

Self-assembly of functional chromophores into chiral nanomaterials

Cristina Oliveras González

Tesi doctoral
Doctorat de Ciència dels Materials

Director/a
David B. Amabilino

Co-director/a
Núria Aliaga Alcalde

Tutor/a
Jordi Hernando Campos

Departament de Química
Facultat de Ciències

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Cristina Oliveras González

Vist i plau

Director/a

David B. Amabilino

Codirector/a

Núria Aliaga Alcalde

Tutor/a

Jordi Hernando Campos

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Thesis abstract

This thesis focuses on the self-assembly studies of chiral porphyrins and the use of these chromophores to drive the organization optically active molecular materials.

Porphyrins and their derivatives are pigments – some found in natural systems - that are made up of four pyrrolic units linked by methine bridges and they form part of an important class of cyclic chromophores. Porphyrins are present in nature developing important processes in biological systems, especially in electron transport or light harvesting systems. It is important to emphasize that these macrocycles have chiral environment arising from self-organization through non-covalent interactions such as hydrogen-bonding, van der Waals interactions, π - π interactions and metal coordination.

The study of the self-assembly of porphyrins and metalloporphyrins has received great attention in recent years because of their optical, electronic and magnetic properties that make these chromophores suitable for a broad range of potential applications such as nanoelectronic devices, solar cells or organic field-effect transistors (OFETs).

The porphyrins and metalloporphyrins studied in this work contain in their structures different moieties capable to direct the self-assembly. Moreover, the presence of a zinc (II) metal ion in the core of the chromophoric ring can influence in their organization due to its ability to coordinate with oxygen, nitrogen and sulfur containing derivatives. The important role of the chiral group in the periphery of the porphyrin ring is noteworthy. Therefore, the number and position of the stereogenic centers directly affect the chiral transfer from molecular level to supramolecular systems.

Bearing these considerations in mind, the design of chiral supramolecular systems based on porphyrins has been carried out in order to determine the influence of chirality in the hierarchy morphology of the aggregates and in consequence the influence of the chiral organization in the efficiency for further applications.

The self-assembly studies in solution and in the solid state of a family of metalloporphyrins which contain in their structure chiral amide groups and pyridyl groups show the influence in the constitution in their optical activity and morphology of the aggregates, all of them formed as a main interaction the coordination between the pyridyl unit with the zinc (II) metal ion.

The self-assembly of a C_3 symmetric molecule based on chiral porphyrins has been studied by CD in different solvents and the morphology of the aggregates by AFM after be deposited on HOPG and mica.

Finally, the supramolecular organization of a chiral metalloporphyrin-block copolymer complex has been studied in solution. Moreover, the CD studies suggested chirality transfer from chiral metalloporphyrin to the superstructure of the complex.

Resum de la tesi

Aquesta tesi es basa en l'estudi de l'auto-assemblatge de porfirines quirals i la utilització d'aquests cromòfors en l'organització de molècules orgàniques de manera quiral.

Les porfirines i els seus derivats són colorants – uns d'ells naturals - formats per quatre anells pirròlics units entre si per un enllaç metilè i les quals formen part d'una família de cromòfors cíclics. Les porfirines estan presents a la natura i juguen un paper important in diferents processos en sistemes biològics, especialment aquells de transport d'electrons or com a captadors de llum. És important remarcar que tots aquests macrocicles posseeixen un ambient quiralt provinent de l'auto-assemblatge a traves de d'enllaços no-covalents tal com ponts d'hidrogen, interaccions febles de van der Waals, interaccions π - π i enllaços de coordinació mitjançant un centre metàl·lic.

L'estudi de l'auto-assemblatge de porfirines i metal·loporfirines ha rebut un gran interès els darrers anys degut a les propietats òptiques, elèctriques i magnètiques que aquests cromòfors presenten. És per aquest motiu, que aquests pigments naturals puguin ser utilitzats en múltiples aplicacions en camps de la nanoelectrònica, celes fotovoltaïques o com a transistors d'efecte de camp orgànic (OFETs).

Les porfirines i metal·loporfirines estudiades en aquest treball contenen en la seva estructura diferents grups capaços de dirigir l'auto-assemblatge. A més a més, la presència de de l'ió zinc (II) enllaçat a l'interior de l'anell porfirínic pot també influir en l'organització de l'agregat, ja que el zinc presenta una gran tendència a coordinar-se amb lligants axials que continguin àtoms d'oxigen, sofre o nitrogen en la seva estructura. És important destacar, l'important rol del grup quiral en els substituents de l'anell de porfirina, ja que el nombre i posició dels centres esterogènics afecten directament en la transferència de quiralitat des de nivell molecular al sistema supramolecular.

Tenint totes aquestes consideracions en ment, el disseny d'estructures supramolecular quirals basades en porfirines ha estat dut a terme per tal de determinar la influència de la quiralitat en la morfologia dels agregats i per tant la influència de l'organització quiral de les estructures supramoleculares en l'eficiència del transport de càrrega per a futures aplicacions.

S'ha pogut observar en els estudis d'auto-assemblatge d'una família de metal·loporfirines amb grups amida quirals i grups piridina en dissolució i en estat sòlit la influència del nombre i posició dels diferents grups en l'activitat òptica dels agregats i en la seva morfologia. S'ha determinat que els agregats s'han format mitjançant la coordinació d'un grup piridina amb el zinc (II) metàl·lic.

S'ha estudiat l'auto-assemblatge d'una molècula simètrica C_3 basada en porfirines quirals en diferents dissolvents de diferents polaritats i la morfologia dels agregats formats quan aquests són dipositats sobre una superfície de grafit o mica.

Finalment, l'organització supramolecular d'un complex format per una metal·loporfirina quiral i un bloc copolímer s'ha estudiat en dissolució, observant-se mitjançant CD una transferència de la quiralitat des de la porfirina lliure al complex.

Abbreviations

AFM : Atomic force microscopy

BCP : Block copolymer

CD : Circular Dichroism

DDQ : 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

HOPG : Highly oriented pyrolytic graphite

HT : Hight tension

IR : Infra red spectroscopy

LDI-Tof : Laser desorption ionization-time of flight

MALDI-Tof : Matrix-assisted laser desorption ionization-time of flight

NMR : Nuclear magnetic resonance

OFET : Organic field-effect transistor

OLED : Organic light-emitting diode

PGSE : Pulsed gradient spin echo

ROESY : Rotating frame overhauser effect spectroscopy

SEM : Scanning electron microscope

TFA : Trifluoroacetic acid

UV-Visible : Ultraviolet-visible absorption spectroscopy

Chapter 1

General introduction

1. General introduction.

1.1. Chirality.

Chirality is the property of an object to be non-superimposable on its mirror image.¹ Therefore, following such definition, a molecule is chiral only if it contains a carbon atom with four different substituents (Figure 1), or if it contains a chiral conformation (as is the case of helical chirality). Chirality is above all, an essential property in living systems, found in amino acids,² proteins and enzymes,³ sugars,⁴ in DNA and RNA,⁵ also in tetrapyrrolic systems, that play important roles in most of life systems.⁶

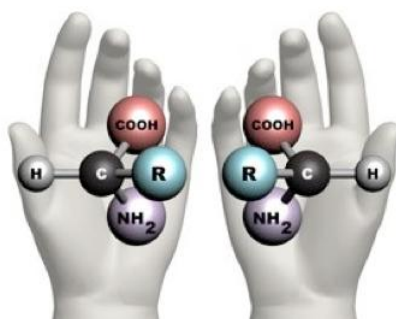


Figure 1. Illustration of two enantiomers of a generic amino acid.

Most molecules involved in the functioning and reproduction of life only exist as one of the two enantiomeric forms, right-handed or left-handed, but the origin of this dissymmetry remains still unclear; one of the most accepted possibilities bases on external influences as the responsible for this natural enantioselection, such as flux under the influence of a magnetic field follow by hierarchical assembly,⁷ although many other postulates have been made as well, all of them difficult to be proved or discerned.⁸

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 - (7) Micali, N.; Engelkamp, H.; van Rhee, P. G.; Christianen, P. C. M.; Scolaro, L. M.; Maan, J. C. *Nat. Chem.* **2012**, *4*, 201-207.
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1.2. Porphyrins and their derivatives.

Porphyrins are pigments – found in natural systems - constituted by four pyrrolic units linked by methine bridges⁹ that form part of an important class of chromophores called porphyrinoids. These compounds differ among them due to structural modifications, as depicted in Figure 2.¹⁰

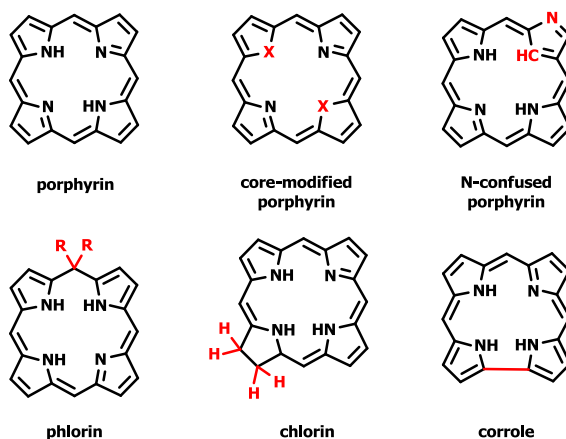


Figure 2. Porphyrinoid chemical structures.

The properties and reactivity of porphyrins and their analogues depends mostly in the lateral substitutions of their macrocycle core.^{11,12} However, it has been widely studied that the insertion of a metal ion in the core of the chromophore ring can also modified the photophysical properties of such systems.¹³

The ionic radii of many metal ions fit well within the inner core of the porphyrin ring, where the metal gets fixed inside the cavity, by coordination bonds with the nitrogen atoms of the pyrrole units.^{14,15}

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Porphyrin chemistry has progressed over the past years because of their optical,¹⁶ electronic¹⁷ and magnetic¹⁸ properties, fact that made them interesting for the development of components of solar cells,¹⁹ information storage²⁰ or sensors.²¹

The porphyrinic macrocycle can be substituted at three different positions of the ring as Figure 3 indicates.

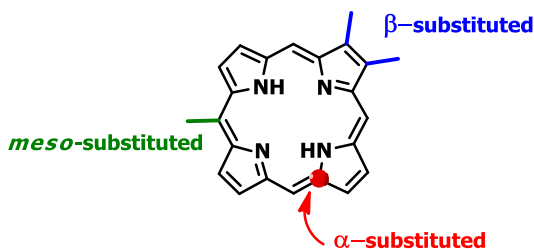


Figure 3. Substitution positions of the porphyrin ring.

The different reactive positions, *alfa*-, *beta*- and *meso*- for the free-base porphyrin afford a great number of porphyrin derivatives, although the majority of them present variations in the *beta*- and/or *meso*-positions. It is worthy to note, that β -substituted porphyrins are present in nature developing important processes in the biological systems as it is the case of heme molecule²² or chlorophyll (Figure 4),²³ while the *meso*-substituted porphyrins have no biological counterparts but wide applications as biomimetic models and useful building blocks for supramolecular chemistry.²⁴

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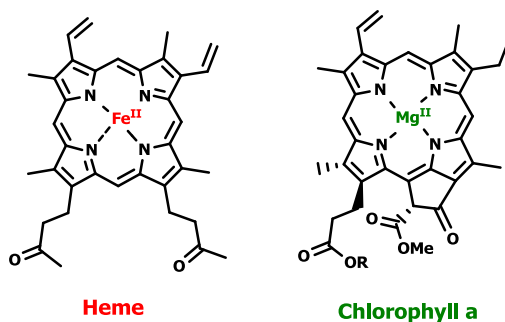


Figure 4. Chemical structure of heme molecule and chlorophyll a.

From a structural point of view, porphyrins are highly π -conjugated systems that show an intense absorptions in the visible and near UV regions, all of them presenting an intense band (Soret band) at around 420 nm with an extinction coefficient over 10^5 mol/L cm^{-1} and four Q-bands with weak intensities between 500 and 700 nm, in the case of free-base porphyrins, or two Q-bands (or less) in the case of metalloporphyrins, due to their higher orbital degeneracy because of the symmetry in the structure.²⁵ The electronic absorption spectra depend on the exocyclic modifications and coordinated metal ion and are well-explained by the Gouterman four-orbital model (Figure 5).²⁶ As the figure shows, this model involves the excitation of the two highest occupied molecular orbitals (HOMO) to the two lowest unoccupied molecular orbitals (LUMO). It is also important to emphasize, that even though this model is widely used, not all the features observed in the absorption spectra can be explained.²⁷

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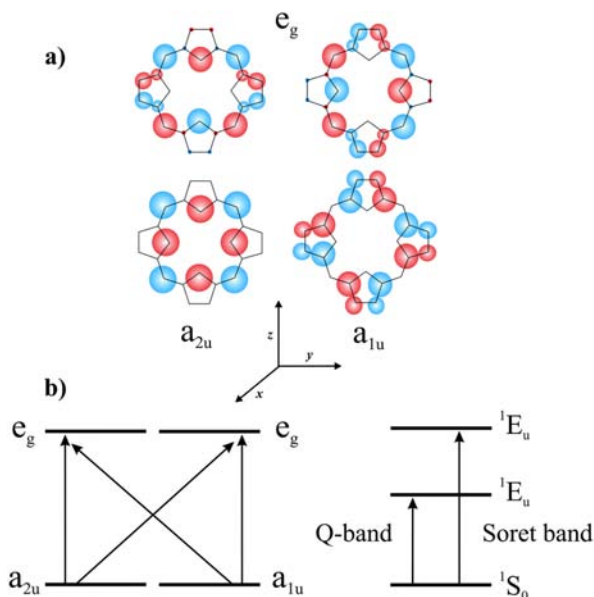
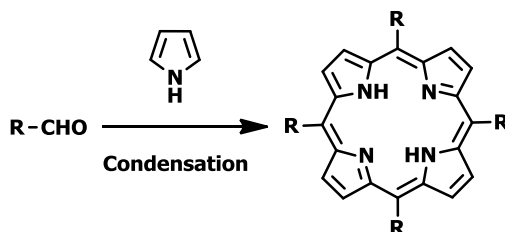


Figure 5. Gouterman Four-orbital model.

There are different ways to synthesize *meso*- and β -substituted porphyrins. The most common route in order to synthesize *meso*-substituted porphyrins is the reaction between aldehydes and pyrroles in acidic media developed in the 1940s by Rothmund,²⁸ modified and improved two decades later by Adler and Longo²⁹, obtaining the porphyrin ring in milder conditions (Scheme 1).



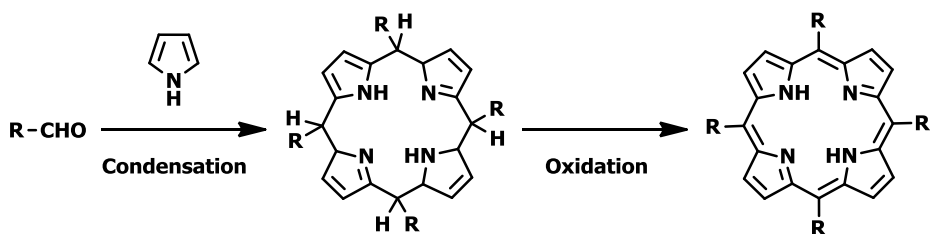
Scheme 1. Adler and Longo method for the synthesis of porphyrins.

In the 1980s, Lindsey³⁰ developed a two-step method where the condensation between the aldehyde and pyrrole were catalyzed by an acid, usually TFA or $BF_3 \cdot OEt_2$, forming a porphyrinogen intermediate and its further oxidation, with DDQ or *p*-chloranil, afforded the *meso*-substituted porphyrin ring in mild conditions as well (Scheme 2).

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Scheme 2. The synthesis of porphyrins by the Lindsey method.

1.3. Self-assembly and supramolecular chemistry.

The self-assembly is defined as spontaneous association of molecules under equilibrium conditions into organized structures as a consequence of a specific interactions among themselves.³¹ The term of supramolecular chemistry was developed by the first time by Jean-Marie Lehn, who won the Nobel Prize in 1987 for his research in this area.³² Jean-Marie Lehn defined this concept as “Chemistry beyond the molecule”, that it was based in the assembly of molecules by non-covalent bonds.³³

The bottom-up approach to supramolecular is based on stacking systems and can be controlled by different non-covalent interactions such as hydrogen-bonding, van der Waals and π - π -interactions or metal coordination instead of the traditional covalent, ionic or metallic bonds.³⁴ Even though the control of the final supramolecular architecture depends on the directionality of the non-covalent interaction involved in the aggregation of the building blocks, possessing hydrogen-bonding and metal coordination provide the strongest directionality and more stable interactions.^{35,36}

It is well-known that self-assembly plays an important role in biological systems such as DNA, which is built up by hydrogen-bonds, or proteins, that assemble to form quaternary structures.³⁷ As mentioned before, most of the biological systems are chiral, therefore the study of the self-assembly of chiral systems have been received great attention in the last decades.^{38,39} Chirality can be expressed in different levels, from molecules to supramolecular systems in which the

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chirality can arise from chiral molecules, a combination of chiral and achiral molecules and also they can be constructed by achiral building blocks.^{40,41}

The optical activity of self-organized molecules can be modified by the number and position of the stereogenic centers in molecules,⁴² Such factor is different from sergeant and soldiers^{43,44} and majority rules effects^{45,46} where both phenomena can drive chiral induction in supramolecular systems but with very few applications. Therefore, it is mandatory to study and tune chirality at will by the incorporation of stereogenic centers.

The study of self-assembled chiral systems based on aromatic chromophores is attractive because they absorb visible light with high efficiency and are good candidates for application in different areas of material science.⁴⁷ Finding these π -functional units in nanostructures such as nanoparticles, fibers, nanorods and wires,⁴⁸ nanolayers and thin films on surface, and even in bulk soft matter systems.⁴⁹

The self-assembly of chiral systems based on synthetic porphyrins is appealing because they present a broad range of potential applications in different areas such as photovoltaic cells,⁵⁰ optoelectronics⁵¹ and nanoelectronic devices,⁵² light harvesting systems^{53,54} and also non-linear optical materials,⁵⁵ owing to their physical-chemical properties.⁵⁶

In general porphyrins can form two different types of aggregates, *H*-aggregate or *J*-aggregate, where non-covalent interactions are the main forces, and the preference to form one or the other

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depends on the functionalization of the porphyrin ring and also of the metal ion coordinated to the core of the chromophores.⁵⁷

The study of the self-assembly of porphyrins by spectroscopic techniques afford information about the kind of aggregate formed in solution by the positions of the absorption bands position; this is possible because their photophysical properties are strongly dependent of the orientation and distance of adjacent chromophores (Figure 6).^{58,59}

Aggregates in solution exhibit changes in the absorption bands compared to their monomeric species. In the case of *H*-aggregates, in which there is a strictly columnar packing with direct overlap of the conjugated systems, a blue shift is observed in the Soret band (hypsochromic shift); on the other hand, a red shift (bathochromic effect) of the Soret band is observed in *J*-aggregates, which present partial overlapping of the porphyrin rings and a kind of staircase type, where one dimensional stacking take place.^{60,61}

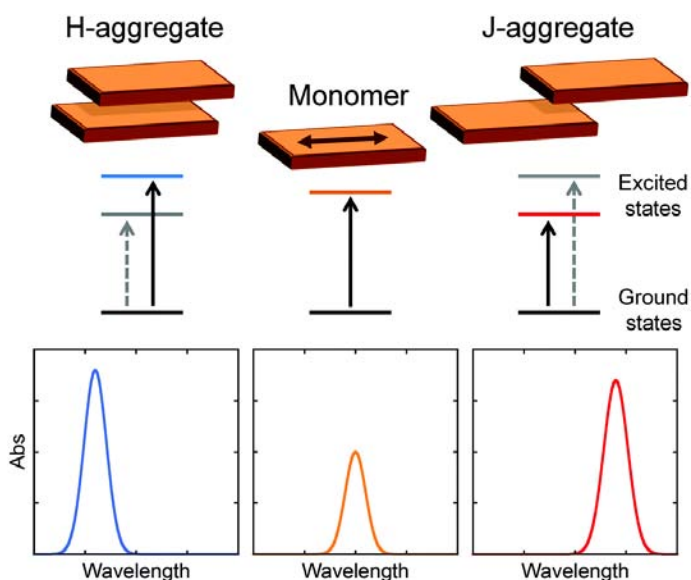


Figure 6. Schematic representation of *H*- and *J*-aggregates and their absorption spectral signatures.

Furhop was one of the pioneers in the study of self-assembled porphyrins in gels and also the study the non covalent chiral fibers of these macrocycles based on derivatives of one of the most

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important natural porphyrins, namely protoporphyrin IX, which exhibit self-assembly in aqueous media due to its amphiphilic character (Figure 7).^{62,63} The fibers that are formed can act as templates for the creation of inorganic and organic nanowires,⁶⁴ leading to multifunctional nanocomposites.⁶⁵

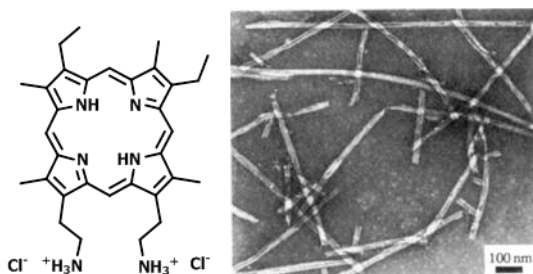


Figure 7. Structure of amine derivative of protoporphyrin IX and TEM image of its fibers.

1.4. Relevant areas for future prospective.

There is presently great research activity into porphyrins; synthesis,^{66,67} catalytic effectiveness,⁶⁸ new applications arising from their electronic¹⁷ and optical properties¹⁶ and also the study of charge transport⁶⁹ in their aggregates.

Chirality together with self-assembly have been studied in recent years by many researchers,^{70,71} although control of helicity in porphyrin stacks through molecular and supramolecular stereochemistry lies practically unexplored. Qiu et al. designed a simple method to prepare self-assembled porphyrins into chiral mesostructured porphyrin-silica hybrids by mean of electrostatic interactions between a cationic organosilane and an anionic water soluble porphyrin into helical stacks.⁷² There, the porphyrin and the chirality are given by the introduction of a chiral agent as dopant element.

So far, in the recent years porphyrins, metalloporphyrins and their derivatives have been receiving great attention because their multiple applications. Photosensitizers used in

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photodynamic therapy (PDT) are one of the applications of porphyrins.⁷³ This therapy has advantages in comparison with others. In the treatment by PDT, cancer cells are irradiated with light that is absorbed by the photosensitizer, in this case a porphyrin. When the photosensitizer returns to its ground state through inter-system crossing singlet oxygen is produced, this is the active cytotoxic agent, destroying the cancer cells. One of the limitations of photosensitizers until now was the weak absorption in the visible region. The advantage of porphyrins as photosensitizers is the absorption in the long wavelength region (600-800 nm) that allows more penetration of light in tissues.

It is well known that porphyrins or metalloporphyrins can be used for catalytic processes because their thermal and metal coordination stability.⁷⁴ The ability of metalloporphyrins to coordinate with sulfur, oxygen and nitrogen compound derivatives made these chromophores suitable for this catalytic purpose.⁷⁵ Metalloporphyrins are involved in catalytic functionalization of saturated C-H bonds via atom/group transfer process.⁷⁶ It is powerful approach to generate new C-O, C-N or C-C bonds from hydrocarbons.

Recently, nanofiber aggregates of porphyrins have been investigating.^{77,78} This kind of molecular organogel system is attractive for applications such as chiroptical tools which are sensitive to changes in temperature, concentration and axial coordination. Jintoku *et al.* investigated the tuning of the self-assembly of L-glutamide containing zinc-porphyrin derivatives with guest molecules in the axial coordination position and the effect on the chiroptical signal.⁷⁹

π -conjugated skeleton of porphyrins made interesting for electron conductivity and together with the optical properties of these chromophores create structures with high impact in the optoelectronic devices.⁸⁰ Therefore, the use of organic polymers as conductive films for further application in optoelectronics are under study to improve the fabrication processes of the inorganic conductors.

As it has been saying, the synthesis of porphyrins to mimicking natural photosynthetic systems has attracted great attention in last years.⁸¹ The development of synthetic light harvesting systems

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based on chromophores covalently linked afforded efficient energy transfer. However, from the synthetic point of view, they are difficult to achieve. Recently, many researchers have focused in the development of artificial light harvesting systems based on self-assembly of dyes which presented similar energy transfer values as natural systems.^{82,83}

Porphyrins and metalloporphyrins also have been used as single molecular units in the field of synthetic molecular machines, such switches or molecular motors that has been inspired by the biomolecular machines.⁸⁴ The different design of the single molecule could tune the properties of the chromophore ring, the fact that different external stimulus such as light, temperature or redox chemistry could be applied for the motion of the molecular motor.

Two main classes of compounds have been used for organic light-emitting diodes (OLEDs) and organic field effect transistors (OFETs), organics and organometallics complexes which presented advantages and disadvantages one respect to the other. Organic conjugated polymers showed easy processability and good electronic properties, nevertheless the low control of their morphology decrease their efficiency in the organic materials. On the other hand, organometallic compounds not presented good processability but in contrast well-ordered thin films are formed for these complexes.⁸⁵ Recently, the design of organic-organometallic complexes have been tested in order to emphasize the advantages of both compounds. In this field metalloporphyrins have been used to alter the morphology of the organic polymer thanks to the π -stacking of the chromophoric cores.⁸⁶

Bearing all these concepts in mind - chirality, porphyrins and self-assembly - this thesis is focused in the study of supramolecular organizations based on chiral porphyrins for future potential applications in areas such light harvesting systems⁸⁷ or electronic and optoelectronic devices.⁸⁸

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