Electronic Supplementary Material (ESI) for Dalton Transactions.

Influence of the chain length and metal:ligand mole ratio on the self-organisation processes of Cu^{2+} complexes of [1+1] 1*H*-pyrazole azamacrocycles

Alberto Lopera,*[a] Ariadna Gil-Martínez,[a] Javier Pitarch-Jarque,[a] Begoña Verdejo,[a] Salvador Blasco,*[a] M. Paz Clares,[a] Hermas R. Jiménez[b] and Enrique García-España*[a]

a Instituto de Ciencia Molecular, Universidad de Valencia, c/ Catedrático José Beltrán Martínez 2, 46980 Paterna (Valencia), Spain.

b Departamento de Química Inorgánica, Facultad de Química, Universidad de Valencia, c/ Doctor Moliner 50, 46100 Burjassot (Valencia), Spain

Suplementary Materials

- Table S1. ^{1}H NMR hyperfine-shifted resonances of the Cu^{2+}-**L2** system in 1:1 molar ratio recorded at 298 K in D_2O at pH 5.

- Table S2. ^{1}H NMR hyperfine-shifted resonances of the Cu^{2+}-**L2** system in 1:1 molar ratio recorded at 298 K in D_2O at pH 10.

- Table S3. Selected bond distances (Å) and angles (°) for the crystal structure of the $[Cu_2(H_{-1}\mathbf{L2})_2]^{2+}$ cation (**2'**).

-**Table S4.** Crystallographic data of $[Cu_2(H(H_{-1}\mathbf{L2}))_2](ClO_4)_4{\cdot}4H_2O$ (**1**), $[Cu_2(H_{-1}\mathbf{L2})_2]{\cdot}2ClO_4$ (**2**), $[Cu_2(H_{-1}\mathbf{L2})_2]Cl_{1.56}Br_{0.44}{\cdot}2.38H_2O$ (**2'**), $[Cu_4(H_{-1}\mathbf{L4})_2(OH)_{2.08}](ClO_4)_{2.92}Br_{0.54}Cl_{0.46}$ (**3**), and $Pd_{2.39}Cu_{1.61}(H_{-1}\mathbf{L4})_2(OH)_2](ClO_4)_2Cl_{1.33}Br_{0.67}{\cdot}2.87H_2O$ (**4**).

- **Figure S1.** Plot of the species distribution diagram of **L**1. [**L1**] = 1.0x10^{-3} M.

- Figure S2. Plot of the species distribution diagram of **L2**. [**L2**] = 1.0x10^{-3} M.

- Figure S3. Plot of the species distribution diagram of **L3**. [**L3**] = 1.0x10^{-3} M.

- Figure S4. Plot of the species distribution diagram of the system Cu(II)-**L1** in 1:1 Cu(II):L molar ratio. [**L1**] = [Cu(II)] = 1.0x10^{-3} M.

- Figure S5. Plot of the species distribution diagram of the system Cu(II)-**L2** in 1:1 Cu(II):L molar ratio. [**L2**] = [Cu(II)] = 1.0x10^{-3} M.

- Figure S6. Plot of the species distribution diagram of the system Cu(II)-**L3** in 1:1 Cu(II):L molar ratio. [**L3**] = [Cu(II)] = 1.0x10^{-3} M.

- Figure S7. Plot of the species distribution diagram of the system Cu(II)-**L1** in 2:1 Cu(II):L molar ratio. [**L1**] = 1.0x10^{-3} M. [Cu(II)] = 2.0x10^{-3} M.

- Figure S8. Plot of the species distribution diagram of the system Cu(II)-**L2** in 2:1 Cu(II):L molar ratio. [**L2**] = 1.0x10^{-3} M. [Cu(II)] = 2.0x10^{-3} M.

- Figure S9. Plot of the species distribution diagram of the system Cu(II)-**L3** in 3:2 Cu(II):L molar ratio. [**L3**] = 1.0x10^{-3} M. [Cu(II)] = 1.5x10^{-3} M.

- Figure S10. Plot of the species distribution diagram of the system Cu(II)-**L4** in 3:2 Cu(II):L molar ratio. [**L4**] = 1.0x10^{-3} M. [Cu(II)] = 1.5x10^{-3} M.

- Figure S11. Plot of the species distribution diagram of the system Cu(II)-**L4** in 2:1 Cu(II):L molar ratio. [**L4**] = $1.0x10^{-3}$ M. [Cu(II)] = $2.0x10^{-3}$ M.

- Figure S12. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L1}_2(Br)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L1**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S13. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L1}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L1**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S14. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L2}_2(Br)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S15. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L2}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S16. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the specie $[Cu_2H_{-2}\mathbf{L3}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L3**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S17. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-1}\mathbf{L3}_2(ClO_4)]^{2+}$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L3**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S18. Plot of the ESR spectrum recorded for the system Cu(II)-**L2** in 1:1 Cu(II):L molar ratio. The pH values are: 2.60 (blue), 3.64 (red), 5.63 (green), 8.88 (purple), and 10.95 (orange). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M. ESR was recorded in ethylene glycol 30% in water. Experimental conditions: ν = 9.47 GHz and T = 77 K. The signals are ESR silent above pH 5.

- Figure S19. UV-vis spectrum for the Cu(II)–**L1** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.27 (blue), 4.04 (red), 6.30 (green) and 10.94 (purple). [**L1**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S20. UV-vis spectrum for the Cu(II)–**L2** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.03 (blue), 5.10 (red), 8.01 (green) and 10.54 (purple). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S21. UV-vis spectrum for the Cu(II)–**L3** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.14 (blue), 4.96 (red), 6.76 (green) and 8.75 (purple). [**L3**] = [Cu(II)] = $1.0x10^{-3}$ M.

- Figure S22. 400 MHz ^{1}H NMR spectra of the Cu^{2+}-L2 system in 1:1 molar ratio recorded at 298 K in D_2O at (a) pH 5 and (b) pH 10. (c) In the region 76/24 ppm, the intensity of the spectrum at pH 10 is multiplied by ten. The asterisks mark the residual solvent (*, H2O; **, HOD).

- **Figure S23.** (a) Partial view of the crystal structure of the cation $[Cu_2(H_{-1}\mathbf{L2})_2]^{2+}$ (**2'**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown. Colour code: carbon (grey), nitrogen (blue), copper (orange). (b)

Stick view with the two macrocycles composing the structure represented in different colours (purple and green) to clarify the discussion in the text.

- Figure S24. Spectroscopic studies of the mixed Cu(II):Pd(II):**L4** system in 1:1:1 molar ratio. The pH was adjusted to 8 and the UV-vis spectrum was recorded at time values (min): 20, 40, 60, 80, 100, 120, 180 and 300. [**L4**] = [Cu(II)] = [Pd(II)] = $1.0x10^{-3}$ M.

- Figure S25. Plot of the absorbance values at 600 nm at different times for the mixed Cu(II):Pd(II):**L4** system in 1:1:1 molar ratio. The UV-vis spectrum was recorded at time values (min): 20, 40, 60, 80, 100, 120, 180 and 300. [**L4**] = [Cu(II)] = [Pd(II)] = $1.0x10^{-3}$ M.

Table S1. ^{1}H NMR hyperfine-shifted resonances of the Cu^{2+}-**L2** system in 1:1 molar ratio recorded at 298 K in D_2O at pH 5.

Signal	δ(ppm)	Nº of protons	Assignments	Temperature Dependence	Δν1/2 (Hz)	T_2[a] (ms)
a	50.0			anti-Curie	b	b
A[c]	58.3				3005	0.11
b	46.7			Curie	b	b
c	41.1	24	α-CH_2	anti-Curie	1140	0.28
d	22.1			anti-Curie	b	b
D[c]	27.5			anti-Curie	2073	0.15
e	19.9			anti-Curie	b	b
f	11.9			anti-Curie	725	0.44
k	-5.0			Curie	725	0.44
g[d]	8.0	4	γ-CH_2	anti-Curie	52	6.1
h[d]	7.6			anti-Curie	48	6.6
i[d]	2.5	2	H_m-Pyrazole	anti-Curie	95	3.4
j	0.6	8	β-CH_2	anti-Curie	249	1.3

(a) Measured from the line width at half-height. (b) Overlap prevents measurement of this value. (c) Measured at 283 K. (d) Tentative assignments.

Table S2. ^{1}H NMR hyperfine-shifted resonances of the Cu^{2+}-**L2** system in 1:1 molar ratio recorded at 298 K in D_2O at pH 10.

Signal	δ(ppm)	Nº of protons	Assignments	Temperature Dependence	Δν1/2 (Hz)	T_2[a] (ms)
a′	58.2	32	α-CH_2	Curie	2400	0.13
b′	41.7			Indep. of T	1020	0.31
c′	33.0			Curie	1374	0.23
e′	2.2			anti-Curie	260	1.2
f′	1.2			anti-Curie	330	0.96
d′	5.6	6	β-CH_2 and H_m-Pyrazole	anti-Curie	148	2.2

(a) Measured from the line width at half-height.

Table S3. Selected bond distances (Å) and angles (°) for the crystal structure of the $[Cu_2(H_{-1}\mathbf{L2})_2]^{2+}$ cation (**2'**).

Distances (Å)		Angles (°)	
Cu1 - N3	1.927(2)	N3 - Cu1 - N4	80.80(10)
Cu1 - N9	1.931(2)	N3 - Cu1 - N5	91.98(11)
Cu1 - N4	2.103(2)	N3 - Cu1 - N9	96.86(10)
Cu1 - N10	2.082(3)	N4 - Cu1 - N10	101.12(10)
Cu1 - N5	2.504(3)	N4 - Cu1 - N5	79.16(10)
Cu1 - N11	2.566(3)	N5 - Cu1 - N9	96.69(10)
Cu2 - N2	1.934(2)	N5 - Cu1 - N10	93.18(11)
Cu2 - N8	1.933(2)	N9 - Cu1 - N10	81.58(10)
Cu2 - N1	2.086(3)	N3 - Cu1 - N11	97.24(10)
Cu2 - N7	2.088(3)	N4 - Cu1 - N11	91.70(10)
Cu2 - N6	2.605(3)	N9 - Cu1 - N11	92.85(10)
Cu2 - N12	2.611(3)	N10 - Cu1 - N11	77.87(10)
Cu1 - Cu2	3.9167(6)	N1 - Cu2 - N2	81.01(10)
		N1 - Cu2 - N6	78.03(11)
		N2 - Cu2 - N6	96.05(10)
		N2 - Cu2 - N8	96.65(10)
		N6 - Cu2 - N7	90.93(10)
		N6 - Cu2 - N8	95.10(10)
		N1 - Cu2 - N12	94.73(12)
		N2 - Cu2 - N12	95.38(10)
		N7 - Cu2 - N12	77.98(11)
		N8 - Cu2 - N12	92.78(11)

Table S4. Crystallographic data of $[Cu_2(H(H_{-1}\mathbf{L2}))_2](ClO_4)_4{\cdot}4H_2O$ (**1**), $[Cu_2(H_{-1}\mathbf{L2})_2]{\cdot}2ClO_4$ (**2**), $[Cu_2(H_{-1}\mathbf{L2})_2]Cl_{1.56}Br_{0.44}{\cdot}2.38H_2O$ (**2'**), $[Cu_4(H_{-1}\mathbf{L4})_2(OH)_{2.08}](ClO_4)_{2.92}Br_{0.54}Cl_{0.46}$ (**3**), and $Pd_{2.39}Cu_{1.61}(H_{-1}\mathbf{L4})_2(OH)_2](ClO_4)_2Cl_{1.33}Br_{0.67}{\cdot}2.87H_2O$ (**4**).

Structure	**1**	**2**	**2'**	**3**	**4**
Empirical formula	$C_{24}H_{54}Cl_4Cu_2N_{12}O_{20}$	$C_{12}H_{23}ClCuN_6O_4$	$C_{24}H_{50.76}Br_{0.44}Cl_{1.56}Cu_2N_{12}O_{2.38}$	$C_{14}H_{28}Br_{0.27}Cl_{1.73}Cu_2N_6O_7$	$C_{28}H_{58.25}Br_{0.67}Cl_{1.33}Cu_{1.12}N_{12}O_{13.03}Pd_{2.88}$
Formula weight / g mol^{-1}	1099.67	414.35	762.99	602.52	1320.73
Temperature / K	293(2)	120.0(1)	293(2)	120.0(1)	120.0(1)
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P −1	P 2_1/c	P 2_1/a	P nma	I 2/m
***a* / Å**	9.2355(5)	11.1975(7)	16.7810(5)	11.1587(5)	12.8708(7)
***b* / Å**	11.6706(7)	8.9313(5)	9.13400(10)	22.0003(10)	19.3357(11)
***c* / Å**	11.9460(9)	16.2321(11)	21.3720(6)	17.5957(7)	19.8511(7)
α / º	112.721(6)	90	90	90	90
β / º	99.370(5)	92.643(2)	95.9810(10)	90	104.852(4)
γ / º	109.507(5)	90	90	90	90
***V* / Å^3**	1054.56(13)	1621.62(17)	3258.02(14)	4319.7(3)	4775.2(4)
Z	1	4	4	8	4
ρ_{calc} g/cm^{-3}	1.732	1.697	1.556	1.853	1.837
μ /mm^{-1}	1.353	1.544	2.015	2.737	2.371
F(000)	568	860	1591	2455	2638
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα

Θ range / º	3.041–49.994	2.919–45.395	2.761–27.498	2.948–32.525	3.023–29.932
Index ranges	−12 ≤ *h* ≤ 11 −12 ≤ *k* ≤ 15 −16 ≤ *l* ≤ 15	−22 ≤ *h* ≤ 22 −17 ≤ *k* ≤ 17 −32 ≤ *l* ≤ 31	−21 ≤ *h* ≤ 21 −11 ≤ *k* ≤ 11 −27 ≤ *l* ≤ 27	−14 ≤ *h* ≤ 16 −33 ≤ *k* ≤ 21 −24 ≤ *l* ≤ 26	−17 ≤ *h* ≤ 17 −27 ≤ *k* ≤ 15 −27 ≤ *l* ≤ 27
Reflections collected	8268	73854	13925	23582	12263
Unique reflections	4730	13349	7452	7246	6206
Data	4730	13349	7452	7246	6206
Restraints	4	0	29	8	29
Parameters	285	303	451	303	338
Goodness-of-fit on F^2	1.073	1.073	1.078	1.030	1.029
Final *R* indices [I>2σ(I)]	*R*1=0.0354 *wR*2=0.0805	*R*1=0.0317 *wR*2=0.0755	*R*1=0.0457 *wR*2=0.1203	*R*1=0.0426 *wR*2=0.0973	*R*1=0.0759 *wR*2=0.2041
Final *R* indices [all data]	*R*1=0.0446 *wR*2=0.0877	*R*1=0.0534 *wR*2=0.0882	*R*1=0.0809 *wR*2=0.1346	*R*1=0.0637 *wR*2=0.1093	*R*1=0.1078 *wR*2=0.2366
CCDC no.	1953929	1990725	1953930	1953933	1953932

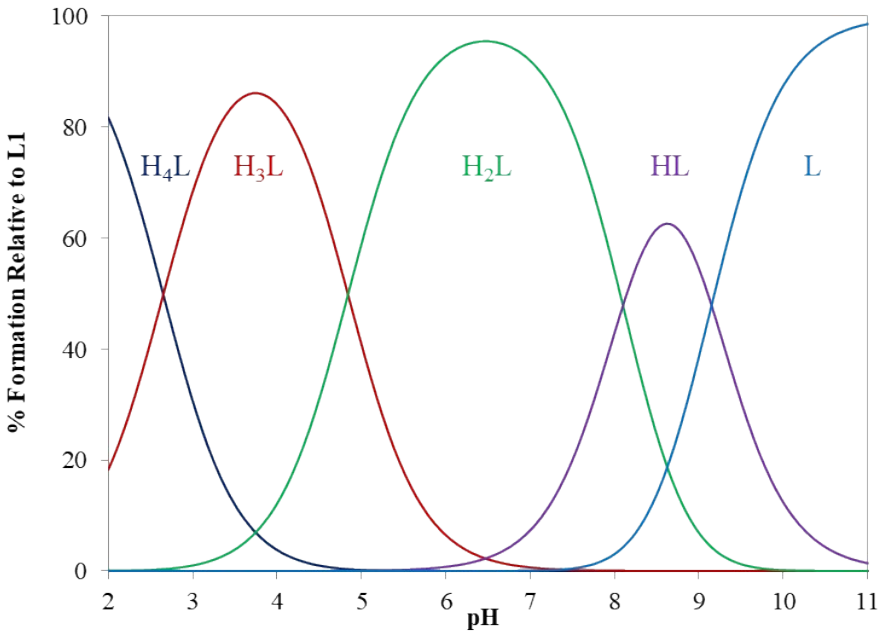

Figure S1. Plot of the species distribution diagram of **L1**. [**L1**] = 1.0x10^{-3} M.

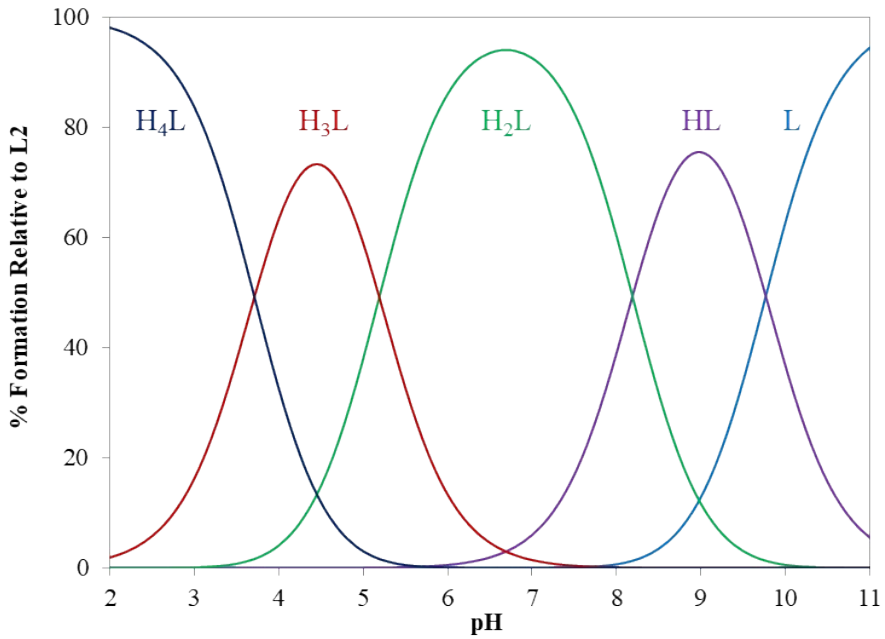

Figure S2. Plot of the species distribution diagram of **L2**. [**L2**] = 1.0x10^{-3} M.

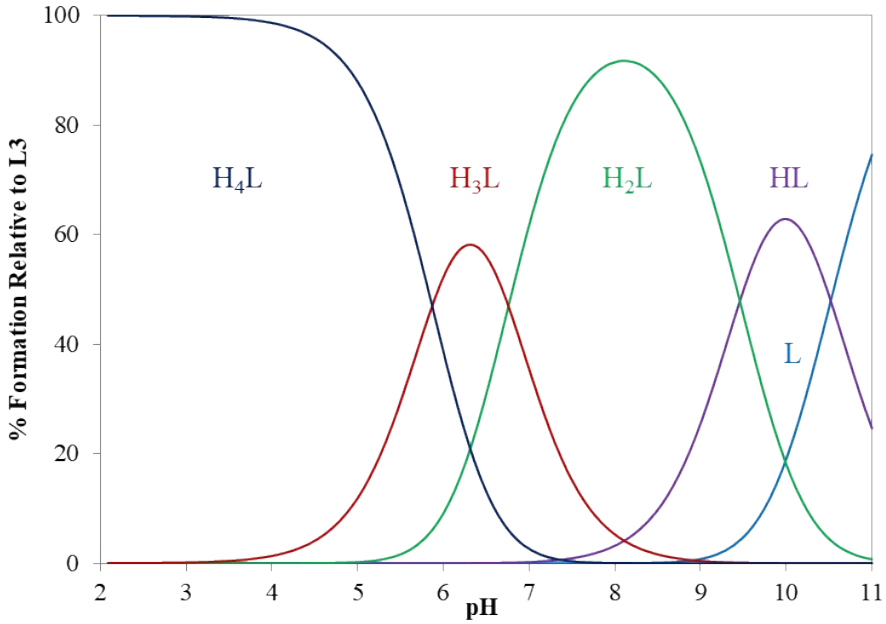

Figure S3. Plot of the species distribution diagram of **L3**. [**L3**] = 1.0×10^{-3} M.

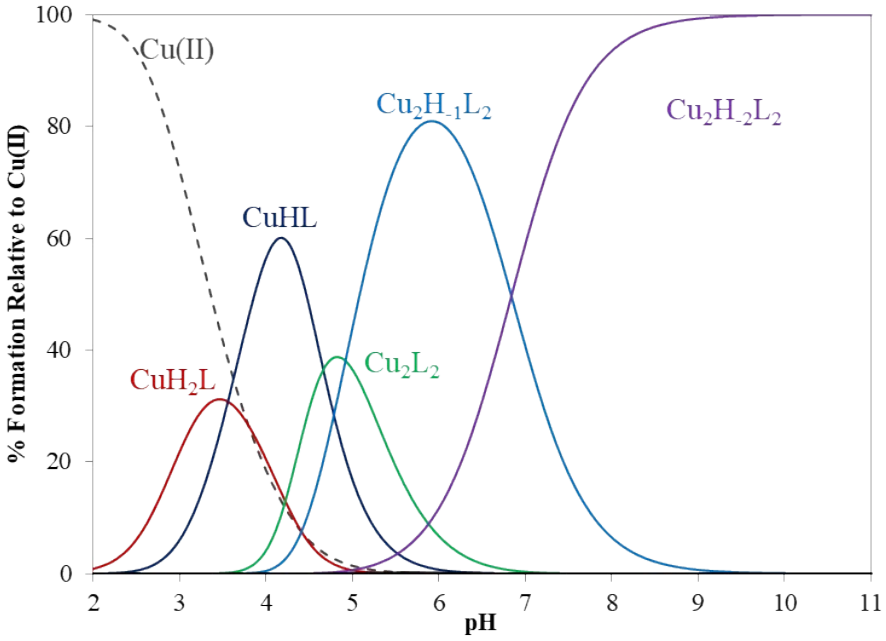

Figure S4. Plot of the species distribution diagram of the system Cu(II)-**L1** in 1:1 Cu(II):L molar ratio. [**L1**] = [Cu(II)] = 1.0×10^{-3} M.

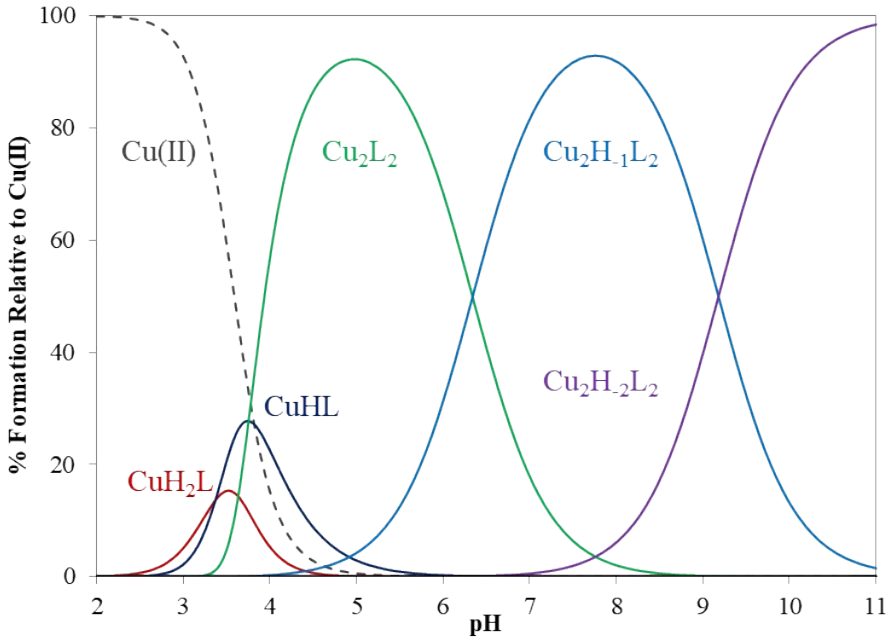

Figure S5. Plot of the species distribution diagram of the system Cu(II)-**L2** in 1:1 Cu(II):L molar ratio. [**L2**] = [Cu(II)] = 1.0×10^{-3} M.

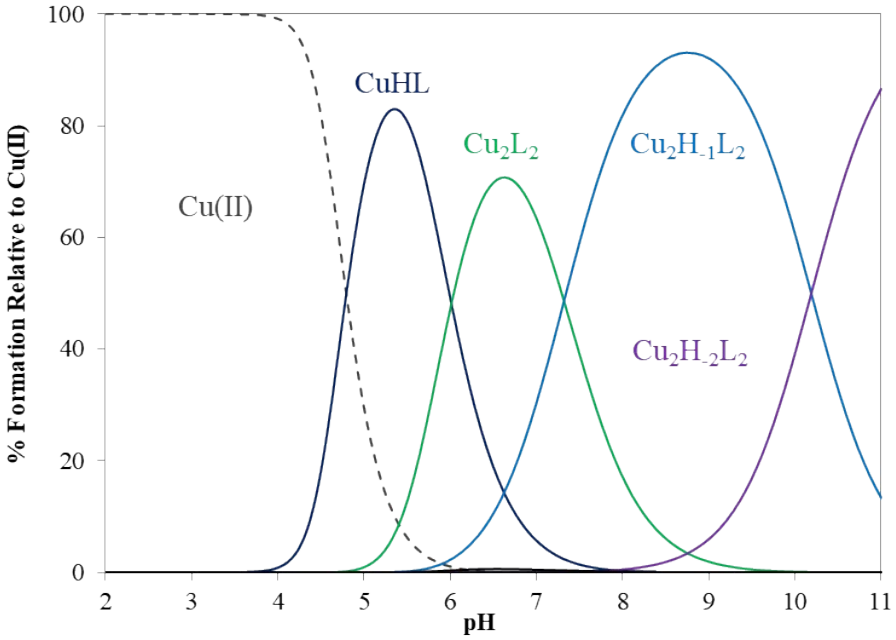

Figure S6. Plot of the species distribution diagram of the system Cu(II)-**L3** in 1:1 Cu(II):L molar ratio. [**L3**] = [Cu(II)] = 1.0×10^{-3} M.

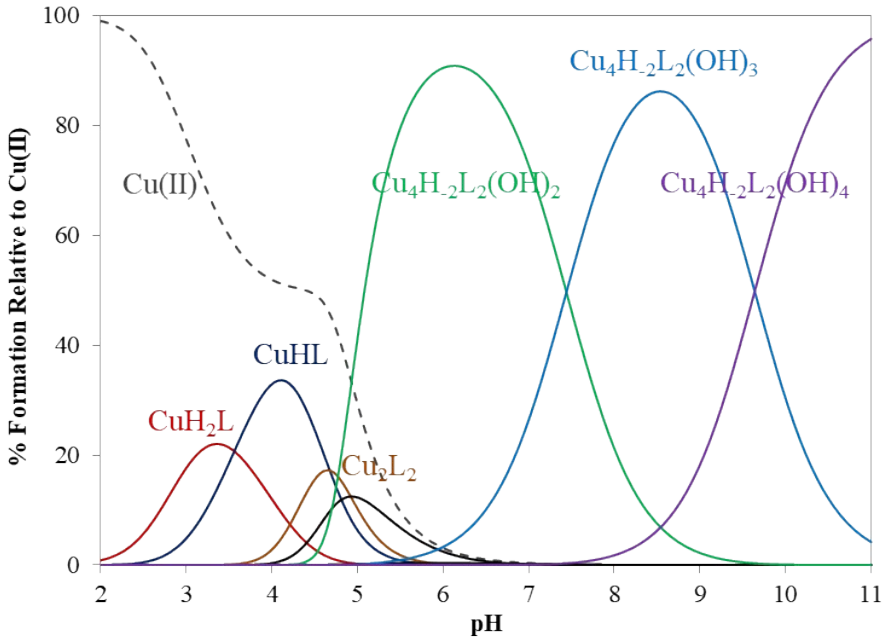

Figure S7. Plot of the species distribution diagram of the system Cu(II)-**L1** in 2:1 Cu(II):L molar ratio. [**L1**] = 1.0×10^{-3} M. [Cu(II)] = 2.0×10^{-3} M.

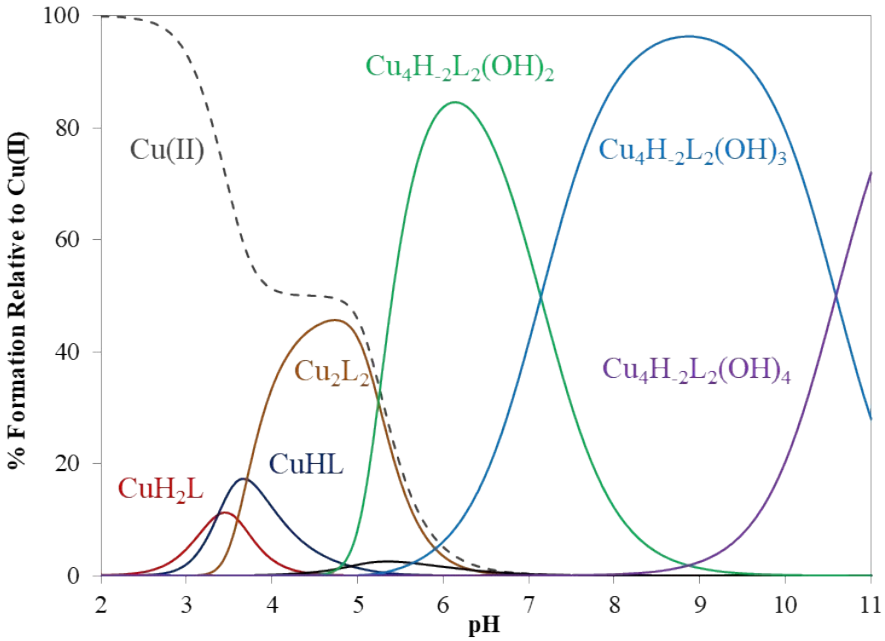

Figure S8. Plot of the species distribution diagram of the system Cu(II)-**L2** in 2:1 Cu(II):L molar ratio. [**L2**] = 1.0×10^{-3} M. [Cu(II)] = 2.0×10^{-3} M.

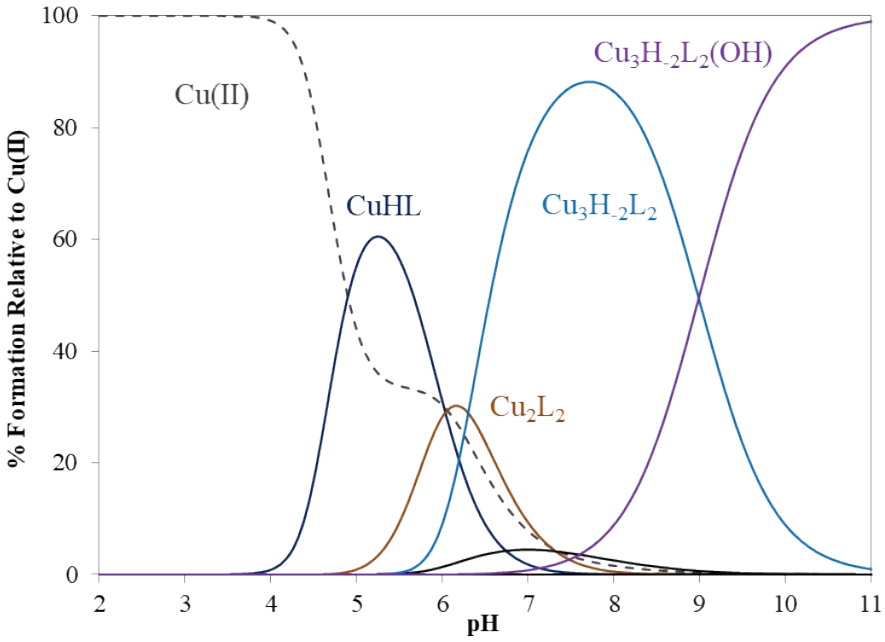

Figure S9. Plot of the species distribution diagram of the system Cu(II)-**L3** in 3:2 Cu(II):L molar ratio. [**L3**] = 1.0×10^{-3} M. [Cu(II)] = 1.5×10^{-3} M.

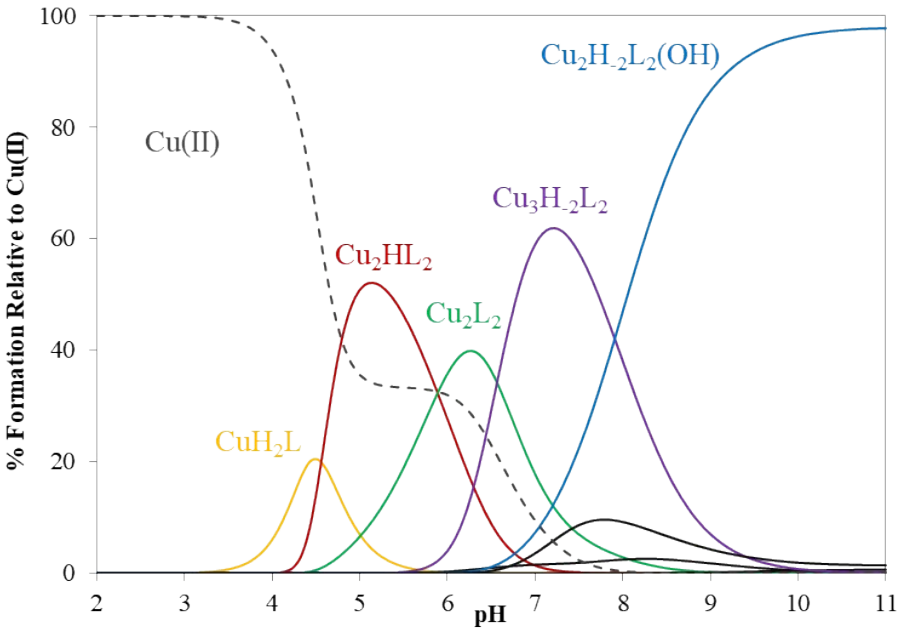

Figure S10. Plot of the species distribution diagram of the system Cu(II)-**L4** in 3:2 Cu(II):L molar ratio. [**L4**] = 1.0×10^{-3} M. [Cu(II)] = 1.5×10^{-3} M.

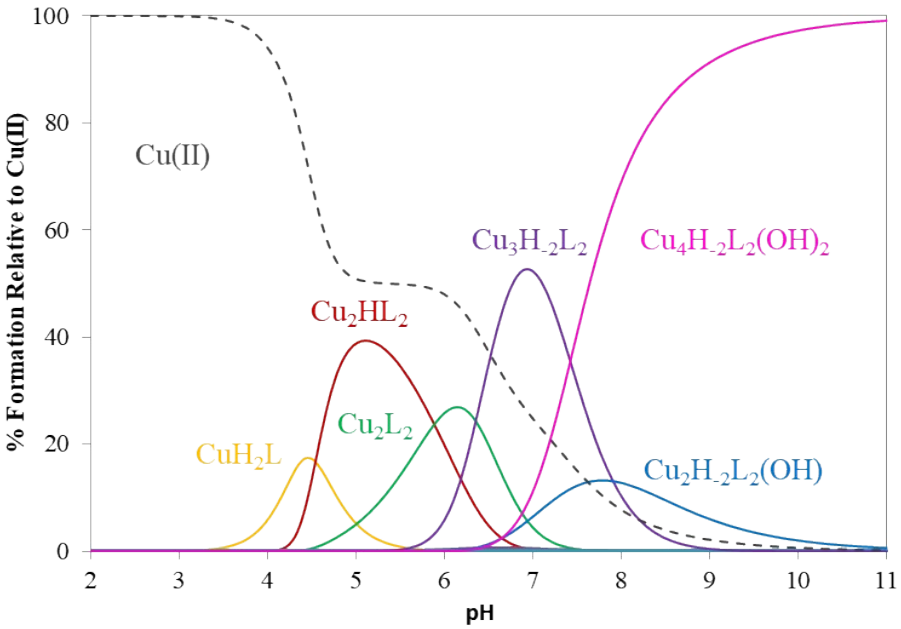

Figure S11. Plot of the species distribution diagram of the system Cu(II)-**L4** in 2:1 Cu(II):L molar ratio. [**L4**] = 1.0×10^{-3} M. [Cu(II)] = 2.0×10^{-3} M.

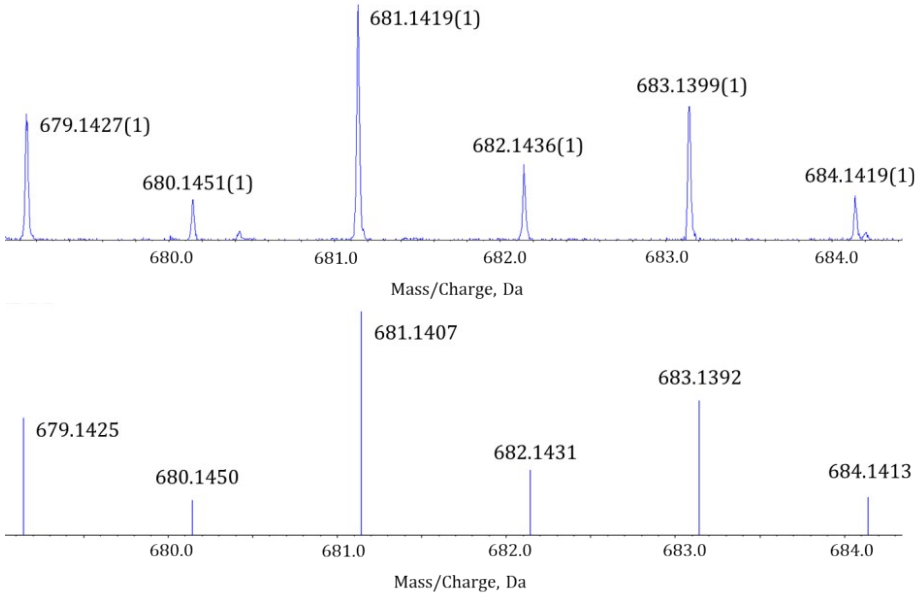

Figure S12. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L1}_2(Br)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L1**] = [Cu(II)] = $1.0x10^{-3}$ M.

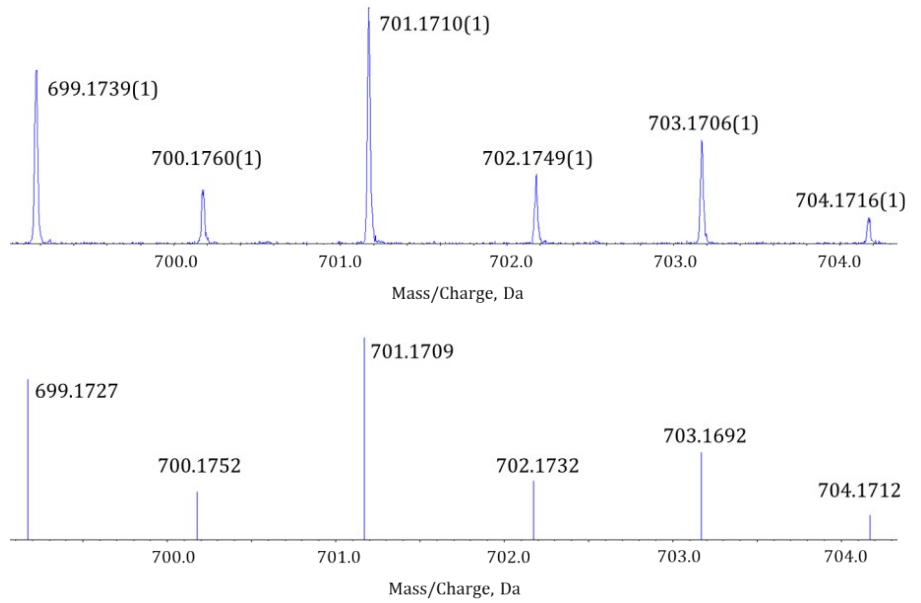

Figure S13. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L1}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L1**] = [Cu(II)] = $1.0x10^{-3}$ M.

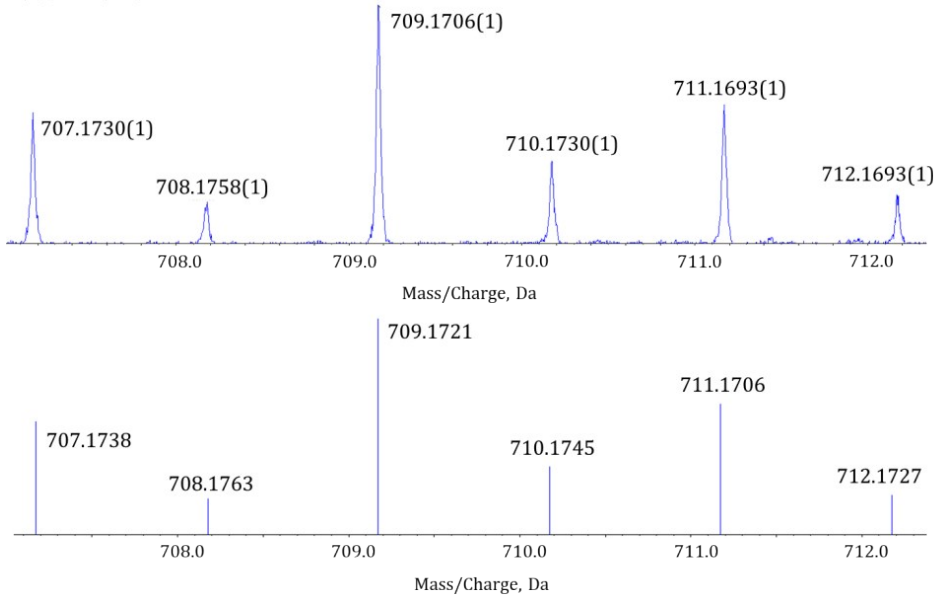

Figure S14. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L2}_2(Br)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M.

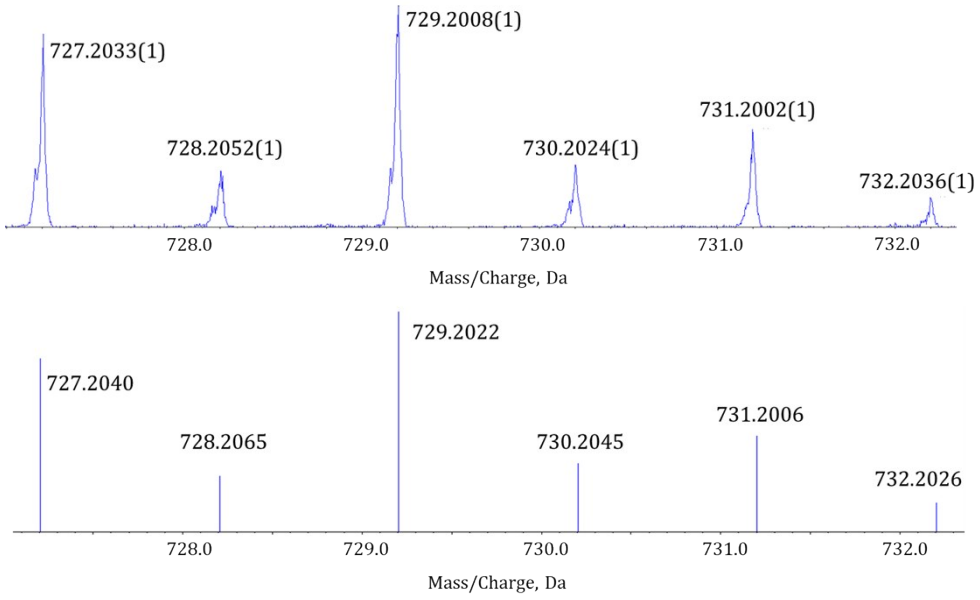

Figure S15. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L2}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L2**] = [Cu(II)] = $1.0x10^{-3}$ M.

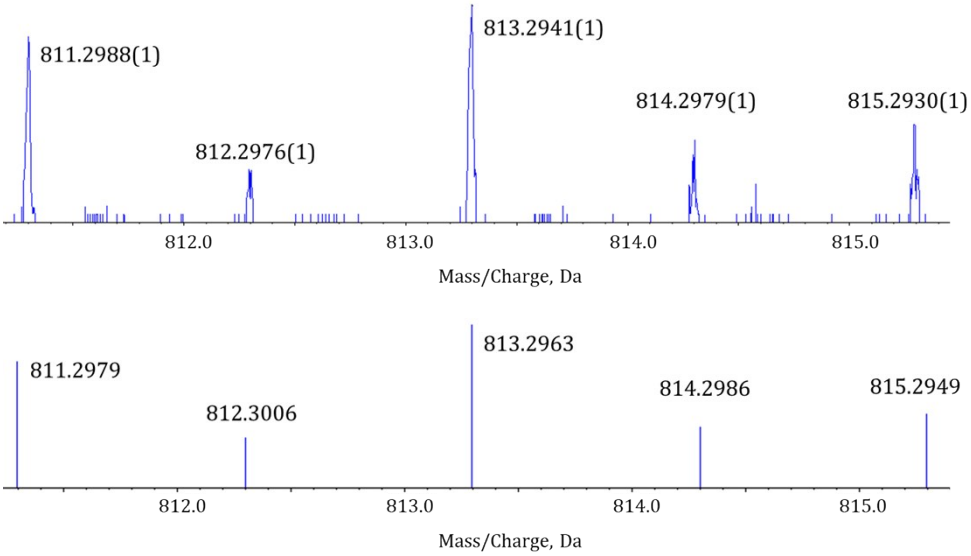

Figure S16. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-2}\mathbf{L3}_2(ClO_4)]^+$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L3**] = [Cu(II)] = 1.0×10^{-3} M.

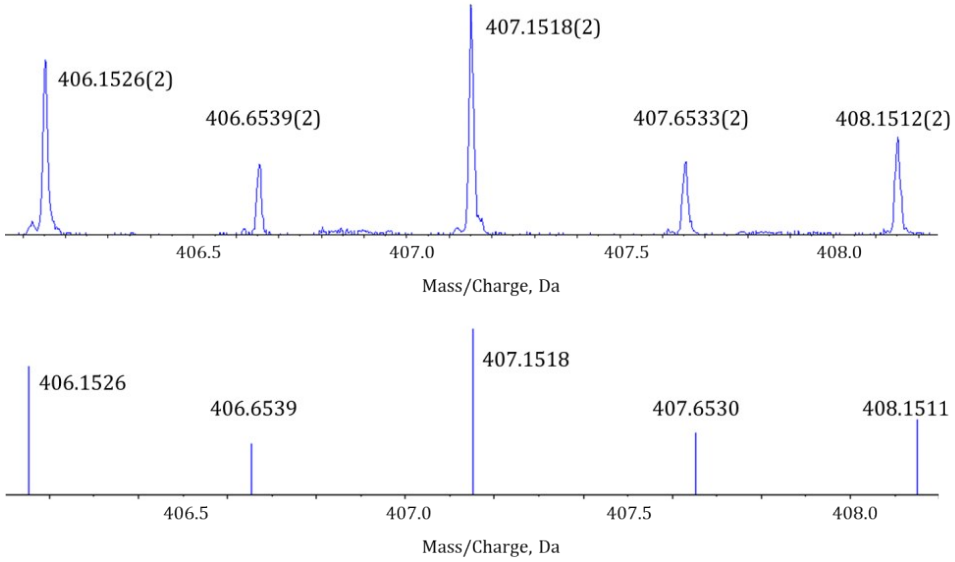

Figure S17. Experimental (top) and simulated (bottom) HR–ESI–Mass peaks for the $[Cu_2H_{-1}\mathbf{L3}_2(ClO_4)]^{2+}$ species. HR–ESI–Mass spectra were recorded in water/methanol (50/50 vol/vol). [**L3**] = [Cu(II)] = 1.0×10^{-3} M.

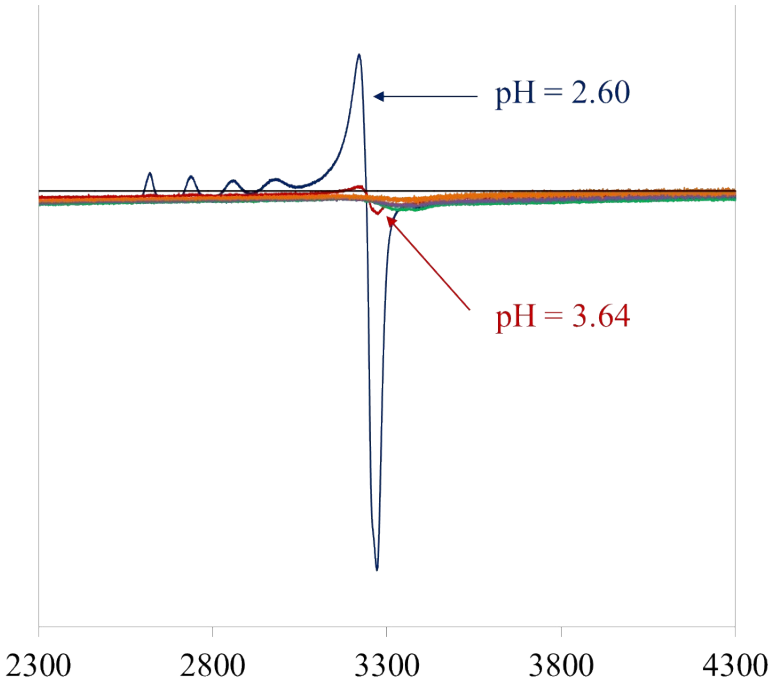

Figure S18. Plot of the ESR spectrum recorded for the system Cu(II)-**L2** in 1:1 Cu(II):L molar ratio. The pH values are: 2.60 (blue), 3.64 (red), 5.63 (green), 8.88 (purple), and 10.95 (orange). [**L2**] = [Cu(II)] = 1.0×10^{-3} M. ESR was recorded in ethylene glycol 30% in water. Experimental conditions: ν = 9.47 GHz and T = 77 K. The signals are ESR silent above pH 5.

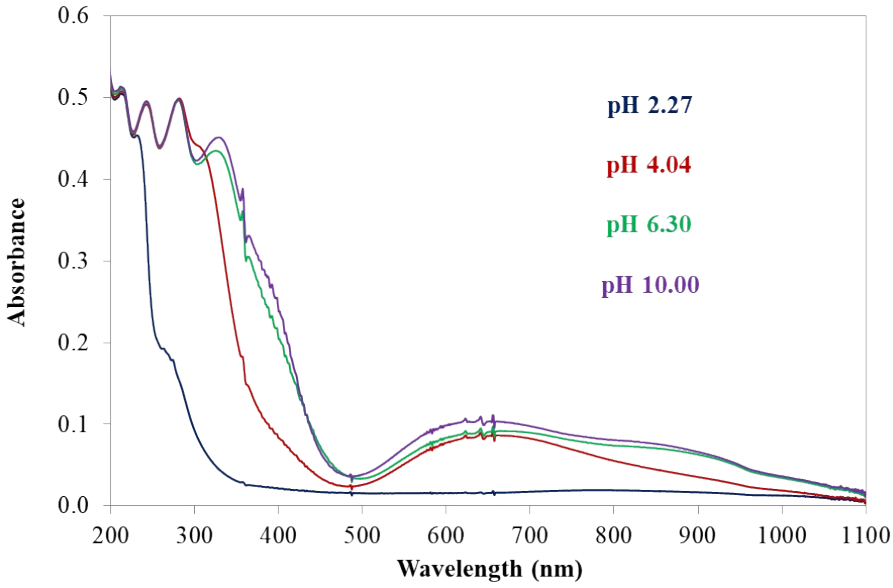

Figure S19. UV-vis spectrum for the Cu(II)–**L1** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.27 (blue), 4.04 (red), 6.30 (green) and 10.94 (purple). [**L1**] = [Cu(II)] = 1.0×10^{-3} M.

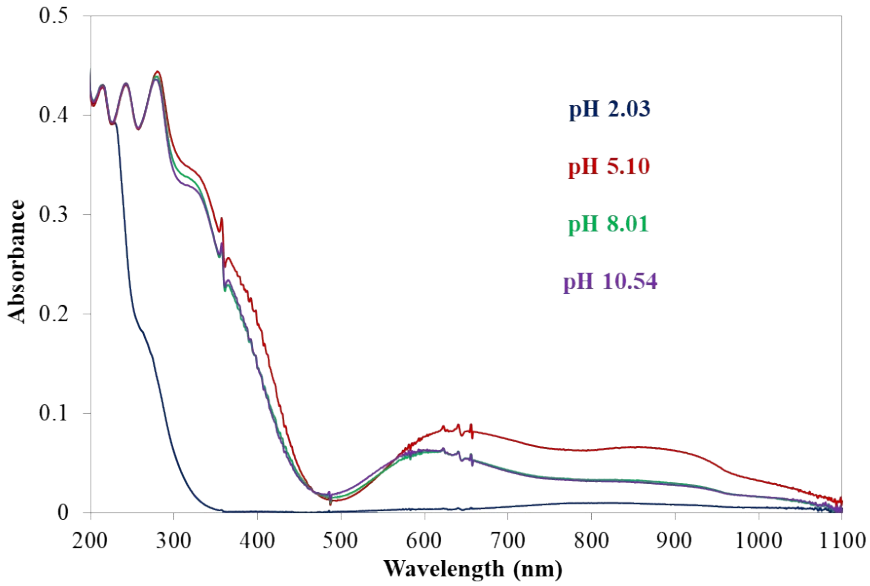

Figure S20. UV-vis spectrum for the Cu(II)–**L2** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.03 (blue), 5.10 (red), 8.01 (green) and 10.54 (purple). [**L2**] = [Cu(II)] = 1.0×10^{-3} M.

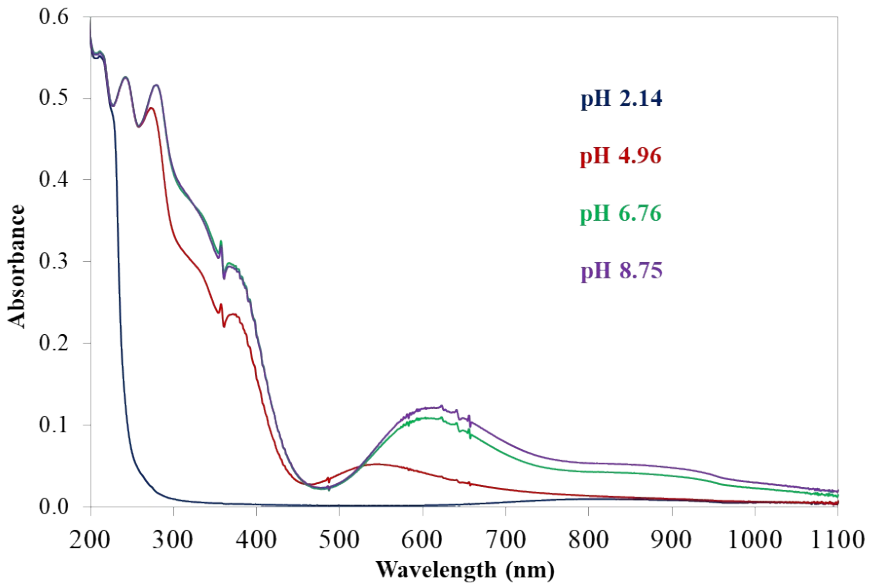

Figure S21. UV-vis spectrum for the Cu(II)–**L3** system in aqueous solution in 1:1 Cu(II):L molar ratio at different pH values: 2.14 (blue), 4.96 (red), 6.76 (green) and 8.75 (purple). [**L3**] = [Cu(II)] = 1.0×10^{-3} M.

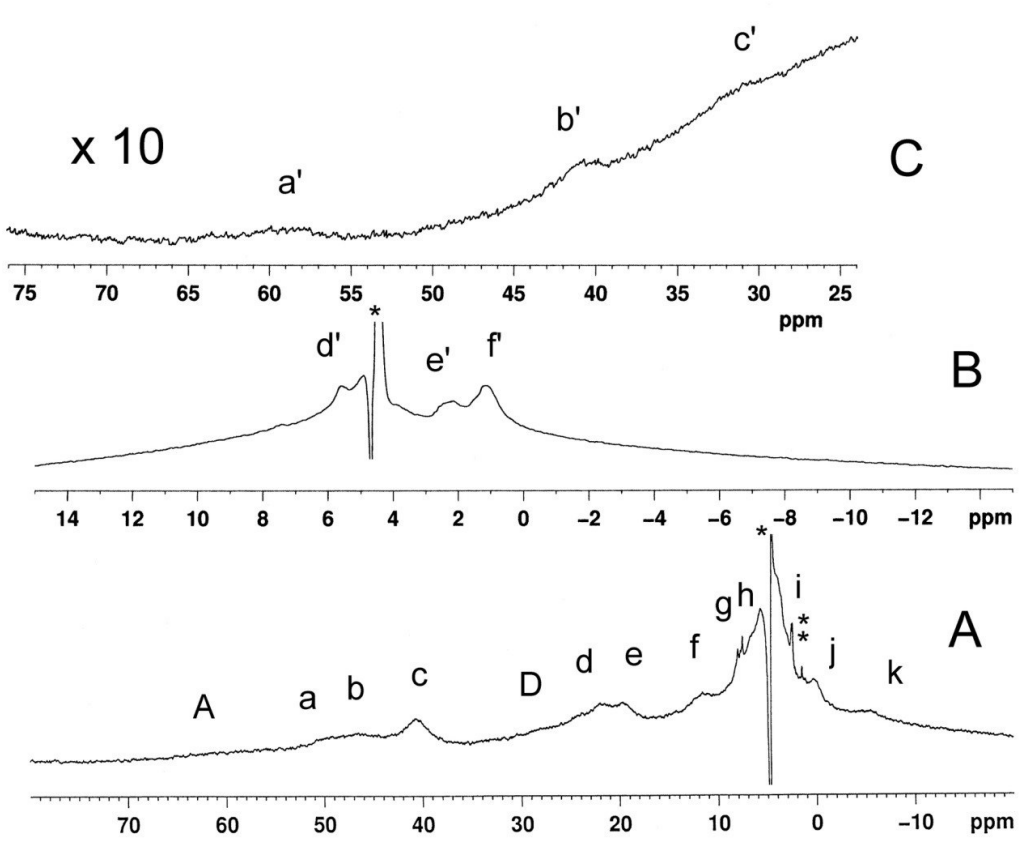

Figure S22. 400 MHz ^{1}H NMR spectra of the Cu^{2+}-L2 system in 1:1 molar ratio recorded at 298 K in D_2O at (a) pH 5 and (b) pH 10. (c) In the region 76/24 ppm, the intensity of the spectrum at pH 10 is multiplied by ten. The asterisks mark the residual solvent (*, H2O; **, HOD).

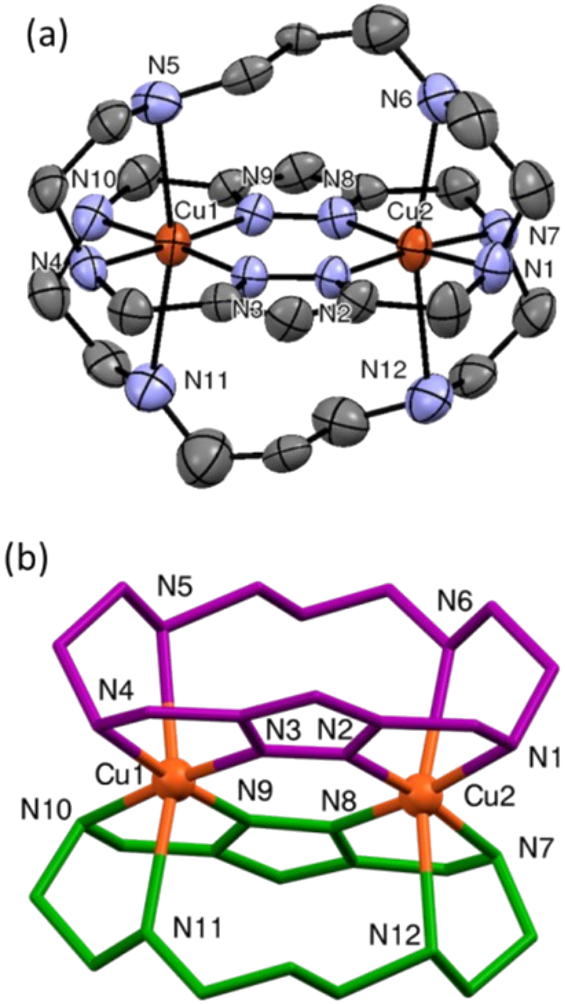

Figure S23. (a) Partial view of the crystal structure of the cation $[Cu_2(H_{-1}\mathbf{L2})_2]^{2+}$ (**2'**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown. Colour code: carbon (grey), nitrogen (blue), copper (orange). (b) Stick view with the two macrocycles composing the structure represented in different colours (purple and green) to clarify the discussion in the text.

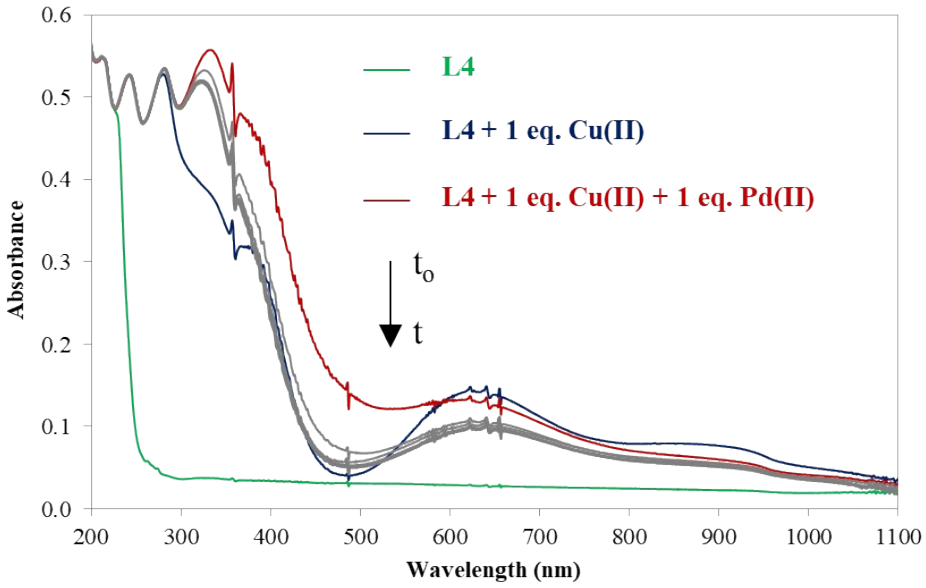

Figure S24. Spectroscopic studies of the mixed Cu(II):Pd(II):**L4** system in 1:1:1 molar ratio. The pH was adjusted to 8 and the UV-vis spectrum was recorded at time values (min): 20, 40, 60, 80, 100, 120, 180 and 300. [**L4**] = [Cu(II)] = [Pd(II)] = 1.0×10^{-3} M.

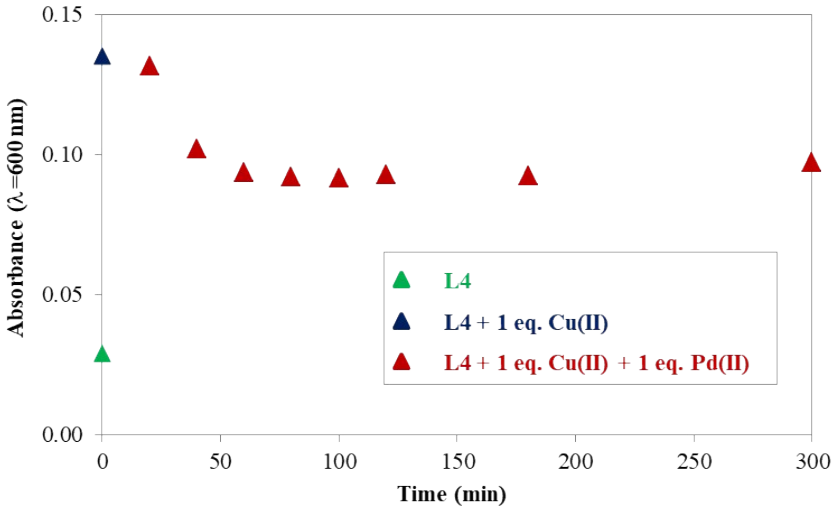

Figure S25. Plot of the absorbance values at 600 nm at different times for the mixed Cu(II):Pd(II):**L4** system in 1:1:1 molar ratio. The UV-vis spectrum was recorded at time values (min): 20, 40, 60, 80, 100, 120, 180 and 300. [**L4**] = [Cu(II)] = [Pd(II)] = 1.0×10^{-3} M.