Escuela Superior de Tecnología y Ciencias Experimentales

Departamento de Química Inorgánica y Orgánica

PhD Thesis

New Pseudopeptidic Bis(Amino Amides): Supramolecular Behaviour in the Presence of Transition Metals

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Annex I

Supporting Information – Chapter 4

Cu^{2+}, Zn^{2+} and Ni^{2+} Complexes of C_2-symmetric pseudopeptides with an aromatic central spacer

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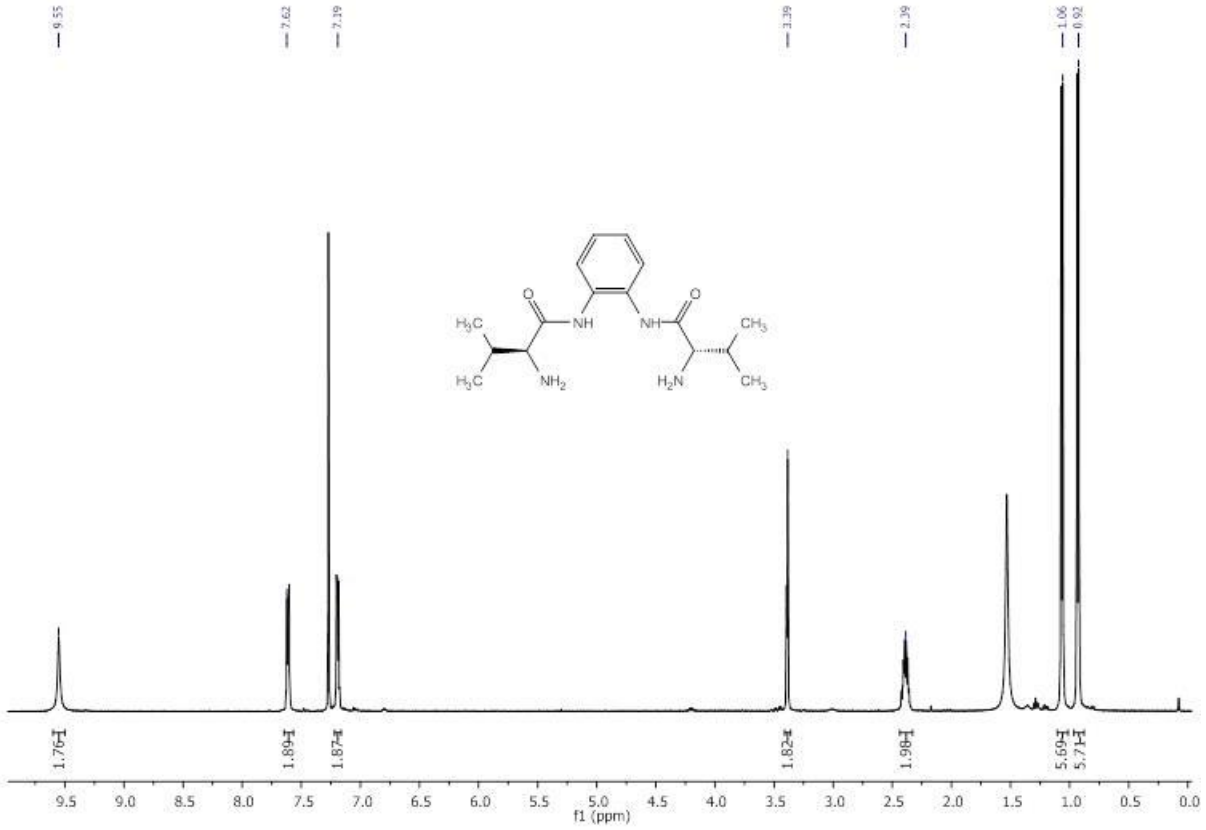


Figure S1. ^{1}H NMR of ligand **5** in $CDCl_3$.

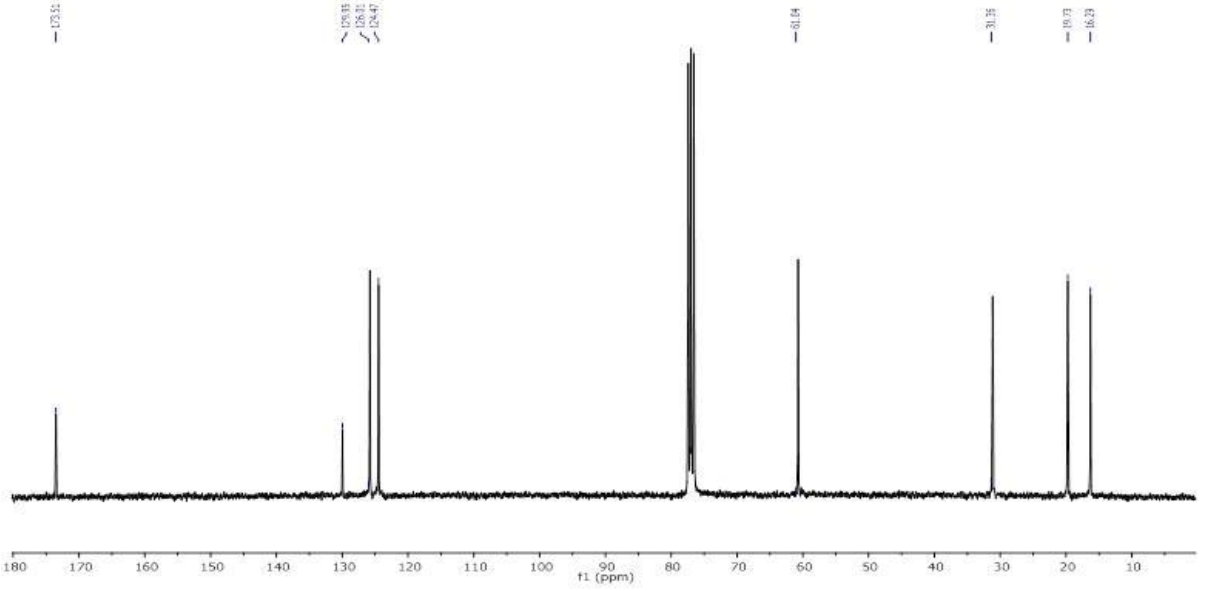


Figure S2. ^{13}C NMR of ligand **5** in $CDCl_3$.

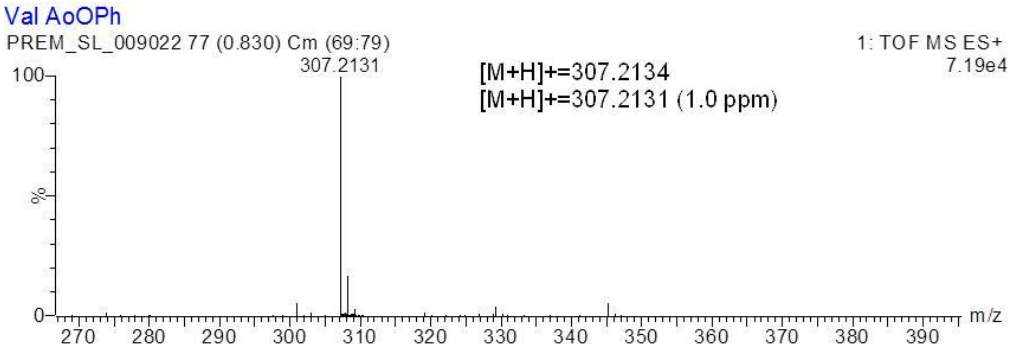


Figure S3. MS of ligand **5**.

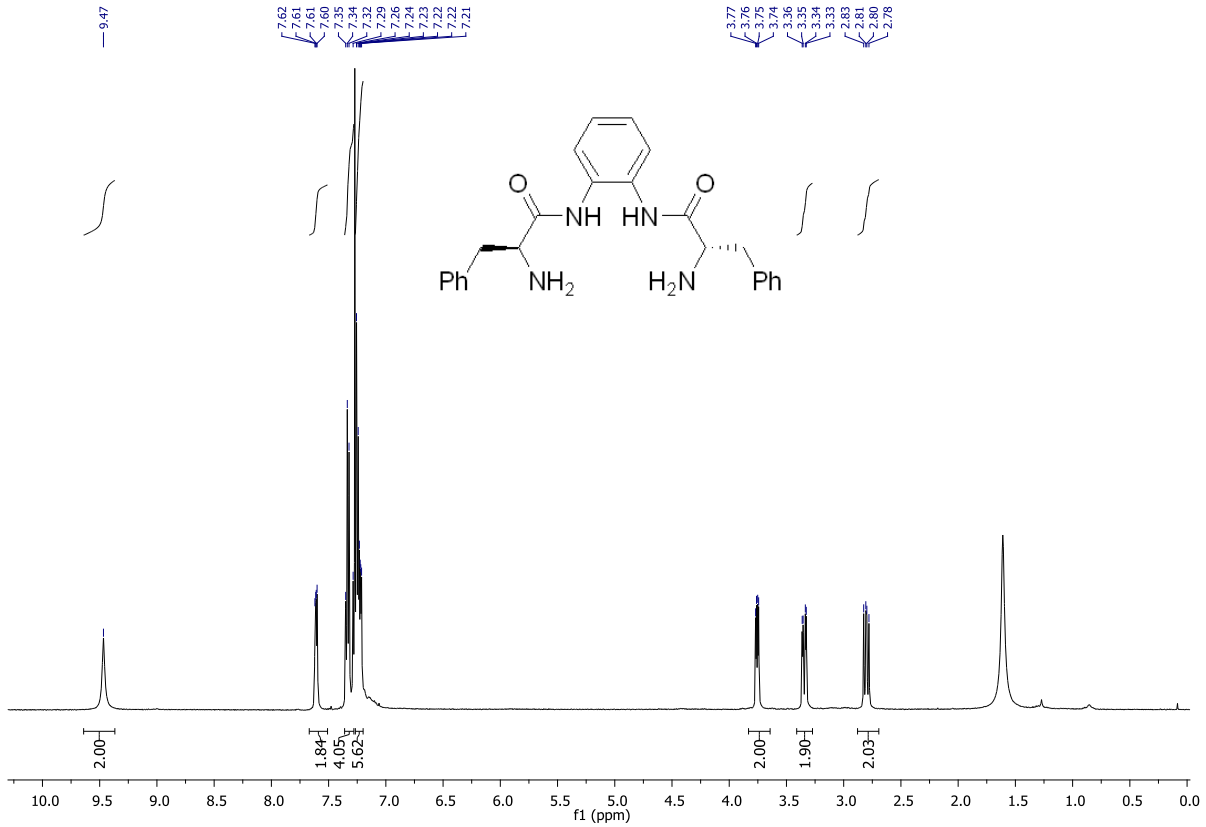


Figure S4. ^{1}H NMR of ligand **6** in $CDCl_3$.

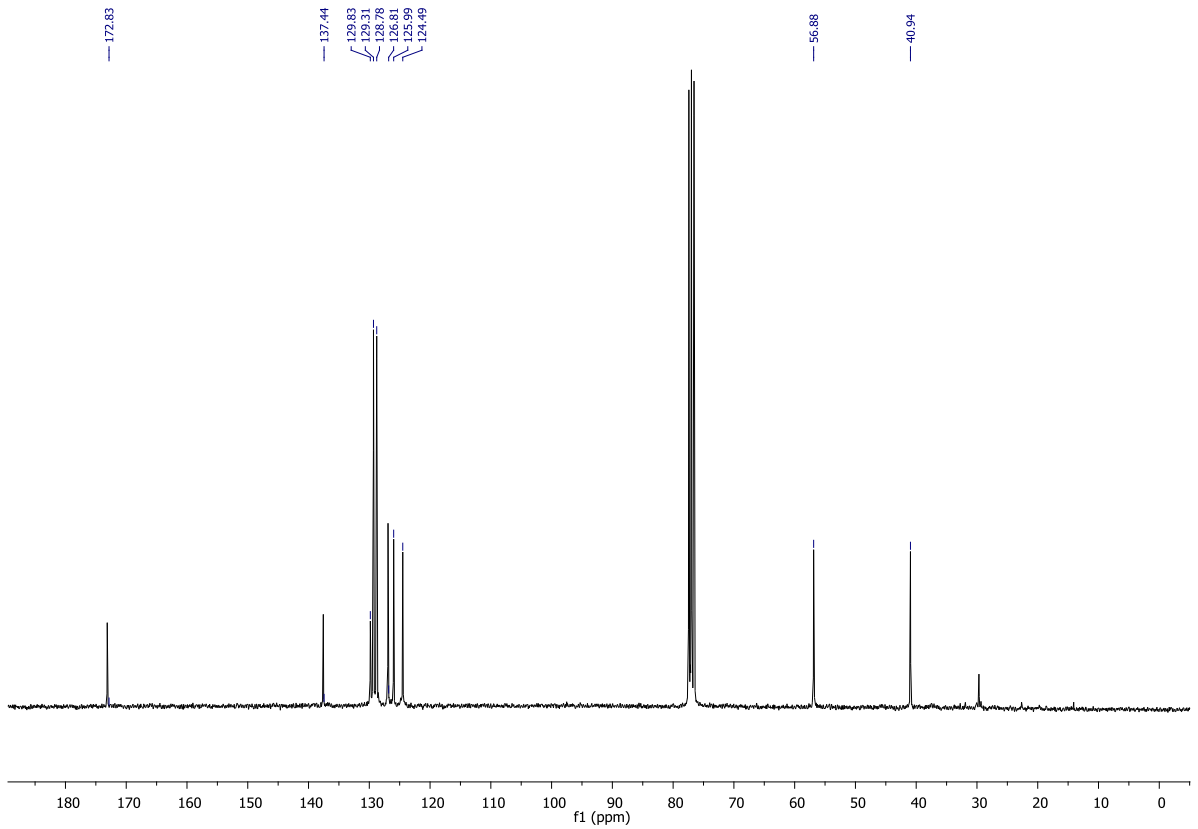


Figure S5. ^{13}C NMR of ligand **6** in $CDCl_3$.

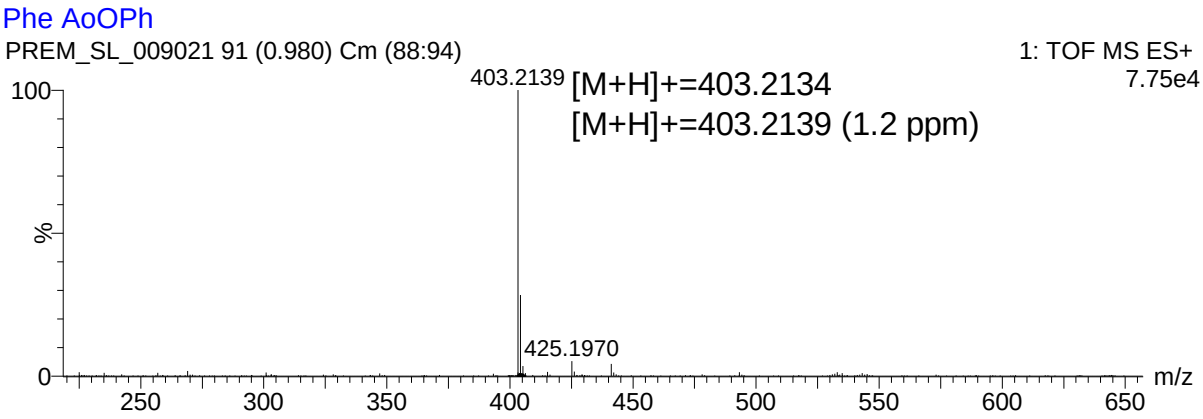


Figure S6. MS of ligand **6**.

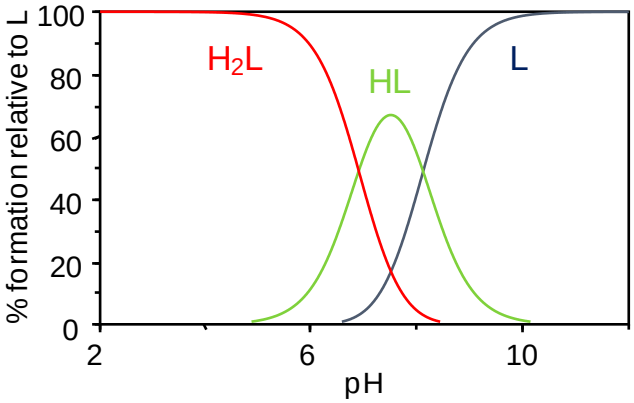


Figure S7. Distribution diagram for the ligand **5** measured in 0.1 M NaCl as a function of pH. Charges have been omitted for clarity.

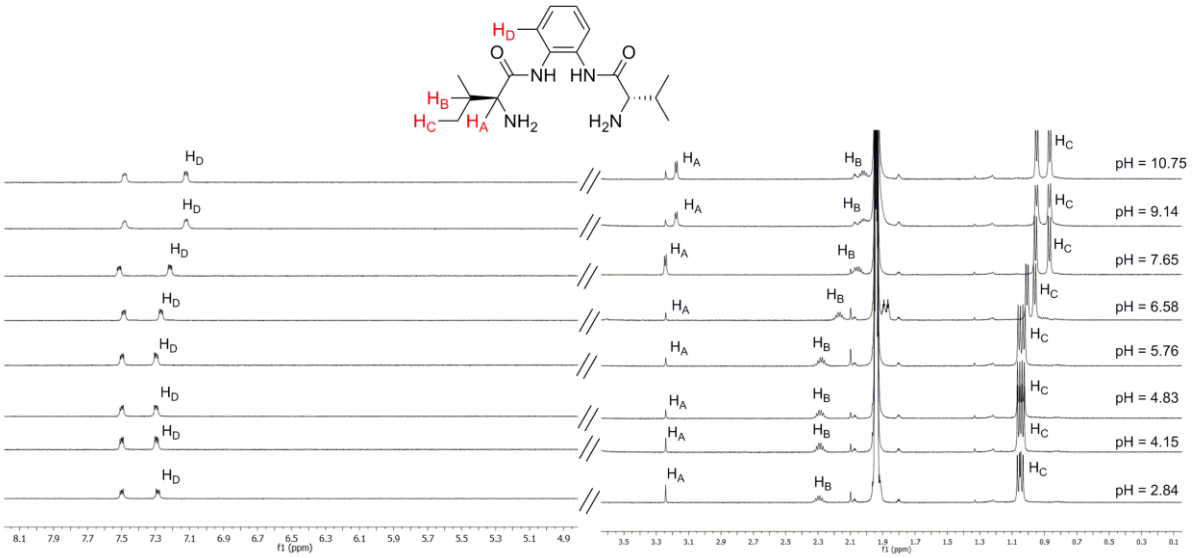
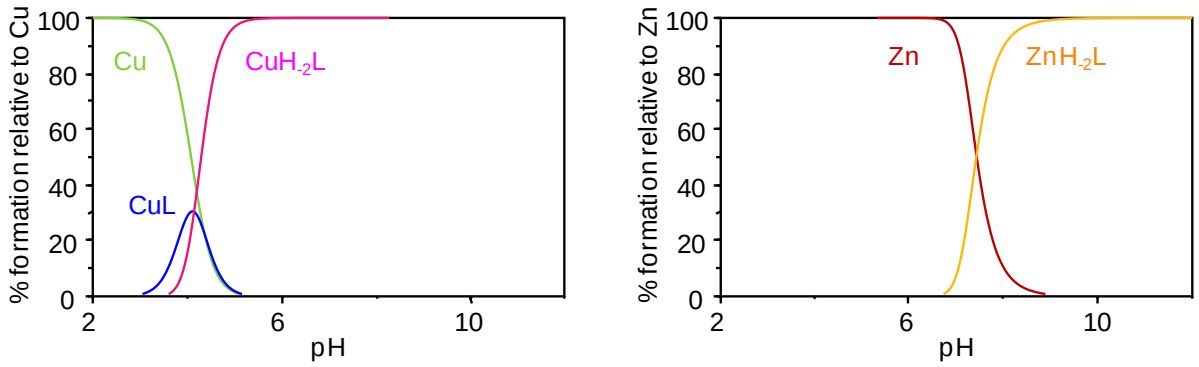


Figure S8. 1H NMR of compound 5 (1 mM) at different pH values in CD_3CN/D_2O 7/3 v/v (from top to bottom, pH values are: 10.75; 9.14; 7.65; 6.58; 5.76; 4.83; 4.15 and 2.84).



(a) **(b)**

Figure S9. Distribution diagrams for ligand **5** with Cu^{2+} (a) and Zn^{2+} (b) as a function of pH using 0.1 M NaCl at 298 ± 0.1 K. Charges have been omitted for clarity. Determined in 0.1 M NaCl using 50 mL solution of a 0.1 mM ligand and $M(OAc)_2$.

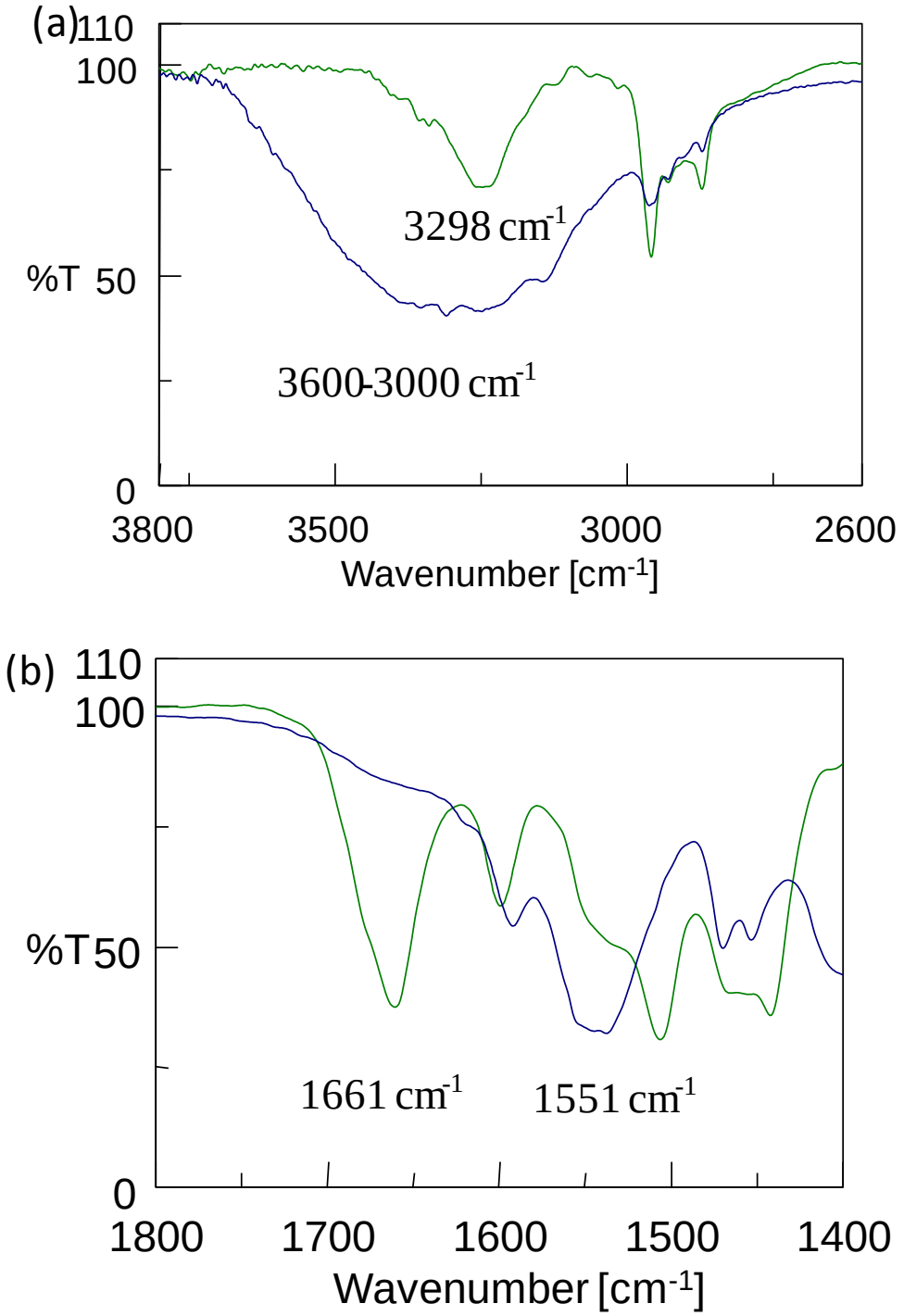
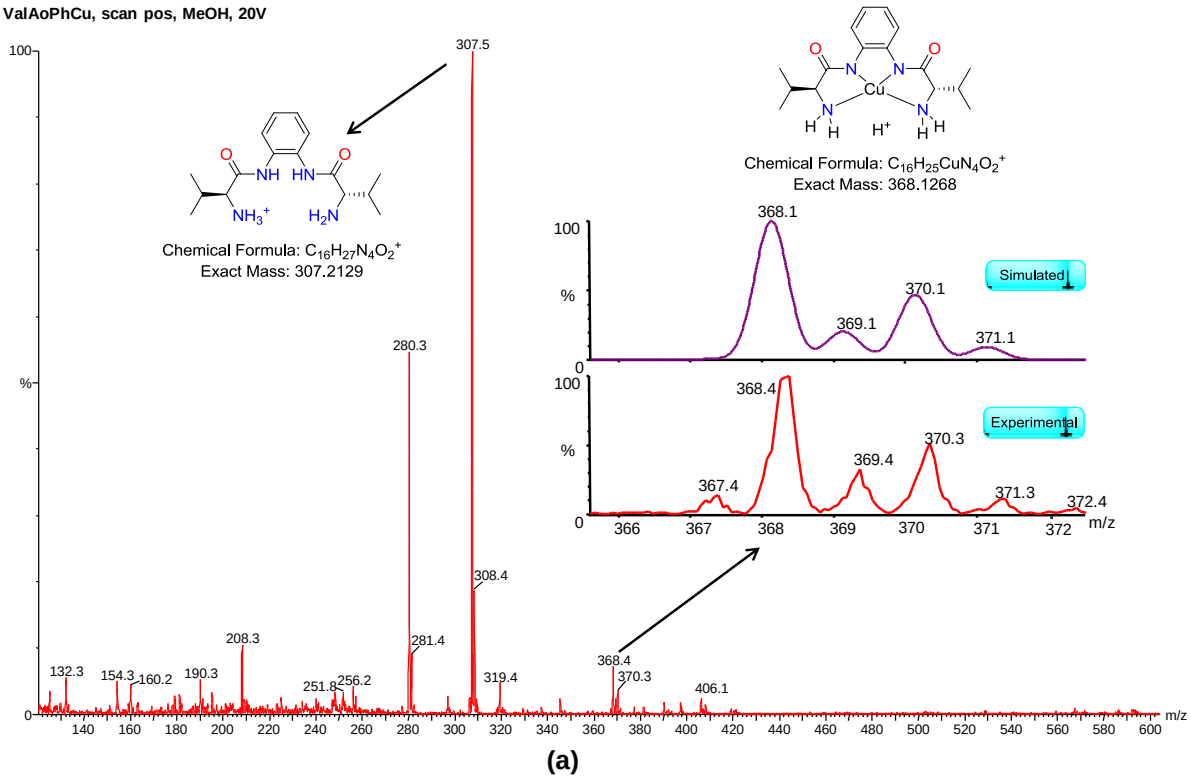
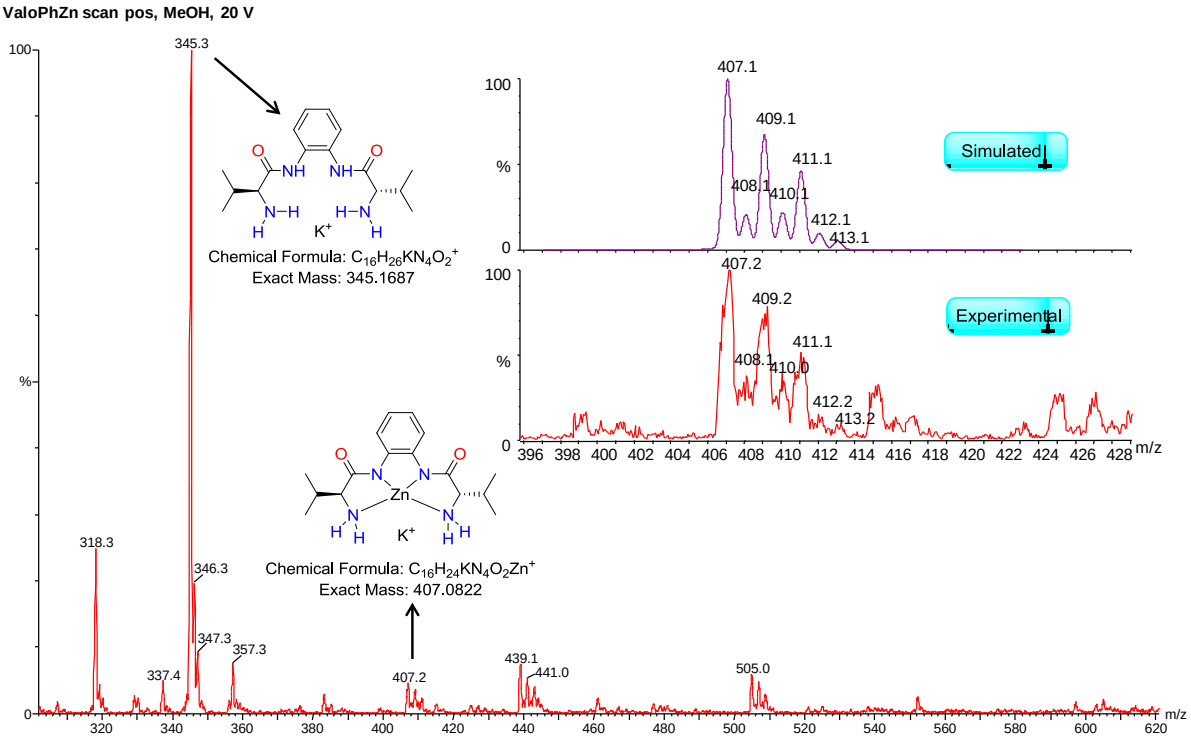


Figure S10. IR spectra for the free ligand **5** (green) and its Cu^{2+} complex **9a** (blue). Changes in the NH (a) and C=O (b) bond stretching frequencies.



(a)



(b)

Figure S11. ESI-MS$^+$ spectra for the systems Cu^{2+}-**5** at pH 4.10 in MeOH (a) and Zn^{2+}-**5** at pH 9.10 in MeOH (b).

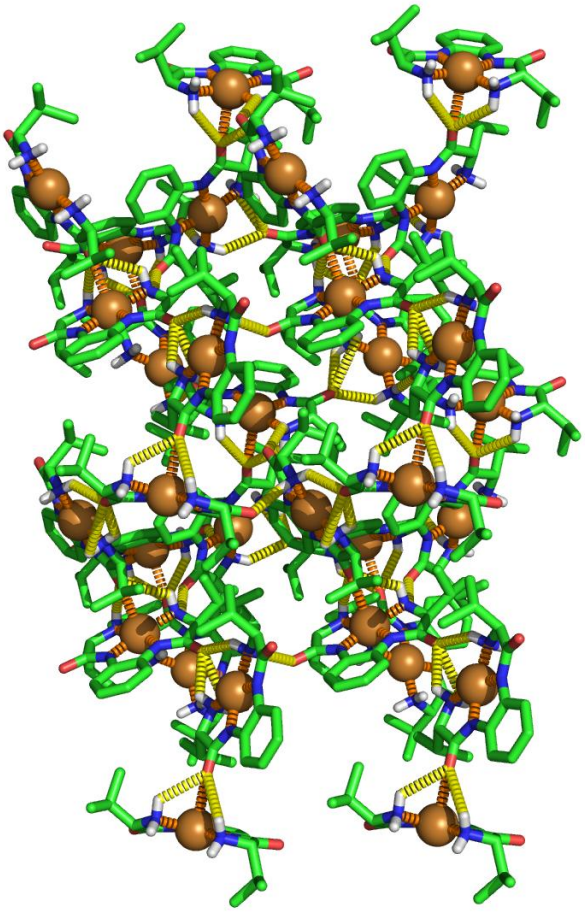


Figure S12. Crystal packing representations found in the solid state structure of the complex **9a**.

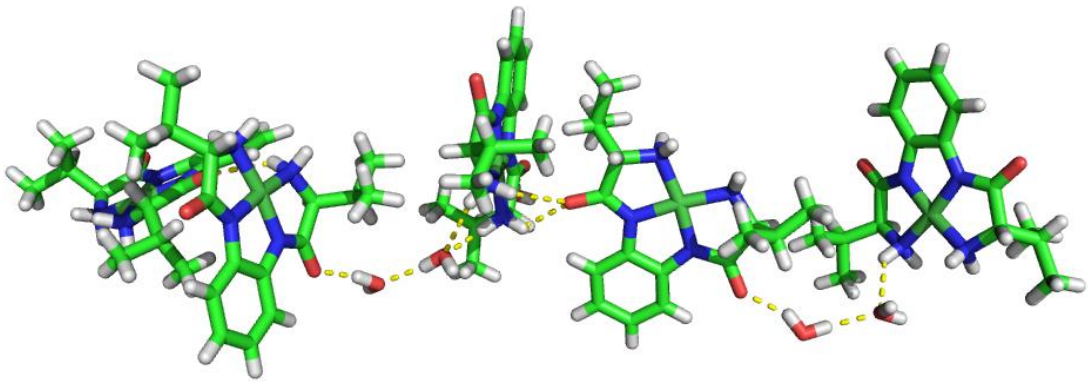


Figure S13. Crystal packing representations found in the solid state structure of the complex **9c**.

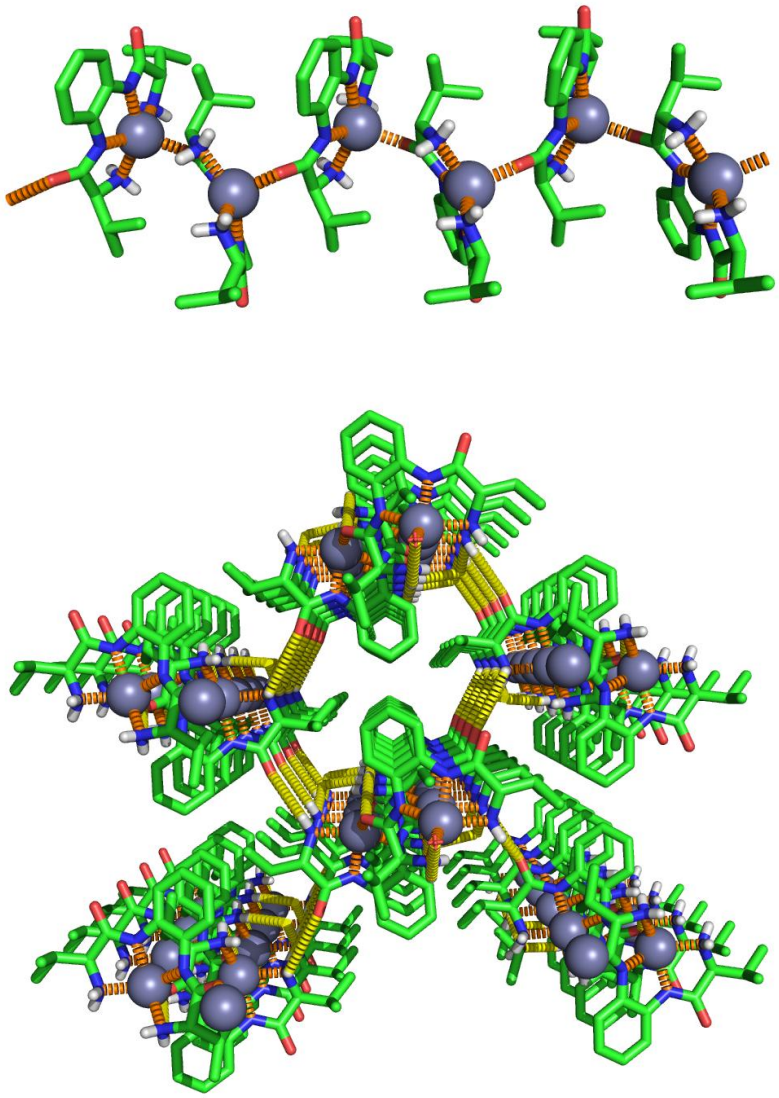


Figure S14. Crystal packing representations found in the solid state structure of the complex **9b**.

Table S1. Crystal data, data collection and refinement parameters of metal complexes **9a-9c**.

	9a	**9b**	**9c**
CCDC number	1474247	1474242	1474246
Temperature/K	293(2)	293(2)	199.95(10)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	11.2386(3)	8.95087(10)	11.1735(3)
b/Å	15.6641(3)	12.63503(10)	15.6927(4)
c/Å	21.5505(5)	19.02315(15)	21.4976(5)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	3793.80(16)	2151.42(3)	3769.44(17)
Z	4	4	4
ρ_{calc}mg/mm^3	1.351	1.327	1.343
m/mm^{-1}	1.799	1.789	1.050
F(000)	1624.0	912.0	1616.0
Crystal size/mm^3	0.36× 0.33 × 0.23	0.30 × 0.05 × 0.04	0.444 × 0.26 × 0.058
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range	6.976 to 145.072°	8.4 to 144.95°	5.866 to 58.902
Index ranges	$-13 \le h \le 11$, $-19 \le k \le 19$, $-25 \le l \le 26$	$-8 \le h \le 10$, $-15 \le k \le 15$, $-22 \le l \le 23$	$-15 \le h \le 14$, $-20 \le k \le 21$, $-29 \le l \le 29$
Reflections collected	18518	19788	41812
Independent reflections	7042 [R_{int} = 0.0586, R_{sigma} = 0.0452]	4202 [R_{int} = 0.0299, R_{sigma} = 0.0208]	9424 [R_{int} = 0.0567, R_{sigma} = 0.0410]
Data/restr./params.	7042/86/541	4202/0/270	9424/3/452
Goodness-of-fit on F^2	1.042	1.045	1.068
R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1306	R_1 = 0.0227, wR_2 = 0.0587	R_1 = 0.0332, wR_2 = 0.0770
R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1349	R_1 = 0.0238, wR_2 = 0.0596	R_1 = 0.0379, wR_2 = 0.0819
Largest diff. peak/hole / e Å^{-3}	0.36/-0.48	0.33/-0.30	0.50/-0.35
Flack parameter	0.01(3)	-0.028(9)	-0.011(4)

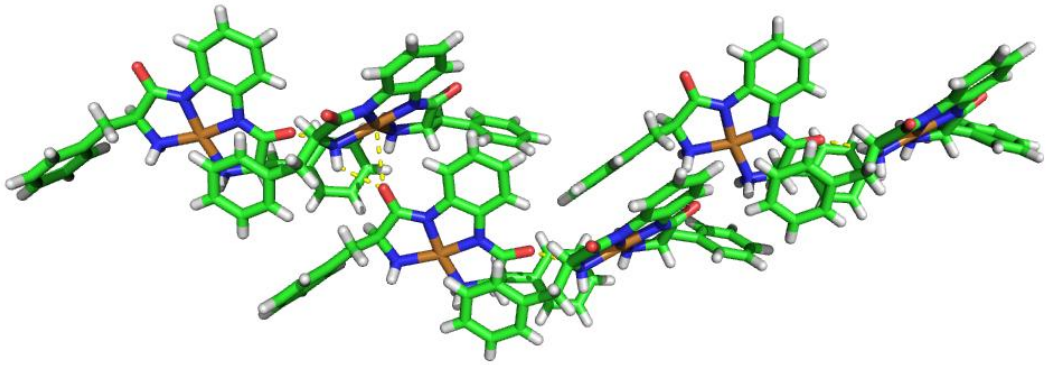


Figure S15. Crystal packing representations found in the solid state structure of the complex **10a.**

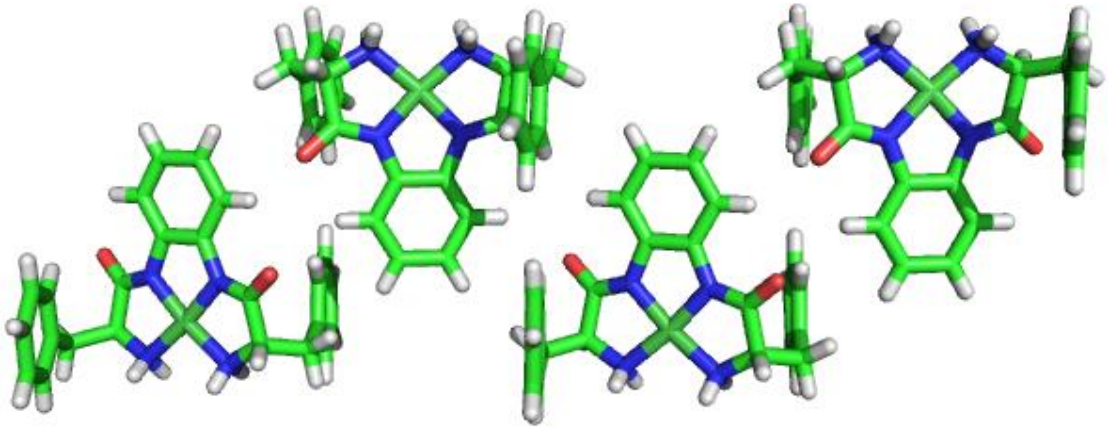


Figure S16. Crystal packing representations found in the solid state structure of the complex **10c**.

Table S2. Crystal data, data collection and refinement parameters of ligand **6** and metal complexes **10a** and **10c**.

	6	**10a**	**10c**
CCDC number	1474244	1474243	1474245
Temperature/K	293(2)	199.95(10)	200
Crystal system	triclinic	triclinic	tetragonal
Space group	P1	P1	$P4_12_12$
a/Å	8.6682(2)	10.1351(2)	11.81680(10)
b/Å	14.7652(3)	10.5175(2)	11.81680(10)
c/Å	18.3708(4)	11.9667(2)	14.84740(18)
α/°	71.785(2)	81.1495(17)	90
β/°	88.7145(19)	67.742(2)	90
γ/°	76.039(2)	62.348(2)	90
Volume/$Å^3$	2163.85(9)	1045.35(4)	2073.24(4)
Z	4	1	8
$\rho_{calc}mg/mm^3$	1.235	1.474	1.477
m/mm^{-1}	0.642	1.711	1.639
F(000)	856.0	482.0	960.0
Crystal size/mm^3	0.2458 × 0.1942 × 0.163	0.51 × 0.33× 0.17	0.2616 × 0.2186 × 0.1611
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range	6.866 to 144.342°	7.98 to 145.46°	9.566 to 144.994
Index ranges	$-10 \le h \le 10$, $-18 \le k \le 17$, $-22 \le l \le 22$	$-12 \le h \le 12$, $-13 \le k \le 12$, $-14 \le l \le 14$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-18 \le l \le 17$
Reflections collected	72801	17715	19255
Independent reflections	16027 [R_{int} = 0.0876, R_{sigma} = 0.0470]	7408 [R_{int} = 0.0221, R_{sigma} = 0.0199]	2060 [R_{int} = 0.0279, R_{sigma} = 0.0103]
Data/restr./params.	16027/4/1177	7408/3/559	2060/0/149
Goodness-of-fit on F^2	1.052	1.053	1.109
R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1454	R_1 = 0.0274, wR_2 = 0.0741	R_1 = 0.0218, wR_2 = 0.0595
R indexes [all data]	R_1 = 0.0598, wR_2 = 0.1552	R_1 = 0.0275, wR_2 = 0.0743	R_1 = 0.0223, wR_2 = 0.0599
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.19	0.24/-0.53	0.16/-0.15
Flack parameter	0.05(15)	-0.019(12)	0.005(8)

Table S3. Hydrogen Bonds for **6**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3D	H3D	O2C[1]	0.90(4)	2.08(4)	2.830(4)	140(4)
C7D	H7D	O2D	0.95	2.27	2.883(6)	121.2
N4C	H4CA	O1D	0.83(5)	2.03(5)	2.845(4)	167(4)
N3A	H3A	O2B[2]	0.88(5)	2.10(5)	2.869(4)	144(4)
C7A	H7A	O2A	0.95	2.26	2.874(5)	121.4
N4B	H4BA	O1A	0.92(5)	1.97(5)	2.863(4)	164(4)

[1]1+X,+Y,+Z; [2]-1+X,+Y,+Z

Table S4. Hydrogen Bonds for **9a**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2A	O2A[1]	0.85(3)	2.04(4)	2.859(6)	163(8)
O2	H2B	O1A[2]	0.85(3)	1.87(3)	2.712(6)	171(8)
O1	H1E	O2[2]	0.85(3)	2.01(3)	2.849(6)	169(9)
O1	H1F	O1B	0.85(3)	1.98(5)	2.747(6)	150(8)
N1A	H1AB	O1[3]	0.89(3)	2.02(4)	2.885(7)	161(9)

[1]2-X,-1/2+Y,1/2-Z; [2]1-X,-1/2+Y,1/2-Z; [3]1/2+X,3/2-Y,1-Z

Table S5. Hydrogen Bonds for **9b**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H3	O2[1]	0.84(4)	1.86(4)	2.694(3)	172(4)

[1]3/2-X,1-Y,-1/2+Z

Table S6. Hydrogen Bonds for **9c**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2A	O2A	0.87(2)	1.83(3)	2.695(3)	170(5)
O1	H1C	O2[1]	0.85	2.02	2.857(4)	170.2
O1	H1D	O2B[2]	0.85	1.96	2.726(3)	149.0

[1]-1/2+X,1/2-Y,1-Z; [2]-1/2+X,3/2-Y,1-Z

Table S7. Hydrogen Bonds for **10a**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1A	H1AA	O2B[1]	0.89	1.96	2.818(3)	161.8
N1A	H1AB	O1B	0.89	2.22	2.825(3)	124.4
N1B	H1BA	O1A[2]	0.89	1.99	2.861(4)	164.4
N1B	H1BB	O2A[3]	0.89	2.01	2.859(3)	159.9

[1]+X,+Y,-1+Z; [2]1+X,+Y,+Z; [3]1+X,-1+Y,+Z

Annex II

Supporting Information - Chapter 5

Selective Cu^{2+} recognition by N,N'-benzylated bis(amino amides)

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Figure S13	LOD determination of **4**:Cu^{2+} complex from serial dilutions of a 2.5 mM solution of the complex by CD experiments in the presence of added base
Figure S14	Identification of Cu^{2+} in the presence of other metal cations using ligand **4** in the absence of added base
Figure S15	ESI mass spectra for ligand **4** in the presence of equimolecular amounts of different metals

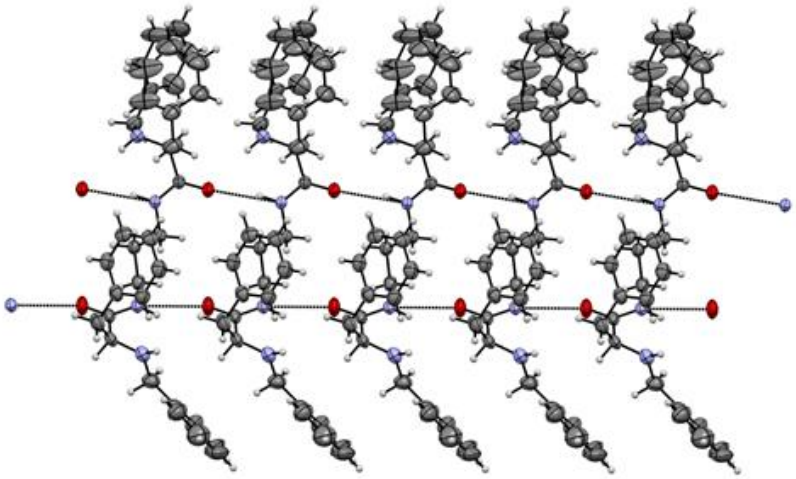


Figure S1. Packing found in the X-ray crystal structure of ligand **3**.

Identification code	**3**	**5a**	**5b**	**6a**	**6b**
Empirical formula	$C_{35}H_{40}N_4O_2$	$C_{35}H_{42}CuN_4O_4$	$C_{35}H_{42}N_4NiO_4$	$C_{27}H_{40}CuN_4O_3$	$C_{27}H_{40}N_4NiO_3$
Formula weight	548.71	646.26	641.43	532.17	527.34
Temperature/K	293(2)	297.9(6)	150.0	141(20)	199.95(10)
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	14.9282(3)	9.6591(3)	10.35136(10)	10.8225(2)	11.0695(3)
b/Å	5.14524(8)	15.9975(4)	15.75766(13)	15.3302(3)	15.2253(4)
c/Å	19.5488(3)	10.4363(3)	19.30342(19)	16.2148(3)	16.1040(5)
α/°	90	90	90	90	90
β/°	98.3145(16)	97.225(3)	90	90	90
γ/°	90	90	90	90	90
Volume/$Å^3$	1485.75(4)	1599.82(8)	3148.64(5)	2690.22(9)	2714.11(13)
Z	2	2	4	4	4
$\rho_{calc}g/cm^3$	1.227	1.342	1.353	1.314	1.291
μ/mm^{-1}	0.602	0.727	1.250	0.846	0.749
F(000)	588.0	682.0	1360.0	1132.0	1128.0
Crystal size/mm^3	0.042 × 0.079 × 0.851	0.39 × 0.275 × 0.105	0.3663 × 0.1019 × 0.0671	0.133 × 0.173 × 0.390	0.2208 × 0.1231 × 0.0868
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.984 to 145.248	5.986 to 51.996	7.242 to 144.258	5.684 to 58.19	5.724 to 58.558
Index ranges	$-18 \le h \le 18$, $-6 \le k \le 6$, $-24 \le l \le 24$	$-11 \le h \le 11$, $-19 \le k \le 19$, $-12 \le l \le 12$	$-9 \le h \le 12$, $-19 \le k \le 19$, $-23 \le l \le 23$	$-14 \le h \le 13$, $-20 \le k \le 20$, $-20 \le l \le 21$	$-14 \le h \le 15$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	27124	30342	29035	29728	30689
Independent reflections	5829 [R_{int} = 0.0497, R_{sigma} = 0.0302]	6280 [R_{int} = 0.0647, R_{sigma} = 0.0379]	6132 [R_{int} = 0.0459, R_{sigma} = 0.0309]	6665 [R_{int} = 0.0543, R_{sigma} = 0.0466]	6801 [R_{int} = 0.0547, R_{sigma} = 0.0434]
Data/restraints/parameters	5829/488/491	6280/7/329	6132/8/421	6665/2/338	6801/2/331
Goodness-of-fit on F^2	1.021	1.036	0.948	1.095	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0527, wR_2 = 0.1409	R_1 = 0.0361, wR_2 = 0.0917	R_1 = 0.0377, wR_2 = 0.0972	R_1 = 0.0340, wR_2 = 0.0700	R_1 = 0.0392, wR_2 = 0.0859
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.1463	R_1 = 0.0401, wR_2 = 0.0954	R_1 = 0.0459, wR_2 = 0.1021	R_1 = 0.0408, wR_2 = 0.0738	R_1 = 0.0521, wR_2 = 0.0947
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.25	0.41/-0.29	0.71/-0.24	0.36/-0.43	0.67/-0.24
Flack parameter	0.14(19)	-0.005(7)	-0.020(10)	-0.001(5)	-0.020(6)

Table S1. Crystallography table of ligand **3 &** Complexes **5a–6b**.

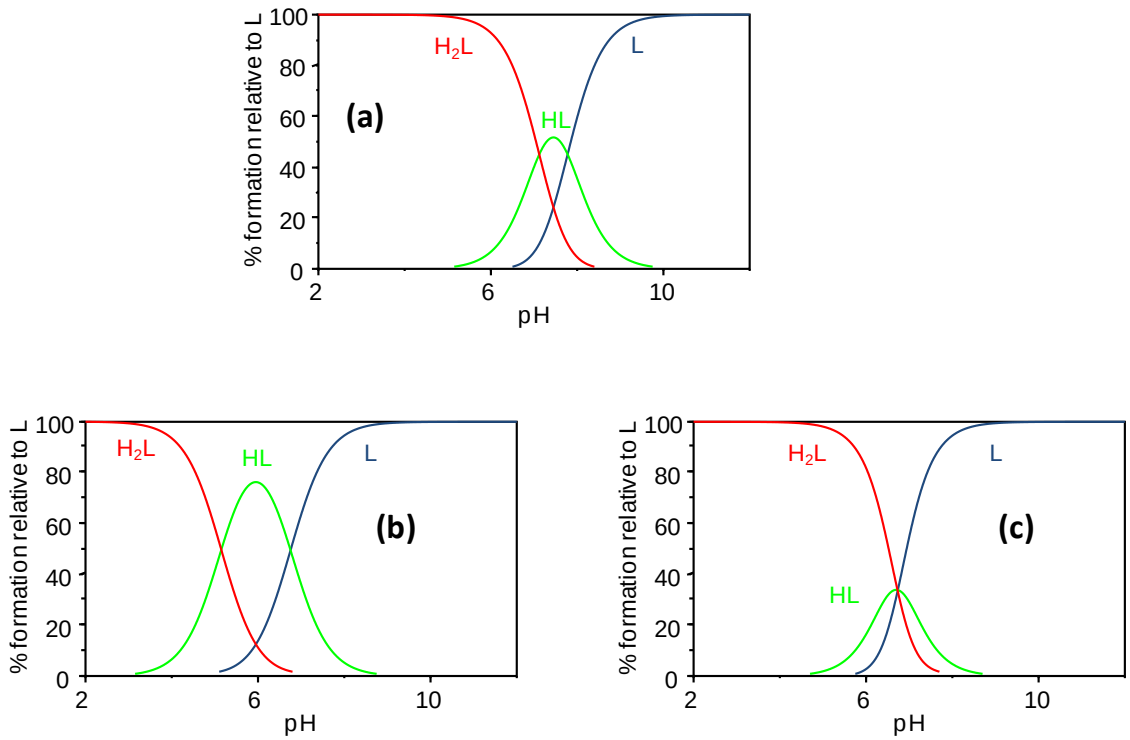


Figure S2. Distribution diagrams for the protonated species of ligand **2** (a), ligand **3** (b) and ligand **4** (c) as a function of pH in 0.1 M NaCl/ACN 7/3 v/v at 298 K. Charges have been omitted for clarity.

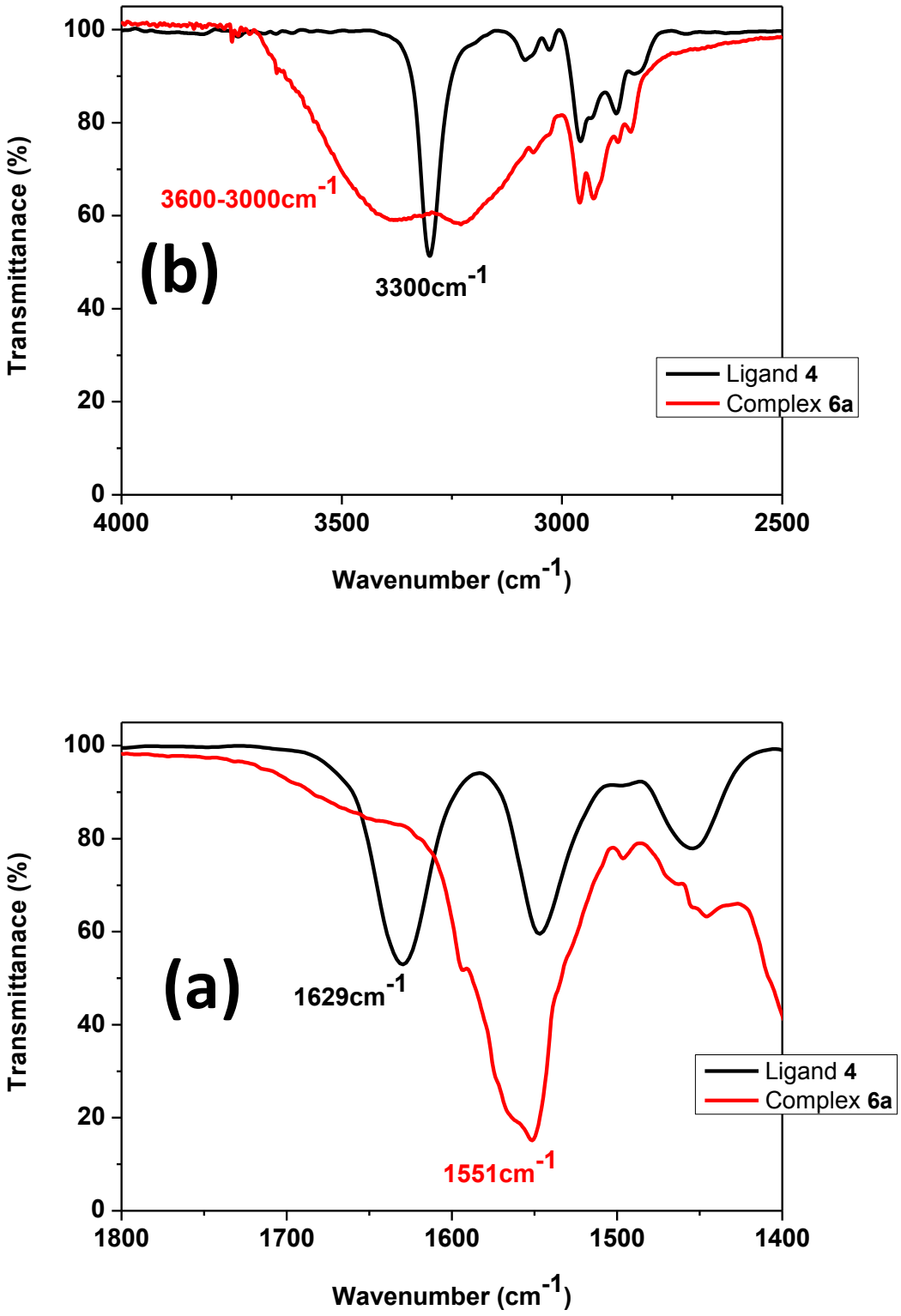


Figure S3. Comparison of FT-IR spectroscopy of ligand **4** and complex **6a** (a) Change in C=O (b) Change in NH band stretching frequencies.

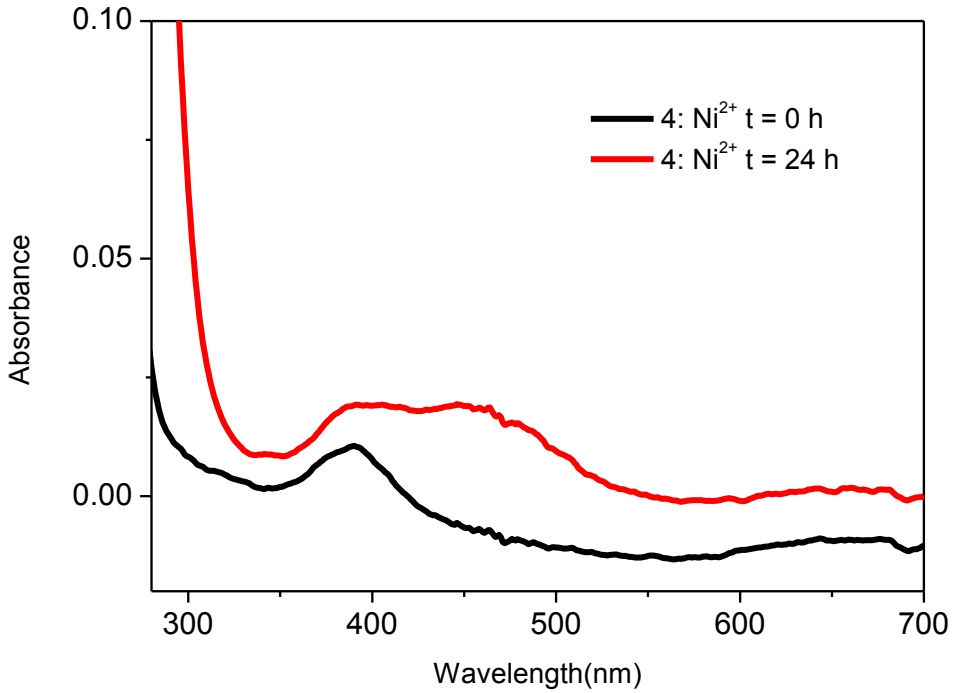


Figure S4. Comparison of UV-Visible spectra for Ni^{2+} complex with ligand **4** (t = 0 h and 24 h). 2.5 mM of $Ni(OAc)_2$ and 30 mM of ligand **4** in MeOH/H_2O 80/20 v/v.

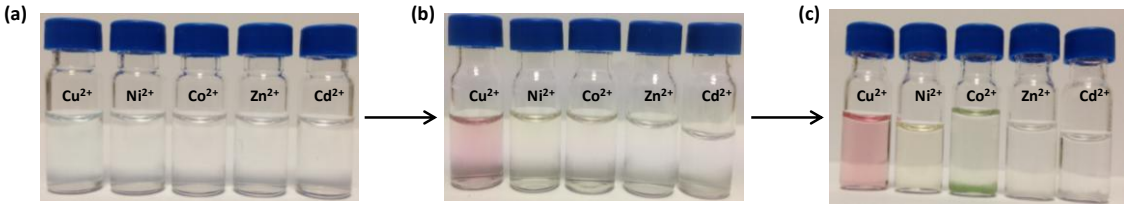
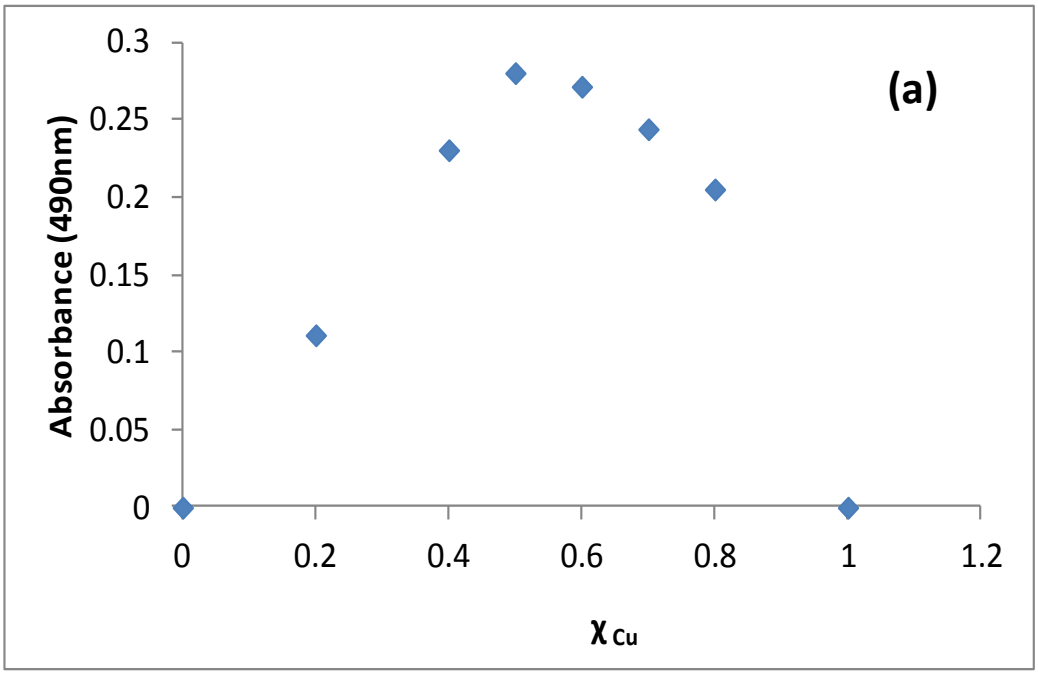


Figure S5. Pictures of vials containing solutions of different metals before and after addition of ligand **4** and base: (a) 2.5 mM solutions of different metal salts in MeOH/H_2O 80/20 v/v; (b) Change of colour upon addition of 1.2 equiv. of the pseudopeptidic ligand; (c) Vials from b after addition of 0.1 M NaOH (2 equiv.).

Table S2. Change in pH of different solutions.

S No	M^{2+}	pH for M^{2+} solution (2.5 mM)	pH for M^{2+}:L (1:1) solution	pH for M^{2+} L (1:1) solution after adding 2 equiv. of 0.1 M NaOH
1	Cu^{2+}	6.0	6.4	9.1
2	Ni^{2+}	6.6	6.7	9.3
3	Co^{2+}	7.2	6.5	9.4
4	Zn^{2+}	7.3	6.2	9.1
5	Cd^{2+}	6.3	7.1	9.8



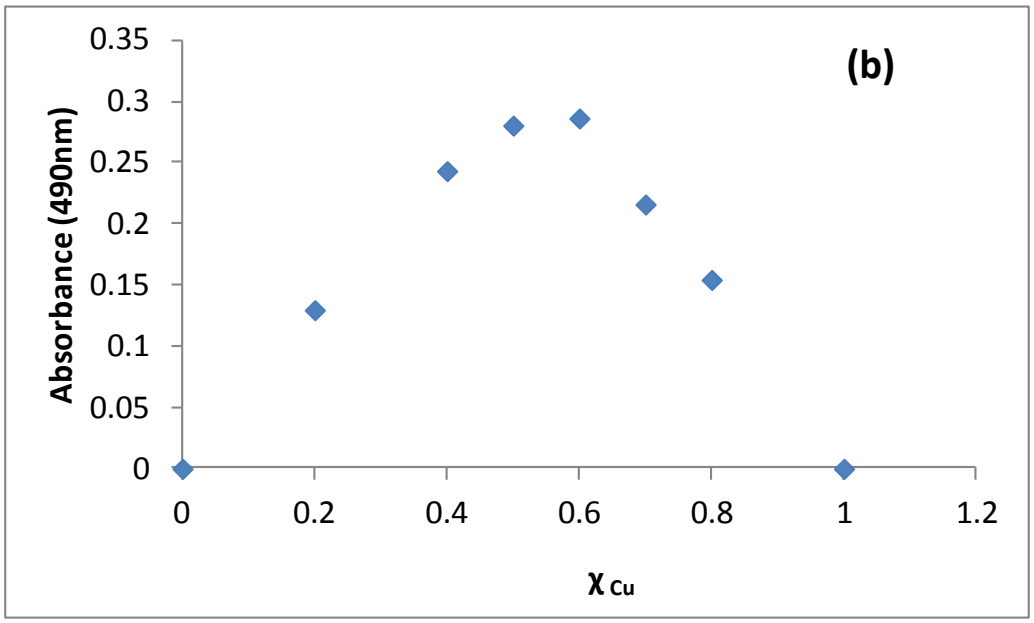


Figure S6. Job plot for ligand **4** (5 mM) and $Cu(OAc)_2$ (5 mM) in MeOH/H_20 80/20 v/v in neutral (a) and basic media (b). Total concentration is 5 mM, MeOH/H_2O 80/20 v/v. The titration protocol is as follows

1. 1 mL Ligand **4** (5 mM) - Measured Absorbance
2. 800 µL Ligand **4** + 200 µL $Cu(OAc)_2$
3. 700 µL Ligand **4** + 300 µL $Cu(OAc)_2$
4. 600 µL Ligand **4** + 400 µL $Cu(OAc)_2$
5. 500 µL Ligand **4** + 500 µL $Cu(OAc)_2$
6. 400 µL Ligand **4** + 600 µL $Cu(OAc)_2$
7. 300 µL Ligand **4** + 700 µL $Cu(OAc)_2$
8. 200 µL Ligand **4** + 800 µL $Cu(OAc)_2$
9. 1 mL $Cu(OAc)_2$ (5 mM)

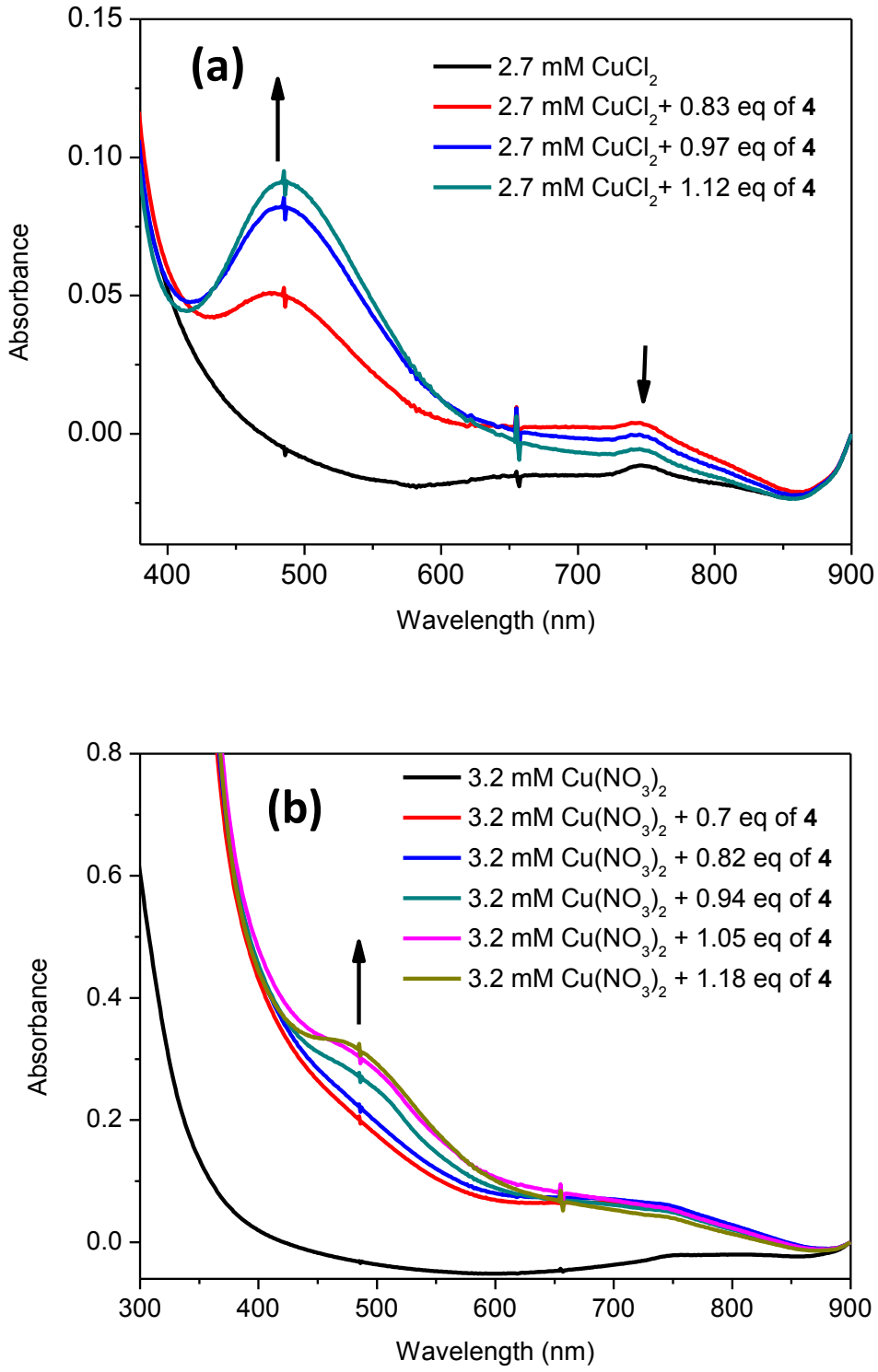


Figure S7. UV-Vis titration of ligand **4** with $CuCl_2$ (a) and $Cu(NO_3)_2$ (b) in the absence of added base in MeOH/H_2O 80/20 v/v.

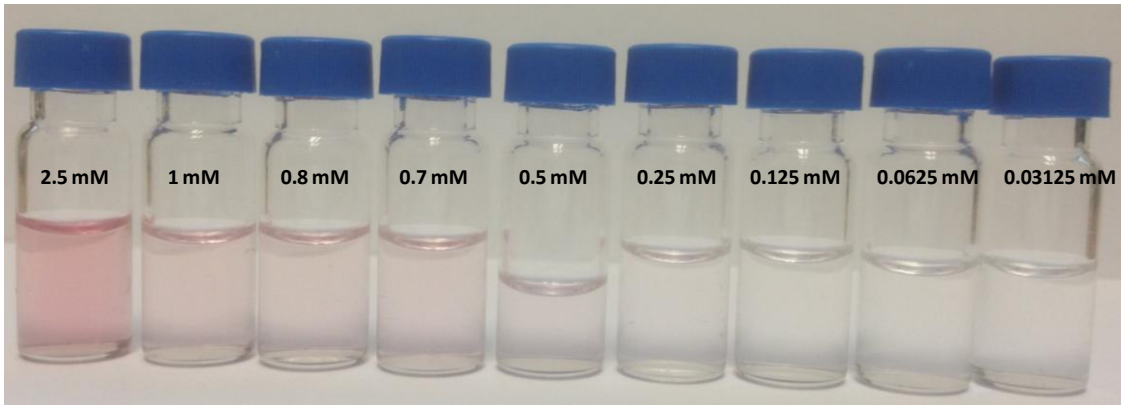
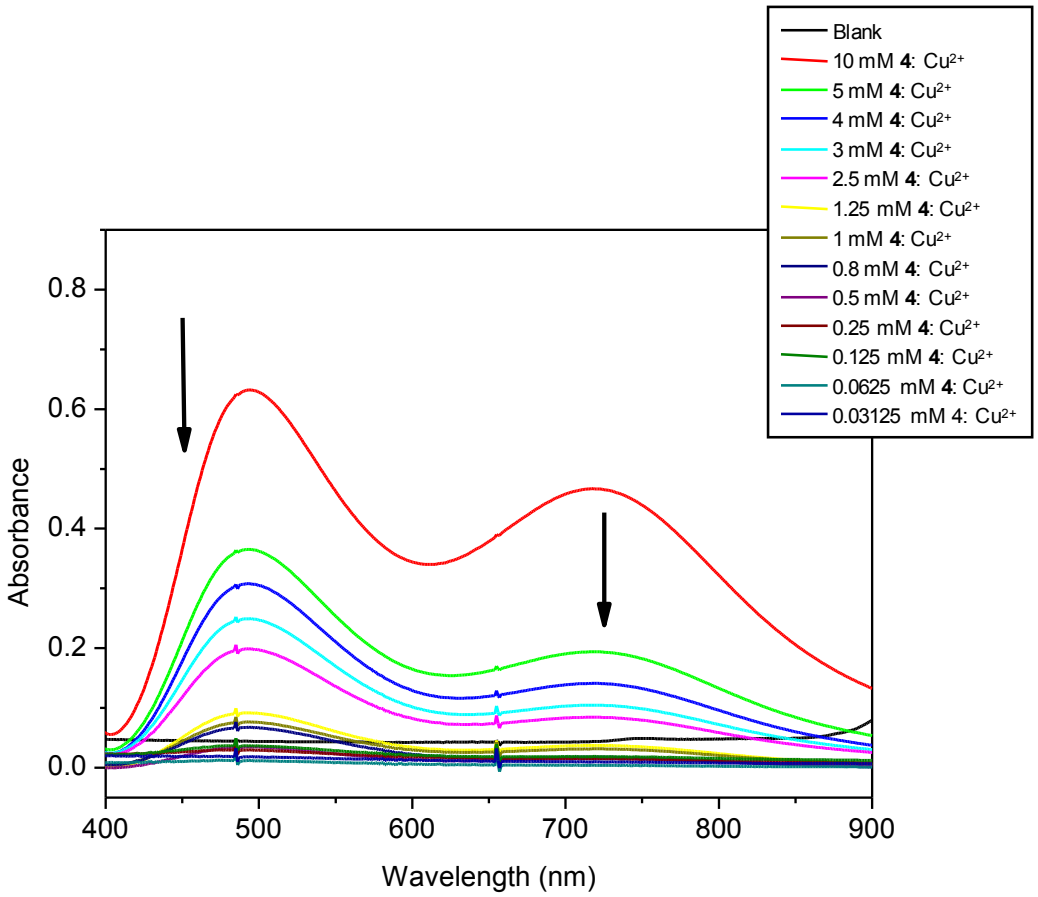


Figure S8. Naked eye LOD determination of Cu^{2+}.**4** complexes after adding the 2 equiv. of base (0.1 M NaOH in water).



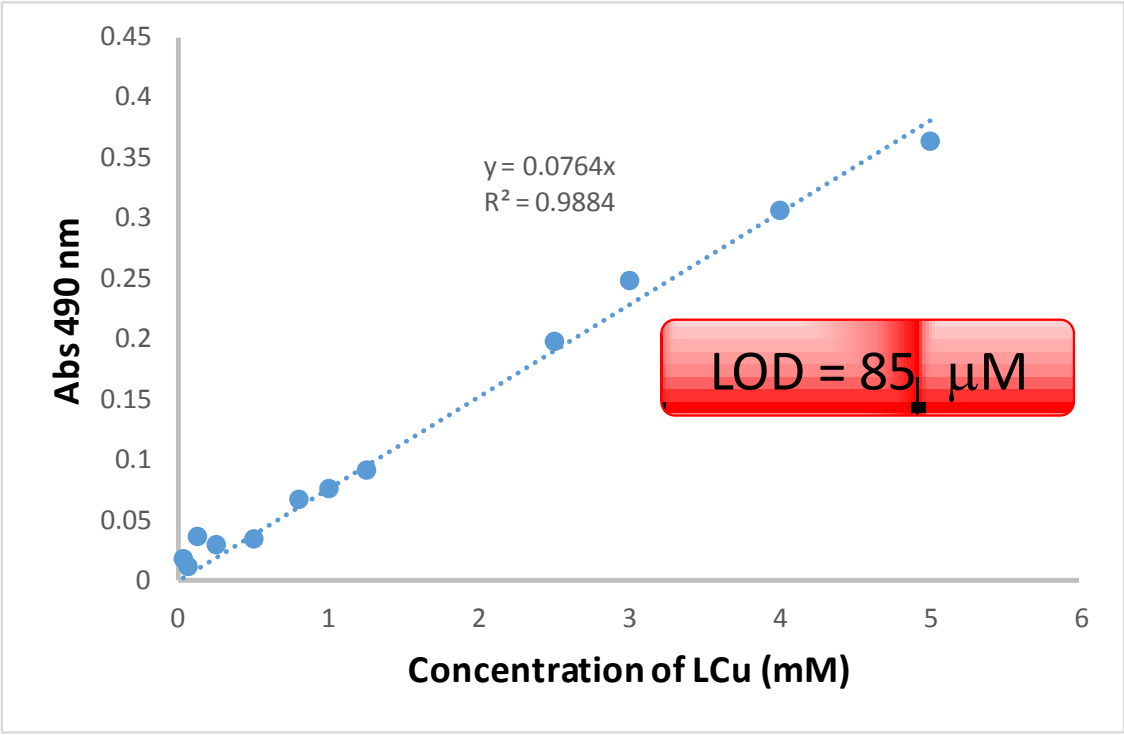
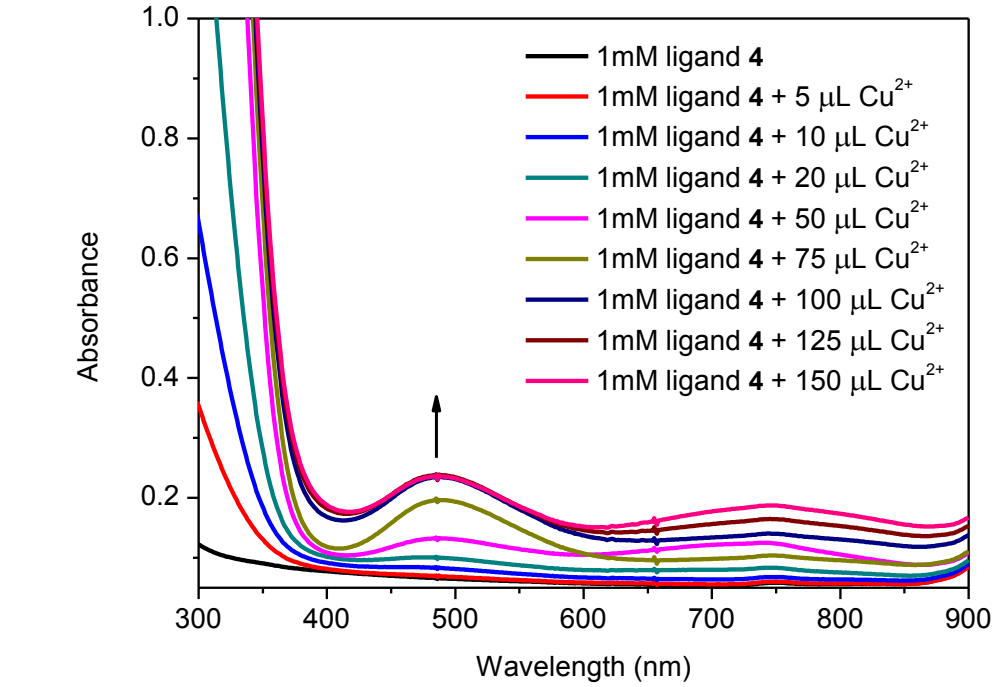


Figure S9. LOD determination by UV-Visible experiments for the **4**:Cu^{2+} complex from dilutions of a 10 mM solution of the complex ((MeOH/H_2O 80/20, v/v) without added base.



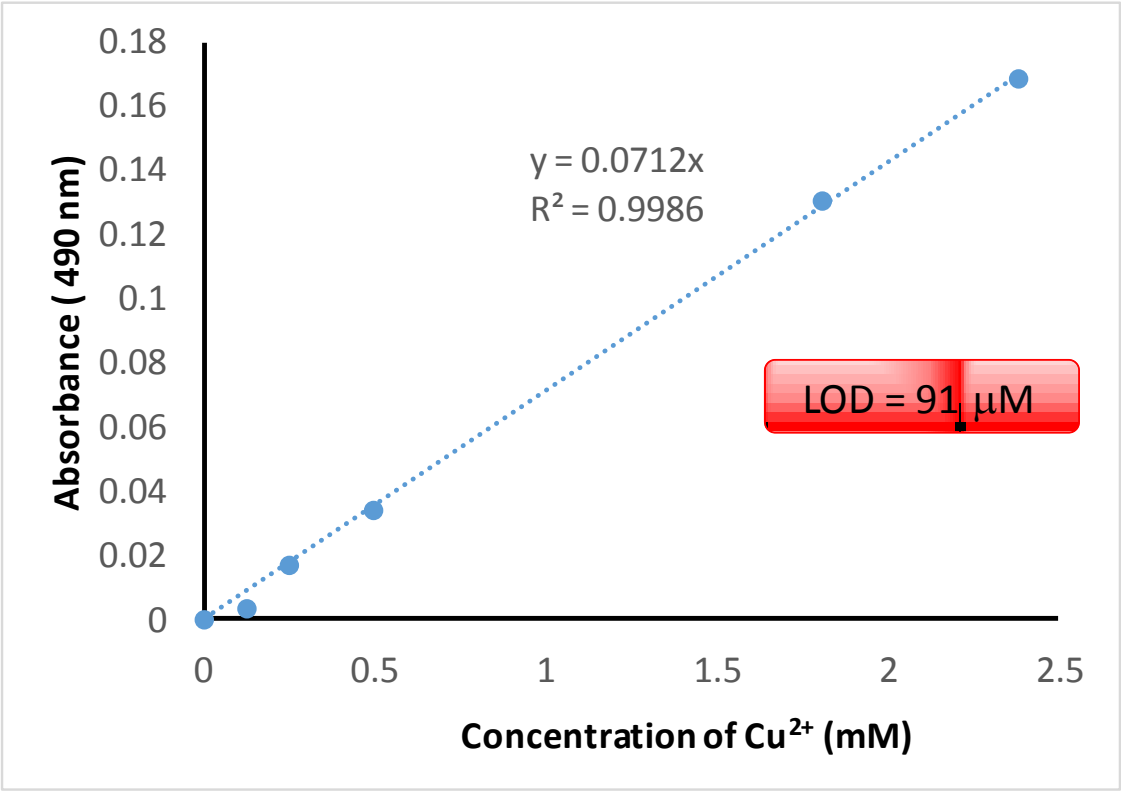
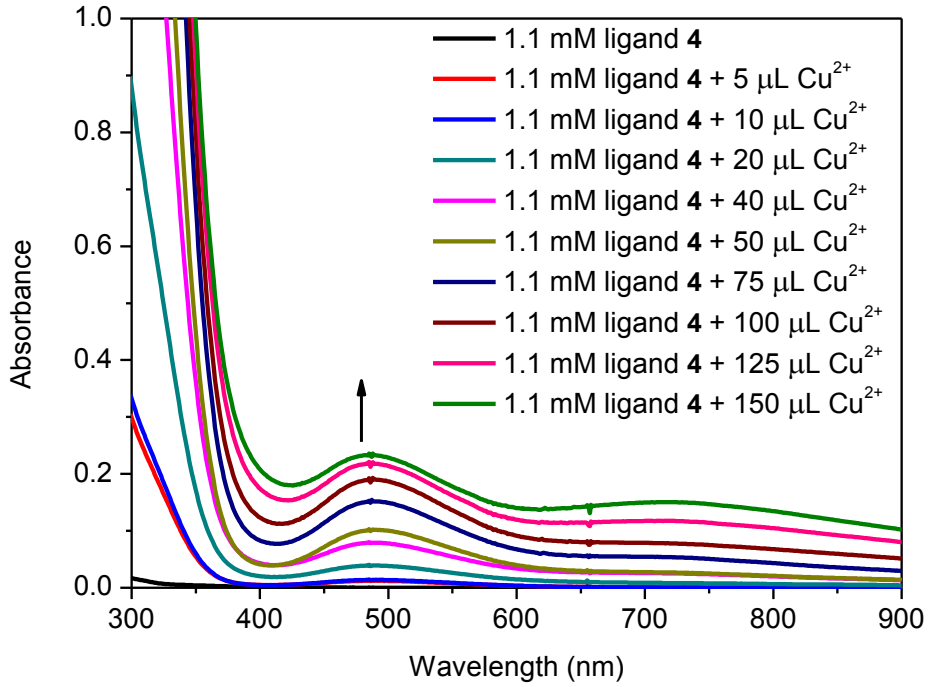


Figure S10. LOD determination by UV-Visible experiments for Cu^{2+} starting from a 1 mM solution of ligand **4** and adding increasing amounts of Cu^{2+} in the absence of added base.



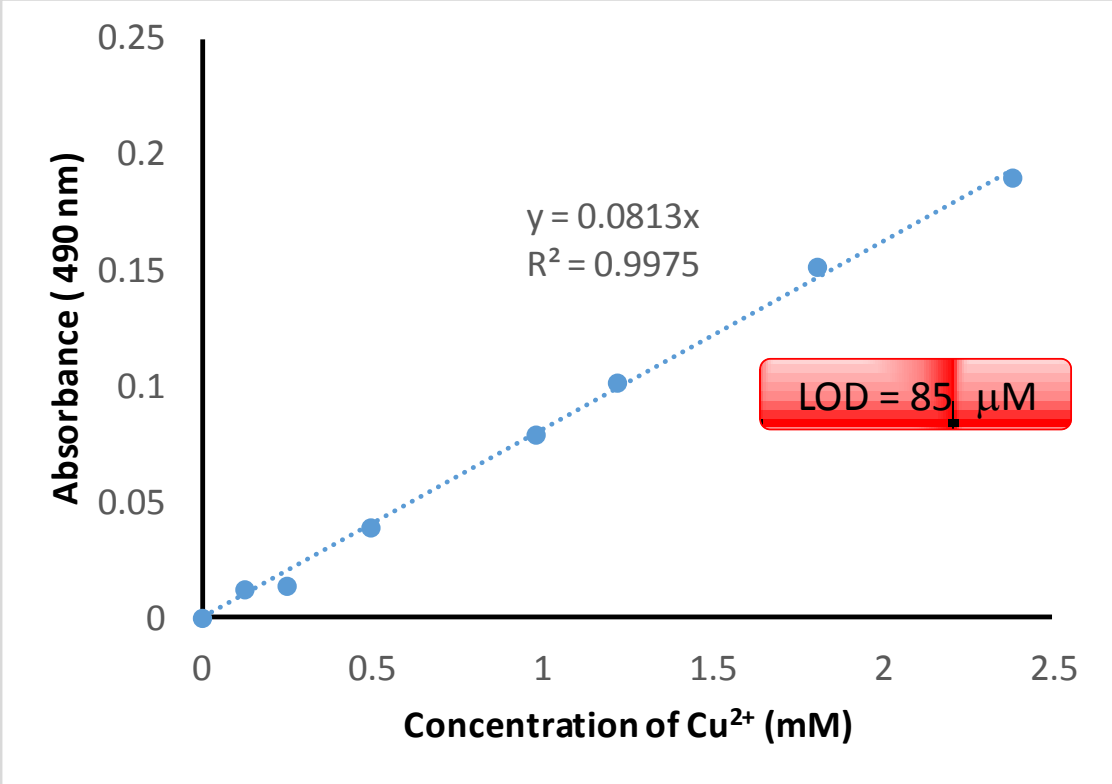
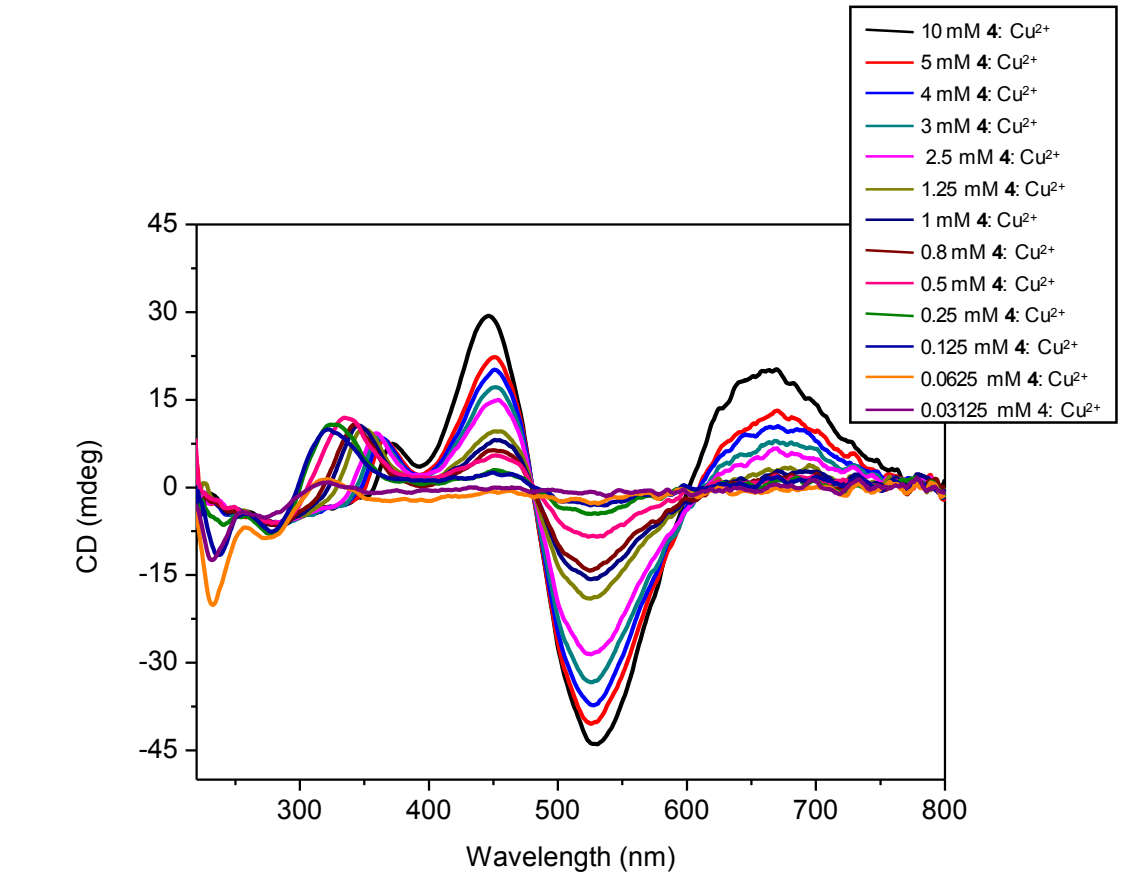


Figure S11. LOD determination by UV-Visible experiments for Cu^{2+} starting from a 1.1 mM solution of ligand **4** and adding increasing amounts of Cu^{2+} in the presence of added base (0.1 M NaOH in water).



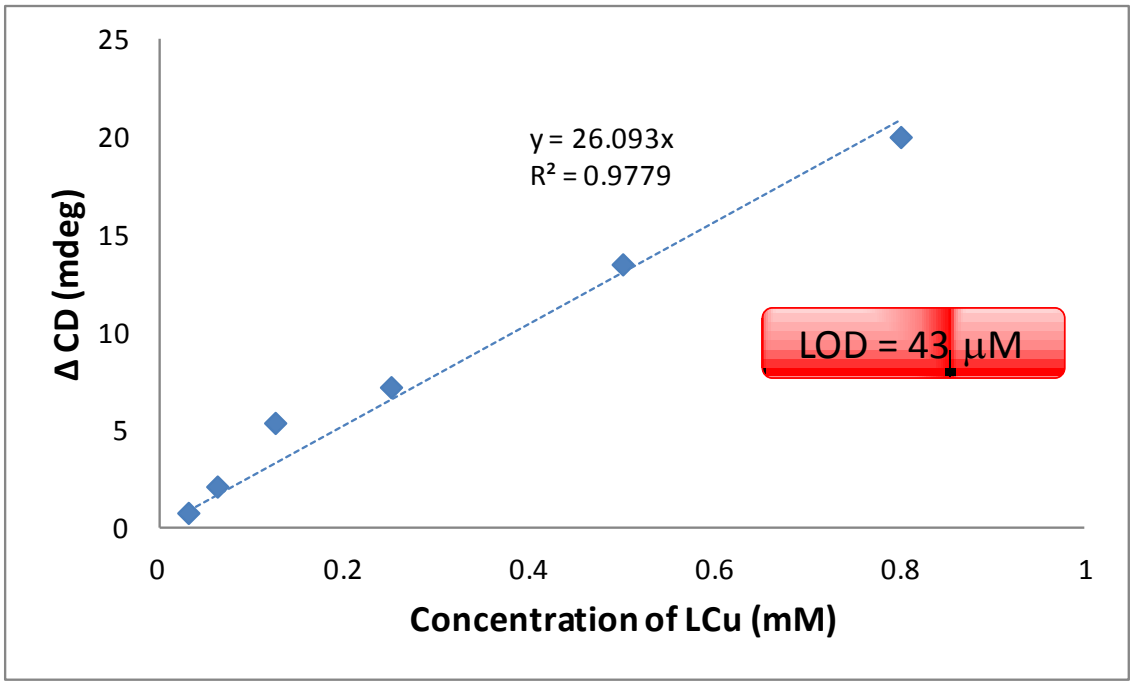
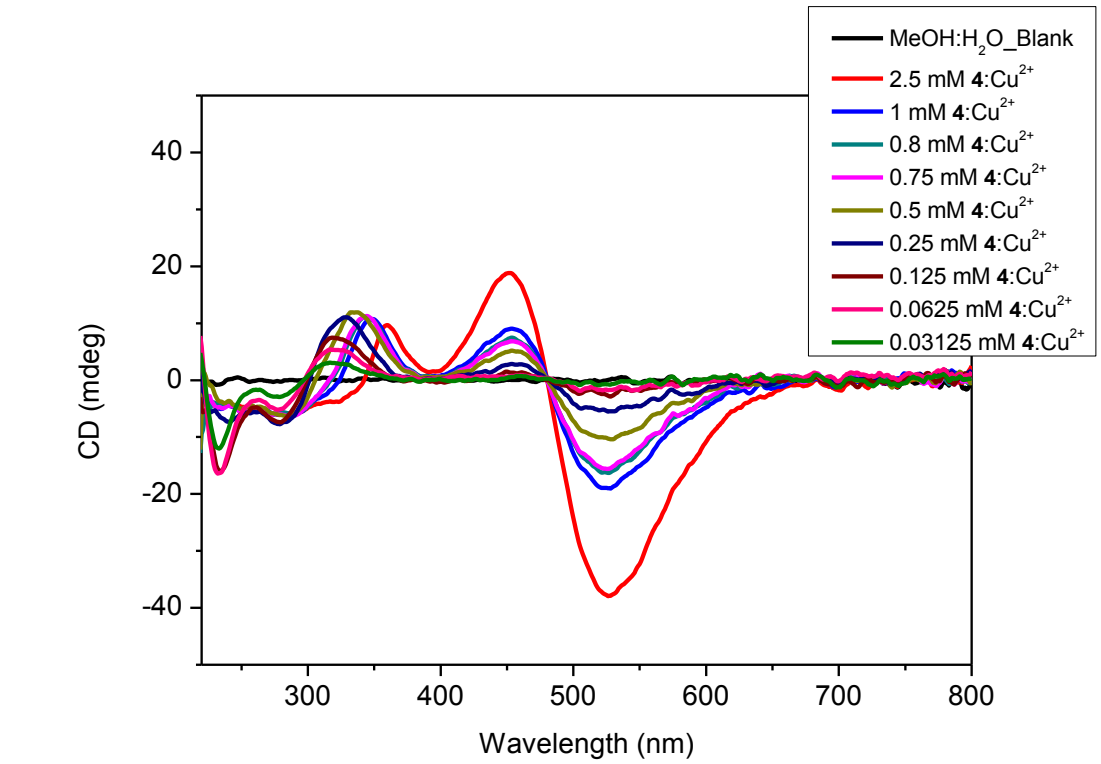


Figure S12. LOD determination of **4**:Cu^{2+} complex from serial dilutions of a 10 mM solution of the complex using the changes in the amplitude of the Cotton effect in the CD spectra in the absence of added base.



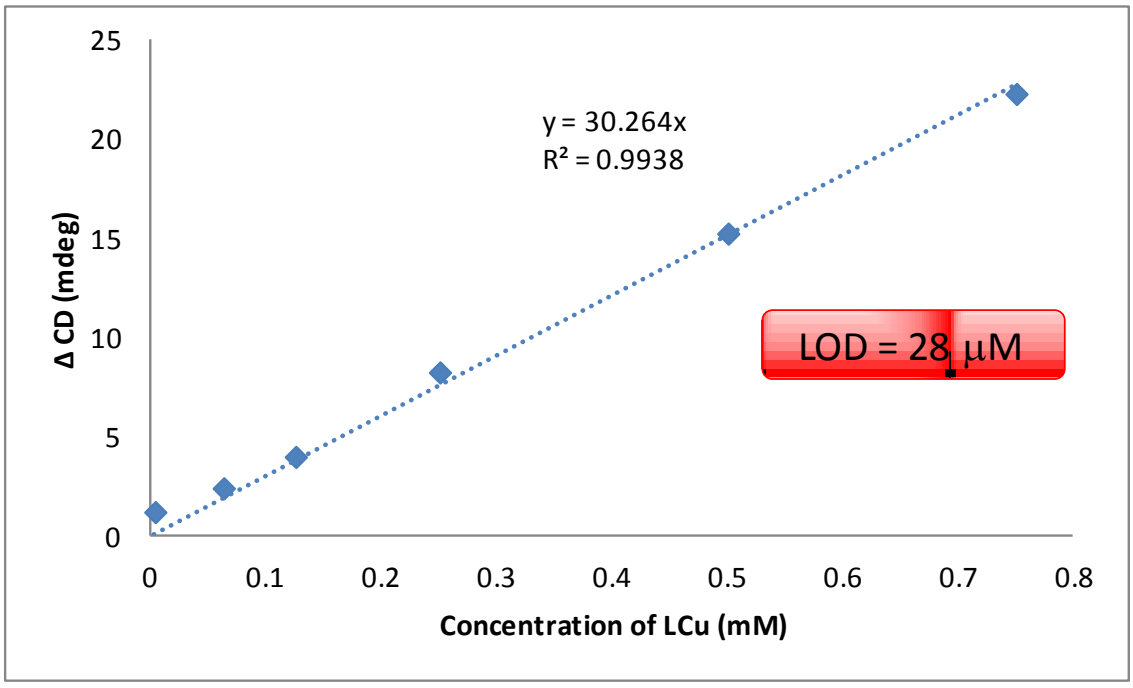


Figure S13. LOD determination of **4**:Cu^{2+} complex from serial dilutions of a 2.5 mM solution of the complex using the changes in the amplitude of the Cotton effect in the CD spectra in the presence of added base.

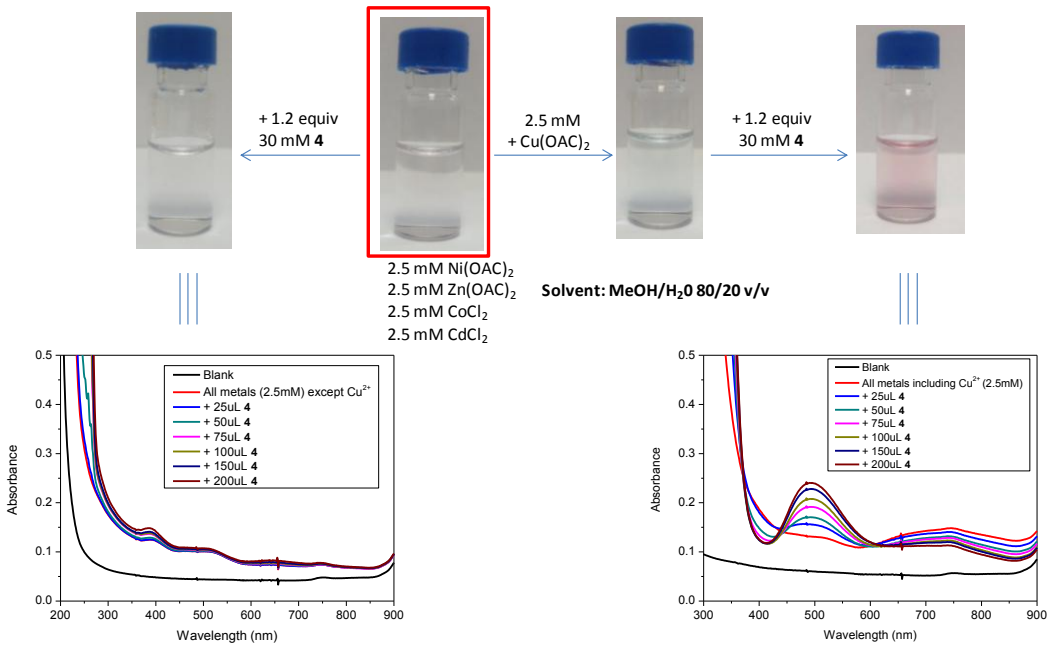
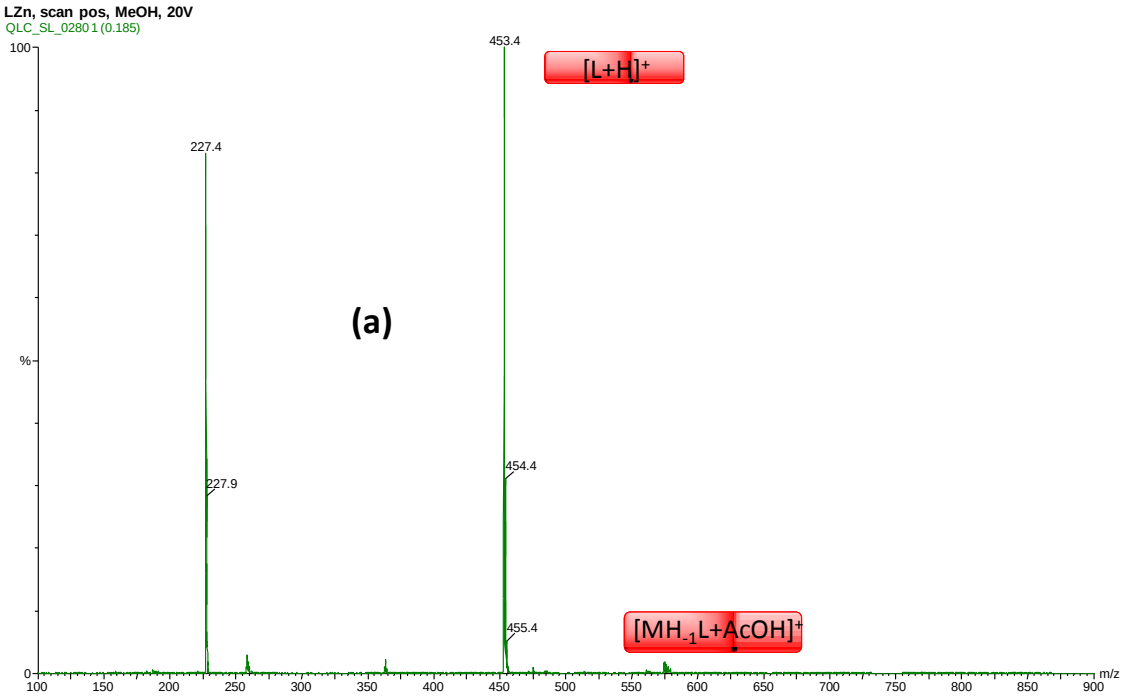
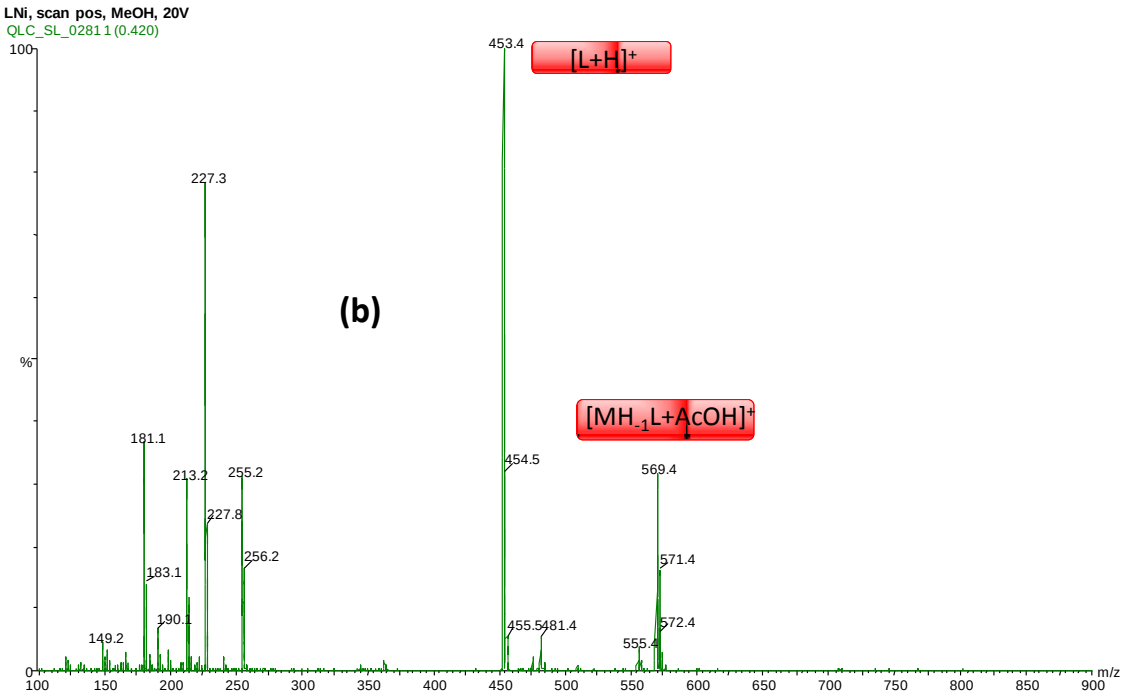
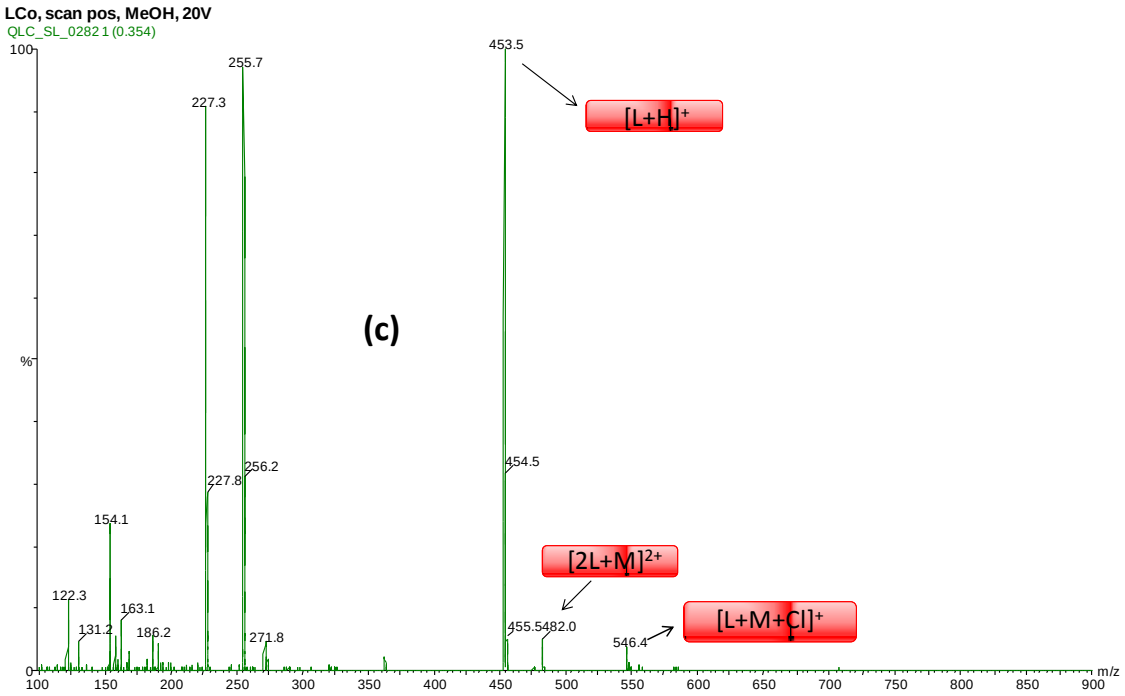
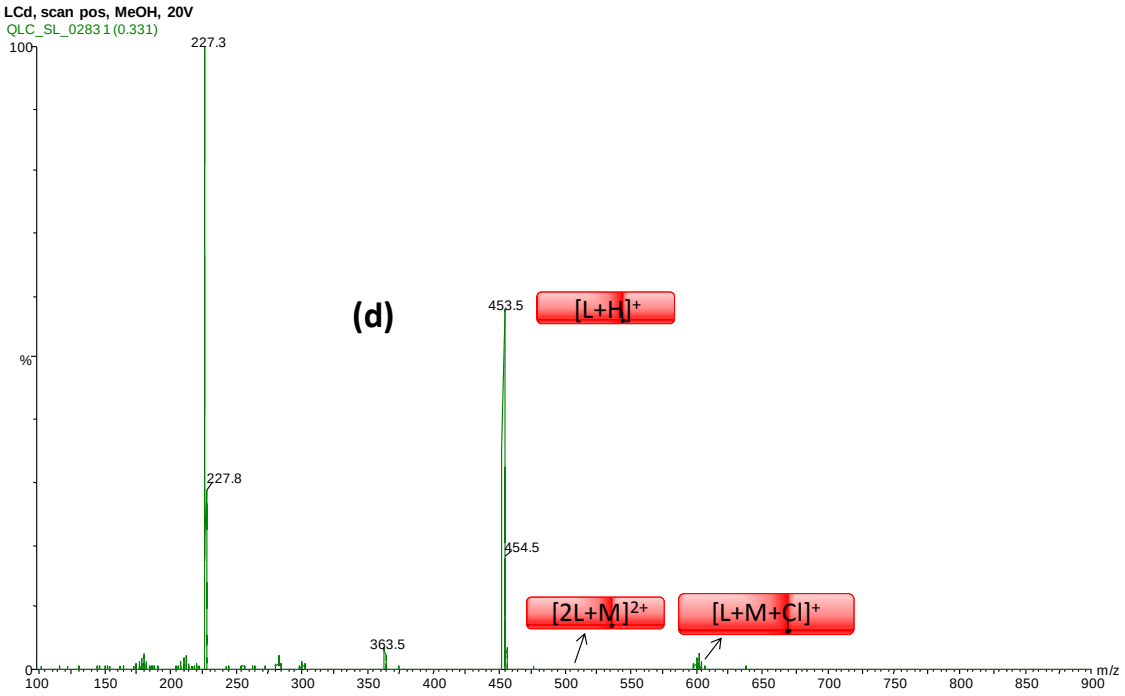


Figure S14. Identification of Cu^{2+} in the presence of other metal cations using ligand **4** in MeOH/H_2O 80/20 v/v in the absence of added base.


LZn, scan pos, MeOH, 20V
QLC_SL_0280 1 (0.185)
100
%
0
453.4
[L+H]+
227.4
(a)
227.9
454.4
455.4
[MH-1L+AcOH]+
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900


LNi, scan pos, MeOH, 20V
QLC_SL_0281 1 (0.420)
100
%
0
453.4
[L+H]+
227.3
(b)
[MH-1L+AcOH]+
181.1
213.2
255.2
227.8
454.5
569.4
256.2
571.4
183.1
190.1
455.5481.4
572.4
149.2
555.4
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900


LCo, scan pos, MeOH, 20V
QLC_SL_0282 1 (0.354)
100
%
0
453.5
255.7
227.3
[L+H]+
(c)
454.5
256.2
227.8
154.1
[2L+M]2+
122.3
163.1
131.2
186.2
271.8
455.5
482.0
546.4
[L+M+Cl]+
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900
m/z


LCd, scan pos, MeOH, 20V
QLC_SL_0283 1 (0.331)
100
%
0
227.3
(d)
453.5
[L+H]+
227.8
454.5
[2L+M]2+
[L+M+Cl]+
363.5
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900
m/z

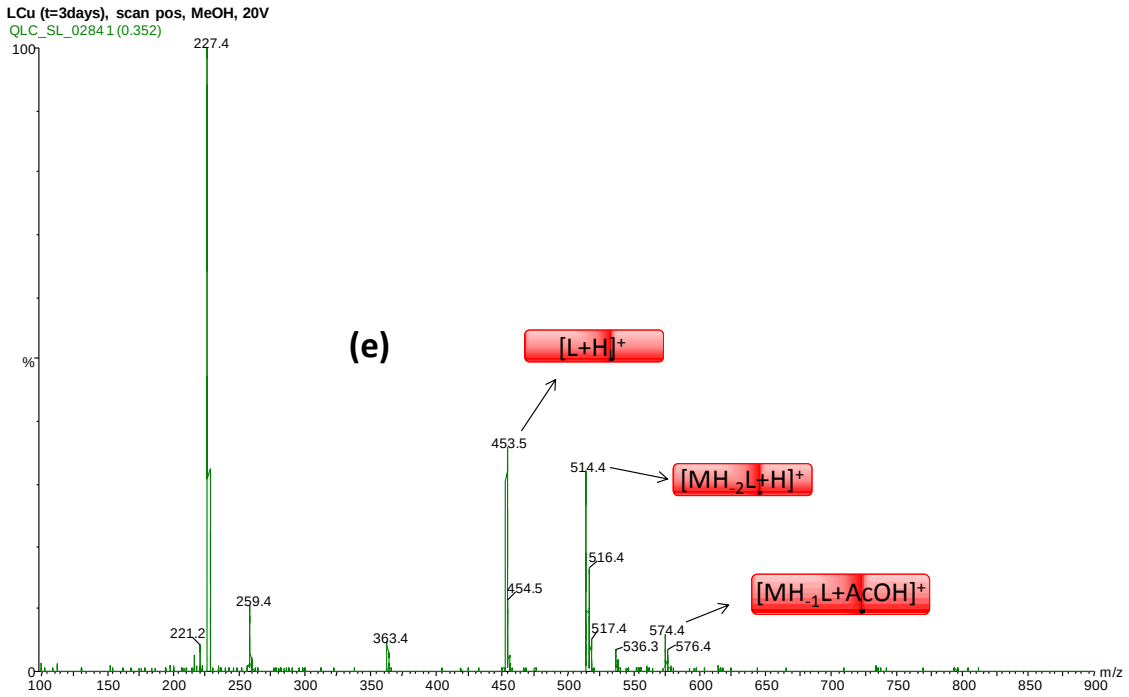


Figure S15. ESI mass spectra for ligand **4** in the presence of equimolecular amounts of different metals in MeOH/H_2O 80/20 v/v. a) Zn^{2+}; b) Ni^{2+}; c) Co^{2+}; d) Cd^{2+}; e) Cu^{2+} after 48 hours. Initial concentrations of both the ligand and the metal were 5 mM.

Annex III

Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Coordination behaviour of new open chain and macrocyclic peptidomimetic compounds with copper(II).

Prashant D. Wadhavane, Lingaraju Gorla, Armando Ferrer[a], Belen Altava, M. Ángeles Izquierdo, M. Isabel Burguete and Santiago V. Luis*

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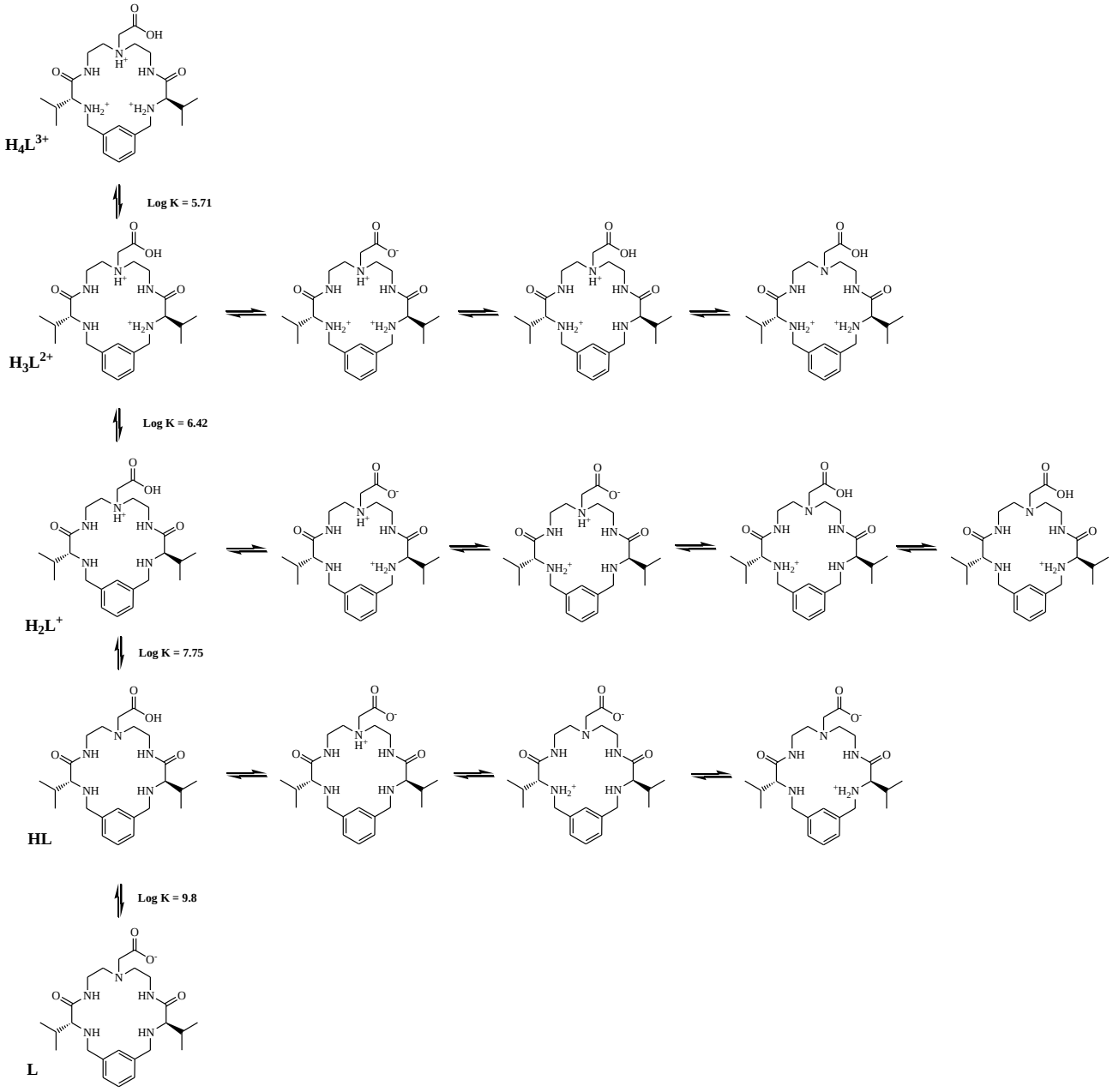
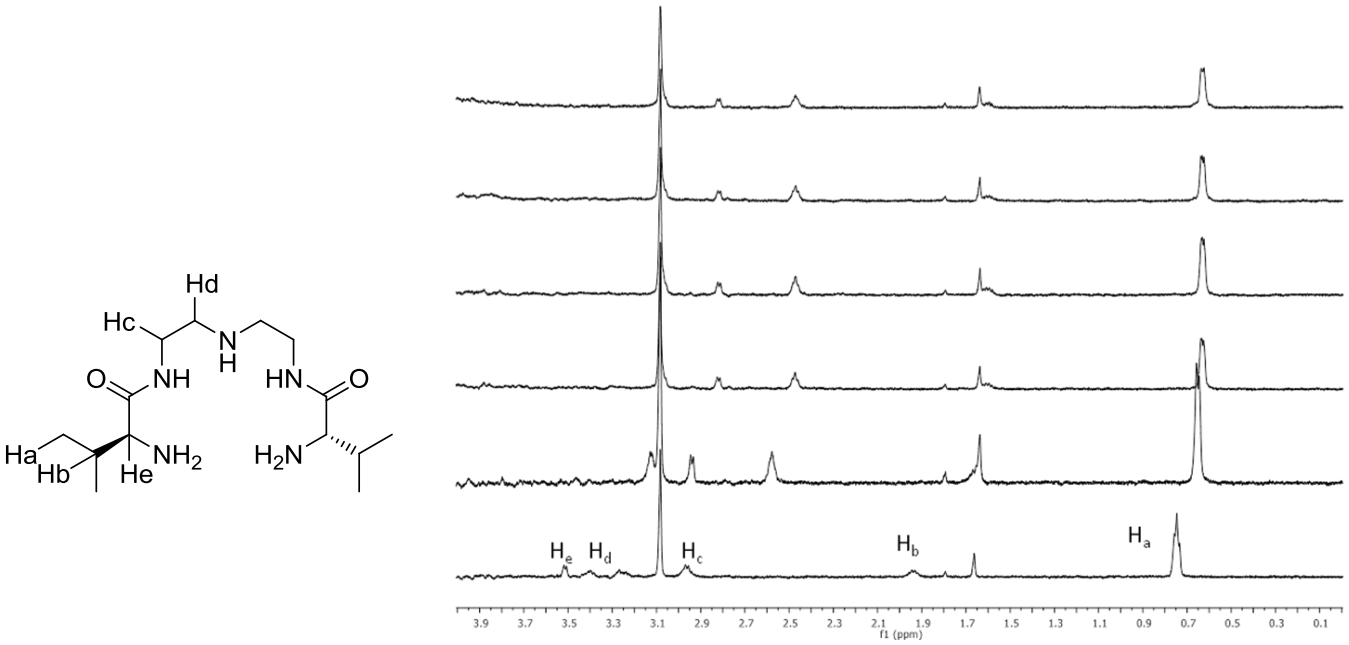
S1 Potential protonation equilibria for pseudopeptide 2.

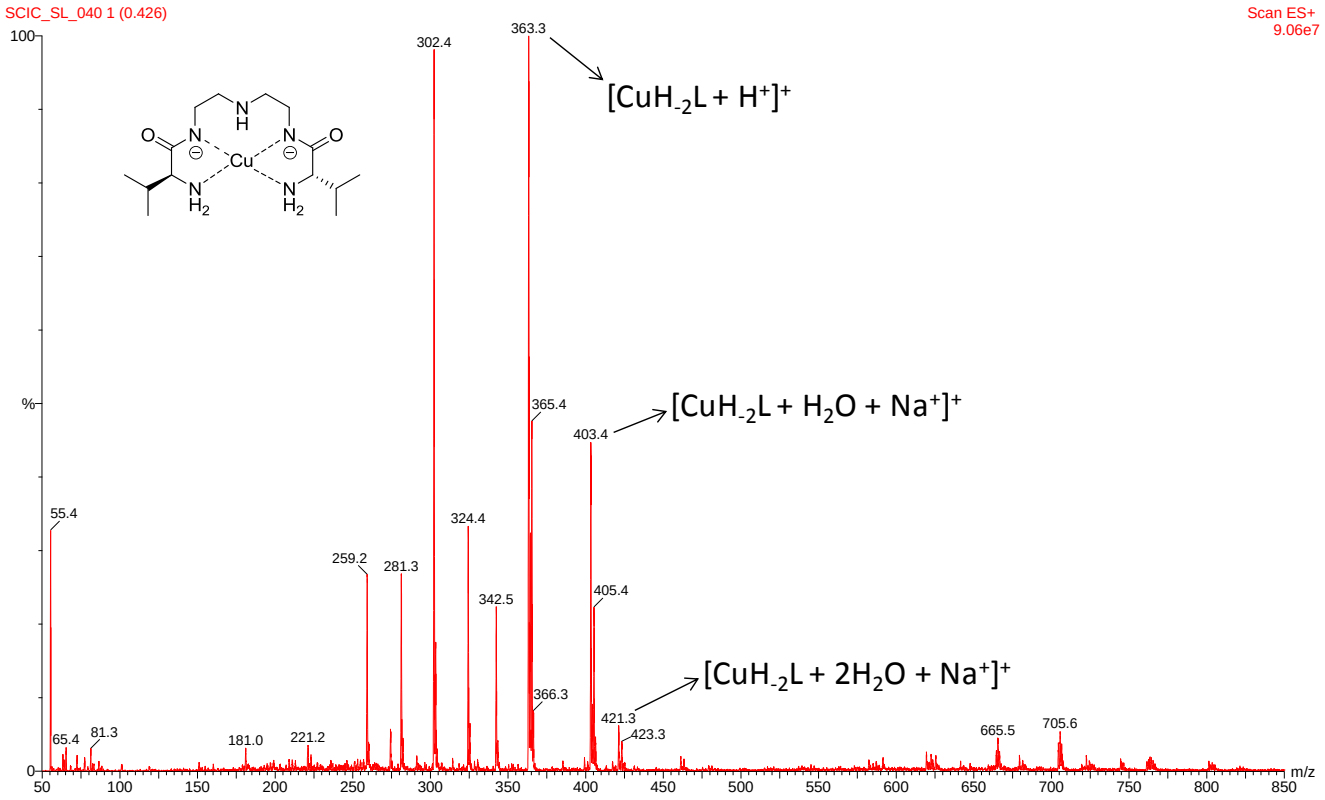


S2 Proton induced shifts for Compound 1 upon changing pH

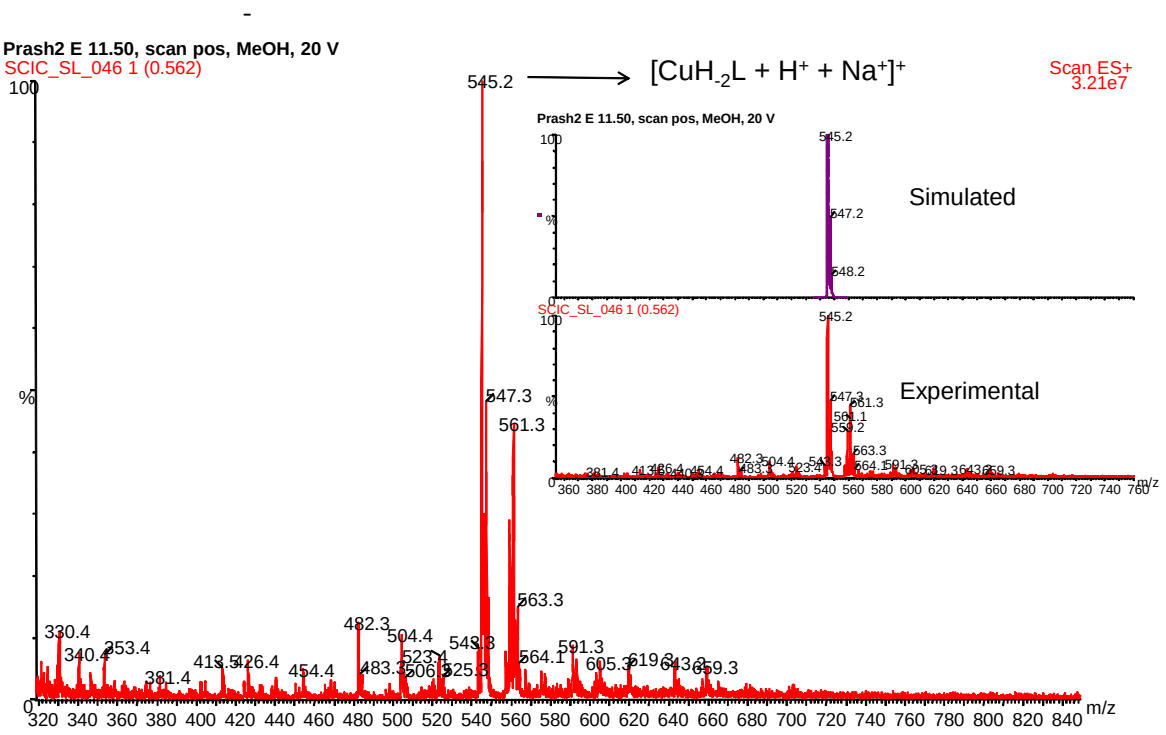


^{1}H NMR of compound **1** (1 mM) at different pH values in H_2O/D_2O 9:1 (from top to bottom, pH values are: 11.3; 10.3; 9.1; 8.6; 6.9 and 5.3).

S3. ESI-MS spectra for Cu (II) complexes.



ESI-MS for **1+Cu** at pH 9.0.

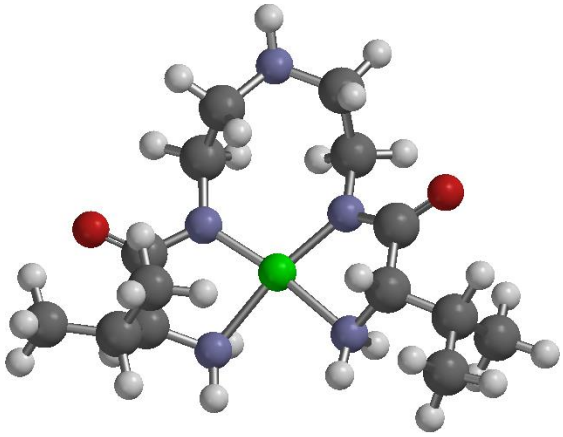


ESI-MS for **2+Cu** at pH 11.5. The species $[CuH_{-2}L+H^{+}+Na^{+}]^{+}$ is monocationic taking into consideration that **L** for **2** has been defined as a monoanionic species.

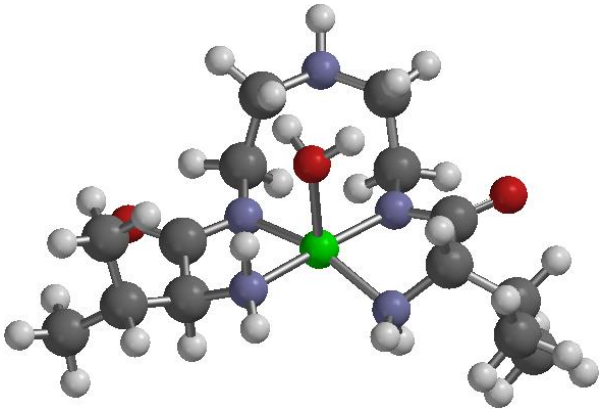
S4. Theoretical studies for Cu(II) Complexes

The calculations were carried out with the program Spartan'14 (version 1.1.0), using the Monte Carlo conformational search performed at the Merck molecular force field (MMFF). The most stable conformers obtained in the conformational search were then optimized by means of density functional theory using the non local hybrid Becke's three-parameter exchange functional (denoted as B3LYP) with LanL2DZ pseudopotential and the associated basis set for Cu and the 6-31G(d) basis set for the rest of atoms using the Gaussian 09 program. The stationary points have been characterized as true minima by the calculation of the normal vibration modes, being all the values positive.

Calculated **1+Cu** complex geometries for [$CuH_{-2}L$] species



square planar

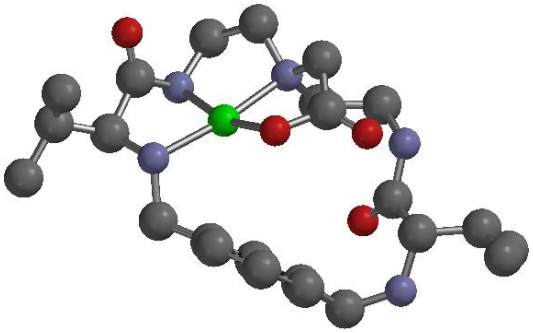


pyramidal

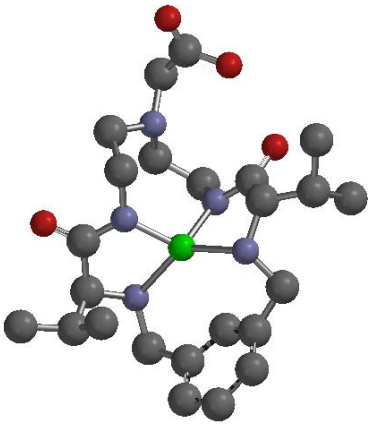
	Square planar	Pyramidal
d (N1-Cu)	1.851 Å	1.877 Å
d (N2-Cu)	1.865 Å	1.879 Å
d (N3-Cu)	2.067 Å	2.067 Å
d (N4-Cu)	2.090 Å	2.089 Å
d (O1-Cu)	-	2.179 Å
d (O2-Cu)	-	-
a (N1-Cu-N2)	105.8°	106.9 °
a (N2-Cu-N4)	83.3°	83.7 °
a (N1-Cu-N3)	85.3 °	84.2 °
a (N3-Cu-N4)	85.9 °	87.2 °
planar distortion	6.1º	15.2º
Relative energy*	1.9	0.0

*Energy difference in kcal/mol

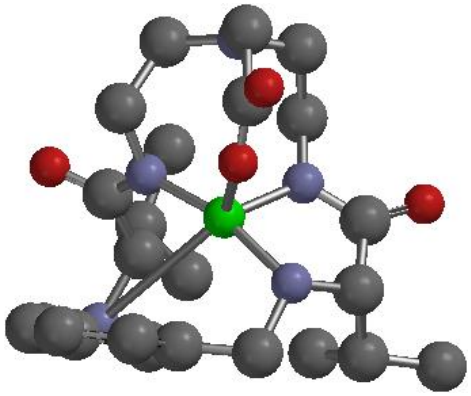
Calculated **2+Cu** complex geometries for $[CuH_{-2}L]$ species



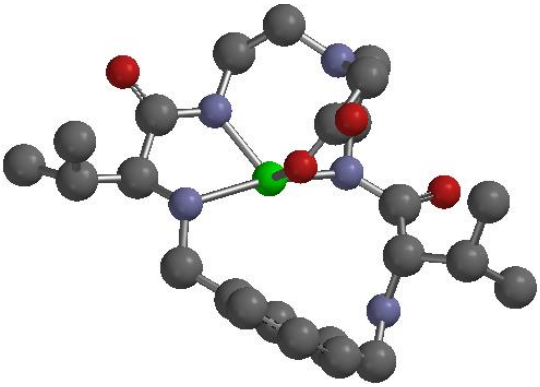
A



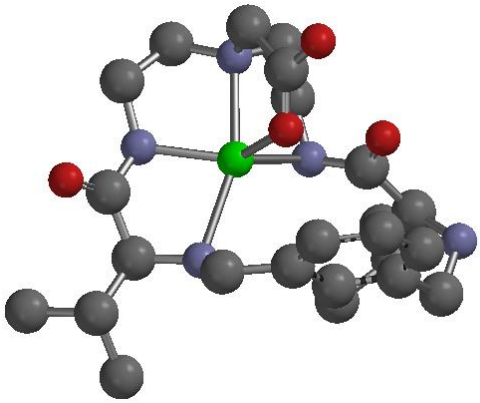
B



C



D



E

	A	B	C	D	E
d (N1-Cu)	2.171 Å	1.839 Å	1.865 Å	2.035 Å	2.091 Å
d (N2-Cu)	-	1.838 Å	1.845 Å	2.047 Å	2.127 Å
d (N3-Cu)	2.025 Å	2.327 Å	2.076 Å	2.431 Å	2.339 Å
d (N4-Cu)	-	2.213 Å	4.103 Å	-	-
d (N5-Cu)	2.024 Å	-	2.113 Å	-	2.237 Å
d (O-Cu)	2.068 Å	-	-	1.904 Å	2.027 Å
Relative energy*	7.6	0.9	3.7	2.5	0.0

*Energy difference in kcal/mol

Annex IV

Supporting Information – Chapter 7

Self-Assembly of pseudopeptidic systems

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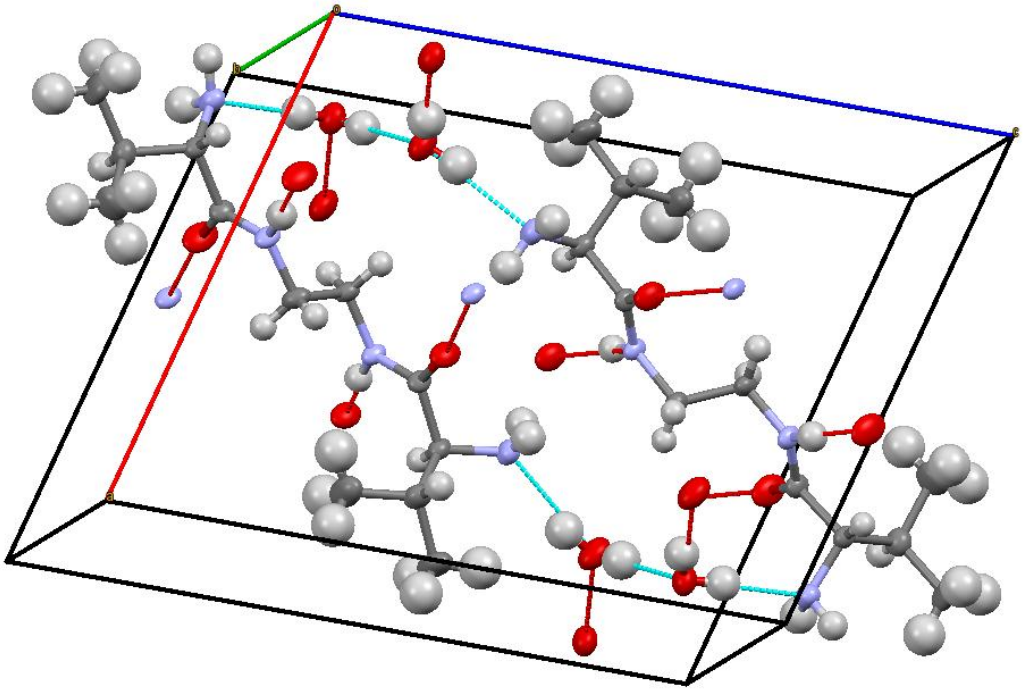

Fig S1. Crystal lattice for **3b**

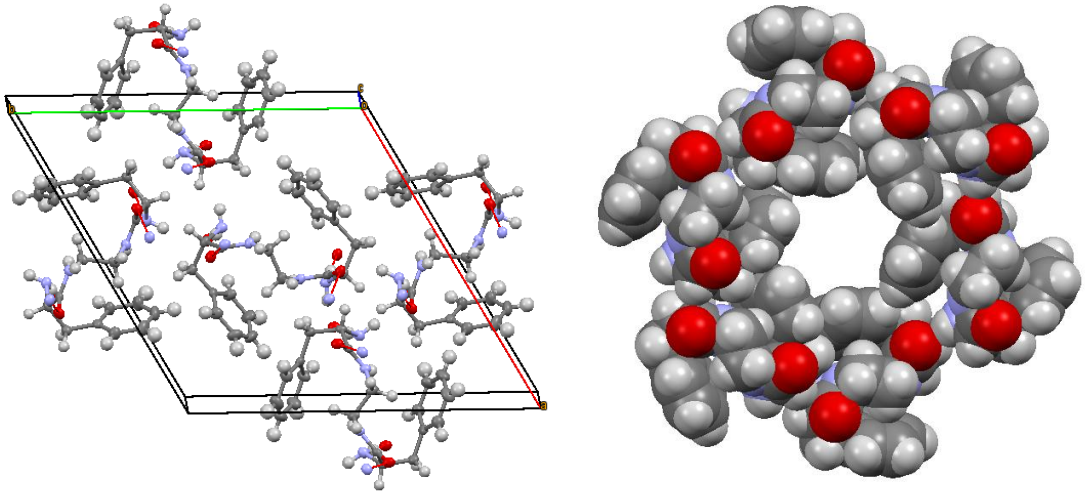

Fig S2. Crystal lattice and the self-assembly structure displaying the aromatic channels for **3a**

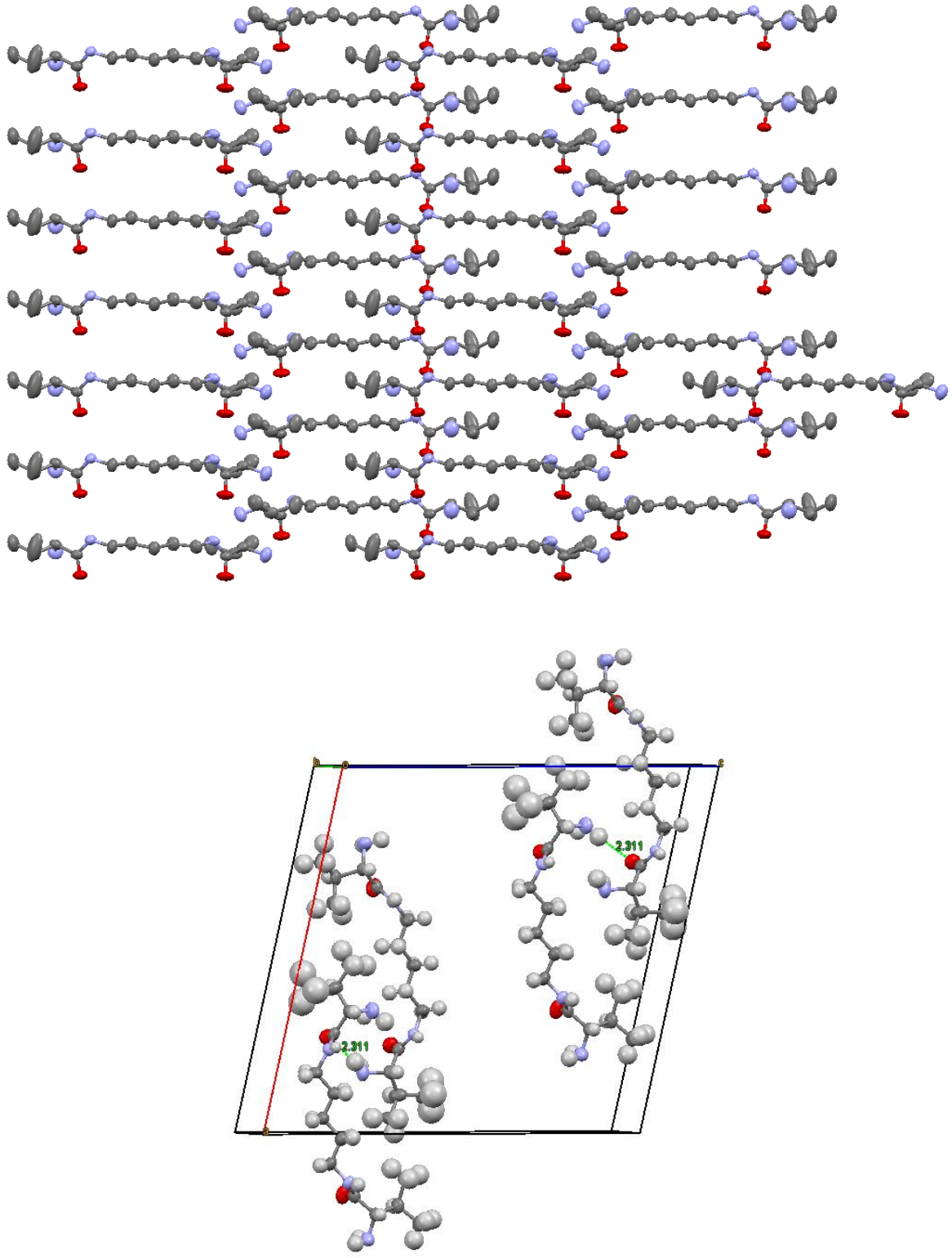

Fig. S3 Packing of compound **4b** in the c plane (up) and crystal lattice of compound **4b** (down)

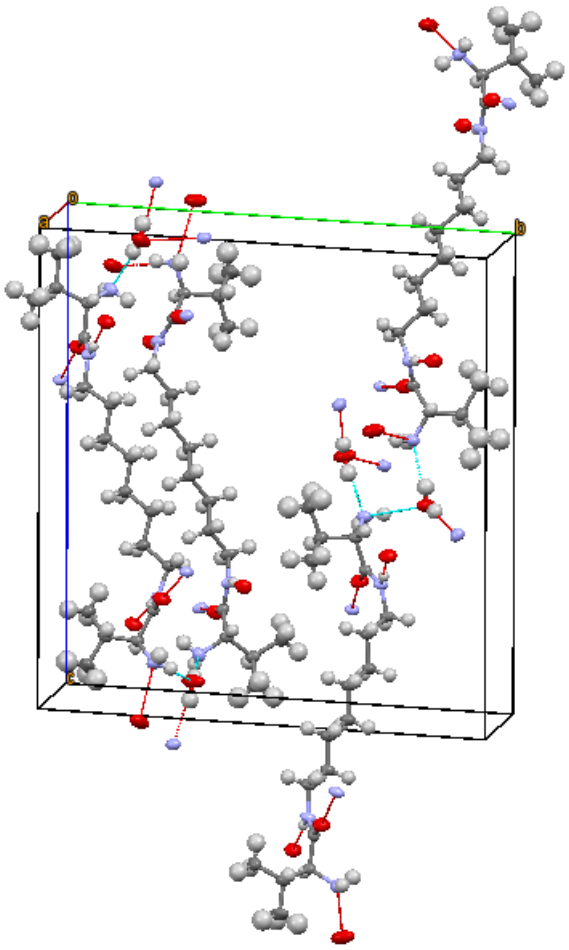

Fig. S4 Crystal lattice of compound **5b** showing H-bonds

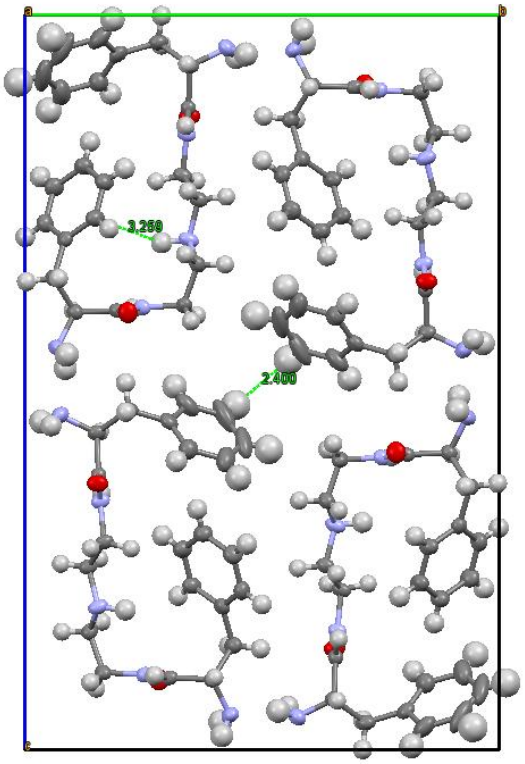

Fig. S5 Crystal lattice of compound **7a** (a plane) showing H-bonds

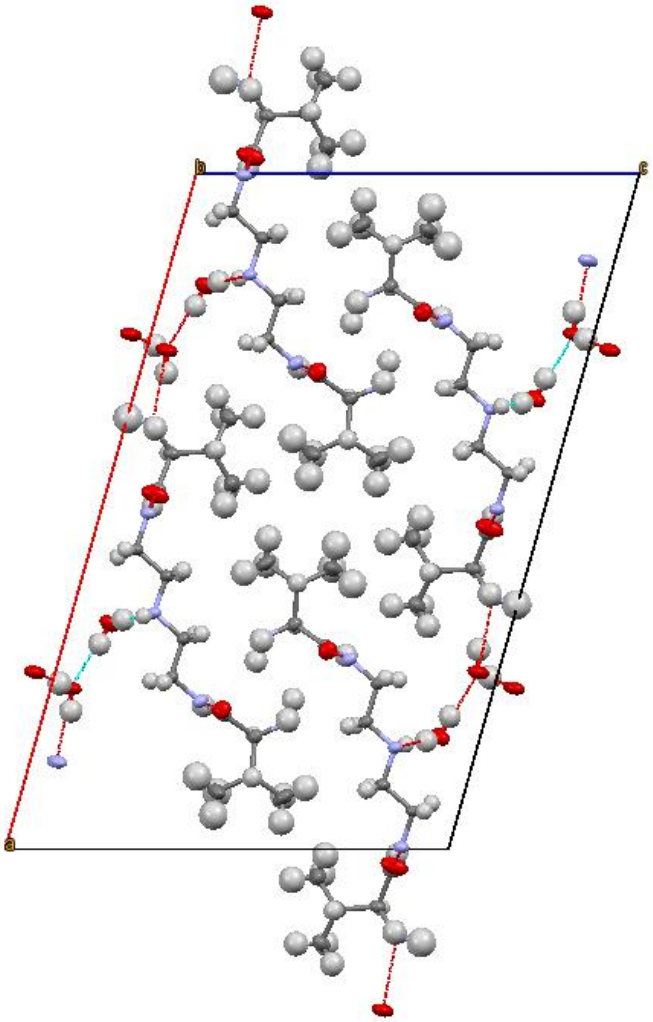

Fig. S6 Crystal lattice of compound **7b** (b plane) showing intermolecular H-bonds

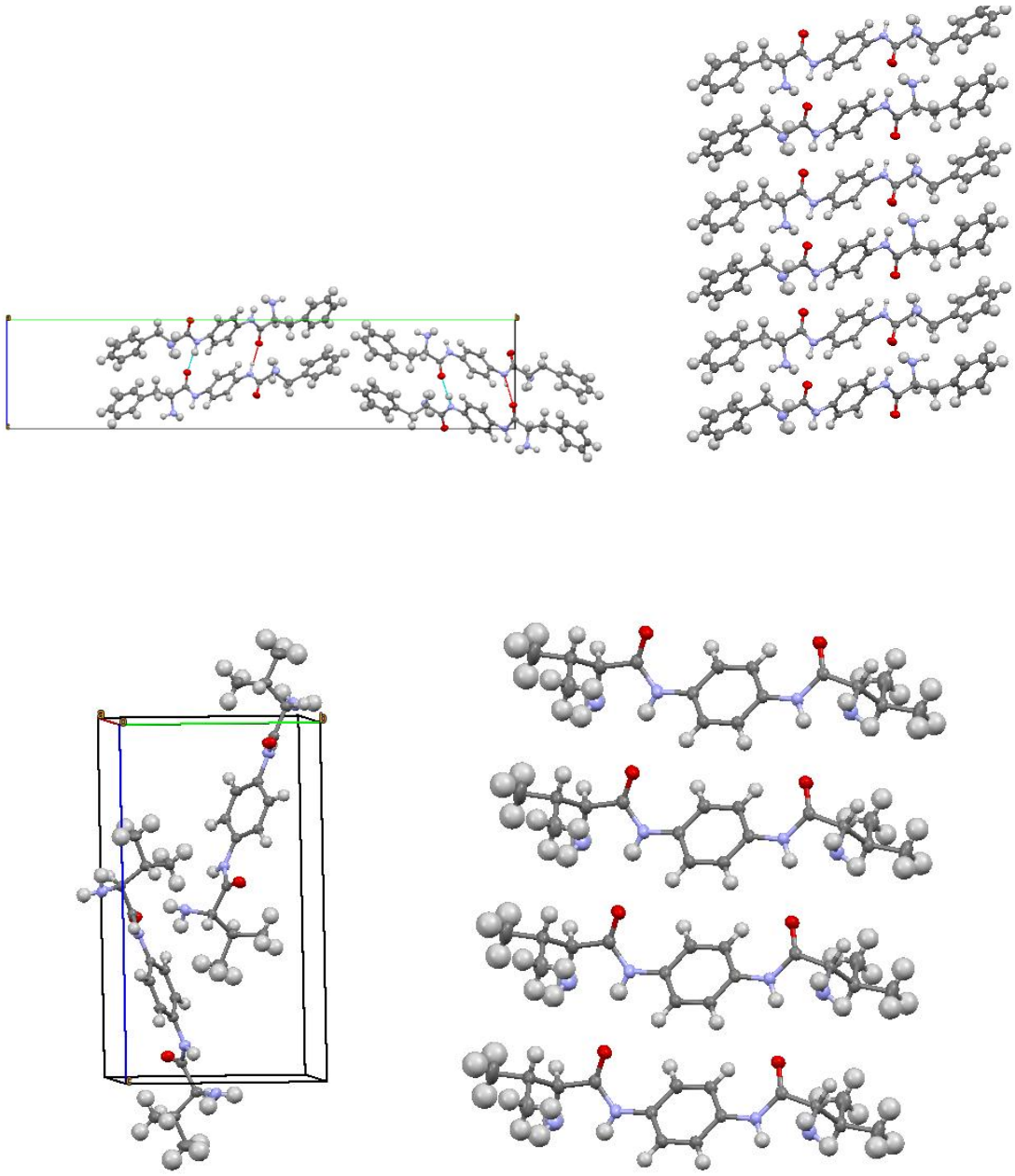

Fig. S7 Crystal lattice and packing of compounds **1a (**up) and **1b (**down)

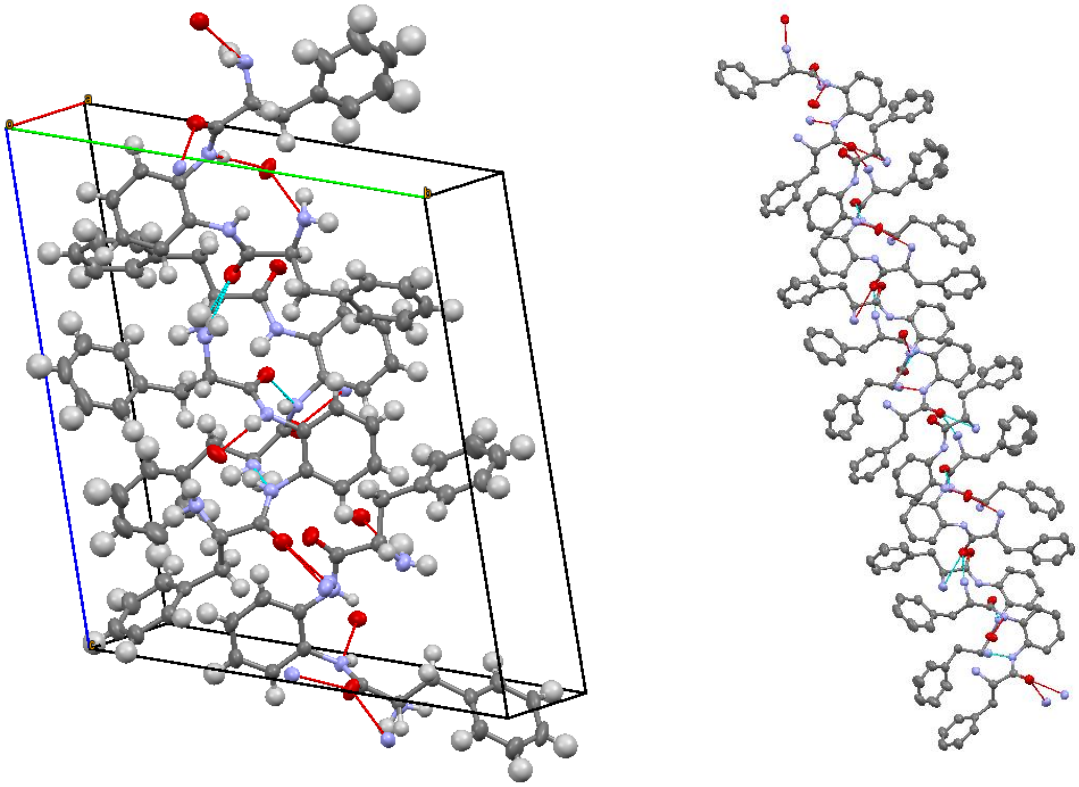

Fig. S8 Crystal lattice of compounds **2a** and packing

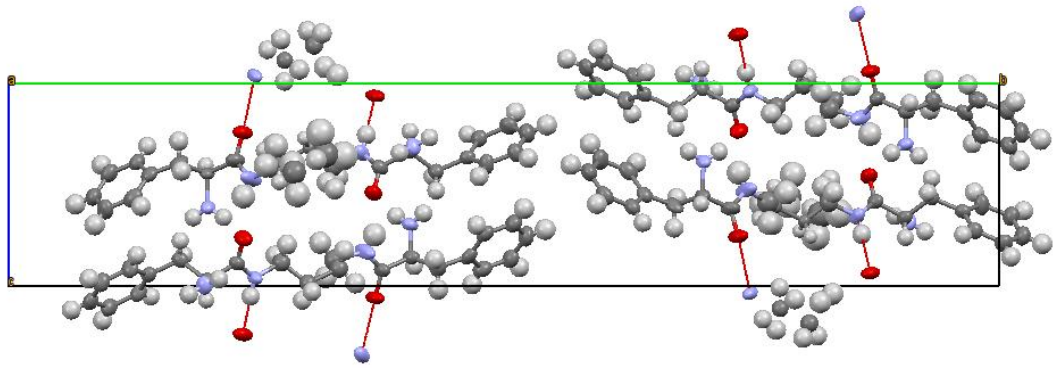

Fig. S9 Crystal lattice of compound **A4Phe**

Identification code	**2a**	**3b**	**6a**
Empirical formula	$C_{24}H_{26}N_4O_2$	$C_{12}H_{30}N_4O_4$	$C_{35}H_{40}N_4O_2$
Formula weight	402.49	294.40	548.71
Temperature/K	200	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P1	$P2_1$	$P2_1$
a/Å	8.6682(2)	12.5640(3)	14.9282(3)
b/Å	14.7652(3)	4.80981(7)	5.14524(8)
c/Å	18.3708(4)	15.8319(3)	19.5488(3)
α/°	71.785(2)	90	90
β/°	88.7145(19)	112.756(3)	98.3145(16)
γ/°	76.039(2)	90	90
Volume/$Å^3$	2163.85(9)	882.26(4)	1485.75(4)
Z	4	2	2
$\rho_{calc}g/cm^3$	1.235	1.108	1.227
μ/mm^{-1}	0.642	0.682	0.602
F(000)	856.0	324.0	588.0
Crystal size/mm^3	0.2458 × 0.1942 × 0.163	0.3977 × 0.1078 × 0.0509	0.042 × 0.079 × 0.851
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.866 to 144.342	7.63 to 131.998	6.984 to 145.248
Index ranges	$-10 \le h \le 10$, $-18 \le k \le 17$, $-22 \le l \le 22$	$-14 \le h \le 12$, $-5 \le k \le 5$, $-18 \le l \le 18$	$-18 \le h \le 18$, $-6 \le k \le 6$, $-24 \le l \le 24$
Reflections collected	72792	8173	27124
Independent reflections	16019 [R_{int} = 0.0876, R_{sigma} = 0.0470]	3066 [R_{int} = 0.0762, R_{sigma} = 0.0748]	5829 [R_{int} = 0.0497, R_{sigma} = 0.0302]
Data/restraints/parameters	16019/4/1178	3066/7/215	5829/488/491
Goodness-of-fit on F^2	1.029	1.078	1.021
Final R indexes [I>=2σ(I)]	R_1 = 0.0501, wR_2 = 0.1404	R_1 = 0.0459, wR_2 = 0.1216	R_1 = 0.0527, wR_2 = 0.1409
Final R indexes [all data]	R_1 = 0.0588, wR_2 = 0.1493	R_1 = 0.0542, wR_2 = 0.1244	R_1 = 0.0568, wR_2 = 0.1463
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.18	0.20/-0.22	0.27/-0.25
Flack parameter	0.04(14)	-0.1(3)	0.14(19)

Table S1 Crystallographic and structural refinements data for Compounds **2a**, **3b**, and **6a**

Identification code	**4a**	**4b**	**5b**
Empirical formula	$C_{23}H_{32}N_4O_2$	$C_{15}H_{31.61}N_4O_{4.25}$	$C_{18}H_{40}N_4O_3$
Formula weight	396.52	336.05	360.54
Temperature/K	293(2)	293(2)	293(2)
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12$	I2	$P2_12_12_1$
a/Å	25.6360(3)	20.4259(4)	4.84556(10)
b/Å	16.5436(2)	4.79492(9)	20.5154(5)
c/Å	5.05085(6)	21.6606(5)	21.9450(4)
α/°	90	90	90
β/°	90	102.636(2)	90
γ/°	90	90	90
Volume/$Å^3$	2142.12(4)	2070.08(8)	2181.51(8)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.230	1.078	1.098
μ/mm^{-1}	0.633	0.648	0.596
F(000)	856.0	734.0	800.0
Crystal size/mm^3	0.3512 × 0.0585 × 0.0346	0.7711 × 0.0913 × 0.0542	0.383 × 0.067 × 0.05
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.896 to 145	6.728 to 131.978	8.058 to 131.994
Index ranges	$-31 \le h \le 31$, $-20 \le k \le 19$, $-5 \le l \le 6$	$-24 \le h \le 24$, $-5 \le k \le 5$, $-25 \le l \le 25$	$-5 \le h \le 4$, $-24 \le k \le 24$, $-26 \le l \le 26$
Reflections collected	19750	9488	19233
Independent reflections	4201 [R_{int} = 0.0391, R_{sigma} = 0.0223]	3413 [R_{int} = 0.0422, R_{sigma} = 0.0384]	3808 [R_{int} = 0.0405, R_{sigma} = 0.0285]
Data/restraints/parameters	4201/6/286	3413/21/240	3808/0/262
Goodness-of-fit on F^2	1.033	1.116	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.1030	R_1 = 0.0778, wR_2 = 0.2391	R_1 = 0.0507, wR_2 = 0.1230
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.1059	R_1 = 0.0808, wR_2 = 0.2454	R_1 = 0.0561, wR_2 = 0.1279
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.16	0.34/-0.37	0.24/-0.20
Flack parameter	-0.03(10)	-0.14(19)	0.09(11)

Table S2 Crystallographic and structural refinements data for Compounds **4a**, **4b**, and **5b**

Identification code	**7a**	**7b**
Empirical formula	$C_{22}H_{31}N_5O_2$	$C_{14}H_{35}N_5O_4$
Formula weight	397.52	337.47
Temperature/K	293(2)	293(2)
Crystal system	orthorhombic	monoclinic
Space group	$P22_12_1$	C2
a/Å	5.01883(14)	26.1681(6)
b/Å	16.5007(5)	4.81178(18)
c/Å	25.5451(7)	16.5261(5)
α/°	90	90
β/°	90	105.807(3)
γ/°	90	90
Volume/$Å^3$	2115.49(10)	2002.20(11)
Z	4	4
$\rho_{calc}g/cm^3$	1.248	1.120
μ/mm^{-1}	0.656	0.672
F(000)	856.0	744.0
Crystal size/mm^3	0.6174 × 0.0395 × 0.0248	0.9442 × 0.0931 × 0.0382
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.92 to 140.994	7.022 to 129.942
Index ranges	$-6 \le h \le 1$, $-18 \le k \le 20$, $-21 \le l \le 30$	$-30 \le h \le 30$, $-5 \le k \le 5$, $-19 \le l \le 19$
Reflections collected	6701	16100
Independent reflections	3869 [R_{int} = 0.0379, R_{sigma} = 0.0488]	3249 [R_{int} = 0.0695, R_{sigma} = 0.0432]
Data/restraints/parameters	3869/7/290	3249/9/246
Goodness-of-fit on F^2	1.036	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1084	R_1 = 0.0548, wR_2 = 0.1514
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.1119	R_1 = 0.0592, wR_2 = 0.1564
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.15	0.24/-0.21
Flack parameter	-0.13(19)	0.2(3)

Table S3 Crystallographic and structural refinements data for Compounds **7a** and **7b**