Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A Water Molecule in the Interior of a 1H-Pyrazole Cu2+ Metallocage.

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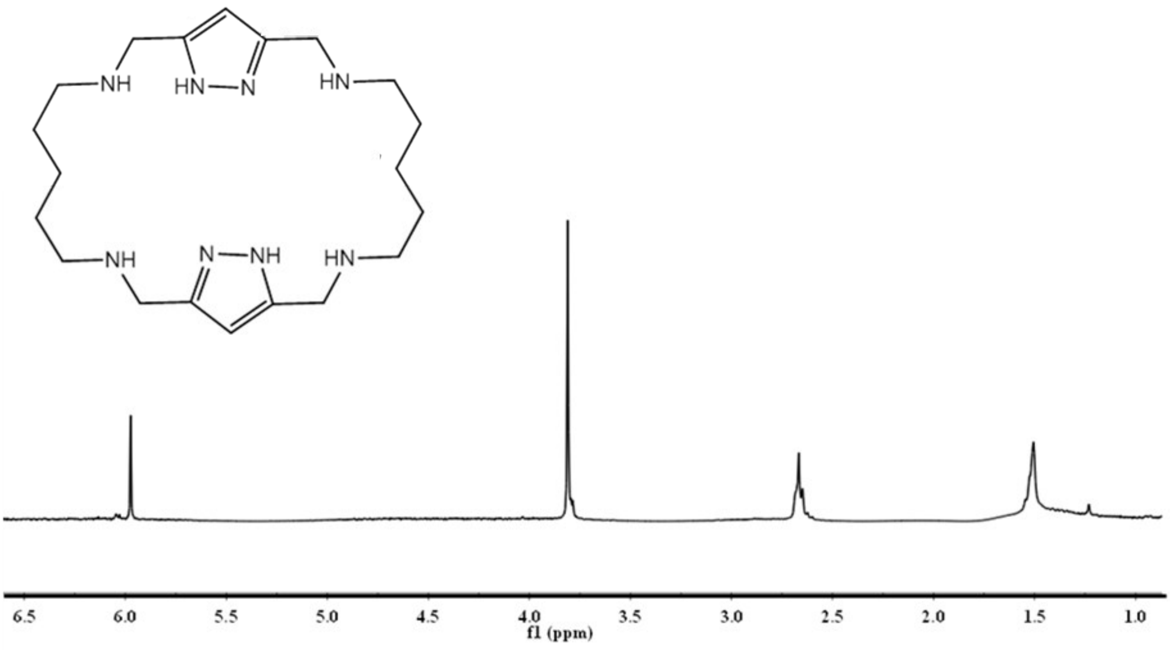
1. Supplementary figures

A)



B)

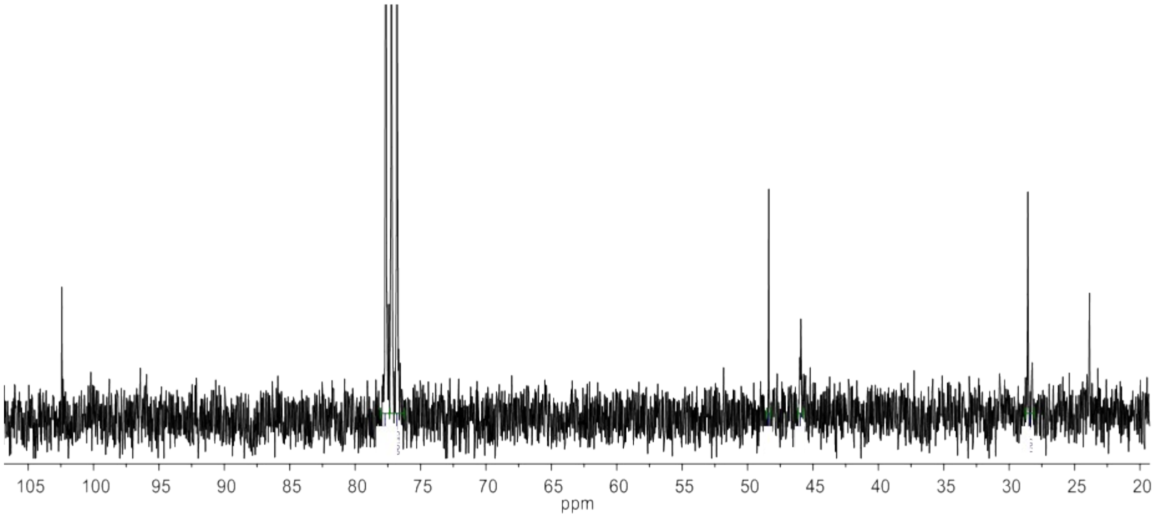


Figure S1. A) ${}^{1}H$ NMR (300 MHz, $CDCl_3$) spectrum of **L**. B) ${}^{13}C$ NMR (75 MHz, $CDCl_3$) spectrum of **L**.

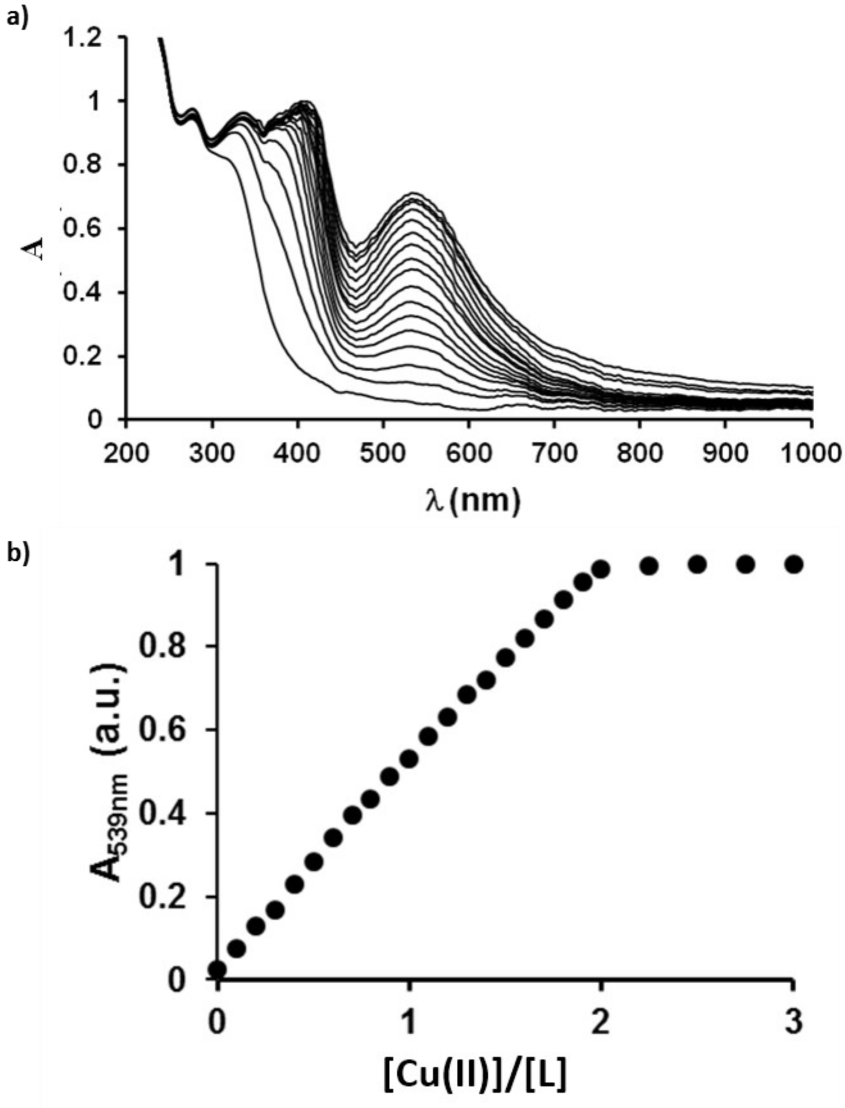


Figure S2 .A) Absorbance spectra of **L** (0.0072 M), adding increasing amounts of an aqueous solution 0.1 M of $Cu(ClO_4)_2$ since molar ratio (1:2) **L**:Cu(II) in water (pH = 8). B) Plot of the absorbance at 539 nm vs. [Cu(II)]/[**L**].

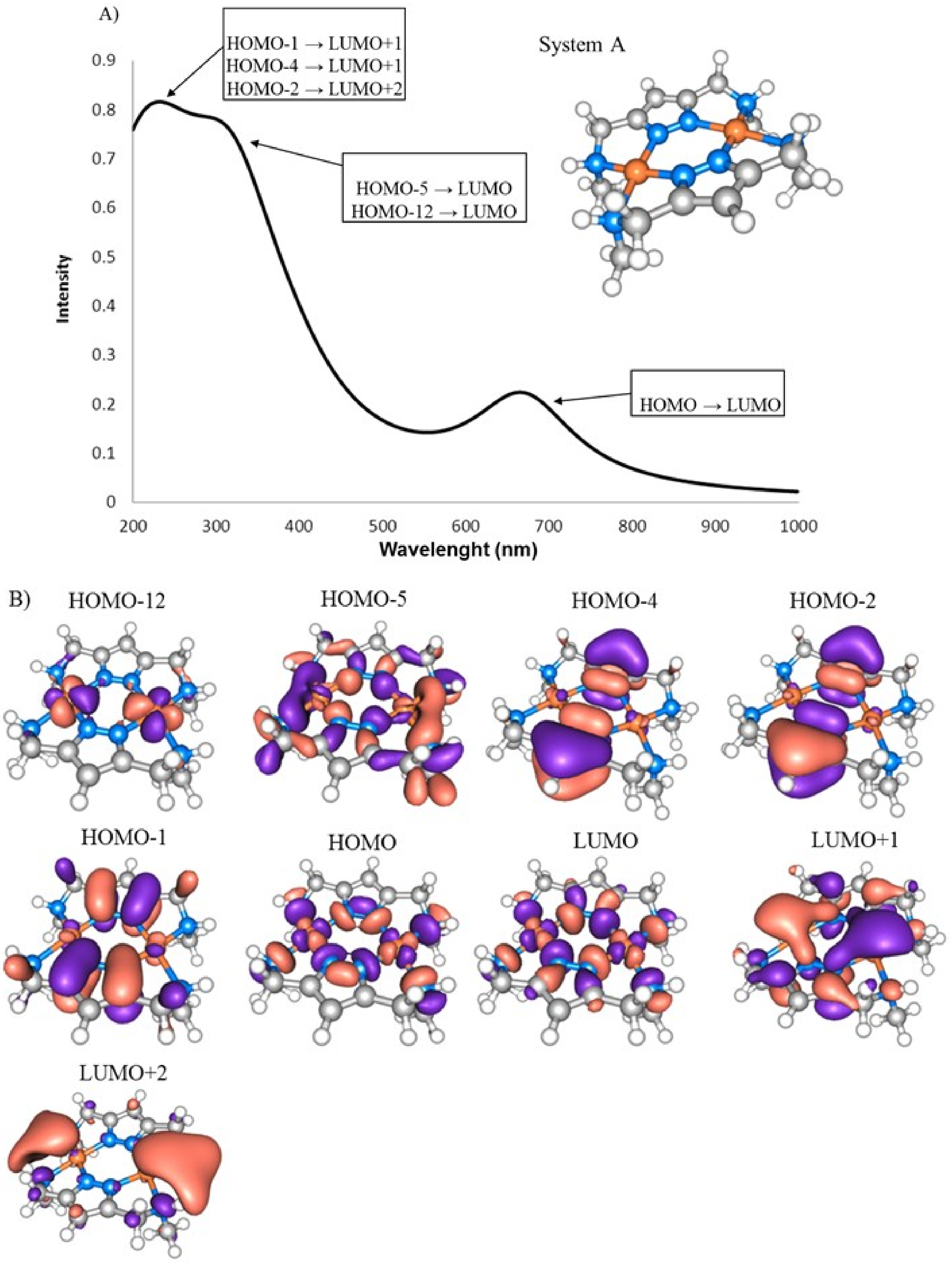


Figure S3. A) Theoretical (TDDFT) absorption spectrum calculated at the B3LYP / 6-31G**//LANL2DZ level for system A. The bands are complex and include several excitations. The main contribution of the main excitations on each band is indicated on the figure. B) Topology of the MOs involved in the main excitations.

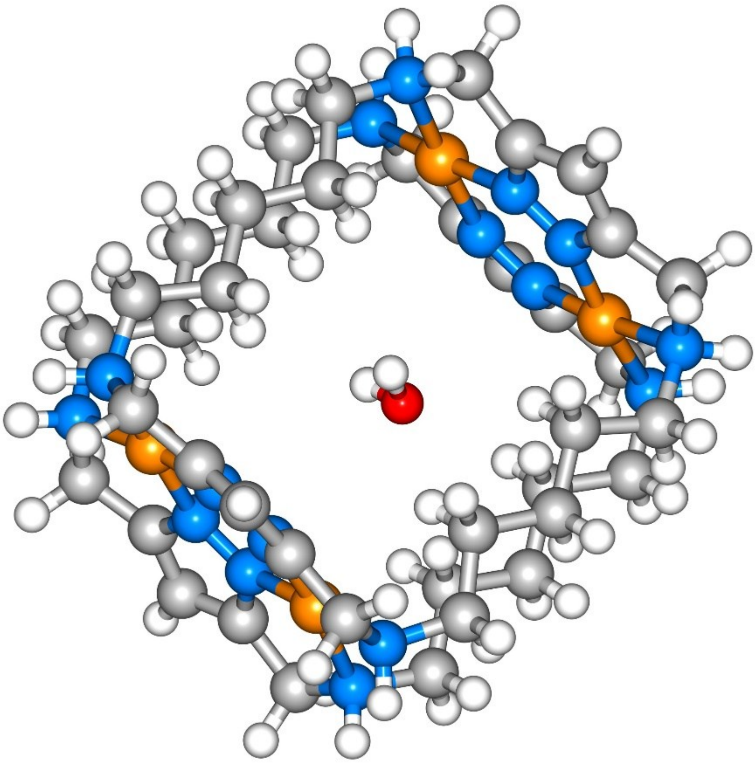


Figure S4. Optimized geometry of the system at the B3LYP/6-31G** level.

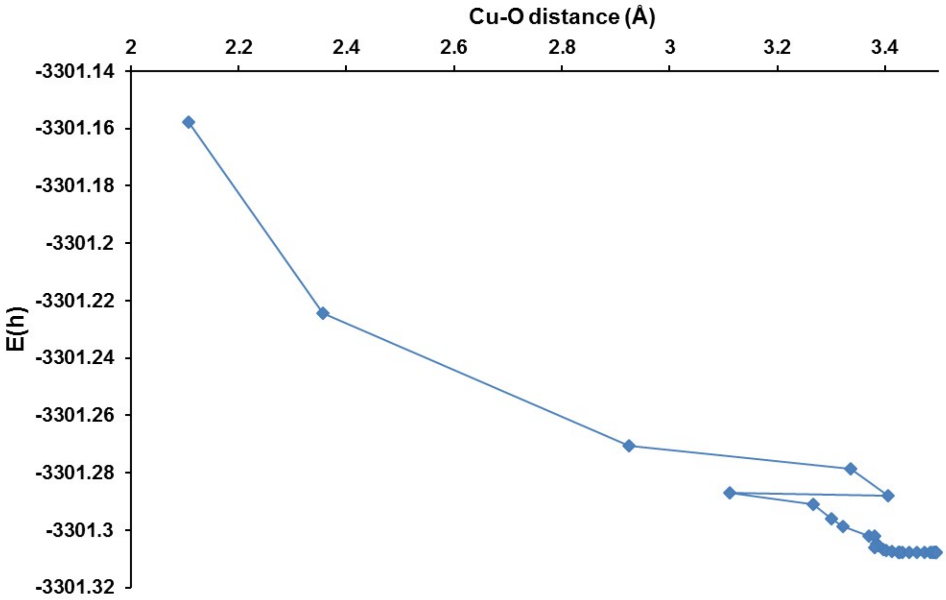
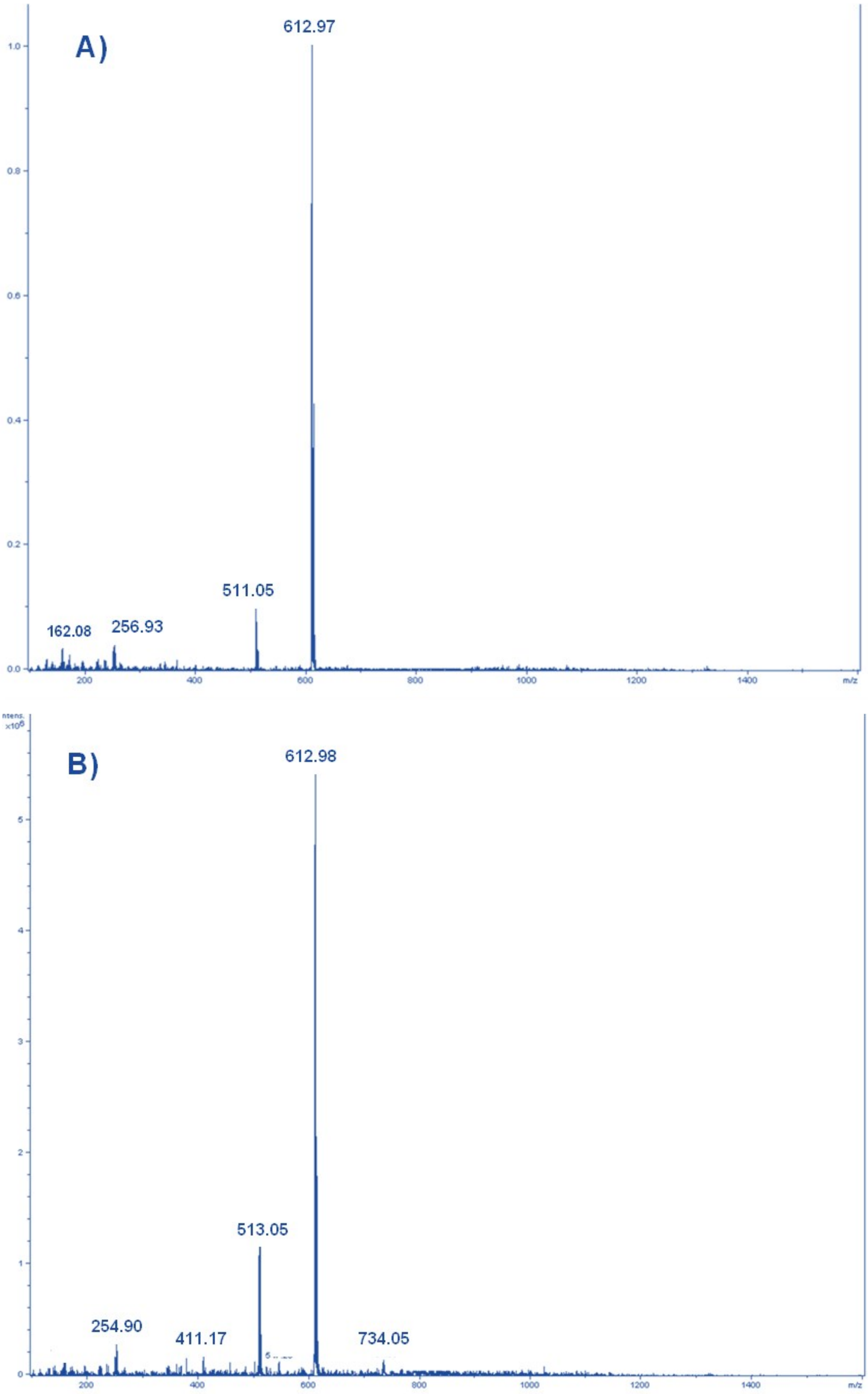


Figure S5. Geometry optimization of the system (B3LYP/6-31G** level). The total system energy vs. the distance between the O and the closest Cu atom at each of the optimization steps is represented. A geometry where the water molecule is at coordination distance of a Cu atom is used as initial guess. The graph shows that the distance Cu-O increses.


A)
612.97
511.05
162.08
256.93
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
1200
1400
m/z
B)
Intens.
x10^6
612.98
513.05
254.90
411.17
734.05
5
4
3
2
1
0
200
400
600
800
1000
1200
1400
m/z

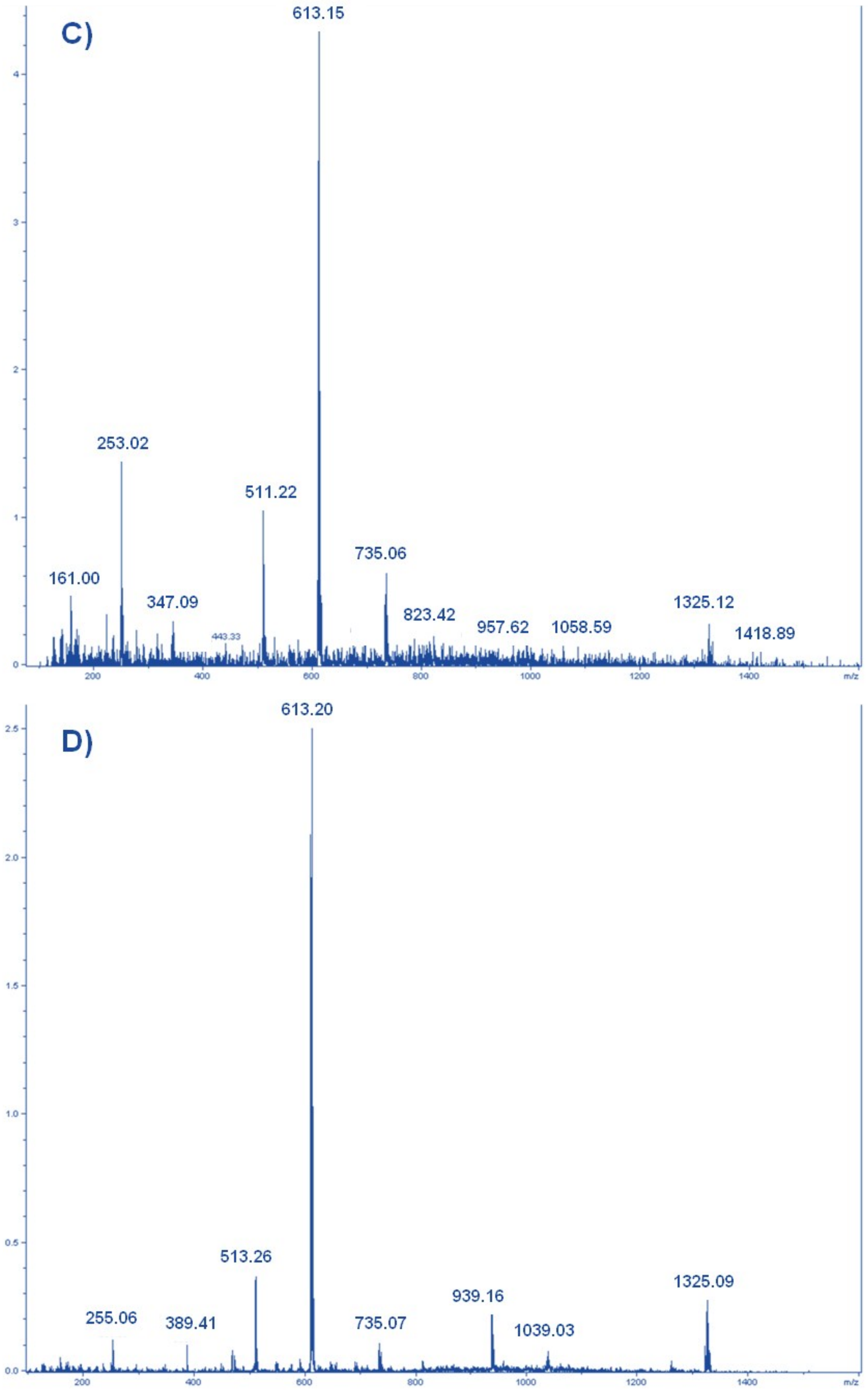


Figure S6. ESI Mass spectra of aqueous solutions on the Cu(II):**L** complexes at pH = 7.4. Concentrations of **L**: A) 0.002 M; B) 0.005 M C) 0.007 M; D) 0.01 M.

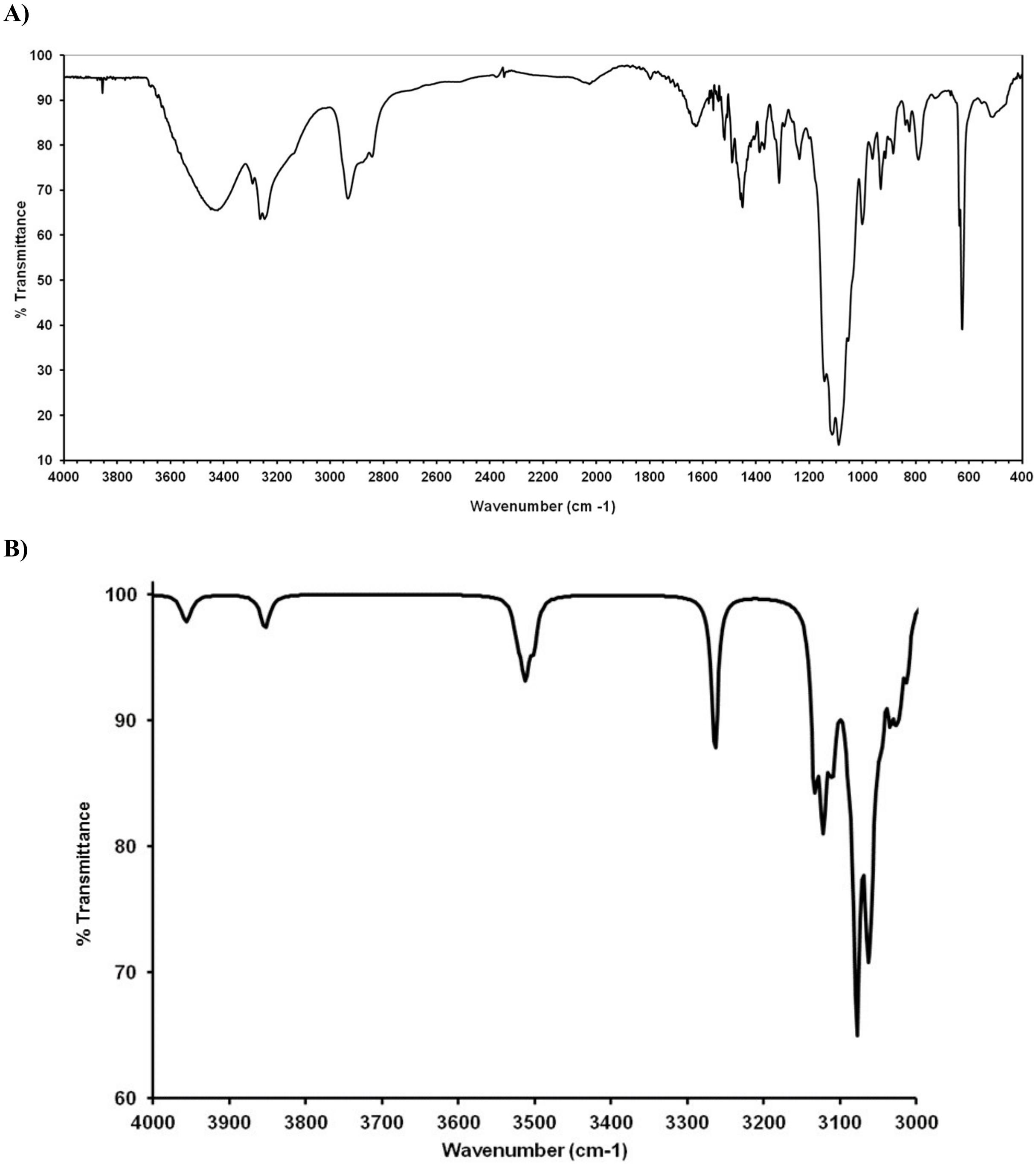


Figure S7. **A**) Experimental IR spectrum (KBr) of complex **3**. **B**) Theoretical (TD-DFT: M06-02X/6-311G(2d,p)) IR spectrum (3000-4000 cm^{-1} range). Transmittance values are calculated from IR intensities. A lorentzian broadening has been applied, with a band width on 1/2 height of 10 nm. The results have been normalized so the point in which the absorption is maximum in this range has been assigned a 65% transmittance. The normalization parameter has been obtained by direct comparison with experimental spectrum. The two small bands centered at 3853 and 3957 cm^{-1} correspond to the symmetric and antisymmetric stretching of the water molecule, respectively.

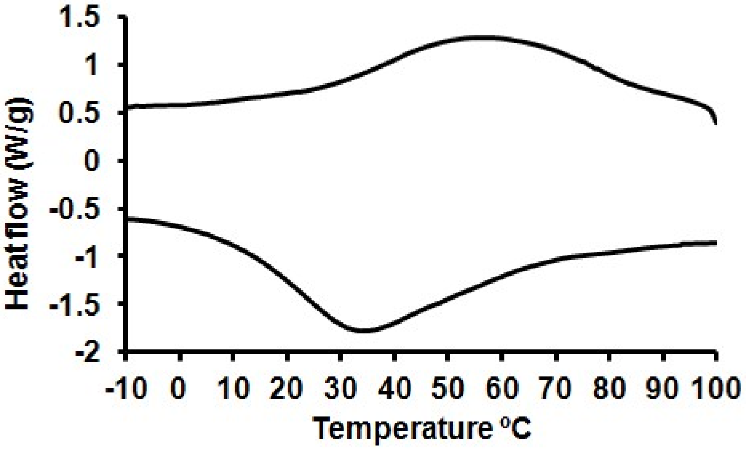


Figure S8. DSC curve of complex **3**.

2. General Experimental Section.

^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AVANCE DRX 300 spectrometer. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Elemental analyses were performed on crystalline samples using an elemental Analyzer (C, H, N, S) CE INSTRUMENTS EA 1110 CHNS. Infrared spectra were obtained on a NICOLET 5700 FT-IR spectrophotometer. ESI Mass spectra were obtained using a MS ESQUIRE 3000 PLUS coupled with a HPLC AGILENT 1100**.** ESI mass spectrometry were carried out by the mass spectrometry services at Servei Central de Suport a la Investigació Experimental (SCSIE) of the University of Valencia.

Differential scanning calorimetric analyses at low temperature were carried out at a scan rate of 10 °C/min using a Mettler Toledo DSC 821e operating in the range -50 - 100ºC. UV-vis spectra were recorded with an Agilent 8453 spectrophotometer. All the solutions were prepared with demineralized water (obtained by a Millipore/Milli-Q system) and methanol purified by standard methods.

3. X-Ray Crystallography

Single crystals of **1** and **2b** were measured in an Enraf Nonius KappaCCD diffractometer using MoKα radiation (λ=0.71073 Å) at 293 K. Single crystals of **2a** and **3** were measured in an Oxford diffraction Supernova diffractometer using MoKα radiation (λ = 0.71073 Å) at 120K. Single crystal of **4** was measured in an Oxford diffraction Supernova diffractometer using MoKα radiation (λ = 0.71073 Å) at 293 K. Structures were solved by direct methods using SHELXT[1] and refined by full-matrix least-squares on all F^2 using SHELXL97 [2] with the WinGX[3] and OLEX2 [18] suites. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. Tables S1 summarize crystal data and structure determination results. Hydrogen bonds have been analyzed with SHELXL97.

The crystal structures included in this contribution have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 892312, 892315, 892316, 1468807 and1468808.

4. Computational details

Density functional theory calculations (DFT) were carried out with the B.01 revision of the Gaussian 09 program package[4], using Becke's three-parameter B3LYP[5,6,7] and M06-02X[8,9] functionals together with the 6-31G**[10] and 6-311G(2d,p)[11] basis sets, extensively used in ab initio quantum chemistry calculations.

The B3LYP functional has become a standard in DFT and has been selected for our calculations given its widespread use. On the other hand, the more recently developed Minnesota M06-class functionals have shown excellent performance for many interesting chemical systems, as shown in three recent reviews.[12, 13, 14] M06-2X performs well for barrier heights and noncovalent interactions at a relatively small computational cost [15], and thus it was considered a good election for the study of this system.

Time-dependent DFT (TDDFT) [16] was used to calculate the UV-Vis spectrum of system A (Figure S3). In this calculation, a 6-31G** + LANL2DZ-ECP basis set was used [17]. This mixed basis set utilizes the Los Alamos Effective Core Potential on the transition metal, while utilizing a Pople type basis set on all other atoms. The LANL2DZ basis set includes a pseudopotential for the inner electrons of the Cu^{II} that reduces the computational effort and introduces an implicit treatment of scalar-relativistic effects.

Table S1. Crystal data and structure refinement for **1**, **2a** and **2b**.

Compound	**1**	**2a**	**2b**
Formula	$C_{20}H_{38}Cl_2N_8O_8$	$C_{120}H_{228}Cl_{12}Cu_{12}N_{48}O_{61}$	$C_{60}H_{112}Cl_6Cu_6N_{24}O_{29}$
Molecular weight	589.48	4507.37	2227.67
T (K)	293(2)	120.00(10)	293(2)
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	P-1	Pnma	Pnma
a (Å)	8.9190(3)	28.221(3)	28.487(2)
b (Å)	9.3360(4)	24.265(10)	24.612(4)
c (Å)	9.7410(3)	12.8478(9)	12.984(5)
α (°)	65.970(2)	90	90
β (°)	89.173(2)	90	90
γ (°)	70.563(2)	90	90
Volume (Å^3)	691.66(5)	8798(4)	9103(4)
Z	1	2	4
ρ (g/cm^3)	1.415	1.701	1.625
λ (Å)	0.71073	0.7107	0.7107
F(000)	312	4648	4592
μ(mm^{-1})	0.293	1.699	1.64
2Θ range	4.892 to 49.99	5.774 to 50	3.304 to 50.006
Reflections collected	4750	24182	19856
Independent reflections	2441	7911	6874
R(int)	0.0247	0.1184	0.1028
Data/restr/param	2441/8/221	7911/225/643	6874/393/683
R1 (I>4σ)	0.0507	0.0996	0.0811
***wR* ^{2}**	0.1403	0.3457	0.2836
GOF (F^2)	1.033	1.016	0.889

Table S2. Crystal data and structure refinement for **3** and **4**.

Compound	**3**	**4**
Formula	$C_{40}H_{76}Cl_4Cu_4N_{16}O_{20}$	$C_{40}H_{70}Cl_4Cu_4N_{16}O_{17}$
Molecular weight	1497.12	1443.08
T (K)	120.00(10)	293(2)
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a (Å)	12.0759(5)	23.5030(7)
b (Å)	14.4835(6)	14.4620(4)
c (Å)	18.6853(8)	17.1670(4)
α (°)	88.419(3)	90
β (°)	80.246(4)	101.7230(10)
γ (°)	70.061(4)	90
Volume (Å^3)	3026.2(2)	5713.4(3)
Z	2	4
ρ (g/cm^3)	1.643	1.678
λ (Å)	0.7107	0.71073
F(000)	1544	2968
μ(mm^{-1})	1.646	1.706
2Θ range	5.85 to 50	3.542 to 49.996
Reflections collected	17350	9815
Independent reflections	10400	5033
R(int)	0.1028	0.0406
Data/restr/param	10400/83/902	5033/121/433
R1 (I>4σ)	0.0475	0.0717
***wR*^{2}**	0.1309	0.2247
GOF (F^2)	1.045	1.038

Table S3. Selected Bond Distances (Å) and Angles (deg) of complex **2a.**

Bond Distances (Å)			**Bond Angles (deg.)**			
Cu1	N7	1.929(10)	N7	Cu1	N8	81.7(4)
Cu1	N2	1.915(11)	N7	Cu1	O2	89.4(5)
Cu1	N8	2.087(12)	N7	Cu1	N1	177.3(6)
Cu1	O2	2.360(14)	N2	Cu1	N7	95.9(5)
Cu1	N1	2.116(12)	N2	Cu1	N8	175.4(6)
Cu2	N6	1.888(9)	N2	Cu1	O2	92.0(6)
Cu2	N5	2.061(10)	N2	Cu1	N1	82.0(5)
Cu2	N3	1.953(10)	N8	Cu1	O2	91.9(6)
Cu2	N4	2.029(12)	N8	Cu1	N1	100.6(5)
Cu3	N10	1.930(14)	N1	Cu1	O2	89.0(6)
Cu3	N10	1.930(14)(#1)	N6	Cu2	N5	81.6(4)
Cu3	N9	2.060(14)(#1)	N6	Cu2	N3	96.2(4)
Cu3	N9	2.060(14)	N6	Cu2	N4	176.6(6)
Cu4	N11	1.930(16)	N3	Cu2	N5	177.8(5)
Cu4	N11	1.930(16)(#1)	N3	Cu2	N4	81.9(5)
Cu4	N12	2.052(17)(#1)	N4	Cu2	N5	100.3(5)
Cu4	N12	2.052(17)	N10	Cu3	N10(#1)	95.0(9)
			N10(#1)	Cu3	N9(#1)	81.3(6)
			N10(#1)	Cu3	N9	175.0(5)
			N10	Cu3	N9(#1)	175.0(5)
			N10	Cu3	N9	81.3(6)
			N9(#1)	Cu3	N9	102.1(8)
			N11(#1)	Cu4	N11	95.6(9)
			N11(#1)	Cu4	N12	175.1(7)
			N11	Cu4	N12	80.2(6)
			N11	Cu4	N12(#1)	175.1(7)
			N11(#1)	Cu4	N12(#1)	80.2(6)
			N12(#1)	Cu4	N12	103.9(9)

Symmetry operations: #1 = +X,3/2-Y,+Z

Table S4. Hydrogen Bonding Contacts for Complex **2a.**

D-H	A	d(D-H)	d(H..A)	<DHA	d(D..A)
N8-H8	O41(#2)	0.98	2.56	3.346(17)	137.7
N8-H8	O43(#2)	0.98	2.04	2.97(2)	158.4
O2-H2A	O4B	0.88	2.04	2.85(3)	152.4
O2-H2A	O4	0.88	2.22	2.81(5)	124.5
O2-H2B	O37	0.88	2.1	2.78(2)	133.8
O2-H2B	O36	0.88	2.48	3.07(2)	124.7
N4-H4	O34(#1)	0.98	2.23	3.05(3)	140.5
N1-H1	O42(#2)	0.98	2.47	3.44(2)	167.9
N12-H12	O21	0.98	2.39	3.044(19)	123.7
N12-H12	O22	0.98	2.61	3.25(3)	123.6
O3-H3D	O44	0.85	2.38	3.04(3)	134.8
O4B-H4BA	O3	0.85	1.76	2.57(3)	157.9
O4B-H4BB	O43(#2)	0.85	2.06	2.83(3)	150.9
O1-O1D	O12(#3)	0.85	2.17	2.96(4)	153.2
O4-H4C	O11(#4)	0.85	2.38	3.00(4)	130.3
O4-H4D	O3	0.85	2.18	2.87(4)	137.5

Symmetry operations: (#1) =1-X,1-Y,2-Z; (#2) =3/2-X,1-Y,-1/2+Z; (#3) =1-X,-1/2+Y,2-Z; (#4) =+X,+Y,-1+Z;

Table S5. Selected Bond Distances (Å) and Angles (deg) of complex **2b.**

Bond Distances (Å)			**Bond Angles (deg.)**			
Cu1	N7	1.929(10)	N2	Cu1	N1	81.4(4)
Cu1	N2	1.915(11)	N2	Cu1	N7	95.9(5)
Cu1	N8	2.087(12)	N2	Cu1	N8	175.2(5)
Cu1	O2	2.360(14)	N7	Cu1	N1	177.3(5)
Cu1	N1	2.116(12)	N7	Cu1	N8	81.4(5)
Cu2	N6	1.888(9)	N8	Cu1	N1	101.3(5)
Cu2	N5	2.061(10)	N5	Cu2	O2	90.2(4)
Cu2	N3	1.953(10)	N3	Cu2	N5	177.7(5)
Cu2	N4	2.029(12)	N3	Cu2	N4	81.8(4)
Cu3	N10	1.930(14)	N3	Cu2	O2	89.0(4)
Cu3	N10(#1)	1.930(14)	N6	Cu2	N5	82.0(5)
Cu3	N9(#1)	2.060(14)	N6	Cu2	N3	95.9(5)
Cu3	N9	2.060(14)	N6	Cu2	N4	176.7(4)
Cu4	N11	1.930(16)	N6	Cu2	O2	91.7(4)
Cu4	N11(#1)	1.930(16)	N4	Cu2	N5	100.3(4)
Cu4	N12(#1)	2.052(17)	N4	Cu2	O2	90.6(4)
Cu4	N12	2.052(17)	N9(#1)	Cu3	N9	101.7(6)
			N10	Cu3	N9	81.8(5)
			N10	Cu3	N9(#1)	175.1(4)
			N10(#1)	Cu3	N9(#1)	81.8(5)
			N10(#1)	Cu3	N9	175.1(4)
			N10	Cu3	N10(#1)	94.5(7)
			N12	Cu4	N12(#1)	101.4(8)
			N11(#1)	Cu4	N12(#1)	83.1(5)
			N11	Cu4	N12	83.1(5)
			N11	Cu4	N12(#1)	175.0(5)
			N11(#1)	Cu4	N12	175.0(5)
			N11	Cu4	N11(#1)	92.4(7)

Symmetry operations: #1 = +X,1/2-Y,+Z

Table S6. Hydrogen Bonding Contacts for Complex **2b.**

D-H	A	d(D-H)	d(H..A)	<DHA	d(D..A)
O4-H4A	O44	0.81	1.7	2.44(5)	151.4
O2-H2A	O12	0.98	2.11	2.92(2)	139.3
O2-H2A	O11	0.98	2.15	2.95(3)	138.8
O2-H2B	O3(#1)	0.99	2.06	2.73(2)	122.3
O1-H1D	O33	0.84	2.23	2.97(2)	147.6
O3-H3A	O4	0.82	1.88	2.64(3)	156

Symmetry operations: (#1) = 1-X,-1/2+Y,1-Z

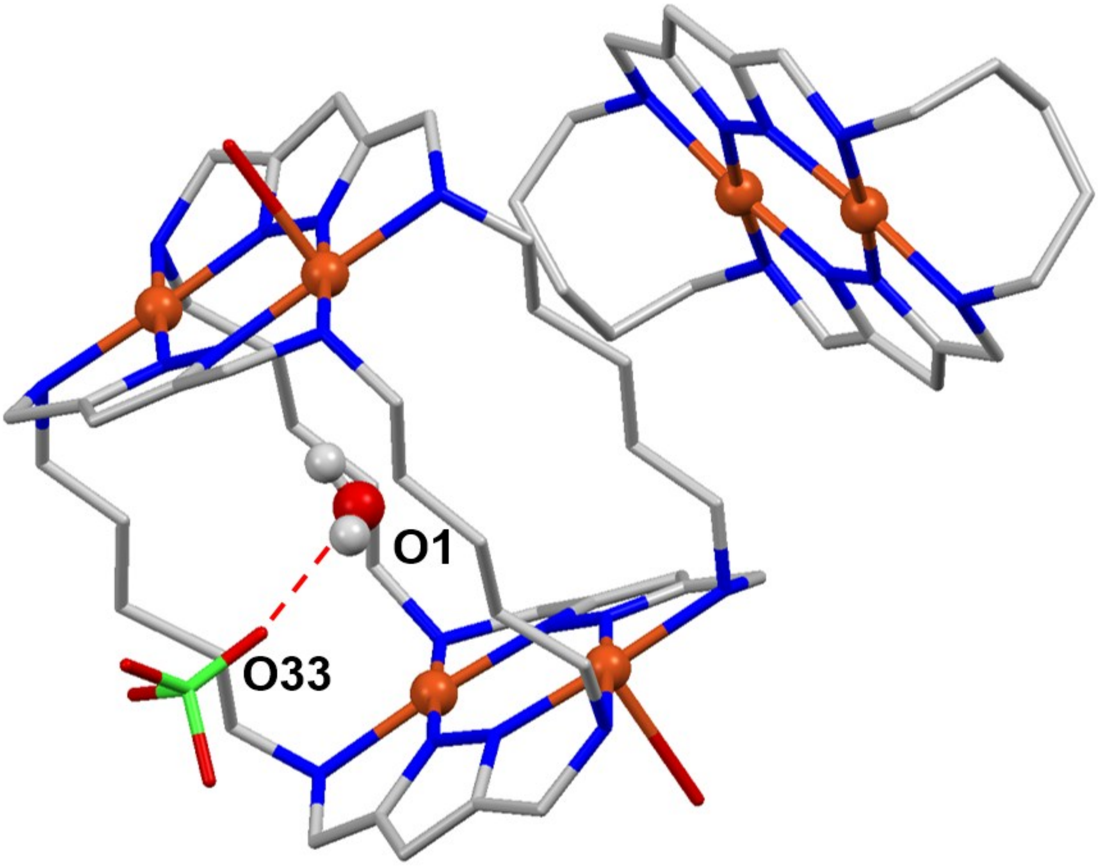


Figure S9. Stick drawing of crystals **2b.**

Table S7. Selected Bond Distances (Å) and Angles (deg) of complex **3.**

Bond Distances (Å)			**Bond Angles (deg.)**			
Cu1	N6	1.945(4)	N6	Cu1	N1	177.00(14)
Cu1	N2	1.931(3)	N6	Cu1	N5	81.81(14)
Cu1	N1	2.078(4)	N6	Cu1	O5	88.90(13)
Cu1	N5	2.076(3)	N2	Cu1	N6	95.93(14)
Cu1	O5	2.409(3)	N2	Cu1	N1	81.39(14)
Cu2	N7	1.923(3)	N2	Cu1	N5	177.46(14)
Cu2	N8	2.090(4)	N2	Cu1	O5	91.75(13)
Cu2	N4	2.060(3)	N1	Cu1	O5	92.51(13)
Cu2	N3	1.937(4)	N5	Cu1	N1	100.84(14)
Cu2	O48	2.324(16)	N5	Cu1	O5	89.36(13)
Cu3	N10	1.924(4)	N7	Cu2	N8	81.84(14)
Cu3	N9	2.067(3)	N7	Cu2	N4	178.14(15)
Cu3	N13	2.079(4)	N7	Cu2	N3	96.19(14)
Cu3	O3	2.436(4)	N7	Cu2	O48	91.5(7)
Cu3	N14	1.929(3)	N8	Cu2	O48	86.6(8)
Cu4	N12(#1)	2.080(4)	N4	Cu2	N8	100.01(14)
Cu4	N15	1.930(4)	N4	Cu2	O48	88.7(7)
Cu4	N11	1.924(3)	N3	Cu2	N8	177.51(14)
Cu4	N16	2.080(4)	N3	Cu2	N4	81.96(14)
			N3	Cu2	O48	91.9(8)
			N10	Cu3	N9	82.07(14)
			N10	Cu3	N13	175.63(15)
			N10	Cu3	O3	96.62(15)
			N10	Cu3	N14	95.29(14)
			N9	Cu3	N13	101.23(15)
			N9	Cu3	O3	90.61(14)
			N13	Cu3	O3	86.25(17)
			N14	Cu3	N9	177.12(14)
			N14	Cu3	N13	81.35(15)
			N14	Cu3	O3	90.85(14)
			N15	Cu4	N12(#1)	177.51(15)
			N15	Cu4	N16	81.85(15)
			N11	Cu4	N12(#1)	81.94(15)
			N11	Cu4	N15	95.75(15)
			N11	Cu4	N16	177.06(16)
			N16	Cu4	N12(#1)	100.44(16)

Symmetry operations: #1 = ^{1}-X,-Y,-Z;

Table S8. Hydrogen Bonding Contacts for Complex **3.**

D-H	**A**	**d(D-H)**	**d(H..A)**	**<DHA**	**d(D..A)**
O5-H5A	O45	0.85	1.96	2.798(7)	169
O3-H3D	O14(#1)	0.85	1.92	2.71(3)	153
O2H2C	O1(#2)	0.822(10)	2.07(9)	2.835(18)	155(20)
O4H4C	O13	0.87	1.6	2.239(17)	128

Symmetry operations: (#1) = -X,1-Y,-Z; (#2) =-X,1-Y,1-Z

Table S9. Selected Bond Distances (Å) and Angles (deg) of complex **4.**

Bond Distances (Å)			**Bond Angles (deg.)**			
Cu1	N3	1.925(5)	N3	Cu1	N4	81.0(2)
Cu1	N2	1.914(6)	N3	Cu1	N1	170.9(2)
Cu1	N4	2.066(6)	N2	Cu1	N3	94.3(2)
Cu1	N1	2.073(6)	N2	Cu1	N4	173.3(2)
Cu2	N2B	1.920(6)	N2	Cu1	N1	81.2(2)
Cu2	N1B	1.918(7)	N4	Cu1	N1	104.1(2)
Cu2	N4B	2.061(7)	N2B	Cu2	N4B	170.8(3)
Cu2	N3B	2.049(7)	N2B	Cu2	N3B	82.5(3)
			N1B	Cu2	N2B	93.7(3)
			N1B	Cu2	N4B	81.6(3)
			N1B	Cu2	N3B	176.0(3)
			N3B	Cu2	N4B	102.3(3)

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