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SUPPLEMENTARY MATERIAL

A Series of Enthalpy/Entropy-Driven Reversible Dissolution/Reorganization Equilibriums in the System of $Cu(NO_3)_2$-HL-GdX_3-H_2O (HL = 5-methylpyrazine-2-carboxylic acid, X = Cl, Br, NO_3, ClO_4)

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Table S1 Crystal data and structure refinement details for **1-5** and $\mathbf{L_{Cu}}$-$\mathbf{L_{Cu5}}$.

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{12}H_{10}CuN_4O_4$	$C_{12}H_{18}Cl_2Cu_2N_4O_8$	$C_6H_5Cl_2CuKN_2O_2$	$C_6H_7BrCuN_2O_3$	$C_{12}H_{20}CuN_6O_{14}$
Formula weight	337.78	544.28	310.66	298.59	535.88
Crystal system	Monoclinic	Triclinic	orthorhombic	Monoclinic	Monoclinic
space group	$P2_1/c$	P-1	Pbca	$P2_1/c$	$P2_1/c$
a (Å)	11.3111(13)	3.8124(19)	9.1599(16)	10.3624(12)	8.374(2)
b (Å)	7.6700(8)	11.366(6)	7.4074(13)	6.5989(8)	16.231(5)
c (Å)	7.5434(9)	11.510(6)	29.564(5)	13.4372(16)	7.673(2)
α (°)	90.00	111.353(8)	90	90.00	90.00
β (°)	105.415(2)	96.305(9)	90	108.446(2)	98.509(5)
γ (°)	90.00	98.768(9)	90	90.00	90.00
V (Å^3)	630.89(12)	451.6(4)	2005.9(6)	871.63(18)	1031.4(5)
Z	2	1	8	4	2
F000	342.0	274.0	1224.0	580.0	342.0
Goodness-of-fit on F^2	1.000	1.029	0.896	1.017	0.890
R indices (all data)	*R1* = 0.0563	R_1 = 0.0906	R_1 = 0.0478	R_1 = 0.0438	*R1* = 0.0594
	wR2 = 0.1031	wR_2 = 0.2092	wR_2 = 0.0812	wR_2 = 0.0679	*wR2* = 0.1126
Final *R* indices	*R1* = 0.0348	R_1 = 0.0735	R_1 = 0.0316	R_1 = 0.0346	*R1* = 0.0398
[*I*>2sigma(*I*)]	*wR2* = 0.0858	wR_2 = 0.1999	wR_2 = 0.0766	wR_2 = 0.0641	*wR2* = 0.1038

$\mathbf{L_{Cu}}$	$\mathbf{L_{Cu1}}$	$\mathbf{L_{Cu2}}$	$\mathbf{L_{Cu3}}$	$\mathbf{L_{Cu4}}$	$\mathbf{L_{Cu5}}$
$C_{12}H_{18}CuN_4O_8$	$C_{12}H_{18}CuN_4O_8$	$C_{12}H_{18}CuN_4O_8$	$C_{12}H_{18}CuN_4O_8$	$C_{12}H_{18}CuN_4O_8$	$C_{12}H_{18}CuN_4O_8$
819.69	819.69	819.69	819.69	819.69	819.69
Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
P-1	P-1	P-1	P-1	P-1	P-1
8.3401(9)	8.3260(10)	8.337(5)	8.3260(10)	8.129(3)	8.374(2)
10.6016(11)	10.5880(14)	10.583(6)	10.5880(14)	10.471(4)	16.231(5)
11.2514(12)	11.2410(16)	11.250(7)	11.2410(16)	10.955(4)	7.673(2)
64.429(2)	64.4220(10)	64.399(11)	64.4220(10)	66.751(6)	90.00
85.378(2)	85.386(2)	85.352(13)	85.386(2)	81.591(7)	98.509(5)
68.450(2)	68.4390(10)	68.436(12)	68.4390(10)	78.088(6)	90.00
831.05(15)	827.68(19)	828.9(9)	827.68(19)	836.1(5)	836.1(5)
1	1	2	1	2	2
422.0	422.0	422.0	422.0	580.0	342.0
1.040	1.045	0.801	1.009	1.121	1.176
R_1 = 0.0499	R_1 = 0.0436	R_1 = 0.2142	R_1 = 0.0863	R_1 = 0.2136	*R1* = 0.2070
wR_2 = 0.1791	wR_2 = 0.1076	wR_2 = 0.0682	wR_2 = 0.1176	wR_2 = 0.2679	*wR2* = 0.2669
R_1 = 0.0838	R_1 = 0.0673	R_1 = 0.0666	R_1 = 0.0494	R_1 = 0.0845	*R1* = 0.0845
wR_2 = 0.1278	wR_2 = 0.0961	wR_2 = 0.0569	wR_2 = 0.1022	wR_2 = 0.2041	*wR2* = 0.2033

[a] $\boldsymbol{R = \Sigma|\,|F_0|-|F_C|\,|/\Sigma|F_0|}$, $\boldsymbol{wR_2 = [\Sigma[w(F_0^2-F_C^2)^2]/\Sigma[(F_0^2)^2]]^{1/2}}$

Table S2 Selected bond lengths [Å] and angles [°] for **1**-**5** and $\mathbf{L_{Cu}}$-$\mathbf{L_{Cu5}}$.

Compound **1**			
Cu(1)-O(1)	1.951(2)	O(1)-Cu(1)-N(1)	83.67(11)
Cu(1)-O(1)	1.951(2)	O(1)-Cu(1)-N(1)	96.33(11)
Cu(1)-N(1)	1.978(3)	O(1)-Cu(1)-N(1)	96.33(11)
Cu(1)-N(1)	1.978(3)	O(1)-Cu(1)-N(1)	83.67(11)
O(1)-Cu(1)-O(1)	180	N(1)-Cu(1)-N(1)	180

Compound **2**			
Cu(1)-O(3)	1.917(6)	O(3)-Cu(1)-Cl(1)	92.99(19)
Cu(1)-O(1)	1.969(5)	O(1)-Cu(1)-Cl(1)	166.27(19)
Cu(1)-N(1)	1.989(6)	N(1)-Cu(1)-Cl(1)	94.07(18)
Cu(1)-Cl(1)	2.246(2)	O(3)-Cu(1)-Cl(1)	95.1(2)
Cu(1)-Cl(1)	2.692(2)	O(1)-Cu(1)-Cl(1)	92.59(19)
O(3)-Cu(1)-O(1)	89.3(2)	N(1)-Cu(1)-Cl(1)	89.96(15)
O(3)-Cu(1)-N(1)	170.4(3)	Cl(1)-Cu(1)-Cl(1)	100.67(8)
O(1)-Cu(1)-N(1)	82.3(2)		

Compound **3**			
Cu(1)-O(2)	1.965(2)	C(1)-K(1)-Cl(2)	154.18(8)
Cu(1)-N(1)	2.015(3)	O(1)-K(1)-Cl(2)	95.25(6)
Cu(1)-Cl(1)	2.2455(10)	O(2)-K(1)-Cl(2)	56.69(6)
Cu(1)-Cl(2)	2.2797(10)	O(2)-K(1)-Cl(2)	91.25(5)
Cu(1)-K(1)	3.7678(11)	O(1)-K(1)-Cl(2)	69.74(5)
K(1)-O(2)	2.812(2)	Cl(2)-K(1)-Cl(2)	147.66(3)
K(1)-O(2)	2.842(2)	C(1)-K(1)-Cl(2)	84.83(7)
K(1)-O(1)	2.930(3)	Cl(2)-K(1)-Cl(2)	71.81(3)
K(1)-Cl(2)	3.0663(13)	O(1)-K(1)-Cl(1)	86.11(6)
K(1)-C(1)	3.147(4)	O(2)-K(1)-Cl(1)	134.99(6)

K(1)-Cl(2)	3.2998(12)	O(2)-K(1)-Cl(1)	63.06(5)
K(1)-Cl(2)	3.3321(13)	O(1)-K(1)-Cl(1)	80.48(5)
K(1)-Cl(1)	3.5258(14)	Cl(2)-K(1)-Cl(1)	61.12(3)
K(1)-Cu(1)	3.7678(11)	C(1)-K(1)-Cl(1)	65.18(7)
K(1)-K(1)	3.8802(16)	Cl(2)-K(1)-Cl(1)	136.38(3)
K(1)-K(1)	4.7575(17)	Cl(2)-K(1)-Cl(1)	149.77(3)
O(2)-Cu(1)-N(1)	81.60(10)	O(1)-K(1)-Cu(1)	107.52(6)
O(2)-Cu(1)-Cl(1)	175.23(8)	O(2)-K(1)-Cu(1)	30.58(5)
N(1)-Cu(1)-Cl(1)	94.55(8)	O(2)-K(1)-Cu(1)	111.64(5)
O(2)-Cu(1)-Cl(2)	87.84(7)	O(1)-K(1)-Cu(1)	105.63(5)
N(1)-Cu(1)-Cl(2)	165.17(8)	Cl(2)-K(1)-Cu(1)	110.85(3)
Cl(1)-Cu(1)-Cl(2)	96.45(4)	C(1)-K(1)-Cu(1)	116.14(7)
O(2)-Cu(1)-K(1)	46.73(7)	Cl(2)-K(1)-Cu(1)	47.68(2)
N(1)-Cu(1)-K(1)	116.49(8)	Cl(2)-K(1)-Cu(1)	36.814(19)
Cl(1)-Cu(1)-K(1)	134.16(3)	Cl(1)-K(1)-Cu(1)	165.45(3)
Cl(2)-Cu(1)-K(1)	61.14(3)	O(1)-K(1)-K(1)	155.89(7)
O(1)-K(1)-O(2)	137.17(8)	O(2)-K(1)-K(1)	47.00(5)
O(1)-K(1)-O(2)	121.36(7)	O(2)-K(1)-K(1)	46.34(5)
O(2)-K(1)-O(2)	93.34(6)	O(1)-K(1)-K(1)	74.93(6)
O(1)-K(1)-O(1)	83.43(5)	Cl(2)-K(1)-K(1)	106.38(4)
O(2)-K(1)-O(1)	110.66(7)	C(1)-K(1)-K(1)	64.20(7)
O(2)-K(1)-O(1)	45.25(7)	Cl(2)-K(1)-K(1)	114.13(4)
O(1)-K(1)-Cl(2)	97.12(6)	Cl(2)-K(1)-K(1)	67.54(3)
O(2)-K(1)-Cl(2)	95.10(6)	Cl(1)-K(1)-K(1)	100.40(3)
O(2)-K(1)-Cl(2)	107.28(6)	Cu(1)-K(1)-K(1)	69.28(2)
O(1)-K(1)-Cl(2)	141.37(6)	O(1)-K(1)-K(1)	83.15(6)
O(1)-K(1)-C(1)	98.75(8)	O(2)-K(1)-K(1)	78.04(5)
O(2)-K(1)-C(1)	108.77(8)	O(2)-K(1)-K(1)	147.16(6)
O(2)-K(1)-C(1)	24.16(8)	O(1)-K(1)-K(1)	166.36(6)

O(1)-K(1)-C(1)	22.63(8)	Cl(2)-K(1)-K(1)	43.55(2)
Cl(2)-K(1)-C(1)	122.34(8)	C(1)-K(1)-K(1)	165.73(8)
O(1)-K(1)-Cl(2)	73.31(6)	Cl(2)-K(1)-K(1)	39.81(2)
O(2)-K(1)-Cl(2)	67.58(5)	Cl(2)-K(1)-K(1)	109.15(3)
O(2)-K(1)-Cl(2)	159.28(6)	Cl(1)-K(1)-K(1)	101.00(3)
O(1)-K(1)-Cl(2)	132.47(6)	Cu(1)-K(1)-K(1)	76.25(2)
Cl(2)-K(1)-Cl(2)	83.35(3)	K(1)-K(1)-K(1)	117.73(4)

Compound **4**

N(2)-Cu(2)	2.016(4)	O(1)-Cu(2)-N(2)	91.56(14)
Br(1)-Cu(2)	2.3798(8)	N(1)-Cu(2)-O(2)	88.71(15)
Cu(2)-N(1)	1.993(4)	O()1-Cu(2)-O(2)	98.60(16)
Cu(2)-O(1)	2.014(3)	N(2)-Cu(2)-O(2)	94.25(15)
Cu()2-N()2	2.016(4)	N(1)-Cu(2)-Br(1)	94.42(11)
Cu()2-O()2	2.203(4)	O(1)-Cu(2)-Br(1)	150.03(11)
N()1-Cu()2-O()1	81.04(14)	N(2)-Cu()2-Br(1)	91.08(11)
N()1-Cu()2-N()2	172.38(16)	O(2)-Cu(2)-Br(1)	110.96(12)

Compound **5**

Cu(1)-O(1)	1.939(3)	O(1)-Cu(1)-N(1)	96.38(12)
Cu(1)-O(1)	1.939(3)	O(1)-Cu(1)-N(1)	83.62(12)
Cu(1)-N(1)	1.979(3)	N(1)-Cu(1)-N(1)	180.00(17)
Cu(1)-N(1)	1.979(3)	O(1)-Cu(1)-O(3)	95.75(10)
Cu(1)-O(3)	2.650(3)	O(1)-Cu(1)-O(3)	84.25(10)
O(1)-Cu(1)-O(1)	180	N(1)-Cu(1)-O(3)	91.19(11)
O(1)-Cu(1)-N(1)	83.62(12)	N(1)-Cu(1)-O(3)	88.81(11)
O(1)-Cu(1)-N(1)	96.38(12)		

L_{Cu}

Cu(1)-O(3)	1.940(4)	O(3)-Cu(1)-N(1)	170.85(19)
Cu(1)-O(1)	1.947(4)	O(1)-Cu(1)-N(1)	170.85(20)
Cu(1-N(2)	1.985(4)	N(2)-Cu(1)-N(1)	170.85(21)
Cu(1)-N(1)	1.995(5)	O(3)-Cu(1)-O(5)	170.85(22)
Cu(1)-O(5)	2.354(4)	O(1)-Cu(1)-O(5)	170.85(23)
O(3)-Cu(1)-O(1)	170.85(16)	N(2)-Cu(1)-O(5)	170.85(24)
O(3)-Cu(1)-N(2)	170.85(17)	N(1)-Cu(1)-O(5)	170.85(25)
O(1)-Cu(1)-N(2)	170.85(18)		

L_{Cu1}

Cu(1)-O(1)	1.934(2)	O(1)-Cu(1)-N(3)	96.08(11)
Cu(1)-O(3	1.943(2)	O(3)-Cu(1)-N(3)	83.08(11)
Cu(1)-N(1)	1.982(3)	N(1)-Cu(1)-N(3)	173.91(12)
Cu(1)-N(3)	1.996(3)	O(1)-Cu(1)-O(5)	94.12(10)
Cu(1)-O(5)	2.348(3)	O(3)-Cu(1)-O(5)	94.71(10)
O(1)-Cu(1)-O(3)	171.17(11)	N(1)-Cu(1)-O(5)	92.47(11)
O(1)-Cu(1)-N(1)	84.00(11)	N(3)-Cu(1)-O(5)	93.59(11)
O(3)-Cu(1)-N(1)	95.90(11)		

L_{Cu2}

Cu(1)-O(3)	1.915(5)	O(3)-Cu(1)-N(1)	95.5(3)
Cu(1)-O(1)	1.972(5)	O(1)-Cu(1)-N(1)	84.1(3)
Cu(1)-N(3)	1.991(6)	N(3)-Cu(1)-N(1)	174.3(3)
Cu(1)-N(1)	1.997(7)	O(3)-Cu(1)-O(5)	93.8(2)
Cu(1)-O(5)	2.323(5)	O(1)-Cu(1)-O(5)	94.7(2)
O(3)-Cu(1)-O(1)	171.5(3)	N(3)-Cu(1)-O(5)	92.2(2)
O(3)-Cu(1)-N(3)	84.6(3)	N(1)-Cu(1)-O(5)	93.6(2)
O(1)-Cu(1)-N(3)	95.0(3)		

L_{Cu3}

Cu(1)-O(1)	1.934(2)	O(1)-Cu(1)-N(3)	96.10(10)
Cu(1)-O(3)	1.944(2)	O(3)-Cu(1)-N(3)	83.05(10)
Cu(1)-N(1)	1.981(3)	N(1)-Cu(1)-N(3)	173.92(11)
Cu(1)-N(3)	1.996(3)	O(1)-Cu(1)-O(5)	94.11(10)
Cu(1)-O(5)	2.348(3)	O(3)-Cu(1)-O(5)	94.72(10)
O(1)-Cu(1)-O(3)	171.16(11)	N(1)-Cu(1)-O(5)	92.47(10)
O(1)-Cu(1)-N(1)	83.97(10)	N(3)-Cu(1)-O(5)	93.59(10)
O(3)-Cu(1)-N(1)	95.94(10)		

L_{Cu4}

Cu(1)-O(3)	1.945(4)	O(3)-Cu(1)-N(3)	83.3(2)
Cu(1)-O(1)	1.955(4)	O(1)-Cu(1)-N(3)	95.3(2)
Cu(1)-N(1)	1.987(6)	N(1)-Cu(1)-N(3)	168.7(2)
Cu(1)-N(3)	1.994(6)	O(3)-Cu(1)-O(5)	97.6(2)
Cu(1)-O(5)	2.239(6)	O(1)-Cu(1)-O(5)	96.7(2)
O(3)-Cu(1)-O(1)	165.7(2)	N(1)-Cu(1)-O(5)	94.8(3)
O(3)-Cu(1)-N(1)	95.8(2)	N(3)-Cu(1)-O(5)	96.5(3)
O(1)-Cu(1)-N(1)	82.8(2)		

L_{Cu5}

Cu(1)-O(3)	1.943(5)	O(3)-Cu(1)-N(3)	83.3(2)
Cu(1)-O(1)	1.953(5)	O(1)-Cu(1)-N(3)	95.4(2)
Cu(1)-N(1)	1.987(7)	N(1)-Cu(1)-N(3)	168.6(2)
Cu(1)-N(3)	1.994(7)	O(3)-Cu(1)-O(5)	97.7(2)
Cu(1)-O(5)	2.239(7)	O(1)-Cu(1)-O(5)	96.6(2)
O(3)-Cu(1)-O(1)	165.7(2)	N(1)-Cu(1)-O(5)	94.9(3)
O(3)-Cu(1)-N(1)	95.8(2)	N(3)-Cu(1)-O(5)	96.5(3)
O(1)-Cu(1)-N(1)	82.7(2)		

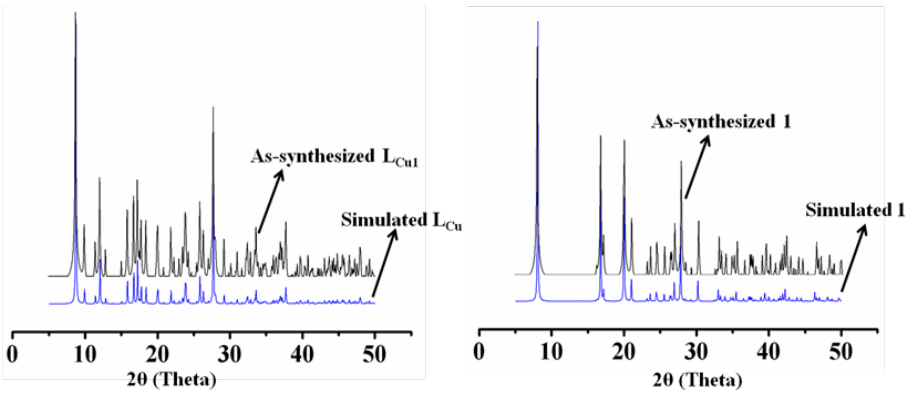
Table S3 Corresponding bond distances (Å) and angle (°) of the coordination environments of Cu(II) ions .

Compound	Configuration	Coordinated-group$_{axial}$	Cu-X$_{axial}$	Cu-X$_{basal}$	(O,N) $_{basal}$-Cu-X$_{axial}$
$\mathbf{L_{Cu}}$	distorted square pyramid geometry	H_2O	d_{Cu-O} = 2.239 Å	d_{Cu-O} = 1.940 Å -1.947 Å d_{Cu-N} = 1.986 Å -1.995 Å	97.676°, 99.432°
1	distorted octahedral geometry	$mpca^-$	d_{Cu-O} = 2.514 Å	d_{Cu-O} = 1.951 Å d_{Cu-N} = 1.978 Å	85.998°, 94.002°
2	distorted square pyramid geometry	Cl^-	d_{Cu-Cl} = 2.695 Å	d_{Cu-Cl} = 2.246 Å d_{Cu-O} = 1.938 Å -1.972 Å d_{Cu-N} = 1.987 Å	91.744°
3	distorted square pyramid geometry	Cl^-	d_{Cu-Cl} = 2.888 Å	d_{Cu-Cl} = 2.246 Å -2.280 Å d_{Cu-O} = 1.965 Å d_{Cu-N} = 2.016 Å	90.414°
4	distorted square pyramid geometry	H_2O	d_{Cu-O} = 2.207 Å	d_{Cu-Br} = 2.380 Å d_{Cu-O} = 2.014 Å d_{Cu-N} = 1.994 Å -2.016 Å	94.828°
5	distorted octahedral geometry	H_2O	d_{Cu-O} = 2.650 Å	d_{Cu-O} = 1.940 Å d_{Cu-N} = 1.978 Å	94.634°, 85.366°

* X$_{axial}$: atoms at the axial sites; X$_{basal}$: atoms at the basal sites; (O,N) $_{basal}$: one O atom and one N atom from chelating ligand at the basal sites; Coordinated-group$_{axial}$: The coordinated group at the axial site.

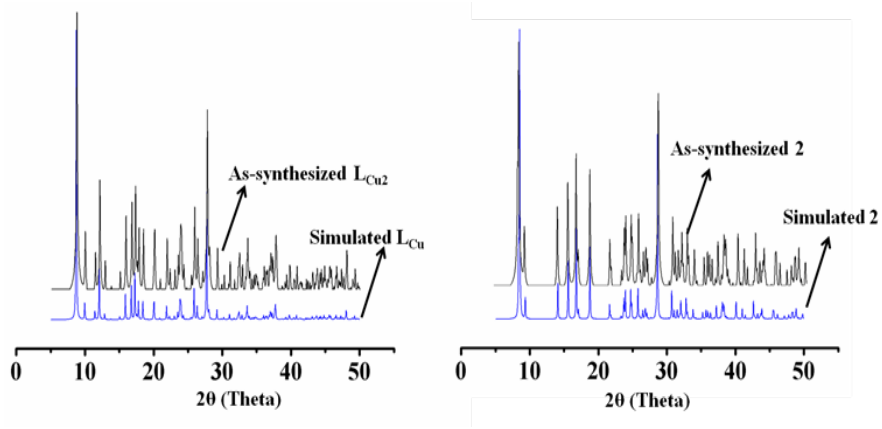
Table S4 Microcalorimetric investigations on reversible dissolution/reorganization processes

Reversible dissolution/reorganization processes	$\Delta_r H^{\theta}_{m(Forward)}$ (kJ·mol^{-1})	$\Delta_r H^{\theta}_{m(Reverse)}$ (kJ·mol^{-1})
1 and $\mathbf{L_{Cu}}$	-81.22	81.18
2 and $\mathbf{L_{Cu}}$	-71.52	71.55
3 and $\mathbf{L_{Cu}}$	-92.62	92.60
4 and $\mathbf{L_{Cu}}$	-68.33	68.37
5 and $\mathbf{L_{Cu}}$	-48.94	48.93



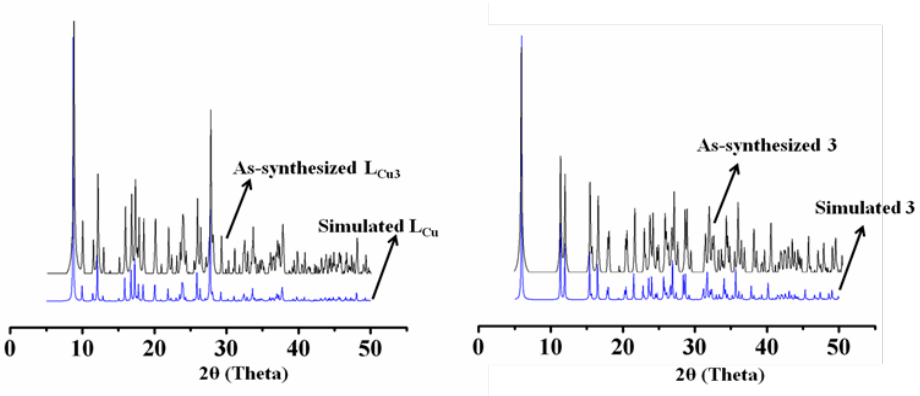
a **b**

Fig. S1 a. PXRD patterns for the metal-containing ligand; **b.** PXRD patterns for **1**.



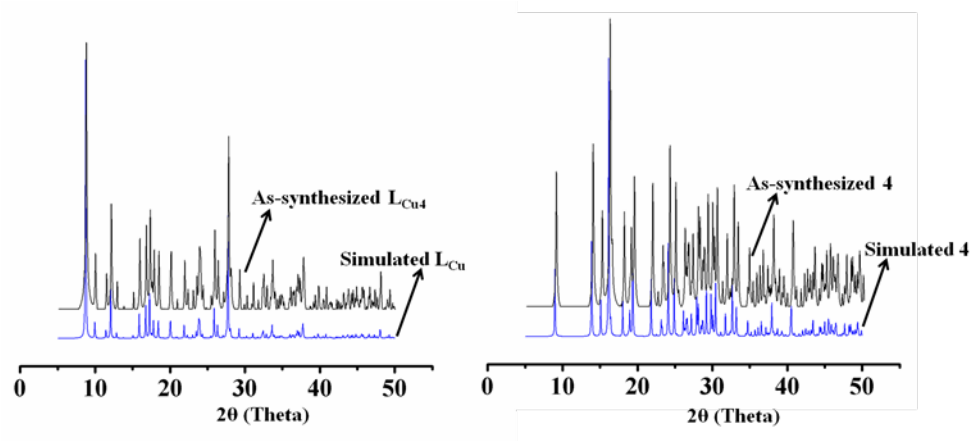
a **b**

Fig. S2 a. PXRD patterns for the metal-containing ligand; **b.** PXRD patterns for **2**.



a **b**

Fig. S3 a. PXRD pattern for the metal-containing ligand; **b.** PXRD pattern for **3;**



a **b**

Fig. S4 a. PXRD pattern for the metal-containing ligand; **a.** PXRD pattern for **4;**

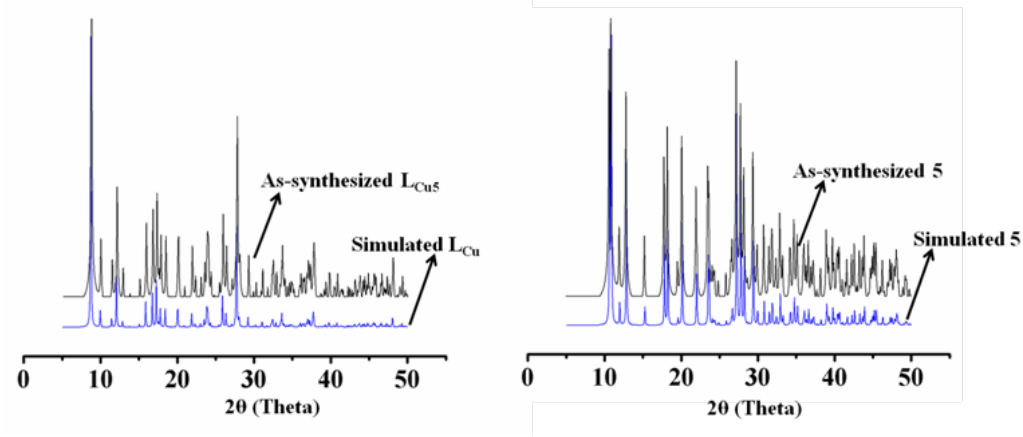


Fig. S5 a. PXRD pattern for the metal-containing ligand; **b.** PXRD pattern for **5.**

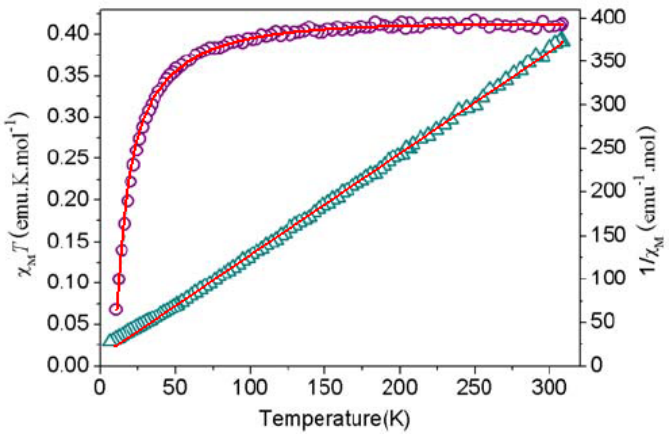


Fig. S6 $\chi_M T$ *vs* T plot for **2**. The solid line is the fit to the experimental data. The inset shows the reverse

susceptibility $1/\chi_M$ of the magnetism complex over temperature.

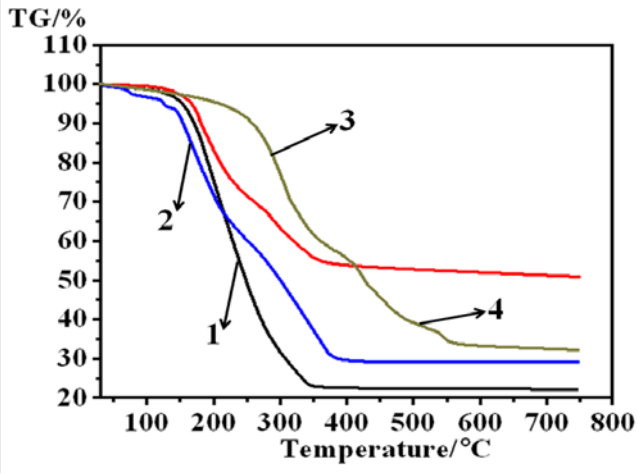


Fig. S7 TG curves of compounds **1**-**4**.