,55mmol), was added slowly. Then, a solution of sulfamic acid (0.151 g; 1.55mmol) in Milli-Q-grade deionized water (10mL) was added and the solution was then stirred at room temperature for 4h. Then, the reaction was quenched with HCl (0.1M, 250mL) and the mixture was extracted with $CHCl_3$.The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give as the desired product (yellow solid). (0.133 g, 80% Yield). ^{1}H NMR (DMSO-d6 400 MHZ) δ_H: 8.12 (d, J=7.7Hz, 1H); 7.99 (d, J=7.7Hz, 1H); 7.69 (d, J=3.6Hz, 1H); 7.42 (d, J=3.6Hz, 1H); ^{13}C NMR (100MHz, DMSO-d6, ppm) δ 159.13; 153.00; 151.44; 149.83; 144.88; 132.54; 125.28; 120.91; 119.82; 113.90; 113.45.

Synthesis of 1,3-Dioctoxybenzene (9): A mixture of resorcinol **8** (11g, 0.1mol), 1-bromooctane (69.6mL, 0.4mol) and K_2CO_3 (69g, 0.5mol) was refluxed for 4 days in dry acetone (500mL). The solvent was removed under reduced pressure and the mixture is extracted with EtOAc (3x100mL). The organic layer was washed with water and dried over anhydrous $MGSO_4$. After removal of solvent under reduced pressure, the product was purified by column chromatography using hexane as a solvent to give the desirable product. (18g, 54% yield). ^1H NMR ($CDCl_3$, 400 MHZ) δ_H: 7.13 (t, J= 8.2Hz, 1H); 6.45 (m, 3H); 3.91 (t, J=6.6 Hz, 4H); 1.75 (m, 4H); 1.43 (m, 4H); 1.33-1.23 (m, 16H); 0.88 (t, J=6.7HZ, 6H).

Synthesis of 2,6-Dioctoxybenzenaldehide (10): A three-neck flask was equipped with an addition funnel and charged with 1,3-Dioctoxybenzene **9** (5g, 0.15mol) and tetramethylethylenediamine (TMEDA) (0.57mL) in 42 mL of THF. The solution was degassed and cooled to 0ºC. Then n-butyllithium (11.2mL, 0.03moL) was added dropwise, (during 20min) and allowed to stir for 3 hours. After warming to room temperature DMF (2.19mL, 0.03mol) was added dropwise and the solution was stirred for 2 hours. The reaction was quenched with water, and the mixture was extracted with ether (3x40mL), dried over $MGSO_4$, and the solvent was removed under vacuum. The product was recrystallized from hexanes to yield a white solid. (3.5g, 65% Yield). ^1H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.11 (s, 2H); 9.23 (d, J= 4.6Hz, 4H); 8.50 (d, J=4.6Hz, 4H); 7.69 (t, J= 8.2Hz, 2H); 7.00 (d, J=8.2Hz, 4H); 3.82 (t, J=6.4 Hz, 8H); 0.92-0.78 (m, 16H); 0.67-0.60 (m, 8H); 0.56-0.40 (m, 36H); -3.03(s, 2H).

Synthesis of 5,15-Bis(2,6-dioctoxyohenyl)porphyrin (11): Dipyrromethane (1.51g, 10.35mmol) and 2,6-Dioctoxybenzenaldehide **10** (3.75g, 10.35mmol) were solved in DCM (1.35L) and degassed. Then, Trifluoroacetic acid (0.69mL, 9.32mmol) was added and the mixture was stirred at 23ºC for 4h under Nitrogen conditions. After that, DDQ (3.53g, 15.25mmol) was added and the mixture was stirred for an additional 1 h. Then, the mixture was basified with Et_3N (1.75mL) and filtered through silica. The solvent was removed under vacuum and the residue was purified by column chromatography using a mixture of Hexane/DCM (2/1) as eluent to give us the desired product (purple powder), (1.6g, 31.50% Yield). ^1H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.11 (s, 2H); 9.23 (d, J=4.5Hz, 4H); 8.95 (d, J=4.5Hz, 4H); 7.69 (t, J= 8.5Hz, 2H); 7.00 (d, J=8.5Hz, 4H); 3.81 (t, J=6.5 Hz, 8H); 0.92-0.87 (m, 8H); 0.85-078 (m, 8H); 0.64-0.59 (m, 8H); 0.55-0.48(m, 28H); 0.45-0.39 (m, 8H); -3.03(s, 2H).

Synthesis of 5-Bromo-10,20-bis(2,6-dioctoxyphenyl)porphyrin (12): A stirred solution of 5,15-Bis(2,6-dioctoxyohenyl)porphyrin **11** (1.6g, 1.64mmol) in DCM (600mL) was slowly added a solution of NBS (0.31g, 1.72mmol) in DCM (100mL). The reaction was stirred at 0ºC for 6h. The reaction was quenched with acetone (20mL), the solvent was removed under vacuum. The residue was purified by column using Hexane/DCM (2:1) as eluent to give us the desired product. (Purple powder) (1.4g, 70% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.02 (s, 1H); 9.63 (d, J=4.8Hz, 2H); 9.18 (d, J=4.8Hz, 2H); 8.90 (m, 4H); 7.70(t, J= 8.1Hz, 2H); 7.01 (d, J=8.4Hz, 4H); 3.85 (t, J=6.6 Hz, 8H); 0.98-0.90 (m, 8H); 0.88-0.80 (m, 8H); 0.69-0.61 (m, 8H); 0.58-0.49 (m, 36H); -2.85 (s, 2H).

Synthesis of [5-Bromo-10,20-bis(2,6-di-octoxyphenyl)porphinato]zinc (II) (13): A mixture of 5-Bromo-10,20-bis(2,6-dioctoxyphenyl)porphyrin (1.44g, 1.36mmol) **12** and $Zn(OAc)_2 \cdot 2H_2O$ (3g, 13.66mmol) in a mixture of DCM (280mL) and MeOH (150mL) was stirred at 23ºC for 3 h. The reaction was quenched with water (60mL), and the mixture was extracted with DCM. The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give as the desired product. (1.34g, 88% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.05 (s, 1H); 9.68 (d, J=4.8Hz, 2H); 9.22 (d, J=4.8Hz, 2H); 8.95 (t, J=4.8Hz, 4H); 7.68(t, J= 8.5Hz, 2H); 6.99 (d, J=8.5Hz, 4H); 3.81 (t, J=6.7 Hz, 8H); 0.91-0.84 (m, 8H); 0.78-0.71 (m, 8H); 0.57-0.40 (m, 44H).

Synthesis of [5,15-Bis(2,6-di-octoxyphenyl)-10-(triisopropylsilyl)ethynyl-porphinato] zinc (II) (14). A mixture of zinc complex **13** (1.34g, 1.19mmol), triisopropylsilylacetylene (0.47mL, 2.99mmol), $Pd(PPh_3)_2Cl_2$ (0.16g, 0.23mmol), CuI (0.066g, 0.35mmol), THF (45mL) and Net_3 (7.3mL) was refluxed for 4 h under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography using Hexane/DCM (3:2) to give as the desired product (purple solid) (1.3g 89.6% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.02 (s, 1H); 9.72 (d, J=4.6Hz, 2H); 9.20 (d, J=4.6Hz, 2H); 8.93 (d, J=4.4Hz, 2H); 8.91 (d, J=4.4Hz, 2H); 7.66 (t, J=8.4Hz, 2H); 6.99 (d, J=8.4Hz, 4H); 3.80 (t, J=6.8Hz, 8H); 1.61-1.57 (m, 21H); 1.09-1.00 (m, 8H); 0.91-0.81 (m, 8H); 0.69-0.44 (m, 44H).

Synthesis of [5-Bis(4-hexylphenyl)amino-15-(TRiisopropylsily)ethynyl-10,20-bis(2,6-di-octooxyphenyl)porphirinato] Zinc(II) (15). To a stirred solution of [5,15-Bis(2,6-di-octoxyphenyl)-10-(triisopropylsilyl)ethynyl-porphinato] zinc (II) **14** (370.0 mg, 0.30 mmol) and Diphenylamine (0.310 g, 0.91mmol) in CH_2Cl_2 (150 mL) was added iodobenzene diacetate (99 mg, 0.310 mmol) and sodium tetrachloroaurate dihydrate (184 mg, 0.465 mmol) at 0 ^{0}C and stirred for 30 minutes at room temperature under open air. After completion of the reaction (monitored by TLC) the reaction mixture were quenched with a saturated solution of sodium thiosulfate and separated the organic layer. Extracted the aqueous layer with CH_2Cl_2; combined organic phase was washed with brine, and dried over Na_2SO_4. The solvent was removed in vacuum obtaining the mixture. This mixture was reacted with $Zn(OAc)_2{\cdot}2H_2O$ in a mixture of DCM (280mL) and MeOH (150mL) and was stirred at 23ºC for 3 h. The reaction was quenched with water (60mL), and the mixture was extracted with DCM. The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give as the desired product (0.382g 82% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 9.63 (d, J=4.6Hz, 2H); 9.16 (d, J=4.6Hz, 2H); 8.83 (d, J=4.4Hz, 2H); 8.67 (d, J=4.4Hz, 2H); 7.61 (t, J=8.4Hz, 2H); 7.20 (d, J=8.4Hz, 4H); 6.91 (t, J=8.5Hz, 8H); 3.79 (t, J=6.2Hz, 8H); 2.43 (t, J=7.5Hz, 4H); 1.53-1.49 (m, 4H); 1.44-1.41 (m, 21H); 1.32-1.27 (m, 12H); 0.95 (m, 8H); 0.88-0.76 (m, 22H); 0.61-0.44 (m, 44H).

Synthesis of LCVC01: To a solution of [5-Bis(4-hexylphenyl)amino-15-(Triisopropylsily)ethynyl-10,20-bis(2,6-di-octooxyphenyl)porphirinato] Zinc(II) **15** (240mg, 0.154mmol) in dry THF (20mL) was added TBAF (0.78mL) 1M in THF. The solution was stirred at 23ºC for 30min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried anhydrous $MGSO_4$ and the solvent was removed under reduced pressure. The residue and 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carboxylic acid **2** (190mg, 0.76) were dissolved in a mixture of dry THF (36mL) and NEt_3 (7mL) and the solution was degassed with dinitrogen for 10min. Then, $Pd_2(dba)_3$ (42mg, 0.046mmol) and $ASPh_3$ (100mg, 0.30mmol) were added to the mixture. The solution was refluxed for 4 hours under dinitrogen. The solvent was removed under reduced pressure. After that, the residue was purified by column chromatography (silica gel) using DCM/CH_3OH =20/1 as eluent. Recrystallization from CH_3OH/Ether to give **LCVC01** (180mg, 74%) ^1H NMR (THFd-8, 400 MHZ) δ_H: 9.97 (d, J=4.6Hz, 2H); 9.04 (d, J=4.6Hz, 2H); 8.81 (d, J=4.6Hz, 2H); 8.55 (d, J=4.6Hz, 2H); 8.54 (s, 1H); 8.30 (d, J=7.6Hz, 1H); 7.67 (t, J=8.4Hz, 2H); 7.20 (d, J=8.4Hz, 4H); 7.04 (d, J=8.4Hz, 4H); 6.92 (d, J=8.4Hz, 4H); 3.87 (t, J=6.3Hz, 8H); 2.47 (t, J=7.4Hz, 4H); 1.58-1.51 (m, 4H); 1.36-1.27 (m, 12H); 1.00-0.57 (m, 66H).

Synthesis of LCVC02: To a solution of [5-Bis(4-hexylphenyl)amino-15-(Triisopropylsily)ethynyl-10,20-bis(2,6-di-octooxyphenyl)porphirinato] Zinc(II) **15** (165mg, 0.106mmol) in dry THF (15mL) was added TBAF (0.54mL) 1M in THF. The solution was stirred at 23ºC for 30min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried anhydrous $MGSO_4$ and the solvent was removed under reduced pressure. The residue and 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)thiophene-2-carboxylic acid **5** (180mg, 0.53mmol) were dissolved in a mixture of dry THF (30mL) and NEt_3 (4.8mL) and the solution was degassed with dinitrogen for 10min. Then, $Pd_2(dba)_3$ (29mg, 0.031mmol) and $ASPh_3$ (71mg, 0.212mmol) were added to the mixture. The solution was refluxed for 4 hours under dinitrogen. The solvent was removed under reduced pressure. Then, the residue was purified by column chromatography (silica gel) using DCM/CH_3OH =20/1 as eluent. Recrystallization from CH_3OH/Ether to give **LCVC02** (115mg, 66%) ^1H NMR (THFd-8, 400 MHZ) δ_H: 9.96 (d, J=4.6Hz, 2H); 9.03 (d, J=4.6Hz, 2H); 8.80 (d, J=4.6Hz, 2H); 8.55 (d, J=4.6Hz, 2H); 8.27 (s, 2H); 8.24 (d, J=4.0Hz, 1H); 7.84 (d, J=4.0Hz, 1H); 7.65 (t, J=8.4Hz, 2H); 7.19 (d, J=8.4Hz, 4H); 7.02 (d, J=8.4Hz, 4H); 6.91 (d, J=8.0Hz, 4H); 3.85 (t, J=6.4Hz, 8H); 2.46 (t, J=7.3Hz, 4H); 1.59-1.51 (m, 4H); 1.28 (m, 12H); 0.97-0.55 (m, 66H). ^{13}C NMR (100MHz, THF-d8, ppm) δ 160.78; 156.76; 153.02; 152.11; 151.53; 151.28; 151.02; 134.90; 132.57; 132.06; 131.27; 130.81; 130.42; 130.34; 129.16;

128.21; 127.29; 122.39; 121.49; 121.46; 115.27; 105.71; 68.73; 35.98; 32.54; 32.36; 30.45; 29.58; 29.50; 29.40; 25.98; 23.32; 23.10; 14.23; 14.10 MS-ESI (*m/z*): $[M+Na]^+$ calculated for $C_{101}H_{121}N_7NaO_6S_2Zn$: 1678.8003; found: 1678.7963.

Synthesis of LCVC03: To a solution of [5-Bis(4-hexylphenyl)amino-15-(Triisopropylsily)ethynyl-10,20-bis(2,6-di-octooxyphenyl)porphirinato] Zinc(II) **15** (150mg, 0.09mmol) in dry THF (15mL) was added TBAF (0.50mL) 1M in THF. The solution was stirred at 23ºC for 30min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried anhydrous $MGSO_4$ and the solvent was removed under reduced pressure. The residue and 5-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)furan-2-carboxylic acid **7** (146mg, 0.45) were dissolved in a mixture of dry THF (24mL) and NEt_3 (4mL) and the solution was degassed with dinitrogen for 10min. Then, $Pd_2(dba)_3$ (24mg, 0.026mmol) and $ASPh_3$ (60mg, 0.18mmol) were added to the mixture. The solution was refluxed for 4 hours under dinitrogen. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM/CH_3OH =20/1 as eluent. Recrystallization from CH_3OH/Ether to give **LCVC03** (112mg, 76%). ^1H NMR (THFd-8, 400 MHZ) δ_H: 9.80 (d, J=4.6Hz, 2H); 9.04 (d, J=4.6Hz, 2H); 8.81 (d, J=4.6Hz, 2H); 8.56 (d, J=4.6Hz, 2H); 8.41 (d, J=7.7Hz, 1H); 8.34 (d, J=7.7Hz, 1H); 7.93 (d, J=3.6Hz, 1H); 7.67 (t, J=8.3Hz, 2H); 7.41 (d, J=3.6Hz, 1H); 7.21 (d, J=8.7Hz, 4H); 7.04 (d, J=8.7Hz, 4H); 6.93 (d, J=6.7Hz, 4H); 3.87 (t, J=6.5Hz, 8H); 2.47 (t, J=7.4Hz, 4H); 1.60-1.51 (m, 4H); 1.30 (m, 12H); 1.01-0.57 (m, 66H). ^{13}C NMR (100MHz, THF-d8, ppm) δ 160.78; 156.75; 153.03; 152.10; 151.88; 151.53; 151.28; 151.02; 134.90; 132.57; 132.05; 131.31; 130.82; 130.34; 129.16; 125.75; 123.93; 122.40; 121.49; 115.27; 114.40 105.17; 68.72; 35.98; 32.54; 32.36; 29.91; 29.60; 29.50; 29.40; 25.98; 23.32; 23.10; 14.23; 14.10 MS-ESI (*m/z*): $[M]^+$ calculated for $C_{101}H_{121}N_7O_7SZn$: 1639.8334; found: 1639.8365.

4.3.2 Device preparation

All the devices for this work have been made as described in Chapter 2.
Two types of TiO_2 films were utilized depending on the measurements being conducted. Highly transparent thin films (8 µm) were utilized for L-TAS measurements. On the other hand, efficient DSC devices were made using 14 µm thick films consisting of 20 nm TiO_2 nanoparticles (Dyesol© paste) and a scatter layer of 4 µm of 400 nm TiO_2 particles (CCIC, HPW-400). All films were sensitized in dye solutions at concentrations of 0.125 mM in Ethanol containing 20mM chenoxydecholic acid were prepared and the film immersed overnight at room temperature. The sensitized electrodes were washed with Ethanol and dried under air. For this work we have used iodine electrolyte consisted of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M *tert*-butylpyridine in acetonitrile;

4.4 RESULTS AND DISCUSSIONS

In Figure 4.1 we can see the absorption spectra of **LCVC01**, **LCV02** and **LCV03 dyes.** Their photophysical and electrochemical characteristics are listed in Table 4.1

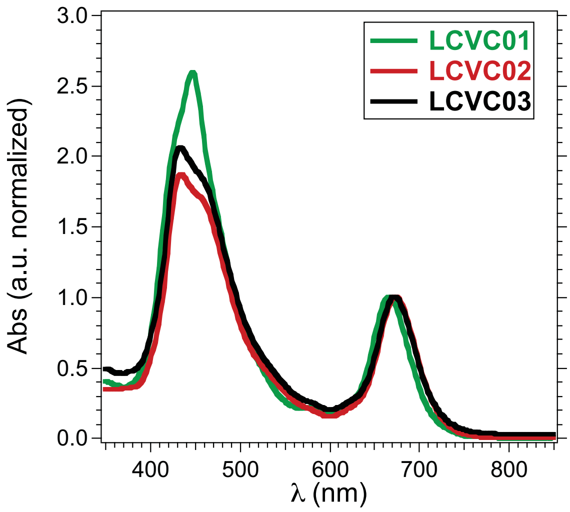


Figure 4.1: Absorption spectra of **LCVC01**, **LCVC02** and **LCVC03**

As shown in Figure 4.1 all the dyes exhibit typical porphyrin spectra with the bands associated to them. At around 450nm we observed an intense Soret band and between 600-700nm a lower intense Q-band. The absorption and emission values of three porphyrins are similar. The oxidation potentials of **LCVC02** and **LCVC03** are the same. However is 20mV lower comparing with the **LCVC01.** This is due to the presence of thiophene and furan between the BDT moiety and the carboxylic acid in **LCVC02** and **LCVC03** respectively. We do not observe a great difference in the HOMO and LUMO levels of the molecules and the values of them are in the case of the LUMO high enough to inject in the TiO_2, and the HOMO level low enough to regenerate from the electrolyte.

Table 4.1. Absorption, emission and electrochemical properties of **LCVC01, LCVC02** and **LCVC03**

Dye	λ_{abs} (nm)[a]	λ_{em} (nm)[a]	E_{ox} (V v's Fc/Fc+)[b]	E_{0-0} (eV)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
LCVC01	448(212); 579(18); 668(87)	705	0.19	1.82	-5.07	-3.25
LCVC02	434(92); 674(47)	715	0.17	1.81	-5.05	-3.24
LCVC03	434(145); 674(70)	690	0.17	1.82	-5.05	-3.23

[a]Measured in Tetrahidrofuran. In parenthesis molar extinction efficient at λ_{abs} (in M^{-1} cm^{-1}). [c]E_{0-0} was determined from the intersection of absorption and emission spectra in dilute solutions. [d]E_{HOMO} was calculated using E_{HOMO}(vs vacuum) = -4.88-E_{ox}(vs Fc/Fc+). [e]E_{LUMO} was calculated using $E_{LUMO} = E_{HOMO} + E_{0-0}$.

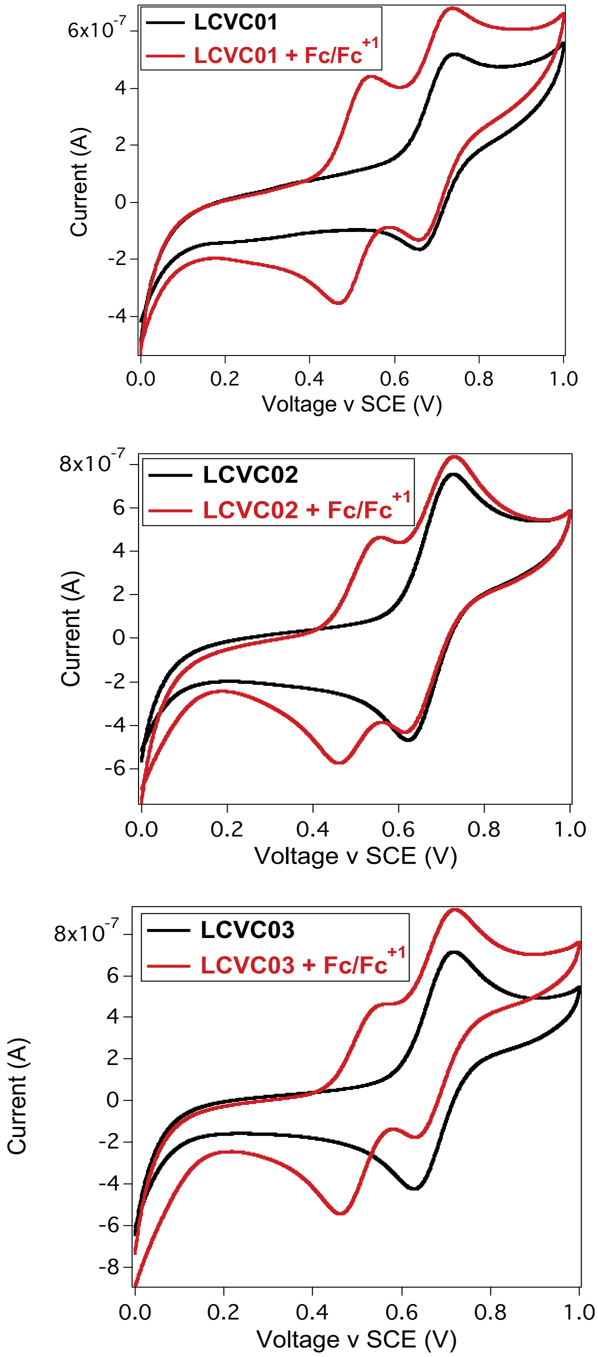


Figure 4.2: Cyclic voltammetry of **LCVC01** (top), **LCVC02** (middle) and **LCVC03** (bottom) recorded in 0.1M tetrabutylammonium hexafluorphosphate in 1:1 acetonitrile:*tert*-butanol at a scan rate of 10 mV s^{-1}. The working electrode consisted of a

platinum wire and the counter electrode a platinum mesh. The reference electrode was the silver calomel electrode (saturated KCl). All solutions were degassed with argon for 5 mins prior to measurement. The red and black scans were recorded in the presence and absence of Ferrocene/Ferrocene+.

Comparing the frontier orbitals of three molecules we observed that probability to find the highest occupied molecular orbital (HOMO) of three dyes is located predominantly on the donor moiety of the molecule. The probability to localize the lowest unoccupied molecular orbital (LUMO) is similar for LCVC02 and LCVC03 showing a significant shift through the acceptor due to the presence of the BDT acting as an electron drawing moiety that we don't observe for LCVC01 dye. With this observation we can say that the in the case of LCVC02 and LCVC03 an increase of Charge Transfer.

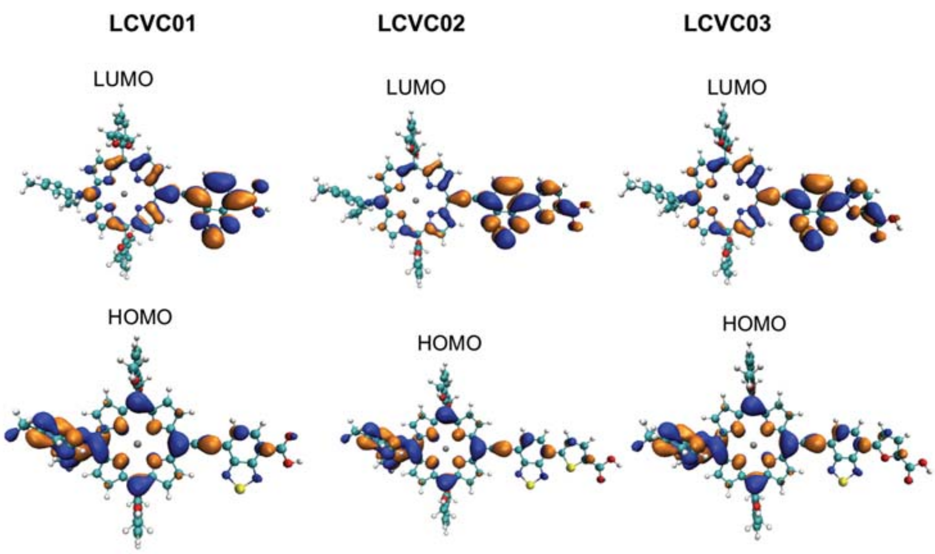


Figure 4.3: Frontier molecular orbitals of **LCVC01**, **LCVC02** and **LCVC03** at the B3LYP/6-31G (d) level

LCVC01, **LCVC02** and **LCVC03** were used to fabricate DSSC solar cells and measured under illumination conditions (AM 1.5G 100 mW/m^2). Device properties are listed in Table 4.2.

Table 4.2: Photovoltaic parameters obtained with **LCVC01**, **LCVC02** and **LCVC03**

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	η (%)*
LCVC01	0.65	7.69	75.40	3.84 (4.52)
LCVC02	0.70	20.00	74.41	10.41 (12.51)
LCVC03	0.58	5.81	74.42	2.55 (2.82)

The photocurrent density observed for **LCVC01** and **LCVC03** is lower when compared to **LCVC02.** The best J_{sc} corresponds to **LCVC02** that displays an impressive 20.00 mA/cm^2, such current is actually as high as the best perovskite solar cells, in contrast with the 7.7 and 5.8 achieved for **LCVC01** and **LCVC03** respectively. The open circuit voltage (V_{oc}) for **LCVC01** is 650mV. As reported before[22] the introduction of a group between the BDT and the anchoring group as in the case of **LCVC02** made that the V_{oc} increase in 50mV. Despite this effect is not observed for **LCVC03** with a low V_{oc} of 580mV. All dyes present similar values of fill-factor (FF). In Figure 4.3(a) is showed the I-V curves of **LCVC01**, **LCVC02** and **LCVC03**. In figure 4.3(b) is showed the incident-photon-to-current conversion (IPCE) of the champion cell of **LCVC02** exhibiting an IPCE up to 800nm. IPCE spectrum shows two maxima due to the Soret and Q bands of the porphyrin at 480nm of 76% and 670nm almost 90%.

Electron density and electron lifetime (Figure 4.4 and 4.5) in these devices were probed using charge extraction and transient photovoltage measurements respectively[24-26]. We observed higher charge density for **LCVC02** when compared to **LCVC01**. However the greater difference is comparing **LCVC03** that presents a lower charge density. From the TPV measurements (Figure 4.5) a slower recombination dynamics can be seen for **LCVC02** and a similar electron lifetime is also observed for **LCVC01**, which explains the similar voltage achieved for these devices. Also in agreement with the shortest electron lifetime for **LCVC03**. The difference obtained can be explained due to the differences in the e^-_{TiO2}/electrolyte$^+$ recombination rate. Some studies reported before[10,27,28] show that the introduction of heteroatoms could bind to I_{3-} and I_2

forming complexes. Due to this, more species are present in the TiO_2 surface accelerating the recombination rate. In our study we have seen how this hypothesis effects a change in the device performance by just the change of only one atom in the molecular structure.

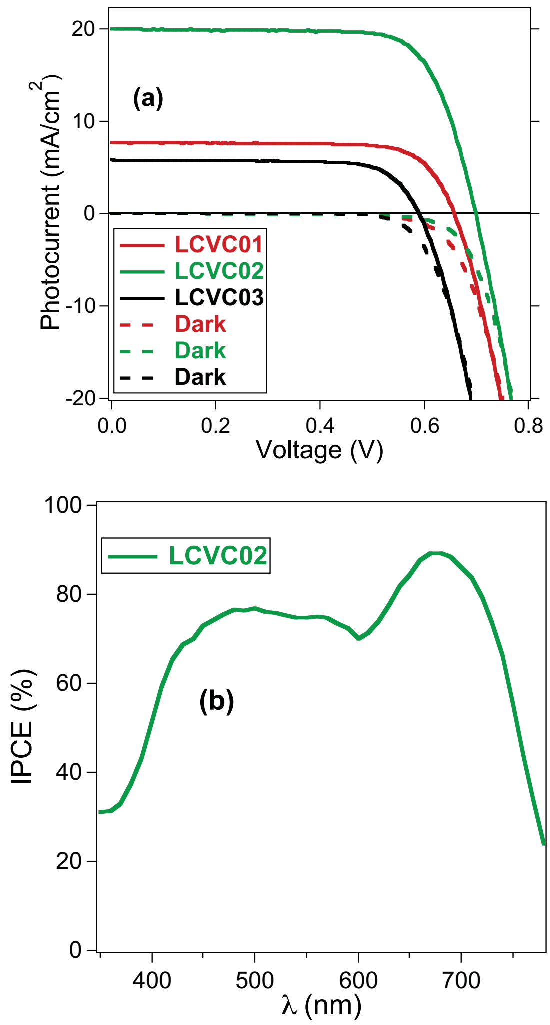


Figure 4.3 (a) I-V curves for **LCVC01, LCVC02** and **LCVC03** (b) IPCE spectra of **LCVC02.** DSC devices recorded under AM 1.5G radiation. Also shown are I-V dark curves.

In order to probe charge recombination and regeneration by the I_3^-/I^- redox couple in transparent DSC devices Laser transient absorption spectroscopy has been used. In figure 4.6 a, b, c we can see the charge recombination decays between the photo-injected electrons at the TiO_2 and the oxidized dye for **LCVC01**, **LCVC02** and **LCVC03** respectively. The data was recorded in absence of electrolyte (black) and corresponds to the long-lived decays assigned to the dye cation formed following photo-excitation. In red color we monitored the same process but in presence of electrolyte (red) with loss of cation signal due to the regeneration by I^-.

In order to estimate the regeneration efficiency we quantified the lifetime at the FWHM (full with at half maximum) of the signal which is 20, 60 and 60μs for **LCVC01**, **LCVC02** and **LCVC03** showing a small difference comparing **LCVC01** with **LCVC02** and **LCVC03** due to the small difference in oxidation potentials having **LCVC01** more positive oxidation potential and presenting more driving force.

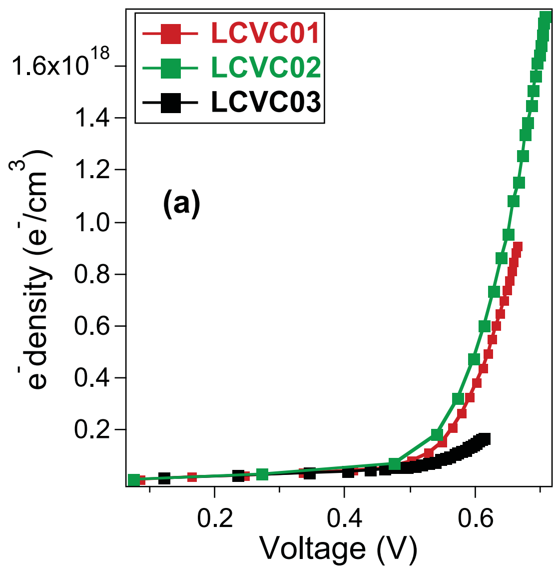


Figure 4.4: Electron density as a function of cell voltage for **LCVC01, LCVC02** and **LCVC03** devices.

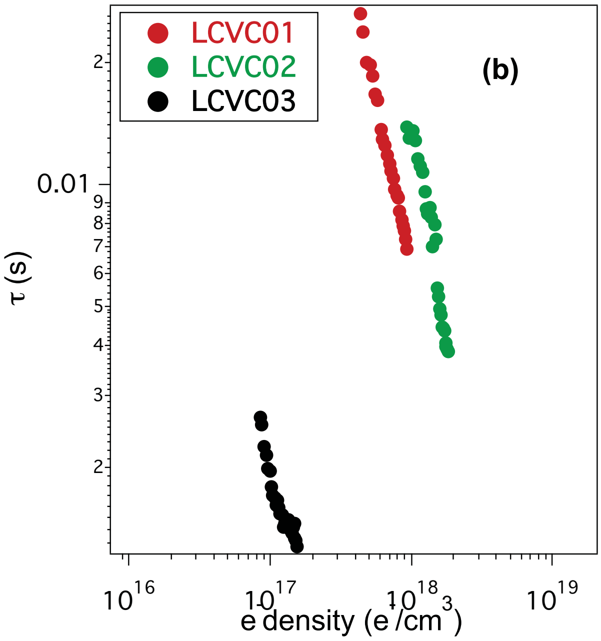
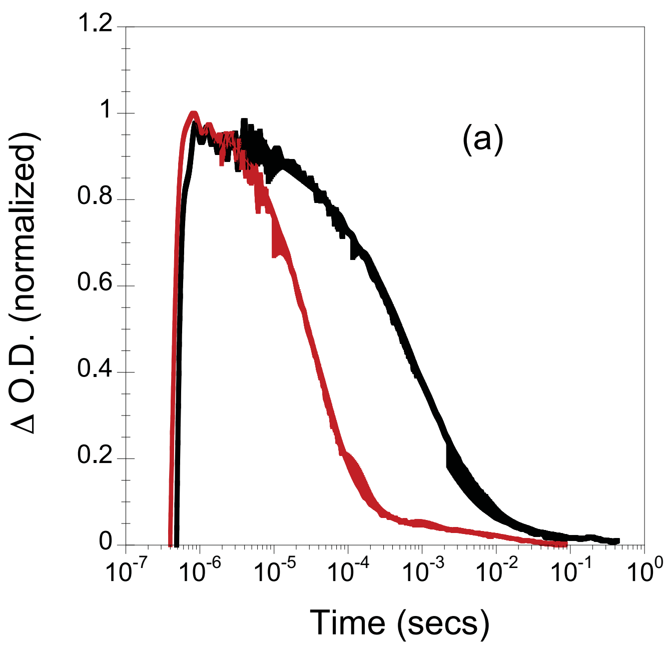
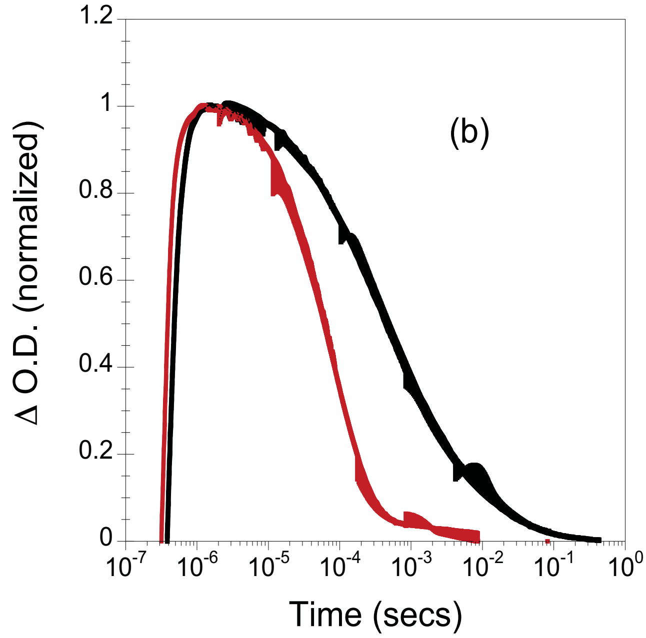


Figure 4.5: Device electron lifetime τ as a function of charge density for **LCVC01, LCVC02** and **LCVC03** devices.





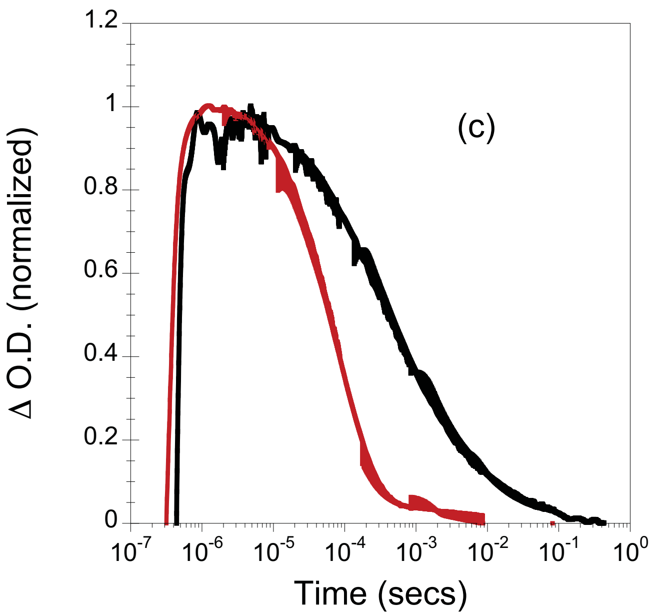


Figure: 4.6 Transient absorption kinetics of (a) **LCVC01**, (b) **LCVC02** and (c) **LCVC03** recorded for 1cm^2 area devices comprising 8 μm TiO_2 films in the presence of a blank electrolyte (black) and an iodide/tri-iodide red/ox electrolyte (red). Kinetics were recorded at 825nm for LCVC01, 775nm forLCVC02 and 825nm for LCVC03 following excitation at 600nm.

4.5 CONCLUSIONS

We have been synthesized a new series of push pull porphyrins using a diphenylamine as a donor moiety and an acid group as anchoring group with the introduction of a BDT group between the porphyrin core and the anchoring group for **LCVC01** and the introduction of a thiophene and a furan between the BDT and the anchoring group for **LCVC02** and **LCVC03** dyes. The DSSC performance gave us a record cell of 10.4% for **LCVC02**, however only a 3.84% and 2.55% were achieved for **LCVC01** and **LCVC03** respectively. As we have studied in the past the thiophene introduced in **LCVC02** reduce recombination reaction. Morever, the introduction of a furan moiety doesn't make the same effect. In that case, the electronegativity of the oxygen atom interacts with the electrolyte oxidized species placing them closely to the TiO_2 surface and accelerating the recombination rate.

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Chapter 5

Novel Porphyrin-based small molecule using indoline as secondary donor for solution processed bulk-heterojunction organic solar cells.

Table of contents

5.1 ABSTRACT

We have synthesized and characterized a new symmetric molecule based on our "push-pull" strategy (**VC53**) using a core of porphyrin as a main donor moiety and the indoline group as secondary electron donor for solution processed bulk-heterojunction organic solar cells obtaining an efficiency of 1.2% with a photocurrent of 5 mA cm^{-2} ensuring efficient electron transfer to PC70BM.

5.2 INTRODUCTION

Bulk-heterojuntion organic solar cells (BHJ-OSC) based on both; polymers[1-4] and small molecules[5] have been intensively developed in recent years and are still in continuous progress due to the great promising alternatives that these organic materials present for solar cells (such us implementation in buildings). These materials can be prepared in multi-scale and, additionally, the use of solution-processed techniques for device fabrication promise to lower the cost of the solar cell[6,7]. In spite of these clear advantages, these kind of devices are always accompanied with some other unsolved scientific matters that defines the entire field development such as studies related on charge generation or the determination of all losses mechanisms and the long-standing question about device stability.[8-13]

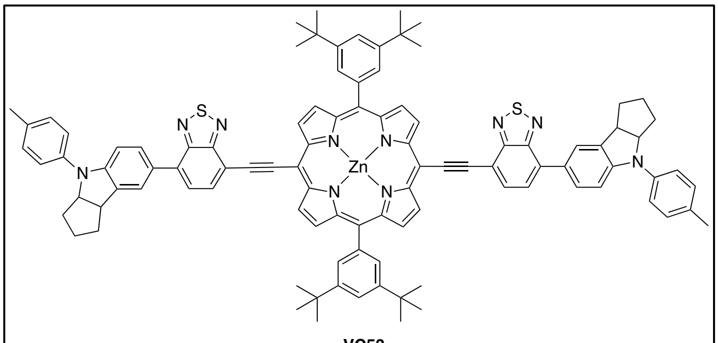
Recent published results for solution-processed small molecule bulk-heterojunction organic solar cells (smOSC) have demonstrated efficiencies reaching 8% under standard measurement conditions[14-16] by using different molecular designs; On the other hand, the approach of using conjugated donor-acceptor (D-A) frameworks facilitate the internal charge transfer because their "push-pull" properties and, in addition, the energetic levels can be easily tunned by introducing different electron donors or acceptor moieties.[17,18]

In addition, the porphyrins (POR) have been also widely studied and used in many BHJ-OSC[17-21] and DSSC[22-25]; PORs are based and inspired on photosynthetic systems, they provide extensive π-conjugated systems, with a fast electron transfer, and an extremely high absorption coefficients. Furthermore, their electrochemical properties can be tuned by both; the

insertion of the metal in the cavity or/and the addition of moieties to the periphery using well-stablished synthetic procedures.[18]
In contrast, the use of porphyrins as small molecule in solution processed BHJ smOSC provides, in general, lower device efficiencies[17-20] than polymeric electron donor materials.

The main reasons are: in first place, the poor solubility of these materials in most common-in-use organic solvents for processing, and, secondly, the weak intermolecular interactions with the acceptor moieties. For both reasons the addition of an additive is usually required.[21] Despite of that, the use of porphyrin in smOSC has recently reach values of efficiencies as high as 7%[26], competing very close with other small molecule moieties.

In the present work, a porphyrin based on symmetric “push-pull” framework has been designed and synthesized. The architecture, described as D-A-D-A-D, is based on a porphyrin core at the centre of the molecular backbone and the indoline[27,28] moieties, as secondary donors placed at the periphery. The benzothiadazole moiety[29] is used as intramolecular acceptor moiety. This design allows a relative low HOMO energy values favouring higher open circuit voltages, V_{oc}, and proper LUMO energy levels that leads to efficient charge dissociation to the main fullerene acceptor.



VC53

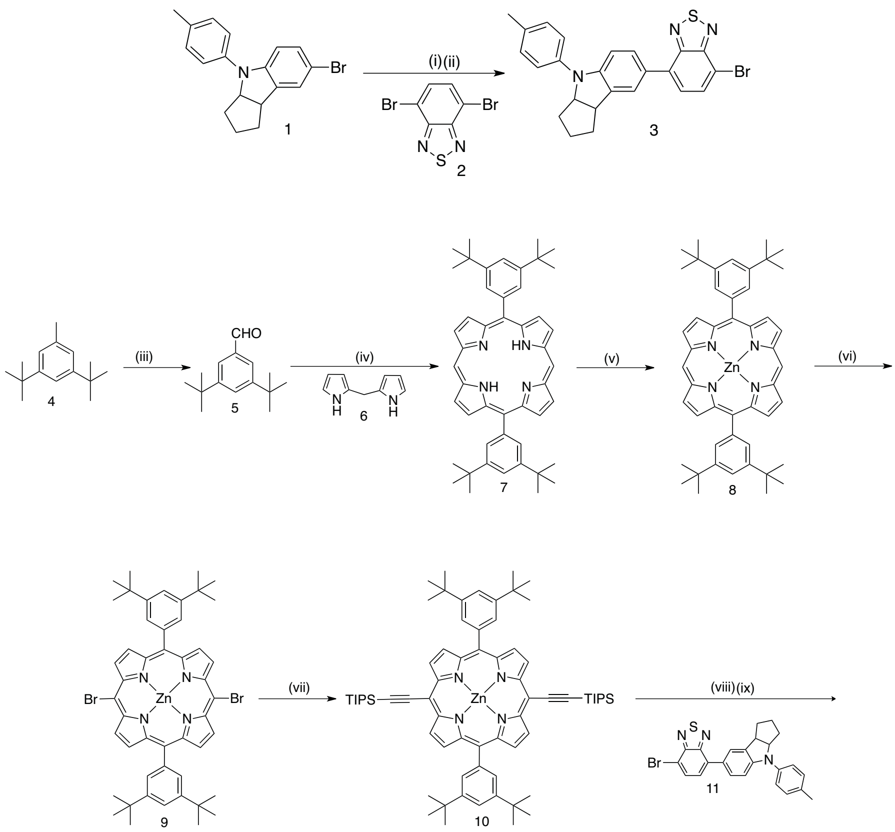
Scheme 5.1: Molecular structure of VC53

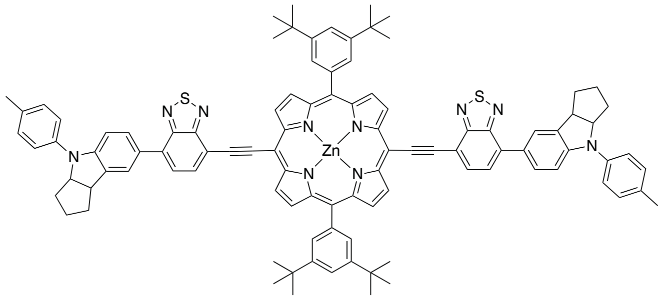
The complete devices were fabricated and analysed in this work. The most relevant parameters are presented below, as well as, the charge recombination measurements that will help to explain what limits the final device performance.

5.3 EXPERIMENTAL SECTION

5.3.1 Synthesis and characterization

The Synthesis of VC53 is shown in Scheme 2. The intermediate **3** was synthesized via in-situ Suzuki coupling. The synthesis of the dye **VC53** was carried out by attaching the intermediate **3** to the *meso* positions via Sonagashira coupling. The intermediates and **VC53** were characterized by ^{1}H-NMR, ^{13}CNMR and MALDI mass spectroscopy.





Scheme 5.2: Synthetic route of **VC53**. (*Reaction conditions):* (i) n-BuLi, THF, $B(OCH_3)_3$, -78ºC; (ii) $Pd(PPh_3)_4$, 2M K_2CO_3 aqueous solution, THF, 6 h, 80ºC; (iii) NBS, AIBN, benzene, 4h, reflux, hexamethylenetetramine, EtOH/H_2O, 4h, reflux, HCl, 30 minutes, reflux; (iv) TFA, DCM, 4 h, 23ºC, DDQ, 1h; (v) $Zn(OAc)_2{\cdot}2H_2O$, DCM/Methanol, 3 h, 23ºC; (vi) NBS, DCM, 6 h, 0ºC; (vii) triisopropylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, THF, Net_3, 4 h, reflux; (viii) TBAF, THF, 30min, RT; (ix) $Pd(PPh_3)_4$, NEt_3, CuI, Toluene, 4 h, reflux;

Synthesis of 4-bromo-7-(4-(*p*-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)benzo[*c*][1,2,5]thiadiazole (3): 7-bromo-4-(*p*-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole **1** (0.300g, 0.914mmol) was added to a round flask with 30mL of THF and was stirred under nitrogen atmosphere at -78ºC. A solution of ^{n}BuLi 2M in hexane (0.41mL, 1.09mmol) was added and the mixture was stirred for 15 minutes at -78ºC. After that, $B(OMe)_3$ (0.15mL, 1.37mmol) was added and the reaction was stirred overnight at -78ºC. The crude was warmed at room temperature. In another Schlenk vessel, $Pd(PPh_3)_4$ (0.094g, 0.025mmol), **2** (0.24g, 0.82mmol), K_2CO_3 2M (4mL), the reaction mixture, and THF (25mL) were mixed and the reaction was stirred at 70ºC for 6 hours. After the reaction, distilled water was added. The crude product was extracted using $CHCl_3$, and the organic layer was dried over $NaSO_4$. The residue was purified by column chromatography (Hexane/Dichloromethane 6:4) to obtain the desired product (0.230g, 54.4% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 7.84 (d, J=7.7Hz, 1H); 7.68 (s, 1H); 7.63 (dd, J=8.4Hz, 2Hz, 1H); 7.48 (d, J=7.7Hz, 1H); 7.20 (m, 4H); 6.97 (d, J=8.4Hz, 1H); 4.84 (m, 1H); 3.91 (m, 1H); 2.33 (s, 3H); 2.06 (m, 1H); 1.92 (m, 2H); 1.79 (m, 1H); 1.64 (m, 2H).

Synthesis of 3,5-di-*tert*-butylbenzaldehyde (5): A solution of 3,5-di-tert-butyltoluene (25g, 0.122mol), N-bromosuccinimide (33.0g, 0.185mol) and azobisisobutyronitrile (AIBN) (0.9g, 0.0055mol) in benzene was heated with reflux under magnetic stirring for 4 hours. The reaction mixture was cooled, filtered through paper and the solvent was evaporated under vacuum. The residue was dissolved in 70mL of a solvent mixture composed by EtOH/H_2O (1:1) and hexamethylenetetramine (50.0g, 0.357mol) was added. The solution was heated under reflux for 4 hours. Concentrate HCl was added (21mL) and the heating under reflux was continued for 30min. The ethanol solution was removed under reduced pressure, and the remaining aqueous layer was extracted with ether. The organic layer was dried over Na_2SO_4 and the solvent removed. Recrystallization from EtOH afforded the desired product as white crystals. (20.0g, 75% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 10.0 (s, 1H); 7.70 (m, 3H); 1.35 (s, 18H).

Synthesis of 5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphyrin (7): dipyrromethane (2.00g, 13.70mmol) and 3,5-di-*tert*-butylbenzaldehyde (2.98g, 13.70mmol) were dissolved in DCM (1.78L) and degassed. Then, trifluoroacetic acid (0.91mL, 12.33mmol) was added and the mixture was stirred at 23ºC for 4h under nitrogen. After that, DDQ (4.70g, 20.55mmol) was added and the mixture was stirred 1 h more. After, the mixture was basified with Et_3N (2.31mL) and filtered through silica. The solvent was removed under vacuum and the residue was purified by column chromatography using a mixture of Hexane/DCM (2/1) as eluent to give us the desired product (purple powder), (2.5g, 26.56% Yield^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.32 (s, 2H) 9.43 (d, J=4.6Hz, 4H); 9.18 (d, J=4.6Hz, 4H); 8.15 (d, J=1.6Hz, 4H); 7.81 (t, J=1.6H, 2H); 1.58 (s, 36H); 3.01 (s, 2H).

Synthesis of [5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphinato]-zinc(II) (8): A mixture of 5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphyrin **7** (2.50g, 3.63mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (5.20g, 36.39mmol) were mixed in DMF (150mL) and the solution was refluxed during 3 h. The reaction was quenched with water

(160mL), and the mixture was extracted using DCM (2x100mL). The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give as the desired product. (2.34g, 86% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 10.32 (s, 2H) 9.44 (d, J=4.6Hz, 4H); 9.20 (d, J=4.6Hz, 4H); 8.14 (d, J=1.6Hz, 4H); 7.83 (t, J=1.6H, 2H); 1.57 (s, 36H).

Synthesis of [5,15-Bis-bromo-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]-zinc(II) (9): To a stirred solution of 5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphinato]-zinc(II) **8** (2.34g, 3.11mmol) in DCM (120mL) NBS was affed (1.10g, 6.22mmol) and the solution was stirred for 30 minutes. After, the reaction was quenched with acetone (20mL) and the solvent was removed under vacuum. The solution was filtered and the residue was washed with MeOH to give us the desired product. (Purple powder) (2.57g, 91% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 9.66 (d, J=4.6Hz, 4H); 8.89 (d, J=4.6Hz, 4H); 8.01 (d, J=1.6Hz, 4H); 7.92 (t, J=1.6H, 2H); 1.57 (s, 36H).

Synthesis of [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-triisopropylsilylethynylporphinato]zinc(II) (10): A mixture of [5,15-Bis-bromo-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]-zinc(II) **9** (0.20g, 0.22mmol), triisopropylsilylacetylene (0.08mL, 0.35mmol), $Pd(PPh_3)_2Cl_2$ (0.03g, 0.04mmol), CuI (4.18mg, 0.02mmol), THF (20mL) and Net_3 (2mL) was stirred for 16h. Then, the solvent was removed under reduced pressure. The residue was purified by column chromatography using Hexane/DCM (3:2) to give as the desired product (purple solid) (0.19g, 77.2% Yield). ^{1}H NMR ($CDCl_3$, 400 MHZ) δ_H: 7.74 (d, J=4.6Hz, 4H); 8.95 (d, J=4.6Hz, 4H); 8.00 (d, J=1.6Hz, 4H); 7.79 (t, J=1.6H, 2H); 1.53 (s, 36H); 1.42 (m, 42H).

Synthesis of VC53: To a solution of **10** (185mg, 0.165mmol) in dry THF (10mL) was added TBAF (2mL) 1M in THF. The solution was stirred at 23ºC for 30min under nitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue and **3** (230mg, 0.498mmol) were dissolved in a mixture of dry toluene (10mL) and NEt_3 (5mL) and the solution was degassed with nitrogen during 10min. After, $Pd(PPh_3)_4$ (38mg, 0.030mmol) and CuI (6.30mg, 0.030mmol) were added to the mixture. The solution was refluxed for 4 hours under nitrogen. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM/CH_3OH =20/1 as eluent to afford pure product (92 mg, yield 36%) ^{1}H-NMR (400 MHz, THF-d8) δ_H: 9.90 (d, J=4.5Hz, 4H); 8.87 (d, J=4.5Hz, 4H); 8.19 (m, 5H); 8.05 (s, 1H); 8.03 (s, 2H); 7.97 (t, J=2.0Hz, 2H); 7.93 (dd J=8.5Hz, 2.0Hz, 2H) 7.86 (d, J=7.5Hz, 2H); 7.27 (d, J=8.5Hz, 4H); 7.18 (d, J=8.5Hz, 4H); 7.00 (d, J=8.5Hz, 2H); 4.92 (m, 2H); 3.92 (m, 2H); 2.33 (s, 3H); 2.09 (m, 4H); 1.94 (m, 1H); 1.86 (m, 1H); 1.63 (s, 36H). MALDI: m/z calcd for $C_{100}H_{90}N_{10}S_2Zn$ 1558.6083, found 1560.6116

5.3.2 Device fabrication

Indium Tin Oxide (ITO) 5 Ohm/square (PSiOTec, Ltd., UK) sodalime glass substrates were first cleaned with acetone to remove the residual photoresist layer. The substrates were then placed in a teflon holder and cleaned by ultrasonic treatment in acetone (1 × 10 min) and in isopropanol (2 × 10 min), and dried under a nitrogen flow. The ITO substrates where ozone-treated in a UV-ozone cleaner for 20 min, and subsequently coated in air with a layer of filtered (0.45 mm, cellulose acetate) solution of Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC StarckBaytron P) (4500 rpm 30 seconds followed by 3500 rpm 30 seconds). The PEDOT:PSS film was dried at 120 ºC under inert atmosphere for 15 min. Active blend was prepared in a concentration of 20 mg/ml (total concentration), using porphyrin (VC53) as a donor derivative and PC70BM in a mixed solution of chlorobenzene and dichlorobenzene 3:1 v/v and 3% of pyridine to help porphyrin solubility; the blend was left under stirring 48 hour; the active layer was spin coated at 8000 rpm in air over the PEDOT:PSS layer obtaining a thin layer 85 nm thick. After the deposition the active layer was exposed to a thermal annealing post-treatment at 130ºC for 2 min.

The cathode layer was deposited by thermal evaporation in an ultra high vacuum chamber (1×10^{-6} mbar). The metals were evaporated through a shadow mask leading to devices with a defined area of 9 mm^2; The LiF (0.6 nm) and the Al (100 nm) layers were deposited at the evaporation rate of 0.1 Å/s and 0.5-1 Å/s respectively.

5.4 RESULTS AND DISCUSSION

The absorption and emission spectra of **VC53** in solution is shown below and their photophysical and electrochemical characteristics are listed in Table 5.1.

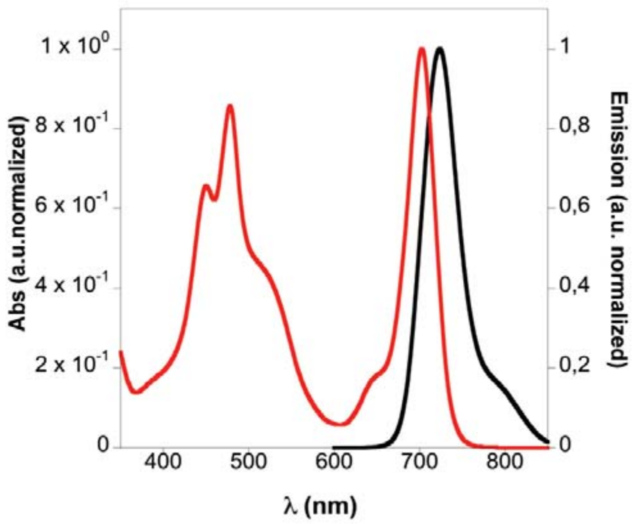


Figure 5.1. The normalized absorption (red) and emission (black) spectra of **VC53** in THF

As we can see, the absorption and emission spectra for **VC53** show the typical bands associated with porphyrins, An Intense Soret Band at 440 nm and 480 nm and also an intense Q band at 702nm. The cyclic voltammetry measurements give as a results a oxidation potential peak of E_{ox} = 0.150V and the corresponding E_{LUMO} calculated was E_{LUMO} =-3.28eV that is energetically high enough to achieve exciton dissociation at the bulk-heterojunction the interface[8]

Table 5.1. UV-Visible, steady-state fluorescence and electrochemical data for **VC53**

Dye	λ_{abs} (nm)[a]	λ_{em} (nm)[a]	E_{ox} (V v's Fc/Fc+)	E_{0-0} (eV)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
VC53	527 (392) 480 (493) 702 (574)	723	0.150	1.75	-5.03	-3.28

[a]Measured in THF. In parenthesis the molar extinction coefficient (ε) at l_{abs} ($10^{-3}M^{-1}$ cm^{-1}). [b]Measured in 0.1M tetrabutylammonium hexafluorophosphate in THF at scan of 30 mVs^{-1}. The working electrode consisted of a platinum wire and the counter electrode a platinum mesh. The reference electrode was the silver calomel electrode (saturated KCl). All solutions were degassed with argon for 5 min prior to measurement. [c]E_{o-o} was determined from the intersection of absorption and emission spectra in dilute solution. [d]E_{HOMO} was calculated using E_{HOMO}(vs vacuum) = -4.48-E_{ox}(vs Fc/Fc$^+$). [e]E_{LUMO} was calculated using $E_{LUMO} = E_{HOMO} + E_{0-0}$

The Light Harvesting Efficiency (LHE) obtained from the UV-visible absorption spectra of thin films is shown in figure 5.2. It is known that one of the main advantages is the great capability of porphyrins to absorb light in a broader light spectra taking into account the contribution of indoline groups; however, the limitation on thickness needed for efficient solar cells reduces the light harvesting efficiency of the film.

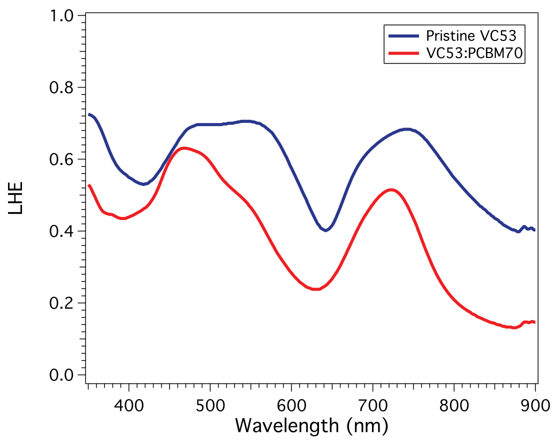


Figure 5.2. The Light Harvesting Efficiency (from the UV-Visible absorption spectra) of a

pristine VC53 film (blue) and VC53:PCBM$_{70}$ film (Red). The thickness of these films corresponds to same thickness obtained in complete devices which is 85-90 nm

Laser transient absorption spectroscopy (L-TAS) was employed with the aim to determine the charge transfer kinetics between the porphyrin and the fullerene as shown in figure 5.3. The thin BHJ film was excited at λ_{ex}= 480nm corresponding to a maximum of the film absorption; The decay transient was measured from micro- to milliseconds time scale and the signal was fitted to a power-law exponential decay (Eq. 5.1), indicating an inhomogeneous distribution of localized states and, due to the slow time scale monitored, the reaction can be assigned to non-geminate recombination process between the porphyrin and the fullerene derivate with a half-lifetime of 3 microseconds and a α parameter of 0.5 at room temperature.[30,31,32]

$\tau = \tau_{\Delta n0} * n^{a}$ (Eq. 5.1)

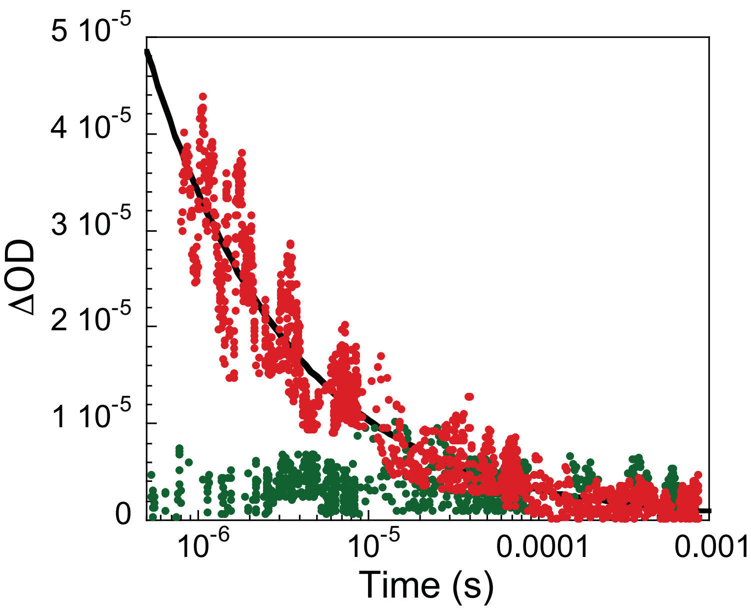


Figure 5.3. Transient absorption decays of VC53:PC$_{70}$BM film (Red) and pristine VC53 film (Green) recorded at λprobe=800nm for λex=480 nm. The black line corresponds to the power law fitting of the measured decay.

The design of this molecule allows favourable molecular aggregation (π-π stacking) due to the presence of the shorter alkyl chains linked over the core of the porphyrin; we expect this translate into an increase of the intra-molecular electron transport minimizing geminate recombination processes.

Once the L-TAS kinetics were measured, we fabricated complete devices as described above in the experimental section; we obtained an average device efficiency of 1.2% under AM 1.5G simulated conditions as shown in figure 5.4.

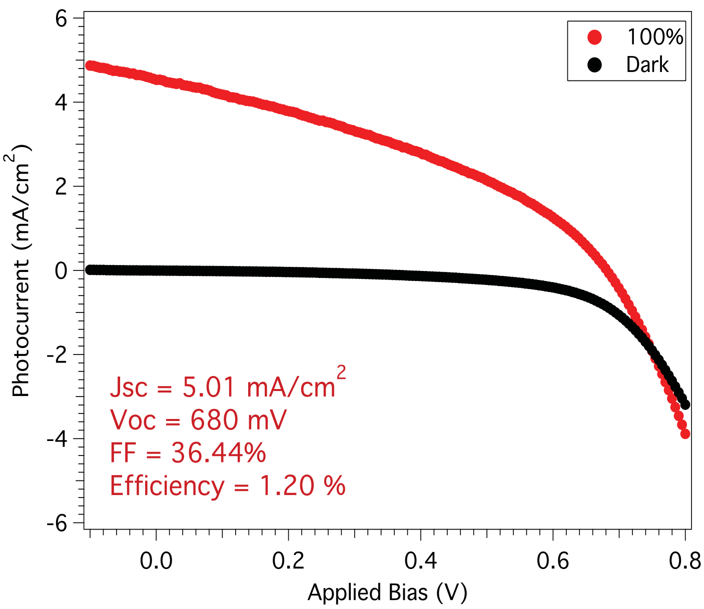


Figure 5.4. Measured current versus voltage (I-V) curves for VC53:$PCBM_{70}$ devices at 100 mW cm^{-2} and in dark.

The photocurrent obtained (J_{sc} = 5 mA cm^{-2}) is notable and correlates well with the LHE measurement shown above. Taking into account the LUMO energy difference between VC53 (-3.28 eV) and the fullerene derivate (-4.0 eV) it seems that exciton dissociation was efficient.[4]

The obtained V_{oc} of 680mV is not noticeably high; however represent a reasonable value taking into account the theoretical maximum value around 1V obtained from energy level positioning difference of both VC53 ($HOMO_{donor}$: -5.03 eV) and fullerene derivate ($LUMO_{acceptor}$: -4.0 eV) using calculation procedures previously reported by other authors.[33]

The FF of 36.5% is unambiguously the main limiting factor of the overall device performance and is known that strongly depends on carrier mobility and the balanced degree between hole and electron charges being generated at the blend and transported through the device active layer to the selective metal contacts. From the results obtained from LHE measurements and taking into account that electron mobility basically depends on the fullerene derivate, we can anticipate that this device present a poor hole mobility that limits the device performance.[34,35]

The CE and TPV measurements were carried out as it have been previously reported by our group among others. [12,13,36] In Figure 5.5, we can appreciate a clear linear region at earlier applied bias until values close to the experimental V_{oc} corresponding to 1 sun illumination, where an exponential trend appears. As we have reported and other authors have confirmed, the linear region is indicative that the device works as a capacitor and charges are likely to be stored at the electrodes[11,37]; On the contrary, under 1 sun illumination the exponential trend can be assigned to the charge being accumulated at the film and producing the splitting of the quasi Fermi levels in both materials. The energy difference between those quasi Fermi levels is equal to the observed Voc at 1 sun.

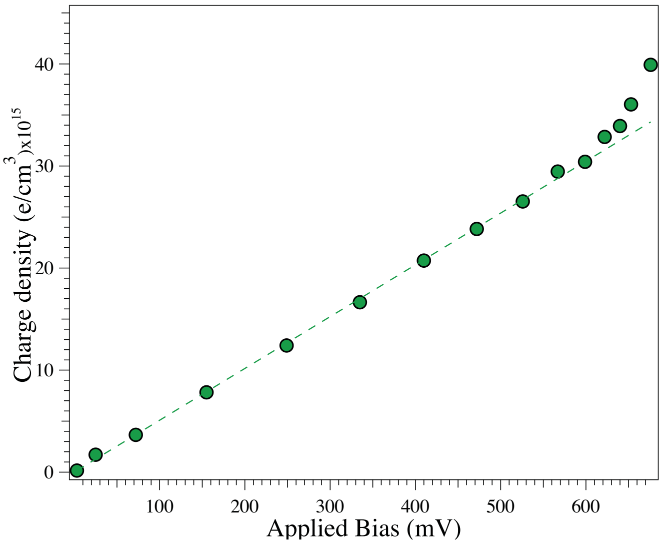


Figure 5.5. Measured charge density at different light bias, dashed line represents the linear trend related to the geometric capacitance of a VC53:$PCBM_{70}$ complete device.

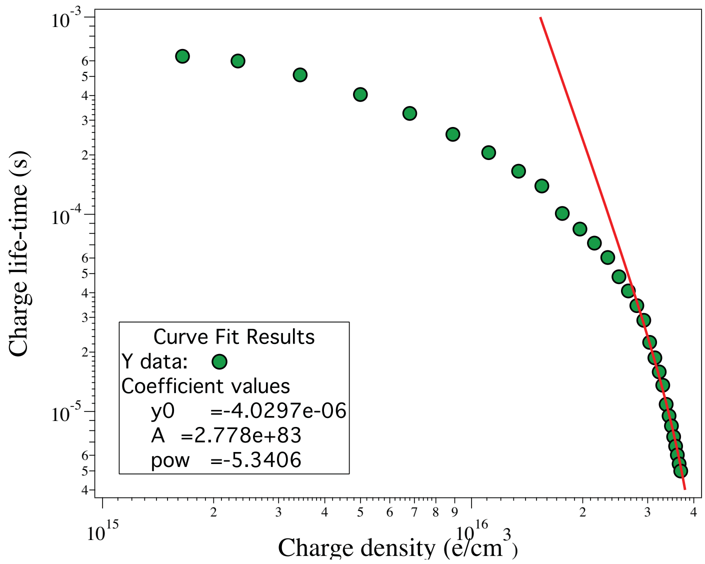


Figure 5.6. Measured charge lifetime at different charge density of a VC53:$PC_{70}BM$ complete device.

In the charge lifetime vs accumulated charge measurements (Figure 5.6), extracted using TPV and CE, we clearly differentiate two regions, the first one corresponding to a smoother decay at times between $4\cdot10^{-4}$s and $1.5\cdot10^{-5}$s that does not corresponds to the real carrier life-time as it measured from the geometric capacitance of the cell and it should be attributed to the discharge time of the capacitor; The second region, measured life-time values below 10^{-5}s, truly correspond to the charge carrier recombination dynamics of the VC53:$PC_{70}BM$ solar cell. The latest data from the TPV were fitted to a power law (Equation 5.1) obtaining an α~5 indicating that the overall charge recombination is not only determined by non-geminate bimolecular recombination kinetics (with expected value of 2) but also by recombination processes at the electrodes interface due likely to the unbalanced mobility between holes and electrons.

5.5 CONCLUSIONS

A new porphyrin has been synthesized and characterized in order to study its applicability in smOPVs. The average efficiency achieved was 1.2% using as acceptor moiety PC70BM. The main limitation observed for this type of molecules is the low mobility of charges (holes) that impedes the use of thicker films that will lead to higher photocurrent. The recombination lifetime measured under working conditions is in the order of other OPV devices including both, small molecules and polymers. Thus, further work on this direction (improving mobility) should be the focus on the design and synthesis of porphyrins for applications in OPV using solution processed methods.

5.6 REFERENCES

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Chapter 6
Final Conclusions

FINAL CONCLUSIONS

In this Thesis, the synthesis and characterization of novel sensitizers for their applications in DSSC and OPVs have been described. For all of the Sensitizers presented the device performance have been done in order to study their applicability for the photovoltaic devices studying how change the efficiency of the devices versus the structure of the molecule.

Basically we can summarize the conclusions as follows:

- **In Chapter 3** we have design a new sensitizer called **VCL01** using as reference the **LS-1** with the difference to include a cyclopentadithiophene unit in the π-bridge in the VCL01 and also the performance in DSC devices is described. We observed for the VCL01 dye a moderate efficiency of 4.81%. However under 120mins of irradiation this efficiency has been increase in almost 50% showing a 7.21%. The increase observed was due to the increase in J_{sc} reflected in the IPCE. And increase in the V_{oc} is also observed due an increase of the electron lifetime seen in the Transient photovoltage measurements. After 120min of irradiation there is an improvement in the interaction between the dye and the TiO_2, promoting a fast electron injection in the semiconductor.

- **In Chapter 4** we have design and synthesized a family of porphyrins called **LCVC01**, **LCVC02** and **LCVC03** in order to study how affect the introduction or not of a group between the BDT and the anchoring group and the importance to choose the correct group. The results achieved indicate that the introduction of a group not always is a good issue. Here we have presented the example of one group (thiophene) with a record efficiency of 10.4% and in other case we have introduced a furan group achieving a modest efficieny of 2.55%. With the photophysical studies of these molecules we have seen that the introduction of a thiophene group in LCVC02 reduce the recombination rate making it a good option. However the introduction of a furan group for LCVC03 not only is showed a worse efficiency if not it seems that the oxygen atom interacts with electrolyte oxidized placing them closely to the semiconductor surface accelerating the recombination reactions.

- **In chapter 5** a porphyrin for OPVs applications have been synthesized. The efficiency achieved was 1.2% with $PC_{71}BM$. Further optimizations and new design for small molecules is needed to achieve good porphyrins with better device performance.

ANNEX

Scientific Contribution

Journal Articles related with this Thesis

Light soaking effects on Charge Recombination and Device Performance in Dye Sensitized Solar Cells Based on Indoline-Cyclopentadithiophene Chromophores. Lydia Cabau, Laia Pellejà, John N. Clifford* Challuri Vijay Kumar* and Emilio Palomares (***J. Mater. Chem. A*, 2013,1, 8994-9000).**

Synthesis of new high efficient Push-pull porphyrins for Dye Sensitized Solar Cells. Lydia Cabau, Antonio Moncho, Challuri Vijay Kumar, John N. Clifford, Núria López and Emilio Palomares. (Writed)

Journal Articles not related with this Thesis

Dye Molecular Structure Device Open-Circuit Voltage Correlation in Ru(II) Sensitizers with Heteroleptic Tridentate Chelates for Dye-Sensitized Solar Cells. Kuan-Lin Wu, Cheng-Hsuan Li, Yun Chi, John N. Clifford, Lydia Cabau, Emilio Palomares, Yi-Ming Cheng, Hsiao-An Pan and Pi-Tai Chou. **(*J. Am. Chem. Soc.*, 2012,134 (17), pp 7488-7496).**

Indoline as Electron Donor Unit in "Push-Pull" Organic Small Molecules for Solution Processed Organic Solar Cells: Effect of The Molecular π-Bridge on Device Efficiency. Fernández Montcada, Nuria; Cabau, Lydia; Kumar, Challuri; Cambaru, Werther; Palomares, Emilio. Submitted

Conferences

Frontiers in organic, dye-sensitized and Hybrid solar cells. VII International Summer School of Krutyn, Poland 2011.

Hybrid and Organic Photovoltaics (HOPV 2014) Lausanne- Switzerland 2014. Poster Presentation
Lydia Cabau; Vijay Kumar Challuri; John N. Clifford; Laia Pellejà; Emilio Palomares. Effect of light soaking on efficiency in Dye Sensitized Solar Cells