Electronic Supplementary Information

Family of $[Cu_2]$, $[Cu_4]$ and $[Cu_5]$ Aggregates: Alteration of Reaction Conditions, Ancillary Bridges and Capping Anions

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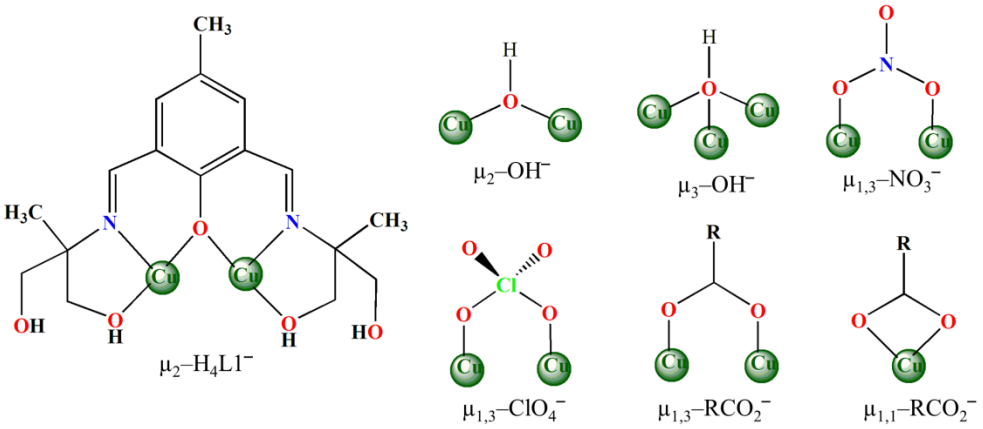
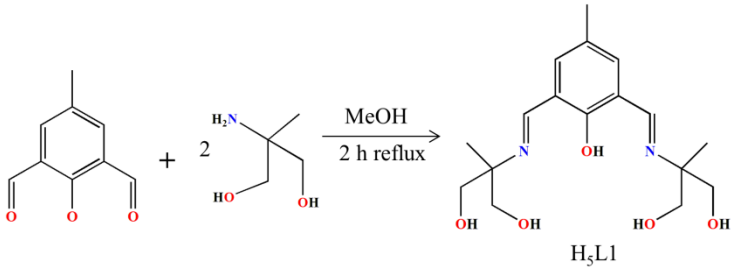
Chart S1 Observed metal binding modes of H_4L1^-, OH^-, NO_3^-, $ClO_4^-$and RCO_2^-



Scheme S1 Synthesis of ligand H_5L1



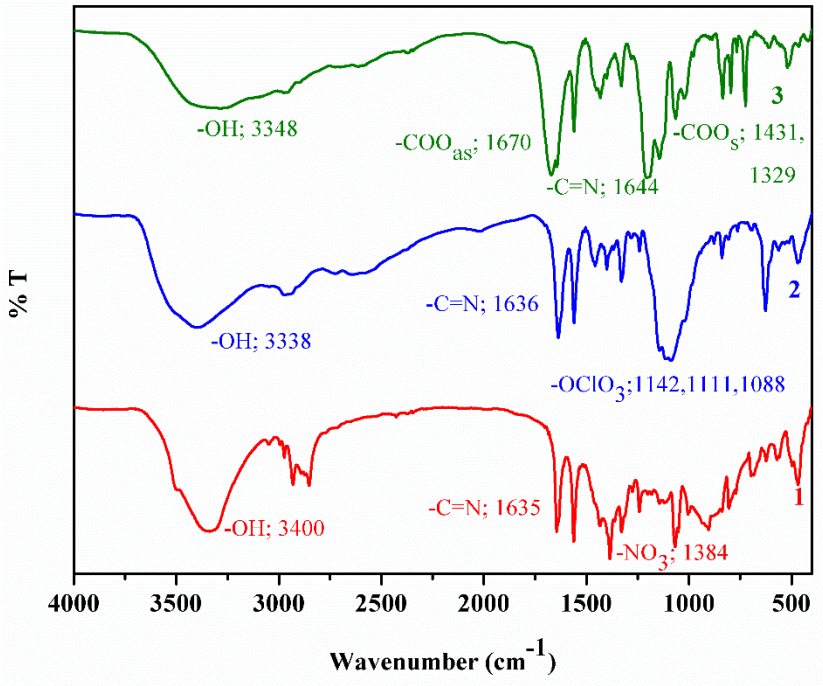


Figure S1 FTIR Spectra of **1-3**

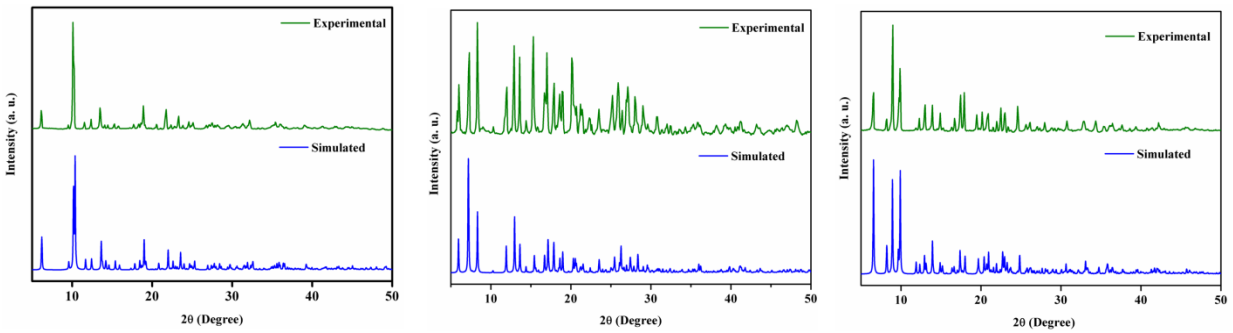


Figure S2 Experimental (olive) and simulated (blue) PXRD traces of **1** (i), **2** (ii) and **3** (iii)

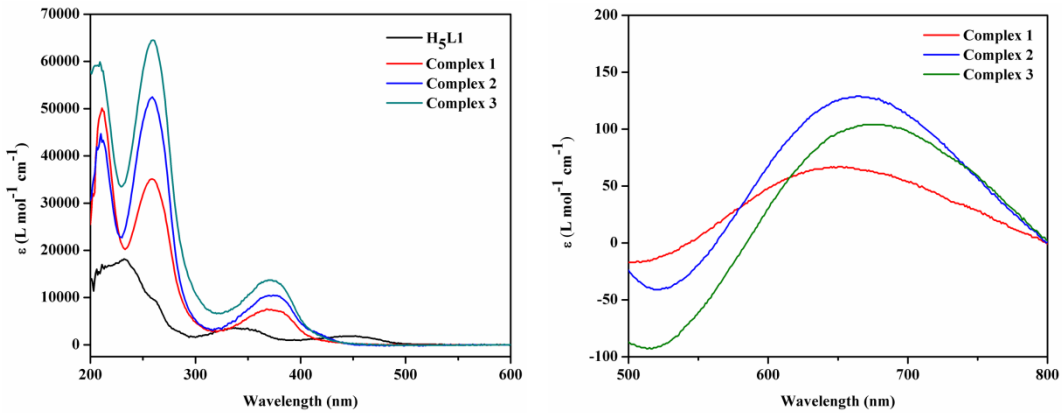


Figure S3 Charge transfer (left) and d-d transition (right) bands for **1**-**3**

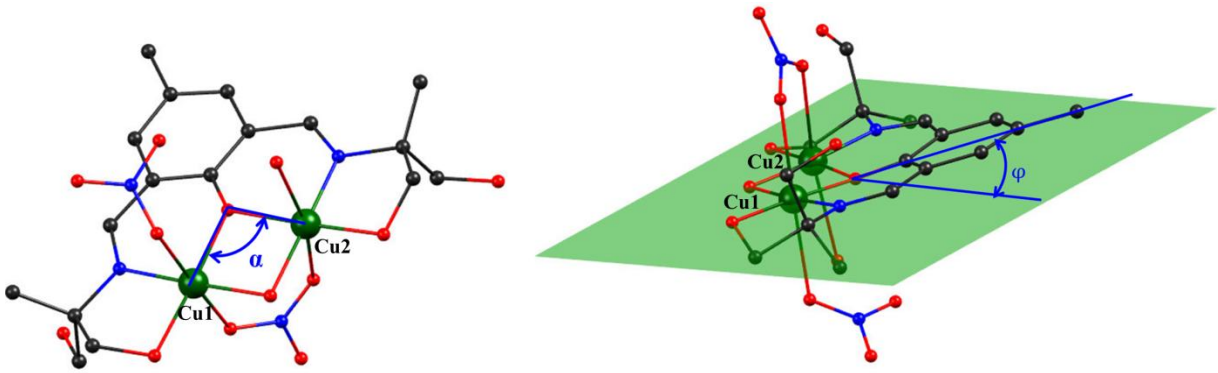


Figure S4 Coordination core in **1** showing the angles α and φ

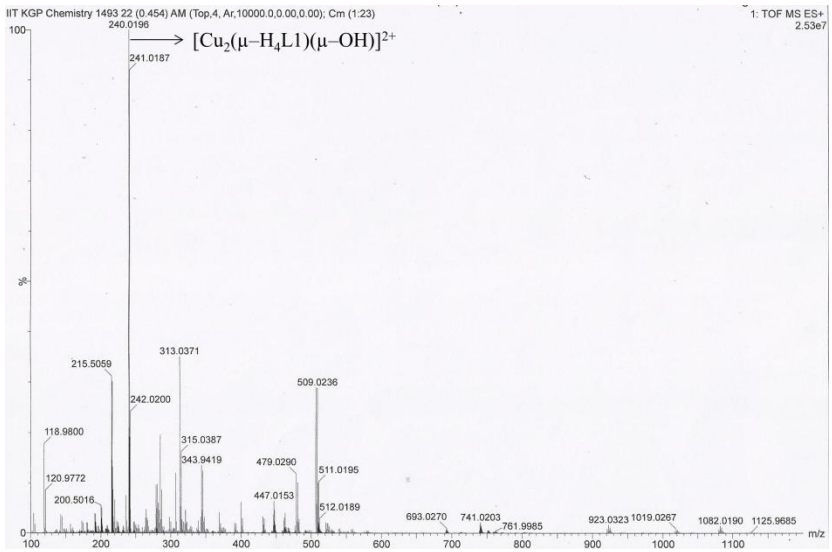


Figure S5 ESI MS spectra of **1** in MeOH

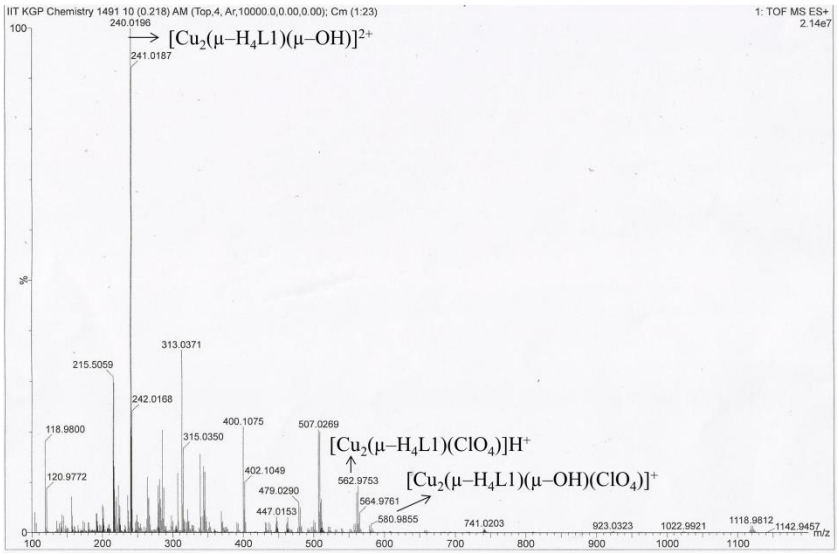


Figure S6 ESI MS spectra of **2** in MeOH

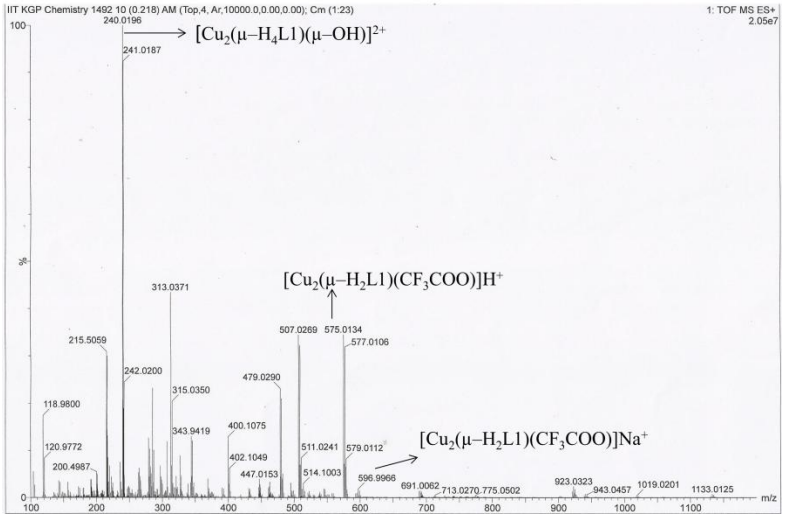


Figure S7 ESI MS spectra of **3** in MeOH

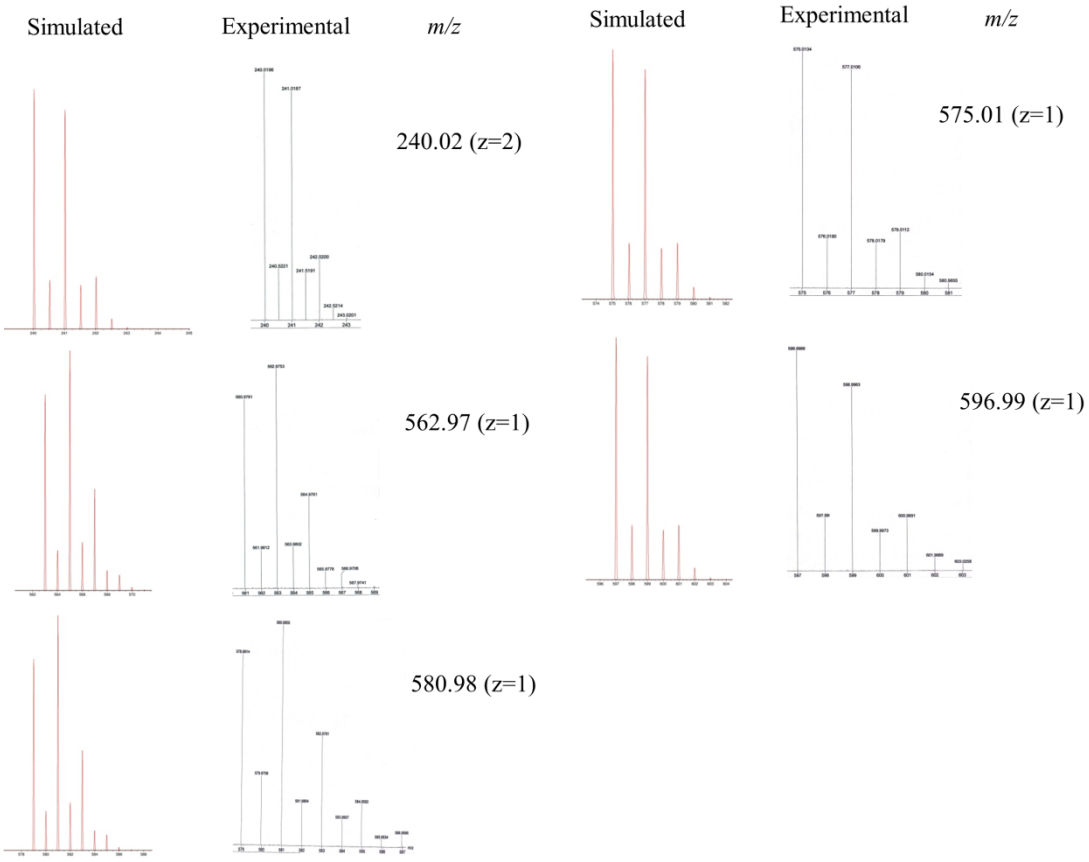


Figure S8 Experimental and simulated isotropic distribution patterns of the peaks of **1**-**3**, respectively, obtained using ESI-MS

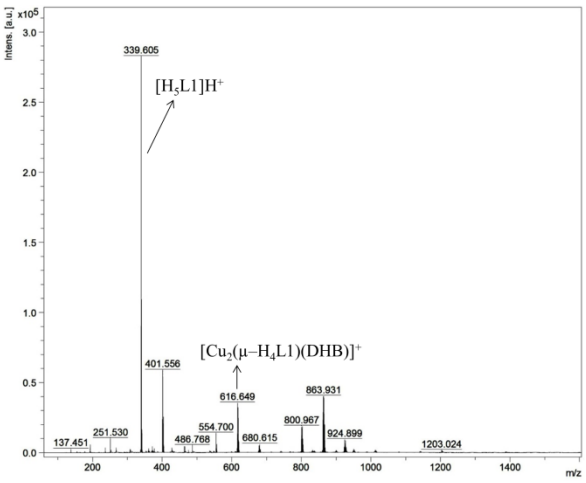


Figure S9 MALDI TOF spectra of **1** in MeOH

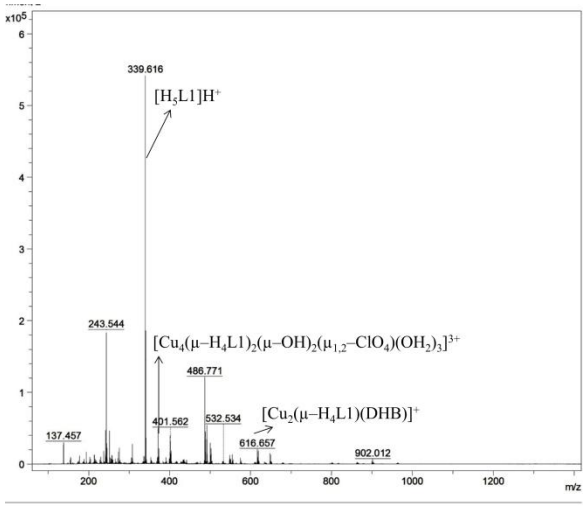


Figure S10 MALDI TOF spectra of **2** in MeOH

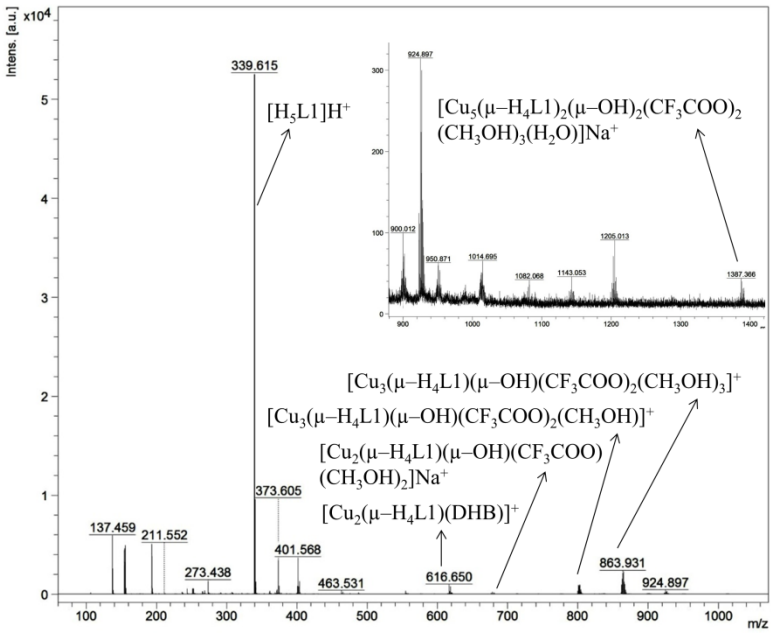
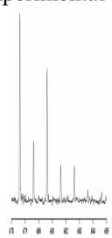
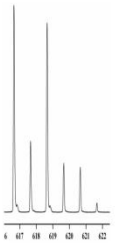
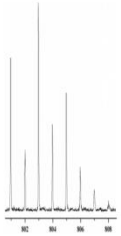
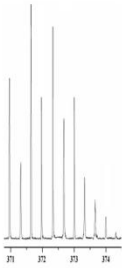


Figure S11 MALDI TOF spectra of **3** in MeOH

Simulated	Experimental	*m/z*	Simulated	Experimental	*m/z*
		339.61 (z =1)			678.61(z =1)
		616.65 (z =1)			802.96(z =1)
		371.42 (z =3)			864.94(z =1)

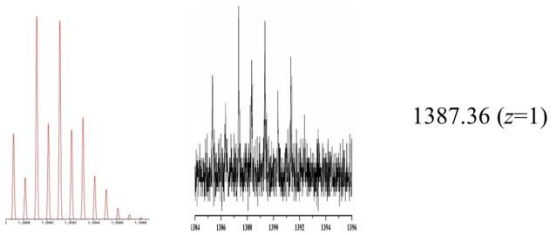


Figure S12 Experimental and simulated isotropic distribution patterns of the peaks of **1-3**, respectively, obtained using MALDI TOF MS

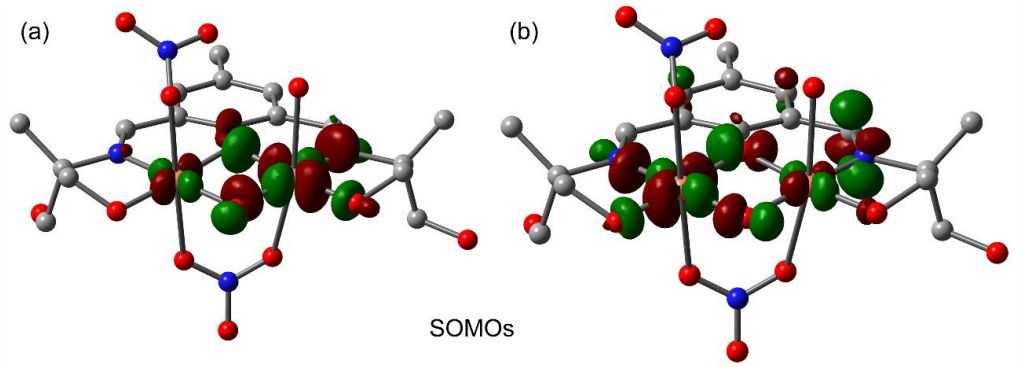


Figure S13 Graphical representation of the SOMOs of complex **1**

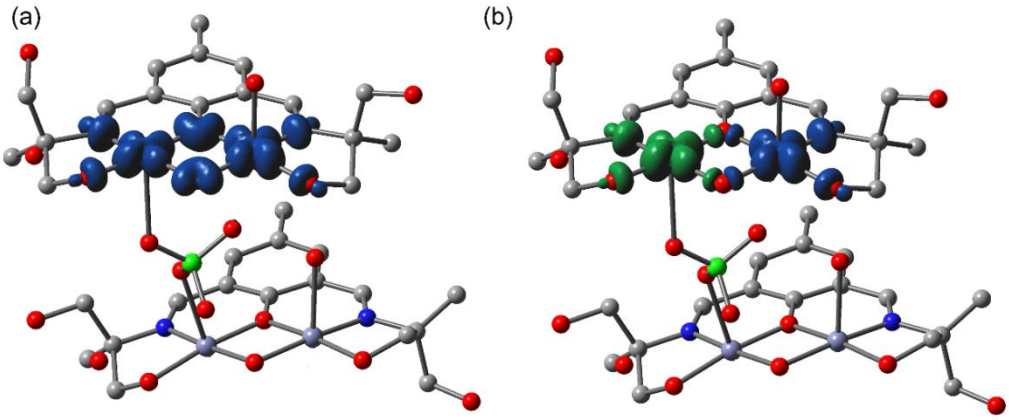


Figure S14 Representation of spin density (contour 0.004 e $Å^{-3}$) at the high spin (a) and low spin (b) configurations of complex **2** (Cu1···Cu2 coupling). Positive spin represented in blue and negative spin in green

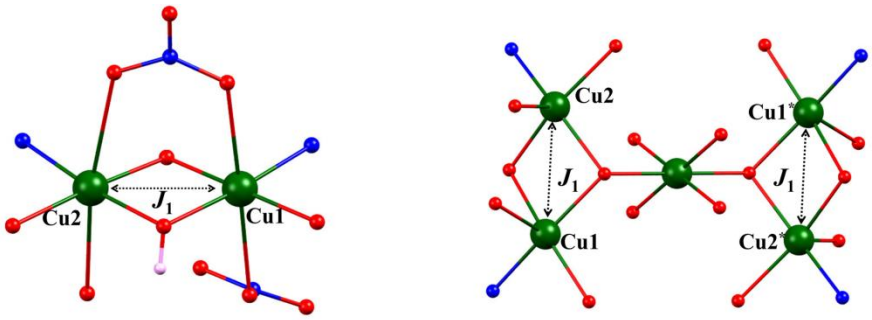


Figure S15 View for exchange interactions used for fitting process for complex **1** (left) and **3** (right)

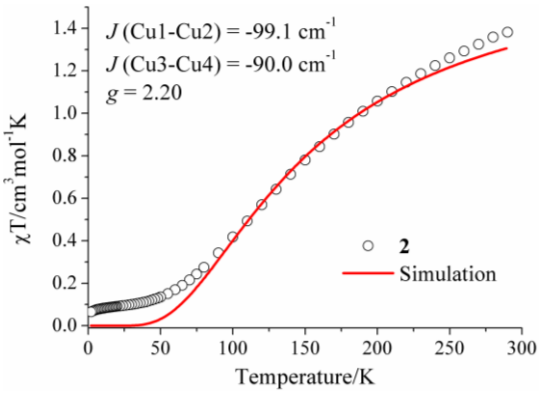


Figure S16. Magnetic susceptibility data for compound **2**. The solid line represents a simulation of the data based on the results of the DFT calculations, using the parameters shown in the Figure, where each of the four Cu(II) ions was assumed to have g = 2.20.

Table S1 Important bond lengths (Å) and angles (°)in **1**, **2** and **3**

Bond lengths (Å)					
Complex **1**					
Cu1 − O1	1.929(5)	Cu1 – N1	1.927(6)	Cu2 – O11	2.549(6)
Cu1 – O2	1.942(5)	Cu2 – O1	1.910(5)	Cu2 – N2	1.921(6)
Cu1 – O3	1.9732(10)	Cu2 – O2	1.958(5)	Cu1 – Cu2	2.8967(13)
Cu1 – O5	2.432(6)	Cu2 – O4	1.945(5)		
Cu1 –O8	2.475(6)	Cu2 – O6	2.574(6)		
Complex **2**					
Cu1 − O1	1.921(2)	Cu2 –N2	1.913(2)	Cu4 – O15	1.958(2)
Cu1 – O2	1.973(2)	Cu3 – O12	1.912(2)	Cu4 – N4	1.921(2)

Cu1 – O3	1.947(2)	Cu3 – O13	1.955(2)	Cu1 – Cu2	2.9243(8)
Cu1 – O11	2.354(3)	Cu3 – O14	1.923(2)	Cu3 – Cu4	2.9213(8)
Cu1 − N1	1.938(2)	Cu3 – O18	2.357(3)		
Cu2 – O1	1.915(2)	Cu3–N3	1.938(3)		
Cu2 – O2	1.941(2)	Cu4 – O8	2.584(2)		
Cu2 – O4	1.943(2)	Cu4 – O12	1.913(2)		
Cu2 – O7	2.638(2)	Cu4 – O13	1.943(2)		
Complex **3**					
Cu1 − O1	1.924(3)	Cu2 – O2	1.995(3)	Cu3 – O8A	2.048(9)
Cu1 – O2	1.975(3)	Cu2 – O3	1.964(4)	Cu1 – Cu2	2.9091(8)
Cu1 – O4	1.947(3)	Cu2 – O6	2.201(3)		
Cu1 – O5	2.301(4)	Cu2 – N1	1.939(4)		
Cu1 – N2	1.929(4)	Cu3 – O2	1.919(3)		
Cu2 – O1	1.939(3)	Cu3 – O7A	1.976(9)		
Bond angles (°)					
Complex **1**					
O1–Cu1–N1	93.9(2)	O1−Cu2−O6	81.5(2)	O3−Cu1−N1	84.3(2)
O1–Cu1–O2	82.9(2)	O2−Cu1−N1	175.5(3)	O3−Cu1−O5	93.33(14)
O1–Cu1–O3	177.26(16)	O2−Cu1−O3	99.05(16)	O3−Cu1−O8	89.02(14)
O1–Cu1–O5	88.7(2)	O2−Cu1−O5	87.5(2)	O4−Cu2−N2	86.0(2)
O1−Cu1−O8	89.0(2)	O2−Cu1−O8	92.6(2)	O4−Cu2−O11	89.3(2)
O1−Cu2−N2	94.3(2)	O2−Cu2−O11	93.7(2)	O4−Cu2−O6	103.1(2)
O1−Cu2−O2	83.0(2)	O2−Cu2−O6	85.8(2)	O5−Cu1−N1	89.3(2)
O1−Cu2−O4	175.5(2)	O2−Cu2−N2	173.8(3)	O5−Cu1−O8	177.6(2)
O1−Cu2−O11	86.2(2)	O2−Cu2−O4	97.2(2)	O6−Cu2−N2	88.4(2)
O6−Cu2−O11	167.58(19)	O8–Cu1–N1	90.5(2)	O11−Cu2−N2	91.7(2)

Cu1−O1−Cu2	98.0(2)	Cu1−O2−Cu2	95.9(2)		
Complex **2**					
O1–Cu1–N1	92.59(9)	O2−Cu2−O7	84.59(8)	O13−Cu3−O18	98.45(9)
O1–Cu1–O2	81.46(9)	O3−Cu1−N1	85.20(10)	O14−Cu3−N3	86.26(10)
O1–Cu1–O3	174.68(9)	O3−Cu1−O11	92.89(12)	O14−Cu3−O18	90.28(10)
O1–Cu1–O11	92.15(12)	O4−Cu2−N2	84.72(10)	O18−Cu3−N3	89.07(10)
O1−Cu2−N2	93.28(10)	O4−Cu2−O7	89.58(9)	O8−Cu4−N4	93.43(9)
O1−Cu2−O2	82.46(9)	O7−Cu2−N2	91.37(9)	O12−Cu4−N4	92.14(9)
O1−Cu2−O4	174.21(9)	O11−Cu1−N1	95.87(12)	O12−Cu4−O13	81.79(9)
O1−Cu2−O7	95.91(8)	O12−Cu3−N3	93.11(10)	O12−Cu4−O15	170.66(10)
O2−Cu1−N1	171.80(10)	O12−Cu3−O13	81.52(9)	O12–Cu4–O8	99.83(9)
O2−Cu1−O3	100.23(9)	O12−Cu3−O14	174.41(9)	O13−Cu4−N4	173.89(10)
O2–Cu1−O11	90.03(12)	O12−Cu3−O18	95.27(10)	O13−Cu4−O15	99.79(9)
O2–Cu2–N2	173.77(10)	O13−Cu3−N3	171.10(10)	O13−Cu4−O8	88.36(8)
O2–Cu2–O4	99.95(9)	O13−Cu3−O14	98.39(9)	O15−Cu4−N4	86.07(10)
O15−Cu4−O8	89.44(9)	Cu1–O2–Cu2	96.70(9)	Cu3–O13–Cu4	97.08(9)
Cu1–O1–Cu2	99.33(9)	Cu3–O12–Cu4	99.59(9)		
Complex **3**					
O1−Cu1−N2	92.69(15)	O2−Cu2−O3	96.67(15)	O2–Cu3–O8A*	87.5(3)
O1−Cu1−O2	82.96(12)	O2−Cu2−O6	87.92(14)	O7A−Cu3−O7A*	180.0
O1−Cu1−O4	170.10(16)	O3−Cu2−N1	85.50(16)	O7A−Cu3−O8A	48.7(4)
O1−Cu1−O5	87.34(14)	O3−Cu2−O6	103.06(16)	O7A−Cu3−O8A*	131.3(4)
O1−Cu2−N1	90.63(15)	O4−Cu1−N2	85.62(16)	O8A−Cu3−O8A*	180.0
O1−Cu2−O2	82.05(13)	O4−Cu1−O5	102.55(15)	Cu1−O1−Cu2	97.73(14)
O1−Cu2−O3	158.12(18)	O5−Cu1−N2	102.67(16)	Cu1−O2−Cu2	94.24(14)
O1−Cu2−O6	98.73(14)	O6−Cu2−N1	105.53(16)		
O2−Cu1−N2	169.49(18)	O2−Cu3−O2*	180.00		

O2−Cu1−O4	97.02(15)	O2−Cu3−O7A	91.7(3)		
O2−Cu1−O5	86.74(14)	O2−Cu3−O7A*	88.3(3)		
O2−Cu2−N1	165.59(17)	O2–Cu3–O8A	92.5(3)		
Cu1−O2−Cu3	118.44(18)	Cu2−O2−Cu3	109.37(18)		

Table S2 Hydrogen bonding parameters for **1-3**

Interactions	Type of H-bond	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (Å)
Complex **1**					
O1W–H1WA···O11		0.86(7)	2.716(8)	1.86(7)	176(11)
O2–H2···O1W		0.85(8)	2.838(8)	2.01(9)	165(10)
O1W–H1WB···O7		0.85(7)	2.845(8)	2.00(7)	172(8)
O3–H3···O12		0.84	2.609(6)	1.78	167
O4–H4···O2		0.85(13)	2.558(8)	1.78(12)	151(14)
O11–H11A···O9	Intra	0.85(3)	2.782(8)	1.95(4)	166(6)
O11–H11B···O7		0.85(6)	2.883(9)	2.04(6)	177(12)
O12–H12···O1W		0.86(6)	2.652(8)	1.80(7)	175(15)
O13–H13B···O9		0.82	2.778(10)	2.14	134
Complex **2**					
O1W–H1WA···O22		0.80(4)	2.857(4)	2.06(4)	175(5)
O2W–H2WA···O30		0.79(4)	2.980(5)	2.24(4)	156(6)
O3–H3···O13		0.80(4)	2.571(3)	1.77(4)	175(4)
O2W–H2WB···O5		0.80(5)	2.744(4)	1.97(6)	163(5)
O4–H4···O16		0.78(3)	2.656(3)	1.88(3)	178(5)
O1W–H1WB···O26		0.81(6)	2.942(4)	2.18(6)	159(7)
O5–H5···O1W		0.83(5)	2.785(4)	1.96(5)	175(6)
O6–H6···O17		0.77(3)	2.808(4)	2.04(3)	176(4)
O13–H13···O10	Intra	0.78(3)	2.818(4)	2.06(3)	163(3)

O14–H14···O2		0.81(5)	2.606(3)	1.81(5)	168(5)
O15–H15···O2W		0.80(3)	2.576(5)	1.79(3)	173(4)
O16–H16···O1W		0.80(3)	2.842(4)	2.05(3)	170(5)
O17–H17···O30		0.79(4)	2.871(5)	2.09(4)	167(6)
O18–H18A···O21		0.80(4)	2.822(5)	2.06(4)	161(5)
O18–H18B···O9	Intra	0.81(4)	2.827(4)	2.03(4)	169(6)
Complex **3**					
O3–H3A···O10		0.93	2.525(5)	1.84	128
O4–H4···O12		0.93	2.552(5)	2.09	110
O10–H10···O9		0.82	2.714(6)	1.99	147
O9–H9···O12		0.82	2.751(5)	1.96	160
O2–H2···O11		0.69	2.724	2.031	177

Table S3 Atomic spin densities (e) computed for the High and Low spin configuration of compound **2** at the B3LYP/6-31+G*, Cu1···Cu2 coupling

Atom Label	High spin	Low Spin
Cu1	0.68	-0.68
Cu2	0.62	0.61
N1	0.13	-0.12
N2	0.15	0.15
O1	0.16	-0.01
O2	0.16	0.01
O3	0.03	-0.03
O4	0.04	0.03

Table S4. Atomic spin densities (e) computed for the High and Low spin configuration of compound **2** at the B3LYP/6-31+G*, Cu3···Cu4 coupling

Atom Label	High spin	Low Spin
Cu3	0.66	-0.66
Cu4	0.67	0.68
N3	0.11	-0.10

N4	0.11	0.11
O12	0.13	-0.01
O13	0.24	0.01
O4	0.02	-0.02
O15	0.02	0.02