Electronic Supplementary Information

Cu(II) frameworks from a "mixed-ligand" approach

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Table S1. Crystal data and structure refinement for complexes **1 - 5**.

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	C20 H14 Cu2 N2 O9	C21 H22 Cu N2 O14	C40 H42 Cu N4 O22	C23 H17 Cu2 N2 O9	C38 H34 Cu N4 O14
Formula weight	553.41	589.95	994.32	592.49	834.24
Temperature	293(2) K	296(2) K	293(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	Pna2(1)	P-1	P-1	C2/c	P21/c
Unit cell dimensions	a = 15.436(2) Å b = 10.2155(17) Å c = 12.2521(19) Å α = 90.00° β = 90.00° γ = 90.00°	a = 7.131(5) Å b = 10.833(8) Å c = 16.834(16) Å α = 103.207(13)° β = 96.130(13)° γ = 107.927(9)°	a = 8.658(5) Å b = 8.814(5) Å c = 13.685(5) Å α = 99.284(5)° β = 95.029(5)° γ = 102.349(5)°	a = 23.809(3) Å b = 11.5102(12) Å c = 18.1434(19) Å α = 90° β = 119.925(1)° γ = 90°	a = 13.744(17) Å b = 7.959(10) Å c = 16.19(2) Å α = 90° β = 94.942(15)° γ = 90°
Volume	1932.0(5) $Å^3$	1182.3(16) $Å^3$	998.7(9) $Å^3$	4309.2(8) $Å^3$	1764(4) $Å^3$
Z	4	2	1	8	2
Density (calculated)	1.903 g/cm^3	1.657 g/cm^3	1.653 g/cm^3	1.827 g/cm^3	1.571 g/cm^3
Absorption coefficient	2.263 mm^{-1}	1.003 mm^{-1}	0.647 mm^{-1}	2.036 mm^{-1}	0.700 mm^{-1}
F(000)	1112	606	515	2392	862
Crystal size (mm^3)	0.19 x 0.23 x 0.30	0.13 x 0.20 x 0.28	0.11 x 0.22 x 0.24	0.17 x 0.26 x 0.34	0.24 x 0.30 x 0.33
θ range for data collection	2.6 to 25.0°	2.5 to 25.0°	2.4 to 25.0°	2.6 to 25.2°	2.5 to 24.9°
Index ranges	-16<=h<=16	-8<=h<=8	-10<=h<=10	-28<=h<=28	-15<=h<=15

	-12<=k<=11	-12<=k<=12	-10<=k<=10	-13<=k<=13	-9<=k<=9
	-6<=l<=14	-20<=l<=20	-16<=l<=15	-21<=l<=21	-19<=l<=18
Reflections collected	4462	8849	7662	21675	11927
Independent reflections	2250 [R_{int} = 0.017]	4121 [R_{int} = 0.031]	3507 [R_{int} = 0.018]	3893 [R_{int} = 0.025]	2992 [R_{int} = 0.089]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2250 / 1 / 311	4121 / 0 / 390	3507 / 0 / 344	3893 / 0 / 334	2992 / 0 / 267
Goodness-of-fit	1.07	1.03	1.11	1.06	0.84
Final R indices [>2σ(I)]	R_{obs} = 0.0241	R_{obs} = 0.0401	R_{obs} = 0.0313	R_{obs} = 0.0229	R_{obs} = 0.0656
	wR_{obs} = 0.0637	wR_{obs} = 0.1039	wR_{obs} = 0.0859	wR_{obs} = 0.0629	wR_{obs} = 0.1581
R indices [all data]	R_{all} = 0.0254,	R_{all} = 0.0553,	R_{all} = 0.0370,	R_{all} = 0.0256	R_{all} = 0.1002
	wR_{all} = 0.0643	wR_{all} = 0.1094	wR_{all} = 0.0886	wR_{all} = 0.0642	wR_{all} = 0.1877
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.632 and -0.244	0.531 and -0.529	0.284 and -0.424	0.323 and -0.380	0.758 and -1.215
CCDC	1033364	1033365	1033366	1555023	1555024

Table S2. Crystal data and structure refinement for complexes **6 - 9**.

Complex	**6**	**7**	**8**	**9**
Empirical formula	C46 H34 Cu4 N4 O21	C38 H30 Cu N4 O14	C37 H27 Cu4 N4 O23	C32 H24 Cu N4 O12
Formula weight	1232.97	830.21	1149.83	720.10
Temperature	296(2) K	296(2) K	296(2) K	296(2) K

Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	P21/c	P-1
Unit cell dimensions	a = 23.644(3) Å b = 11.6083(16) Å c = 18.180(3) Å α = 90.00° β = 119.007(1)° γ = 90.00°	a = 21.289(3) Å b = 10.6498(16) Å c = 15.634(2) Å α = 90° β = 105.939(2)° γ = 90°	a = 10.208(6) Å b = 16.333(9) Å c = 27.106(15) Å α = 90° β = 94.515(14)° γ = 90°	a = 7.9068(7) Å b = 9.2354(9) Å c = 11.096(1) Å α = 104.380(1)° β = 106.168(1)° γ = 101.919(1)°
Volume	4363.9(11) $Å^3$	3408.3(8) $Å^3$	4505(4) $Å^3$	719.97(12) $Å^3$
Z	4	4	4	1
Density (calculated)	1.877 g/cm^3	1.618 g/cm^3	1.695 cm^3	1.661 g/cm^3
Absorption coefficient	2.019 mm^{-1}	0.724 mm^{-1}	1.952 mm^{-1}	0.838 mm^{-1}
F(000)	2488	1708	2308	369
Crystal size (mm^3)	0.09 x 0.19 x 0.24	0.16 x 0.32 x 0.16	0.14 x 0.22 x 0.24	0.19 x 0.24 x 0.28
θ range for data collection	2.6 to 28.7°	2.4 to 28.0	2.4 to 25.2°	2.4 to 29.4°
Index ranges	-31<=h<=31 -15<=k<=15 -24<=l<=23	-28<=h<=28 -14<=k<=14 -20<=l<=20	-12<=h<=12 -19<=k<=19 -32<=l<=32	-10<=h<=10 -12<=k<=12 -13<=l<=15
Reflections collected	26547	20891	43882	7126
Independent reflections	5557 [R_{int} = 0.035]	4079 [R_{int} = 0.036]	8140 [R_{int} = 0.032]	3597 [R_{int} = 0.014]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5557 / 325 / 358	4079 / 0 / 263	8140 / 664 / 613	3597 / 1 / 227
Goodness-of-fit	1.06	0.99	1.10	1.05
Final R indices [>2σ(I)]	R_{obs} = 0.0289	R_{obs} = 0.0304 wR_{obs} = 0.0814	R_{obs} = 0.0468 wR_{obs} = 0.1447	R_{obs} = 0.0397 wR_{obs} = 0.1024

	wR_{obs} = 0.0770			
R indices [all data]	R_{all} = 0.0335 wR_{all} = 0.0794	R_{all} = 0.0394 wR_{all} = 0.0850	R_{all} = 0.0504 wR_{all} = 0.1467	R_{all} = 0.0486 wR_{all} = 0.1075
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.648 and -0.489	0.305 and -0.336	2.126 and -0.925	0.562 and -0.320
CCDC	1555020	1555022	1555025	1555021

Table S3. Selected interatomic distances (Å) and angles (°) for complex **1**.

Cu(1)–O(9)	2.380(4)	Cu(1)#1–O(5)	1.937(3)	Cu(2)–O(6)#6	2.416(3)
Cu(1)–N(1)	1.983(3)	Cu(1)#3–O(8)	1.933(3)	Cu(2)–O(7)#4	1.950(3)
Cu(1) –O(1)	1.934(3)	Cu(2)–O(1)	1.944(3)	Cu(2)#2–O(6)	2.416(3)
Cu(1)–O(5)#5	1.937(3)	Cu(2)–O(3)	1.934(3)	Cu(2)#3–O(7)	1.950(3)
Cu(1)–O(8)#4	1.933(3)	Cu(2)–N(2)	1.982(3)		
O(8)#4–Cu(1)–O(1)	94.95(12)	O(1)–Cu(1)–O(9)	93.04(16)	O(1)–Cu(2)–N(2)	81.84(14)
O(8)#4–Cu(1)–O(5)#5	90.48(12)	O(5)#5–Cu(1)–O(9)	86.26(15)	O(7)#4–Cu(2)–N(2)	176.98(15)
O(1)–Cu(1)–O(5)#5	174.57(12)	N(1)–Cu(1)–O(9)	96.54(15)	O(3)–Cu(2)–O(6)#6	106.33(13)
O(8)#4–Cu(1)–N(1)	167.24(15)	O(3)–Cu(2)–O(1)	164.45(12)	O(1)–Cu(2)–O(6)#6	87.29(12)
O(1)–Cu(1)–N(1)	81.90(14)	O(3)–Cu(2)–O(7)#4	90.45(12)	O(7)#4–Cu(2)–O(6)#6	96.82(12)
O(5)#5–Cu(1)–N(1)	92.82(14)	O(1)–Cu(2)–O(7)#4	95.41(12)	N(2)–Cu(2)–O(6)#6	84.33(14)
O(8)#4–Cu(1)–O(9)	95.97(15)	O(3)–Cu(2)–N(2)	91.89(15)	Cu(1)-O(1)-Cu(2)	115.14(13)

Symmetry transformations used to generate equivalent atoms:
(1) x, y, z+1; (2) –x, –y+1, z+1/2; (3) –x+1/2, y+1/2, z+1/2; (4) –x+1/2, y–1/2, z–1/2; (5) x, y, z–1; (6) –x, –y+1, z–1/2

Table S4. Selected interatomic distances (Å) and angles (°) for complex **2**.

Cu(1)–O(1)	1.932(2)	Cu(1)–O(30)#3	2.633(4)	Cu(2)–O(3)	1.925(2)
Cu(1)–O(1)#1	1.932(2)	Cu(1)–O(30)#4	2.633(4)	Cu(2)–O(3)#2	1.925(2)
Cu(1)–N(1)	1.959(3)	Cu(2)–N(2)	1.947(3)	Cu(2)–O(2)	2.667(3)
Cu(1)–N(1)#1	1.959(3)	Cu(2)–N(2)#2	1.947(3)	Cu(2)–O(2)#2	2.667(3)
O(1)–Cu(1)–O(1)#1	180.00(7)	O(3)#2–Cu(2)–N(2)#2	84.17(9)	O(30)#4–Cu(1)–N(1)#1	93.58(9)
O(1)–Cu(1)–N(1)#1	96.69(10)	N(2)–Cu(2)–N(2)#2	180.000(1)	O(2)–Cu(2)–O(3)	94.02(8)
O(1)#1–Cu(1)–N(1)#1	83.31(10)	O(1)–Cu(1)–(O30)#3	83.44(9)	O(2)–Cu(2)–N(2)	92.90(8)
O(1)–Cu(1)–N(1)	83.31(10)	O(1)–Cu(1)–(O30)#4	96.56(9)	O(2)–Cu(2)–O(2)#3	180
O(1)#1–Cu(1)–N(1)	96.69(10)	O(30)#3–Cu(1)–N(1)	93.58(9)	O(2)–Cu(2)–O(3)#2	85.98(8)
N(1)#1–Cu(1)–N(1)	180.000(1)	O(30)#4–Cu(1)–N(1)	86.42(9)	O(2)–Cu(2)–N(2)#2	87.10(8)
O(3)–Cu(2)–O(3)#2	180.0	O(30)#3–Cu(1)–(O30)#4	180.00(12)	O(2)#2–Cu(2)–O(3)	85.98(8)
O(3)–Cu(2)–N(2)	84.17(9)	O(1)#1–Cu(1)–O(30)#3	96.56(9)	O(2)#2–Cu(2)–N(2)	87.10(8)
O(3)#2–Cu(2)–N(2)	95.83(9)	O(30)#3–Cu(1)–N(1)#1	86.42(9)	O(2)#2–Cu(2)–O(3)#2	94.02(8)
O(3)–Cu(2)–N(2)#2	95.83(9)	O(1)#1–Cu(1)–O(30)#4	83.44(9)	O(2)#2–Cu(2)–N(2)#2	92.90(8)

Symmetry transformations used to generate equivalent atoms:
(1) –x+1, –y, –z+1; (2) –x+1, –y+1, –z+1; (3) 1+x, y, z; (4) –x, –y, 1–z

Table S5. Selected interatomic distances (Å) and angles (°) for complex **3**.

Cu(1)–N(1)	2.0006(17)	Cu(1)–N(2)	1.947(2)	Cu(1)–O(1)	2.3377(17)
Cu(1)–N(1)#1	2.0006(17)	Cu(1)–N(2)#1	1.947(2)	Cu(1)–O(1)#1	2.3377(17)
N(2)–Cu(1)–N(2)#1	180.0	N(1)#1–Cu(1)–N(1)	180.000(1)	N(2)–Cu(1)–O(1)#1	103.64(7)
N(2)–Cu(1)–N(1)#1	92.94(7)	N(2)–Cu(1)–O(1)	76.36(7)	N(2)#1–Cu(1)–O(1)#1	76.36(7)
N(2)#1–Cu(1)–N(1)#1	87.06(7)	N(2)#1–Cu(1)–O(1)	103.64(7)	N(1)#1–Cu(1)–O(1)#1	74.00(7)
N(2)–Cu(1)–N(1)	87.06(7)	N(1)#1–Cu(1)–O(1)	106.00(7)	N(1)–Cu(1)–O(1)#1	106.00(7)
N(2)#1–Cu(1)–N(1)	92.94(7)	N(1)–Cu(1)–O(1)	74.00(7)	O(1)–Cu(1)–O(1)#1	180.0

Symmetry transformations used to generate equivalent atoms: (1) –x+2, –y, –z+2

Table S6. Selected interatomic distances (Å) and angles (°) for complex **4**.

Cu(1)–O(3)	1.9281(15)	Cu(1)–O(9)	2.2815(18)	Cu(2)–N(2)	1.9756(17)
Cu(1)–O(5)	1.9548(14)	Cu(2)–O(4)	1.9285(15)	Cu(2)–O(6)#1	2.3909(16)
Cu(1)–O(1)	1.9588(13)	Cu(2)–O(7)	1.9512(15)	Cu(2)#2–O(6)	2.3909(16)
Cu(1)–N(1)	1.9793(17)	Cu(2)–O(1)	1.9655(13)		
O(3)–Cu(1)–O(5)	85.13(6)	O(5)–Cu(1)–O(9)	102.40(7)	O(7)–Cu(2)–N(2)	93.03(7)
O(3)–Cu(1)–O(1)	93.16(6)	O(1)–Cu(1)–O(9)	93.54(6)	O(1)–Cu(2)–N(2)	81.89(6)
O(5)–Cu(1)–O(1)	163.88(6)	N(1)–Cu(1)–O(9)	85.18(8)	O(4)–Cu(2)–O(6)#1	87.28(6)
O(3)–Cu(1)–N(1)	169.10(7)	O(4)–Cu(2)–O(7)	90.35(7)	O(7)–Cu(2)–O(6)#1	99.02(6)
O(5)–Cu(1)–N(1)	96.40(7)	O(4)–Cu(2)–O(1)	95.29(6)	O(1)–Cu(2)–O(6)#1	91.93(6)
O(1)–Cu(1)–N(1)	82.36(6)	O(7)–Cu(2)–O(1)	167.91(6)	N(2)–Cu(2)–O(6)#1	89.58(6)
O(3)–Cu(1)–O(9)	105.08(7)	O(4)–Cu(2)–N(2)	175.71(7)	Cu(1)-O(1)-Cu(2)	108.66(6)

Symmetry transformations used to generate equivalent atoms:
(1) –x+1/2, y+1/2, –z+1/2; (2) –x+1/2, y–1/2, –z+1/2; (3) –x+1/2, –y+1/2, –z+1; (4) –x+1, y, –z+1/2

Table S7. Selected interatomic distances (Å) and angles (°) for complex **5**.

Cu(1)–N(1)	2.029(5)	Cu(1)–N(2)	1.971(5)	Cu(1)–O(1)	2.470(5)
Cu(1)–N(1)#1	2.029(5)	Cu(1)–N(2)#1	1.971(5)	Cu(1)–O(1)#1	2.470(5)
O(1)–Cu(1)–N(1)	75.05(16)	N(1)–Cu(1)–N(2)	88.44(19)	N(1)#1–Cu(1)–N(2)	91.56(19)
O(1)–Cu(1)–N(2)	73.04(18)	O(1)#1–Cu(1)–N(1)	104.95(16)	N(2)–Cu(1)–N(2)#1	180.00
O(1)–Cu(1)–O(1)#1	180.00	N(1)–Cu(1)–N(1)#1	180.00	O(1)#1–Cu(1)–N(1)#1	75.05(16)
O(1)–Cu(1)–N(1)#1	104.95(16)	N(1)–Cu(1)–N(2)#1	91.56(19)	O(1)#1–Cu(1)–N(2)#1	73.04(18)
O(1)–Cu(1)–N(2)#1	106.96(18)	O(1)#1–Cu(1)–N(2)	106.96(18)	N(1)#1–Cu(1)–N(2)#1	88.44(19)

Symmetry transformations used to generate equivalent atoms:
(1) –x, –y, –z+1

Table S8. Selected interatomic distances (Å) and angles (°) for complex **6**.

Cu(1)–O(3)	1.9344(13)	Cu(1)–O(11)	2.2840(15)	Cu(2)–O(7)	1.9579(14)
Cu(1)–O(1)	1.9644(12)	Cu(2)–O(4)	1.9111(14)	Cu(2)–N(2)	1.9622(16)
Cu(1)–O(5)	1.9702(13)	Cu(2)–O(1)	1.9548(12)	Cu(2)–O(6)#1	2.4614(16)
Cu(1)–N(1)	1.9749(15)				
O(1)–Cu(1)–O(3)	93.82(6)	O(5)–Cu(1)–O(11)	100.78(6)	O(4)–Cu(2)–O7	89.50(7)
O(1)–Cu(1)–O(5)	164.74(6)	O(5)–Cu(1)–N1	96.00(7)	O(4)–Cu(2)–N(2)	175.60(7)
O(1)–Cu(1)–O(11)	94.24(6)	O(11)–Cu(1)–N1	86.10(6)	O(4)–Cu(2)–O(6)#1	87.27(7)
O(1)–Cu(1)–N1	82.21(6)	O(1)–Cu(2)–O(4)	94.49(6)	O7–Cu(2)–N(2)	93.73(8)
O(3)–Cu(1)–O(5)	84.98(6)	O(1)–Cu(2)–O7	170.89(6)	O(6)#1–Cu(2)–O7	92.70(7)
O(3)–Cu(1)–O(11)	105.02(6)	O(1)–Cu(2)–N(2)	82.75(7)	O(6)#1–Cu(2)–N(2)	89.59(6)
O(3)–Cu(1)–N1	168.48(6)	O(1)–Cu(2)–O(6)#1	95.67(6)	Cu(1)-O(1)-Cu(2)	108.99(6)

Symmetry transformations used to generate equivalent atoms:
(1) 1/2–x, –1/2+y, 1/2–z

Table S9. Selected interatomic distances (Å) and angles (°) for complex **7**.

Cu(1)–N(1)	2.0268(12)	Cu(1)–N(2)	1.9836(13)	Cu(1)–O(1)	2.3479(12)
Cu(1)–N(1)#1	2.0268(12)	Cu(1)–N(2)#1	1.9836(13)	Cu(1)–O(1)#1	2.3479(12)

N(2)#1–Cu(1)–N(2)	180.0	N(1)–Cu(1)–N(1)#1	180.00(5)	N(2)#1–Cu(1)–O(1)#1	77.43(5)
N(2)#1–Cu(1)–N(1)	92.64(5)	N(2)#1–Cu(1)–O(1)	102.57(5)	N(2)–Cu(1)–O(1)#1	102.56(5)
N(2)–Cu(1)–N(1)	87.36(5)	N(2)–Cu(1)–O(1)	77.43(5)	N(1)–Cu(1)–O(1)#1	105.24(5)
N(2)#1–Cu(1)–N(1)#1	87.36(5)	N(1)–Cu(1)–O(1)	74.76(5)	N(1)#1–Cu(1)–O(1)#1	74.76(5)
N(2)–Cu(1)–N(1)#1	92.64(5)	N(1)#1–Cu(1)–O(1)	105.24(5)	O(1)–Cu(1)–O(1)#1	180.0

Symmetry transformations used to generate equivalent atoms:
(1) –x, –y, –z

Table S10. Selected interatomic distances (Å) and angles (°) for complex **8**.

Cu(1)–N(2)	1.969(4)	Cu(2)–O(15)	1.965(3)	Cu(3)–O(19)	2.557(6)
Cu(1)–O(1)	1.956(3)	Cu(2)–O(11)#2	2.326(3)	Cu(4)–N(4)	1.975(4)
Cu(1)–O(5)	1.934(3)	Cu(2)#3–O(11)	2.325(3)	Cu(4)–O(3)	1.938(3)
Cu(1)–O(13)	2.196(4)	Cu(3)–N(3)	1.969(4)	Cu(4)–O(8)	1.970(3)
Cu(1)–O(14)	1.995(3)	Cu(3)–O(3)	1.951(3)	Cu(4)–O(17)#1	1.926(3)
Cu(2)–N(1)	1.977(4)	Cu(3)–O(7)	1.941(3)	Cu(4)#1–O(17)	1.926(3)
Cu(2–)O(1)	1.951(3)	Cu(3)–O(10)#3	1.934(3)	Cu(4)–O(19)	2.498(5)
Cu(2)–O(6)	1.964(3)	Cu(3)#2–O(10)	1.934(3)		
O(5)–Cu(1)–O(1)	93.34(12)	O(15)–Cu(2)–N(1)	97.57(15)	O(7)–Cu(3)–O(19)	95.68(15)
O(5)–Cu(1)–N(2)	160.49(16)	O(6)–Cu(2)–N(1)	170.56(15)	O(10)#4–Cu(3)–O(19)	99.97(15)
O(1)–Cu(1)–N(2)	82.43(14)	O(1)–Cu(2)–O(11)#2	107.73(12)	O(17)#1–Cu(4)–O(3)	178.17(14)
O(5)–Cu(1)–O(14)	88.64(13)	O(15)–Cu(2)–O(11)#2	88.02(13)	O(17)#1–Cu(4)–N(4)	96.51(15)
O(1)–Cu(1)–O(14)	168.38(13)	O(6)–Cu(2)–O(11)#2	98.67(14)	O(3)–Cu(4)–N(4)	82.94(14)
N(2)–Cu(1)–O(14)	91.91(15)	N(1)–Cu(2)–O(11)#2	90.06(15)	O(17)#1–Cu(4)–O(8)	87.44(14)
O(5)–Cu(1)–O(13)	100.42(15)	O(10)#3–Cu(3)–O(7)	89.44(14)	O(3)–Cu(4)–O(8)	92.64(13)
O(1)–Cu(1)–O(13)	107.21(14)	O(10)#3–Cu(3)–O(3)	178.47(14)	N(4)–Cu(4)–O(8)	164.57(16)
N(2)–Cu(1)–O(13)	99.01(16)	O(7)–Cu(3)–O(3)	91.33(13)	N(4)–Cu(4)–O(19)	101.65(15)
O(14)–Cu(1)–O(13)	83.65(14)	O(10)#3–Cu(3)–N(3)	96.34(16)	O(3)–Cu(4)–O(19)	83.11(15)
O(1)–Cu(2)–O(15)	164.25(13)	O(7)–Cu(3)–N(3)	166.22(16)	O(8)–Cu(4)–O(19)	92.45(15)
O(1)–Cu(2)–O(6)	91.42(13)	O(3)–Cu(3)–N(3)	82.62(15)	O(17)#5–Cu(4)–O(19)	98.74(16)
O(15)–Cu(2)–O(6)	86.39(14)	N(3)–Cu(3)–O(19)	95.62(17)	Cu(1)-O(1)-Cu(2)	109.49(14)
O(1)–Cu(2)–N(1)	82.45(14)	O(3)–Cu(3)–O(19)	81.28(14)	Cu(3)-O(3)-Cu(4)	107.35(15)

Symmetry transformations used to generate equivalent atoms:
(1) –x+2, –y+2, –z+1; (2) –x+2, y–1/2, –z+1/2; (3) –x+2, y+1/2, –z+1/2 (4) 2-x, 1/2+y, 1/2-z (5) 2-x, 2-y, 1-z

Table S11. Selected interatomic distances (Å) and angles (°) for complex **9**.

Cu(1)–N(1)	1.9860(17)	Cu(1)–N(2)	2.0209(18)	Cu(1)–O(1)	2.4329(16)
Cu(1)–N(1)#1	1.9861(17)	Cu(1)–N(2)#1	2.0209(18)	Cu(1)–O(1)#1	2.4329(16)
N(1)–Cu(1)–N(1)#1	180.00(9)	N(2)–Cu(1)–N(2)#1	180.0	N(1)–Cu(1)–O(1)	75.91(6)
N(1)–Cu(1)–N(2)	87.21(7)	N(1)–Cu(1)–O(1)#1	104.09(6)	N(1)#1–Cu(1)–O(1)	104.09(6)
N(1)#1–Cu(1)–N(2)	92.79(7)	N(1)#1–Cu(1)–O(1)#1	75.91(6)	N(2)–Cu(1)–O(1)	73.25(6)
N(1)–Cu(1)–N(2)#1	92.79(7)	N(2)–Cu(1)–O(1)#1	106.75(6)	N(2)#1–Cu(1)–O(1)	106.75(6)
N(1)#1–Cu(1)–N(2)#1	87.21(7)	N(2)#1–Cu(1)–O(1)#1	73.25(6)	O(1)#1–Cu(1)–O(1)	180.0

Symmetry transformations used to generate equivalent atoms:
(1) –x+1, –y+1, –z+1; (2) –x+1, –y, –z+2

Table S12. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **1**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(2)–H(21)···O(6)#1	2.920(5)	2.22(5)	162(5)	O(9)–H(92)···O(2)#2	2.963(6)	2.37(6)	157(8)
O(9)–H(91)···O(4)	2.721(6)	1.90(8)	162(6)				

Symmetry transformations used to generate equivalent atoms:
(1) –x, 1-y, z-1/2; (2) 1/2+x, 3/2-y, z
[a]D= donor atom
[b]A= acceptor atom

Table S13. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **2**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(5)–H(5A)···O(20)	2.540(5)	1.72(5)	175(3)	O(30)–H(31)···O(4)#4	2.760(4)	2.06(4)	163(4)
O(8)–H(8A)···O(30)#1	2.604(4)	1.82(3)	171(5)	O(30)–H(32)···O(4)#5	2.783(5)	1.93(4)	166(3)
O(10)–H(10A)···O(40)	2.552(5)	1.94(4)	174(5)	O(40)– H(41)···O(50)#6	2.748(5)	1.87	170
O(20)–H(21)···O(2)#2	2.860(5)	2.14(5)	168(7)	O(50)–H(51)···O(9)	2.748(5)	1.93(6)	157(6)
O(20)–H(22)···O(7)#3	2.843(5)	2.02(6)	167(6)	O(50)–H(52)···O(6)#7	2.798(4)	1.96	164

Symmetry transformations used to generate equivalent atoms:
(1) –x+1, –y, –z+1; (2) –x+1, –y+1, –z+1; (3) –x, 1–y, –z; (4) x, y–1, z; (5) 2–x, 1–y, 1–z; (6) –x–1, –y–1, –z; (7) x–1, y–1, z
[a]D= donor atom
[b]A= acceptor atom

Table S14. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **3**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(1)–H(1A)···O5#1	2.442(3)	1.54(3)	176(3)	O10–H(10A)···O7#4	2.782(3)	2.01(4)	178(5)
O(2)–H(2A)···O6#1	2.572(3)	1.81(4)	175(4)	O10–H(10B)···O4#5	2.776(4)	2.09(4)	170(4)
O(3)–H(3A)···O11	2.549(3)	1.69(4)	169(4)	O11–H(11A)···O10#6	2.666(4)	1.96(4)	174(4)
O(8)–H(8A)···O9	2.599(3)	1.86(3)	169(3)	O11–H(11B)···O7#7	2.858(3)	2.36(4)	126(4)
O(9)–H(9A)···O1#2	2.767(3)	2.02(3)	163(3)	O11–H(11B)···O5#8	2.996(4)	2.34(4)	149(4)
O(9)–H(9B)···O11#3	2.894(4)	2.19(4)	146(4)				

Symmetry transformations used to generate equivalent atoms:
(1) x, y, 1+z; (2) 3–x, 1–y, 2–z; (3) 1+x, 1+y, z; (4) 3–x, 1–y, 1–z; (5) 2–x, –y, 1–z; (6) x–1, y, z; (7) x–1, y–1, z; (8) 2–x, –y, 1–z
[a]D= donor atom
[b]A= acceptor atom

Table S15. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **4**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(2)–H(2A)···O(8)#1	2.762(3)	1.9700	163.00	O(9)–H(9B)···O(6)	2.06(4)	2.790(3)	148(4)
O(9)–H(9A)···O8)	2.862(3)	2.19(4)	162(4)				

Symmetry transformations used to generate equivalent atoms:
(1) 1/2–x, 1/2+y, 1/2-z
[a]D= donor atom
[b]A= acceptor atom

Table S16. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **5**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(1)–H(1A)···O(3)	2.627(7)	1.8500	157.00	O(7)–H(7A)···O(6)	2.831(9)	1.90(10)	164(8)
O(2)–H(2A)···O(7)#1	2.548(8)	1.7500	162.00	O(7)–H(7B)···O(4)#1	2.646(8)	1.69(8)	171(6)
O(5)–H(5A)···O(4)#2	2.608(7)	1.8300	158.00				

Symmetry transformations used to generate equivalent atoms:
(1) 1–x, -y, 1-z; (2) x, 1/2-y, 1/2+z
[a]D= donor atom
[b]A= acceptor atom

Table S17. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **6**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(9)–H(9AA)···O(7)#1	3.068(3)	2.4100	138.00	O(11)–H(11A)···O6	2.806(3)	2.1600	136.00
O(2)–H(2B)···O(8)#2	2.779(3)	1.9600	174.00	O(11)–H(11B)···O8	2.875(3)	2.0800	168.00
O(10)–H(10A)···O(5)#3	2.965(5)	2.1200	176.00				

Symmetry transformations used to generate equivalent atoms:
(1) x-1/2, 1/2+y, z; (2) 1/2-x, y-1/2, 1/2-z; (3) 1/2-x, 1/2+y, 1/2-z
[a]D= donor atom
[b]A= acceptor atom

Table S18. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **7**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(1)–H(1A)···O(4)#1	2.5749(17)	1.73(2)	170(2)	O(5)–H(5A)···O(6)#2	2.6966(18)	1.8800	172.00
O(2)–H(2A)···O(3)#2	2.7133(18)	1.8900	176.00	O(7)–H(7A)···O(3)#3	2.8176(19)	2.0700	152.00

Symmetry transformations used to generate equivalent atoms:
(1) –x, 1-y, -z; (2) 1/2-x, 1/2-y, 1-z; (3) 1/2-x, 1/2+y, 1/2-z
[a]D= donor atom
[b]A= acceptor atom

Table S19. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **8**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(2)–H(2A)···O(12)#1	2.611(5)	1.8100	166.00	O(14)–H(14A)···O(4)#5	3.042(5)	2.4100	125.00
O(4)–H(4A)···O(2)#2	2.770(5)	1.9800	161.00	O(14)–H(14A)···O(12)#5	2.647(5)	2.3300	100.00
O(13)–H(13B)···O(18)#3	2.765(5)	2.0200	136.00	O(14)–H(14B)···O(8)#5	3.352(5)	2.5900	140.00
O(14)–H(14A)···O(2)#4	3.364(5)	2.4500	166.00	O(19)–H(19A)···O(30)#5	2.872(16)	2.1800	164.00
O(14)–H(14A)···O(3)#5	2.940(5)	2.5400	106.00	O(19)–H(19B)···O(40)#6	2.809(15)	2.2000	156.00

Symmetry transformations used to generate equivalent atoms:
(1) 2–x, y-1/2, 1/2-z; (2) 2-x, 1/2+y, 1/2-z; (3) 1-x, 2-y, 1-z; (4) 1-x, 1/2+y, 1/2-z (5) x-1, y, z (5) x-1, y, z; (6) 2-x, 2-y, 1-z
[a]D= donor atom
[b]A= acceptor atom

Table S20. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for **9**.

D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b	D^a – H···A^b	D^a ···A^b	H···A^b	< D^a H A^b
O(1)–H(1A)···O(4)#1	2.683(3)	1.91(3)	170(4)	O(5)–H(5)···O(4)	2.414(3)	1.6100	168.00
O(2)–H(2A)···O(3)#1	2.663(3)	1.8500	172.00				

Symmetry transformations used to generate equivalent atoms:
(1) 1-x, 1-y, 1-z
[a]D= donor atom
[b]A= acceptor atom

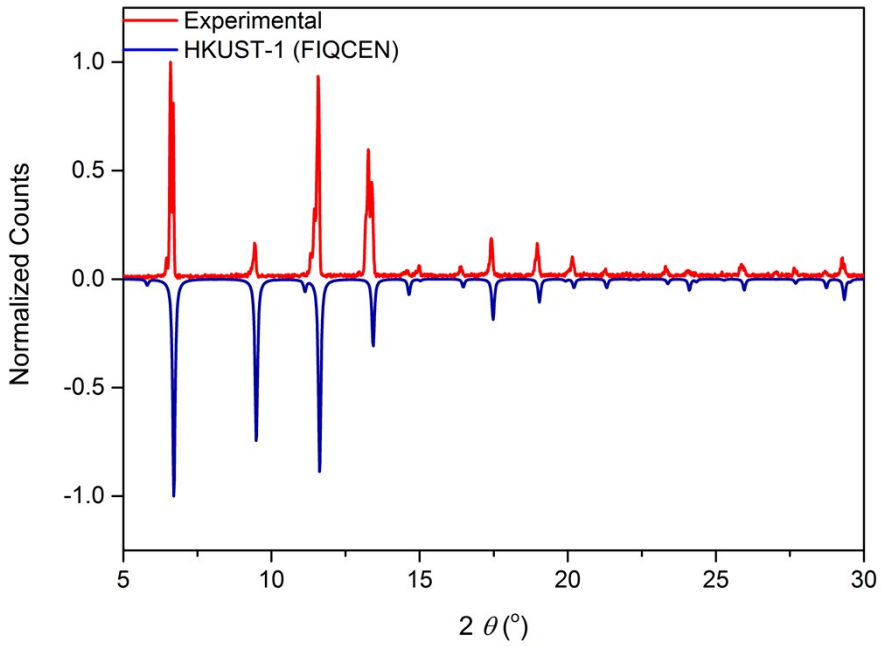

Fig. S1. The powder x-ray diffraction pattern of the product isolated from the reaction system $CuCl_2/(py)_2CO/H_3btc/H_2O_2$ (top) and the simulated pattern of HKUST-1 (bottom).

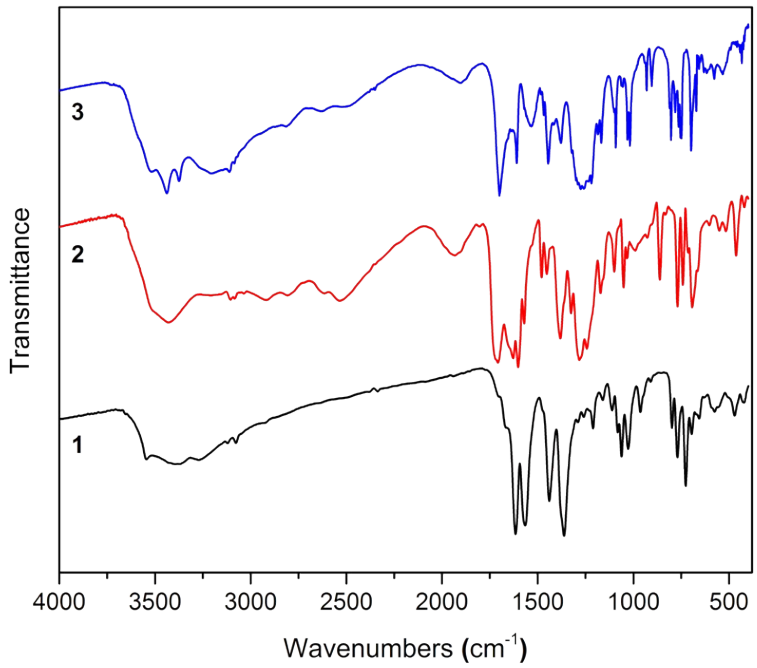

Fig. S2. The IR spectra (KBr disks) of complexes **1**, **2** and **3** in the 4000 − 400 cm^{-1} region.

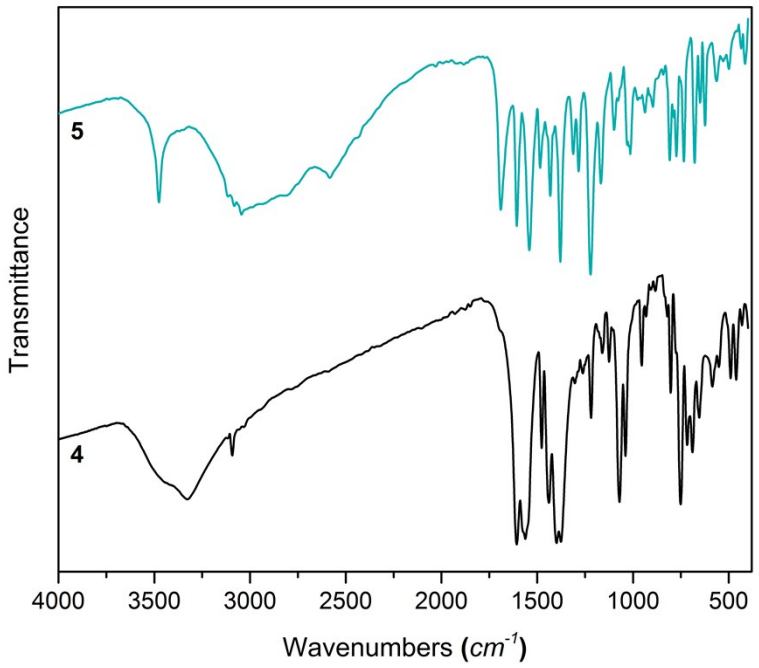

Fig. S3. The IR spectra (KBr disks) of complexes **4** and **5** in the 4000 − 400 cm^{-1} region.

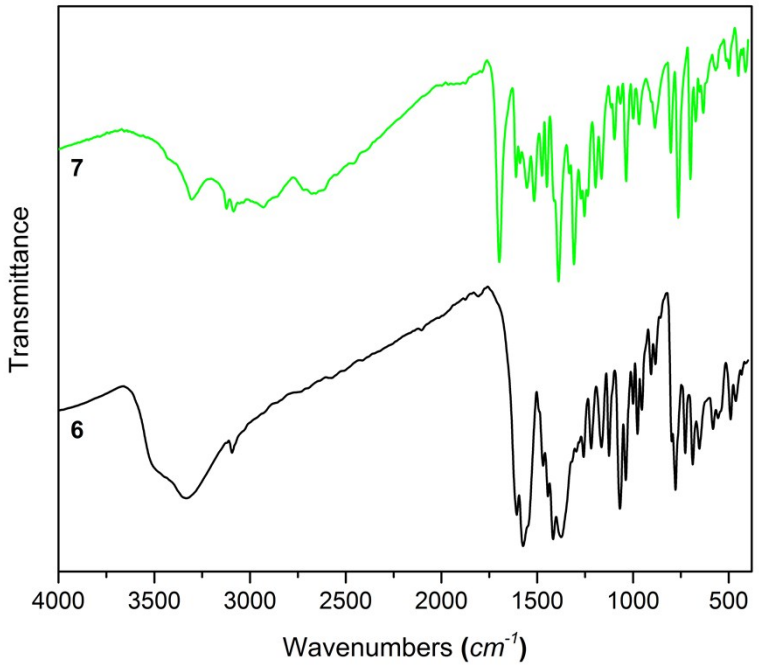

Fig. S4. The IR spectra (KBr disks) of complexes **6** and **7** in the 4000 − 400 cm^{-1} region.

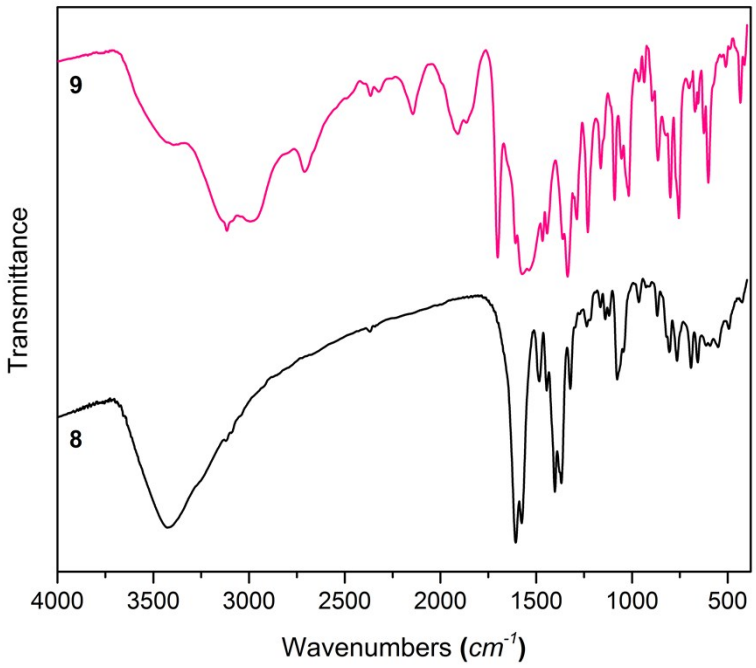

Fig. S5. The IR spectra (KBr disks) of complexes **8** and **9** in the 4000 − 400 cm^{-1} region.

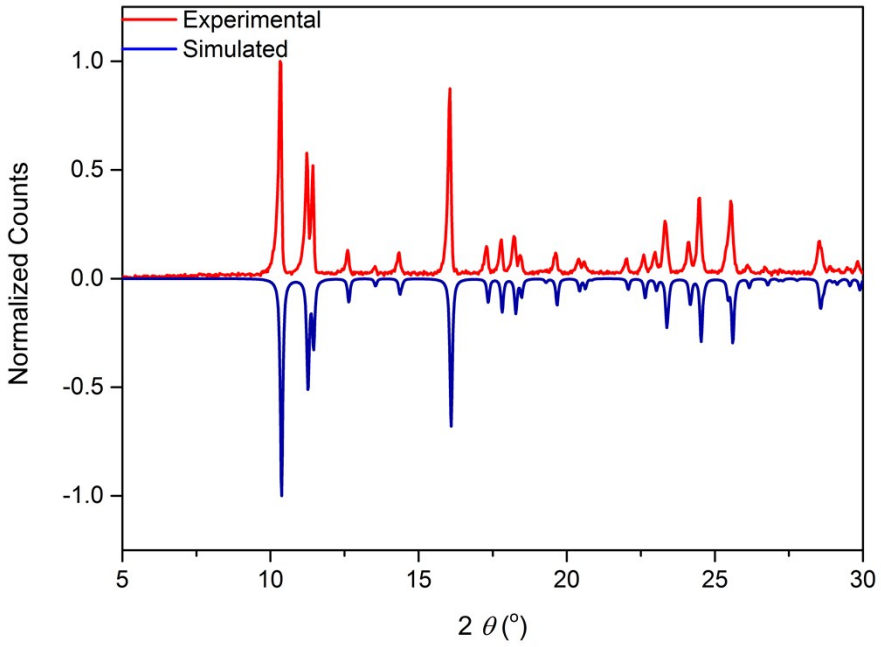

Fig. S6. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **1**.

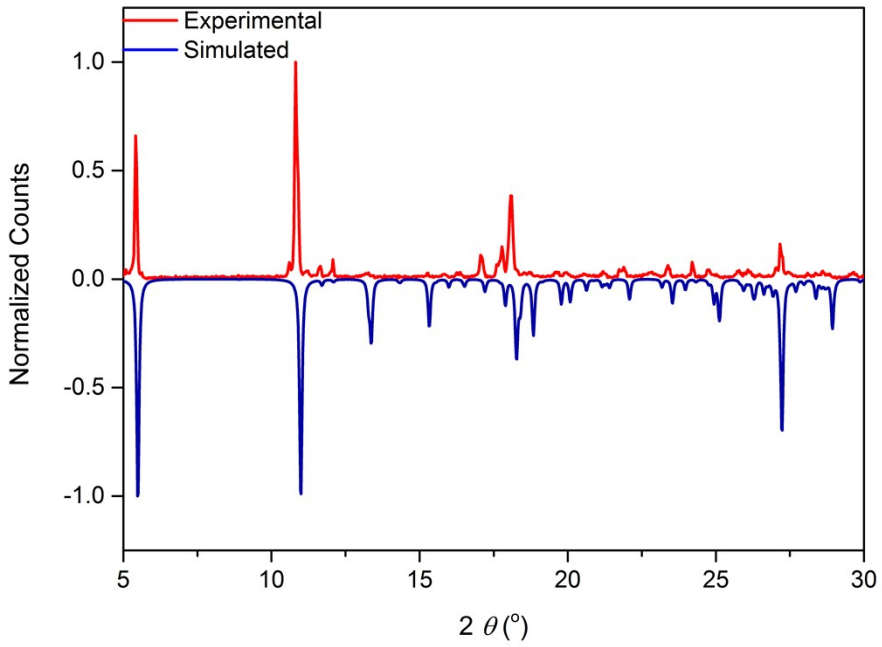

Fig. S7. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **2**.

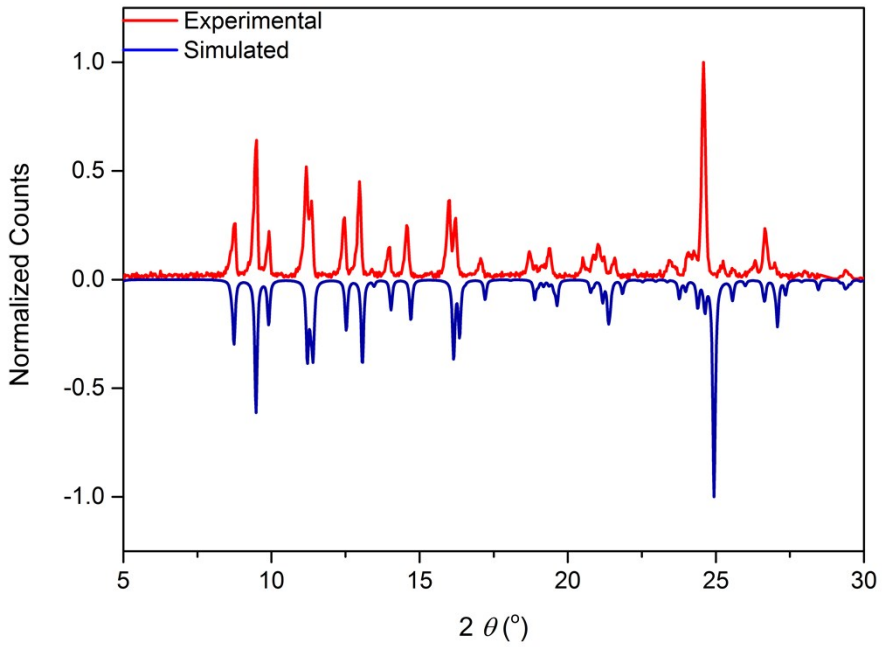

Fig. S8. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **3**.

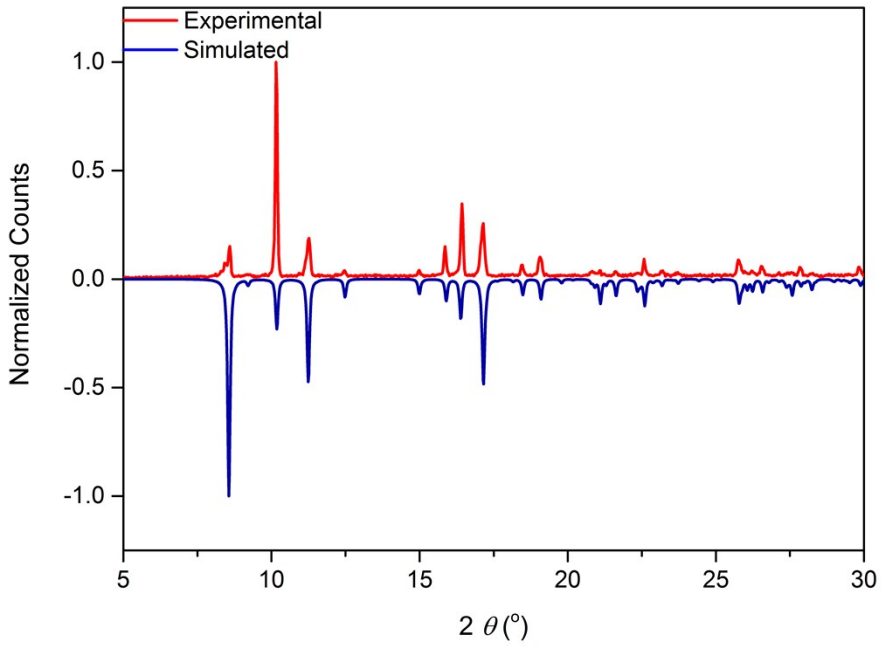

Fig. S9. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **4**.

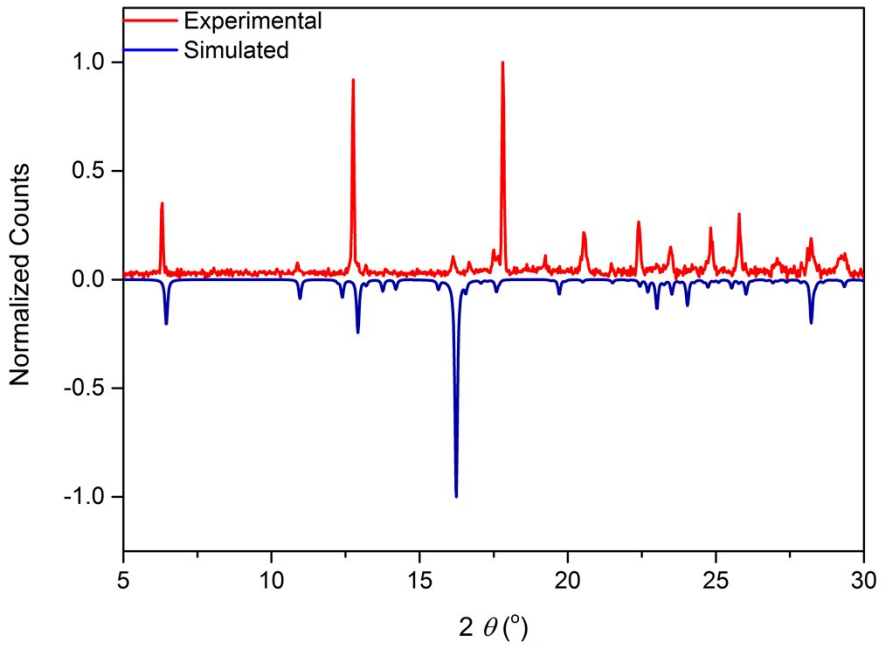

Fig. S10. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **5**.

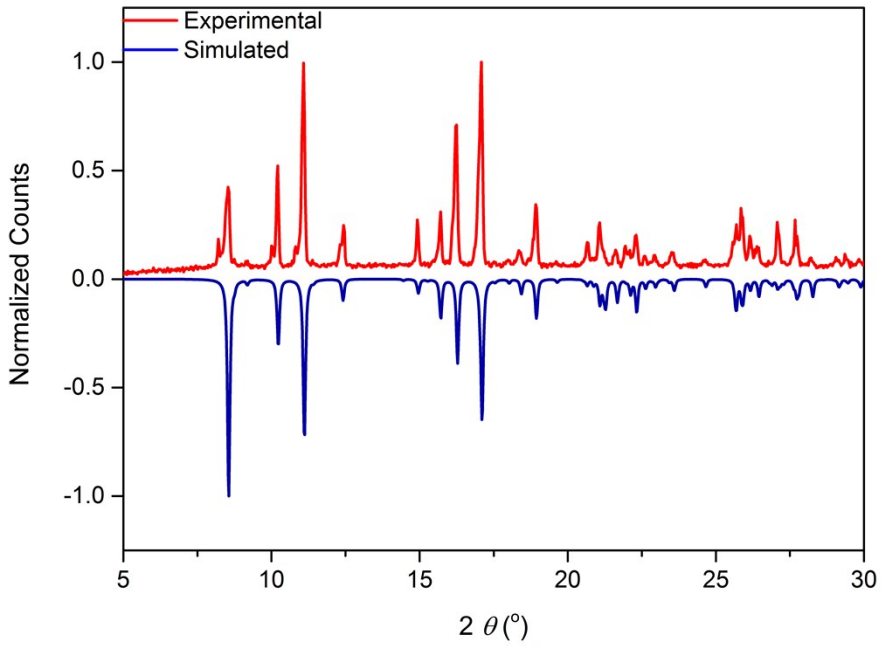

Fig. S11. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **6**.

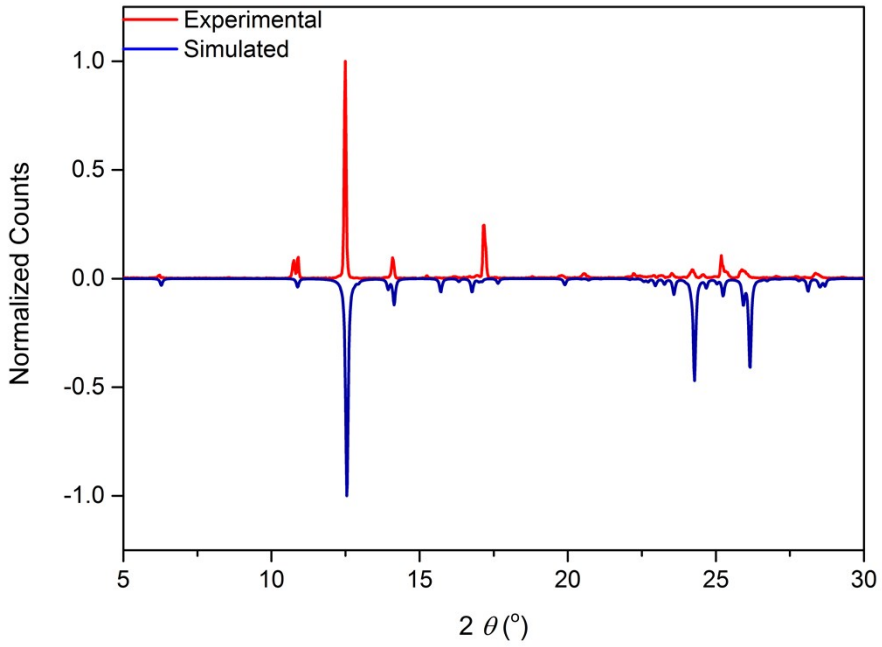

Fig. S12. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **7**.

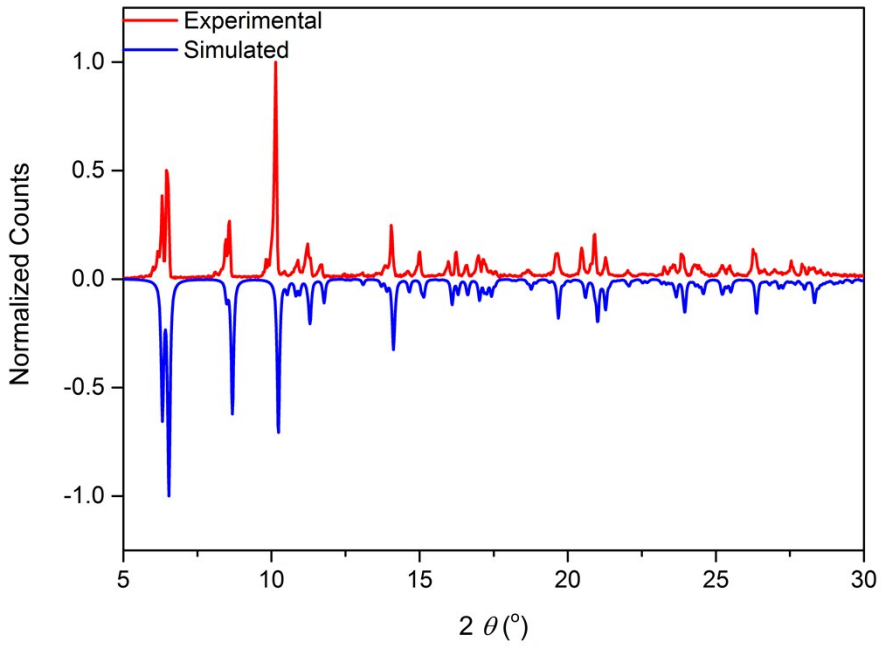

Fig. S13. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **8**.

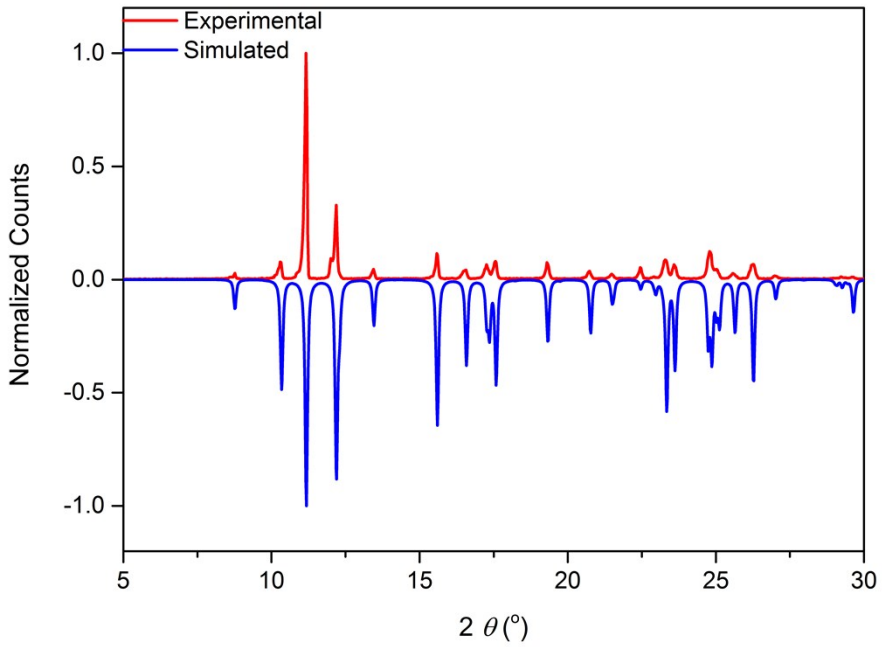

Fig. S14. The experimental (red line, top) and calculated (blue line, bottom) PXRD patterns of **9**.

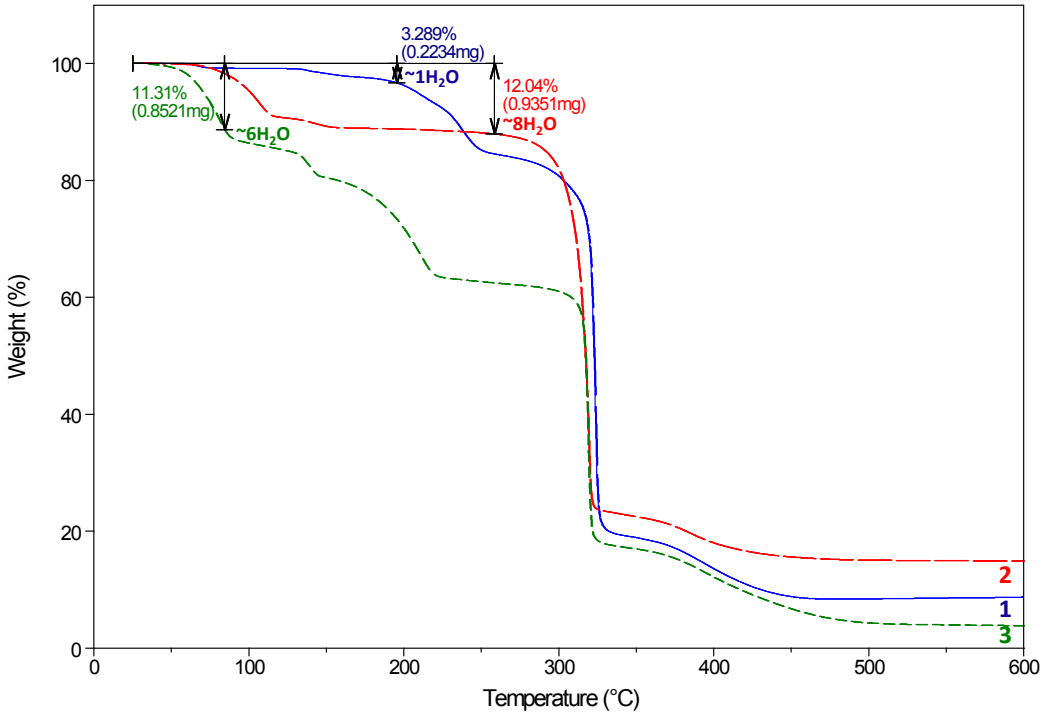

Fig. S15. The TGA curves for complexes **1**, **2** and **3**.

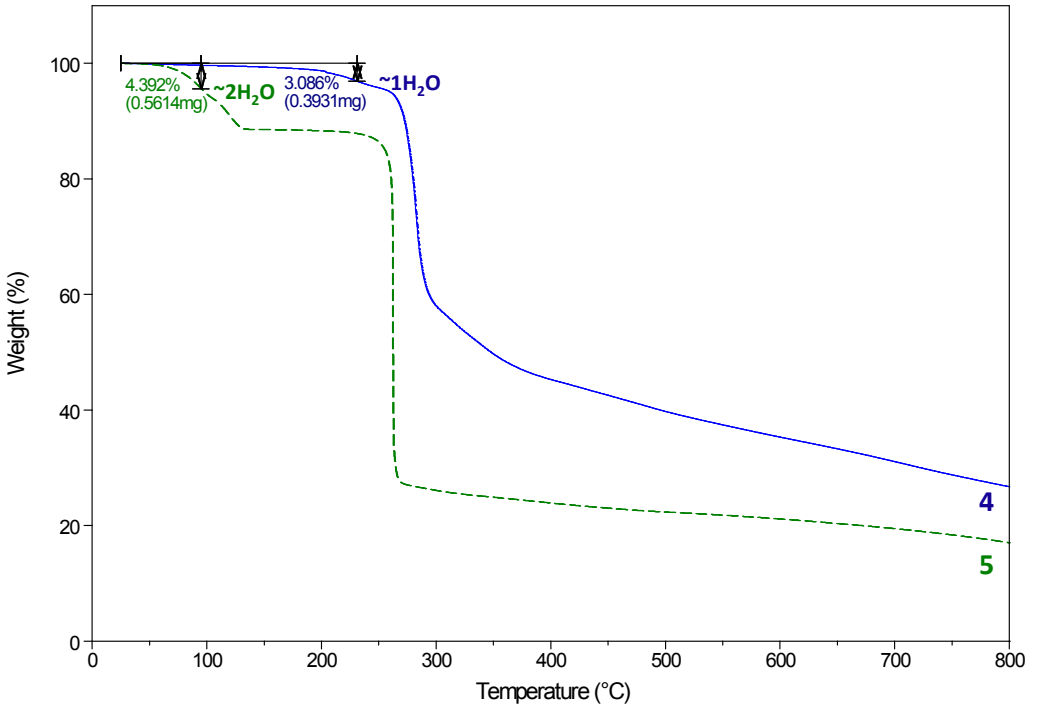

Fig. S16. The TGA curves for complexes **4** and **5**.

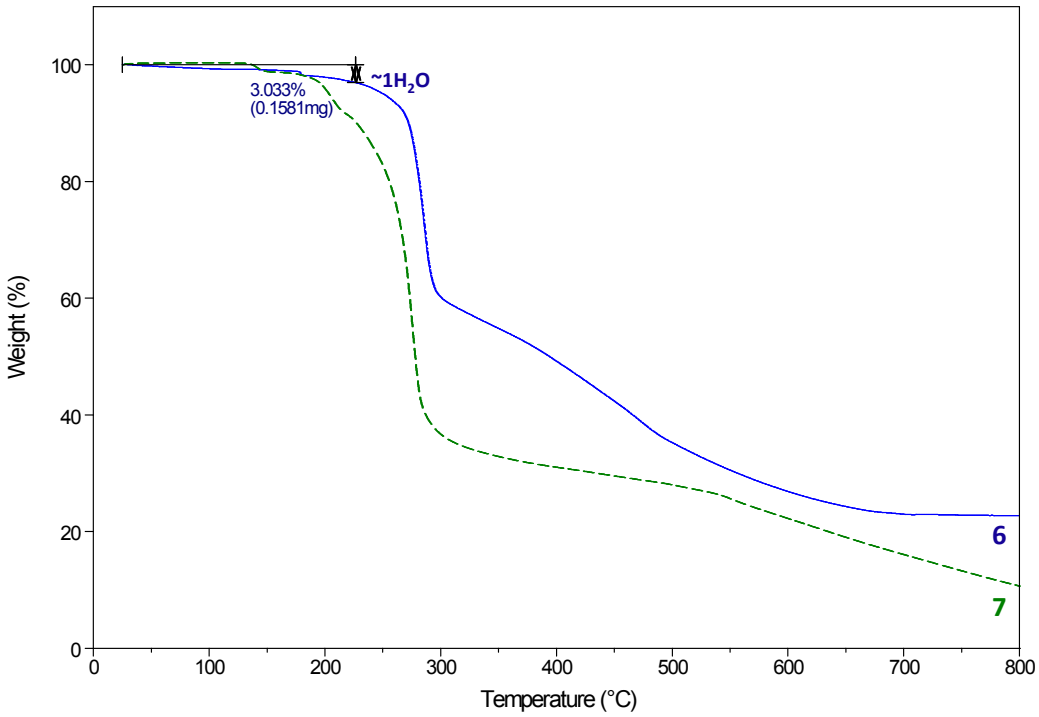

Fig. S17. The TGA curves for complexes **6** and **7**.

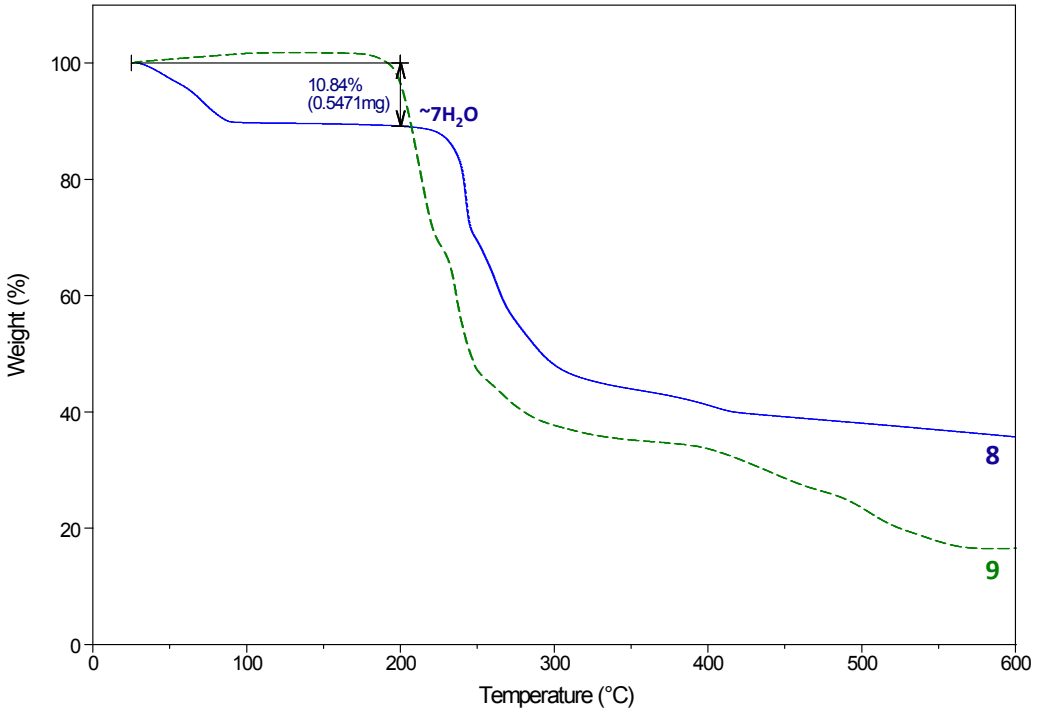

Fig. S18. The TGA curves for complexes **8** and **9**.

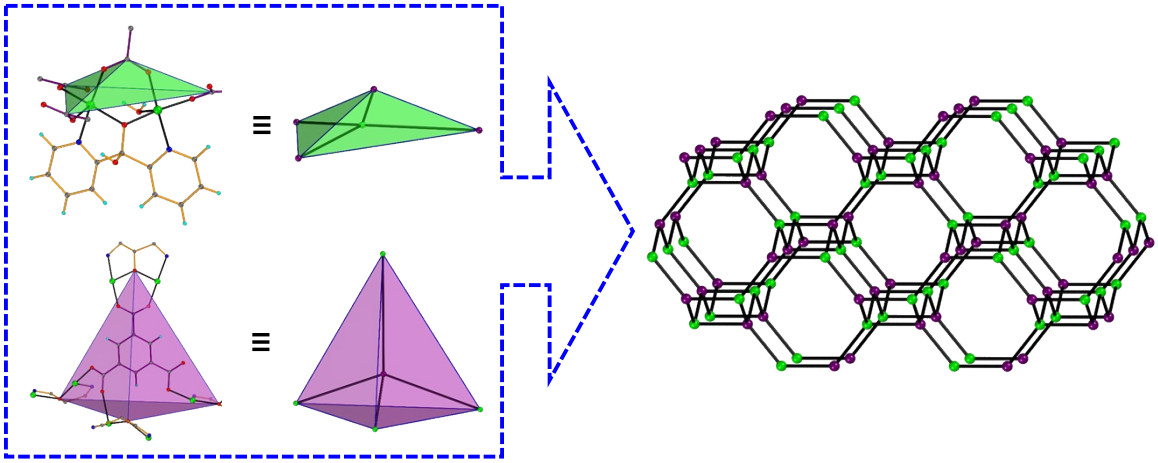

Fig. S19. The deconstruction of the framework of **1** to produce the underlying network with **sra** topology (right). Green and purple spheres represent the $[Cu_2\{(py)_2C(OH)O\}(H_2O)]^{3+}$ and btc^{3-} tetrahedral nodes, respectively.

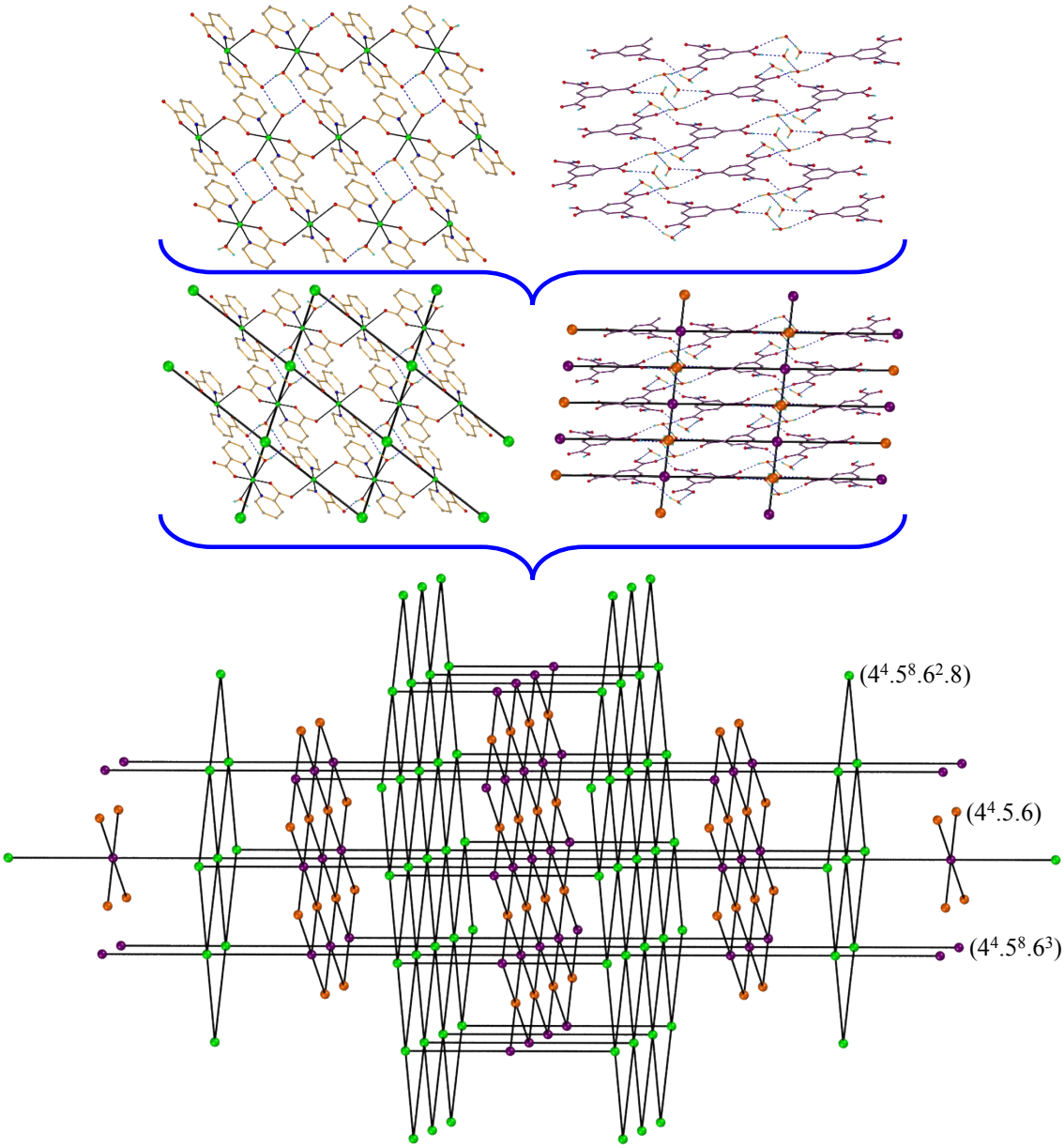

Fig. S20. The deconstruction of the hydrogen-bonded framework of **2** to produce the underlying (4,6,6-coordinated) tri-nodal network with a unique topology and point symbol $(4^4.5.6)(4^4.5^8.6^2.8)(4^4.5^8.6^3)$ (bottom).

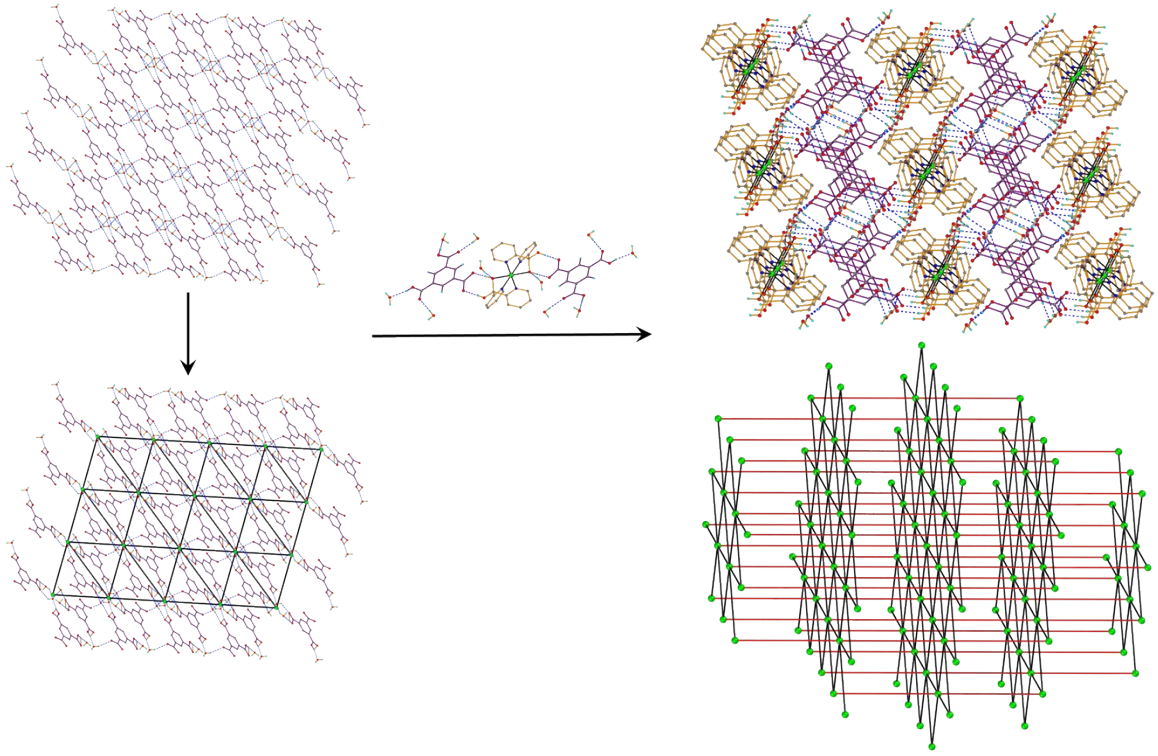

Fig. S21. The deconstruction of the hydrogen-bonded framework of **3** to produce the underlying network with **hex** topology (bottom right). Red lines represent connection of the anionic hydrogen-bonded H_2btc^-/H_2O layers by the $[Cu\{(py)_2C(OH)_2\}_2]^{2+}$ cations.

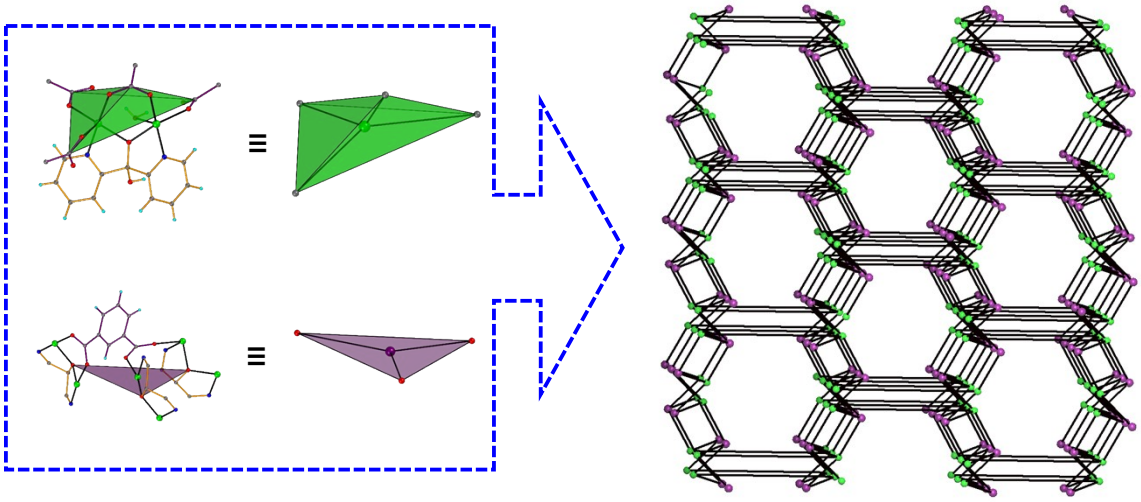

Fig. S22. The deconstruction of the framework of **4** to produce the underlying network with topological type **3,4T1** and point symbol $(4.6.8)(4.6^2.8^3)$ (right). Green and purple spheres represent the tetrahedral $[Cu_2\{(py)_2C(OH)O\}(H_2O)]^{3+}$ and trigonal planar bdc^{2-} nodes, respectively. Compound **6** has the same structure and topology with 5-HO-bdc^{2-} instead of bdc^{2-}.

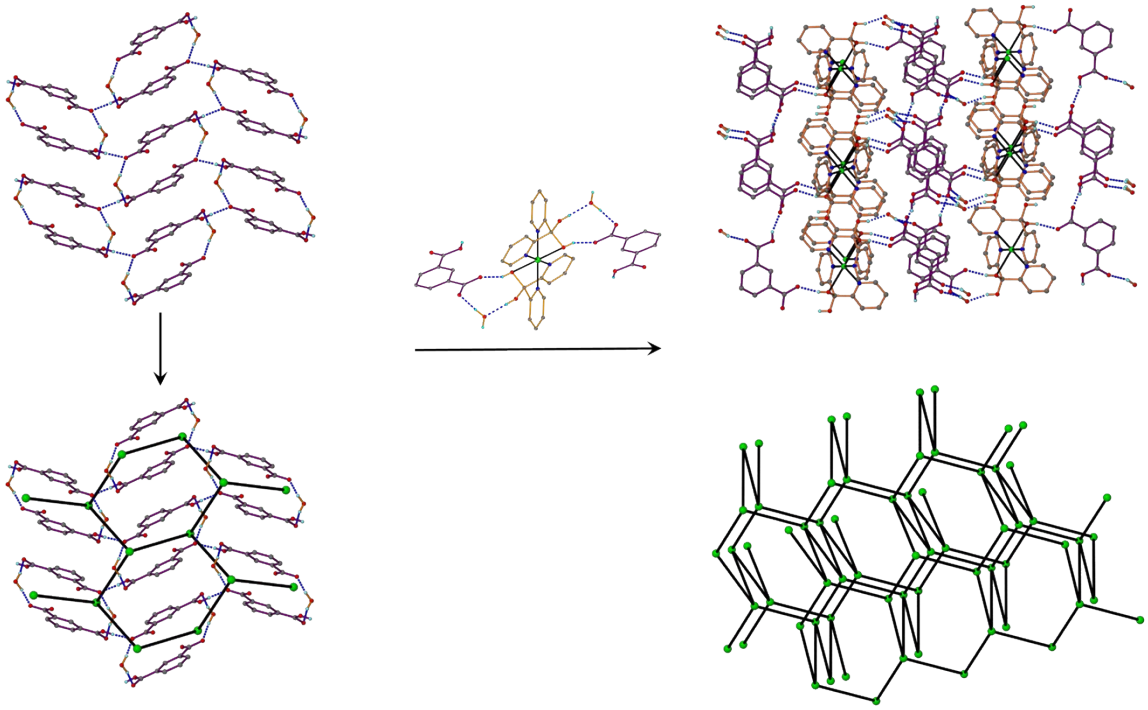

Fig. S23. The deconstruction of the hydrogen-bonded framework of **5** to produce the underlying network with **dia** topology (bottom right).

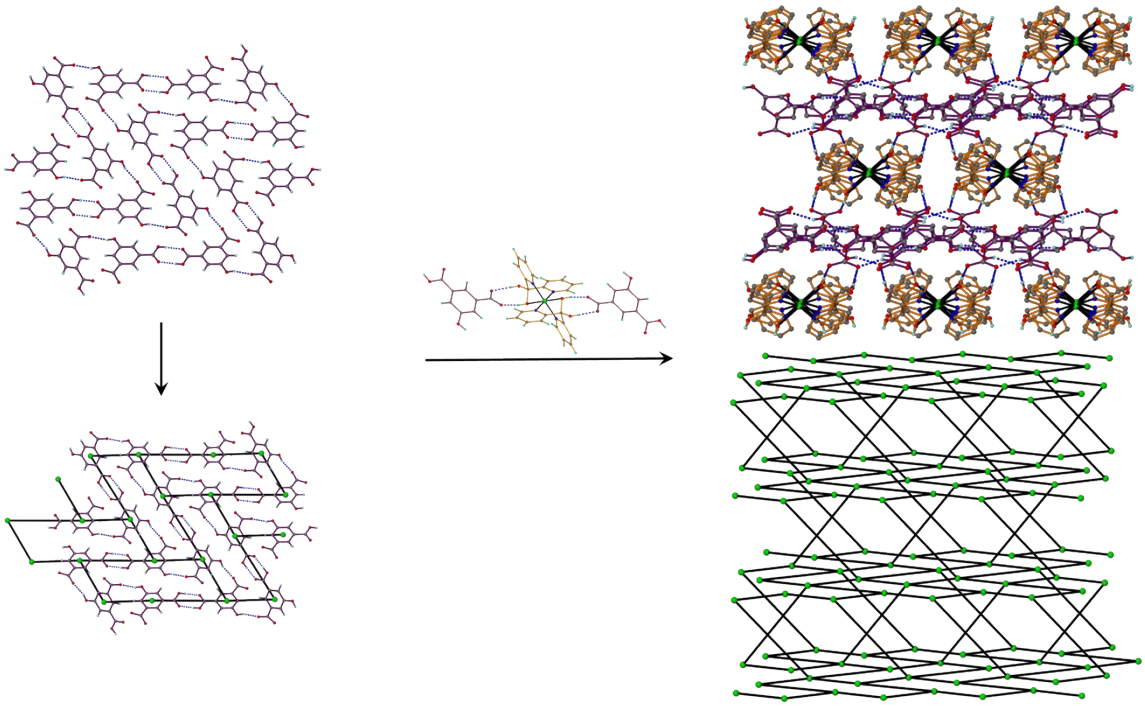

Fig. S24. The deconstruction of the hydrogen-bonded framework of **7** to produce the underlying network with **dia** topology (bottom right).

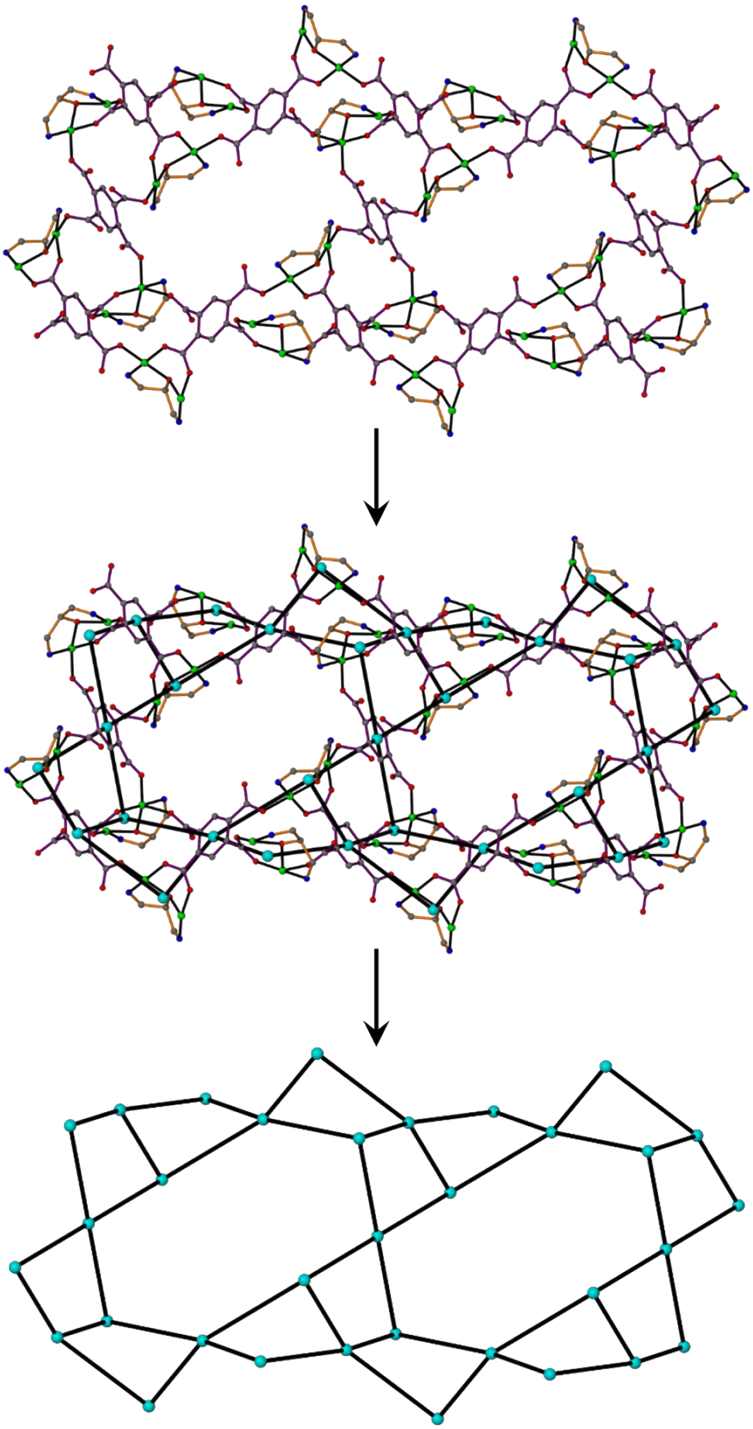

Fig. S25. The deconstruction of the framework of **8** to produce the underlying network with topological type **3,4,4L15** and point symbol $(4^2.6)_4(4^2.8^2.10^2)(4^3.6^2.8)_2$.

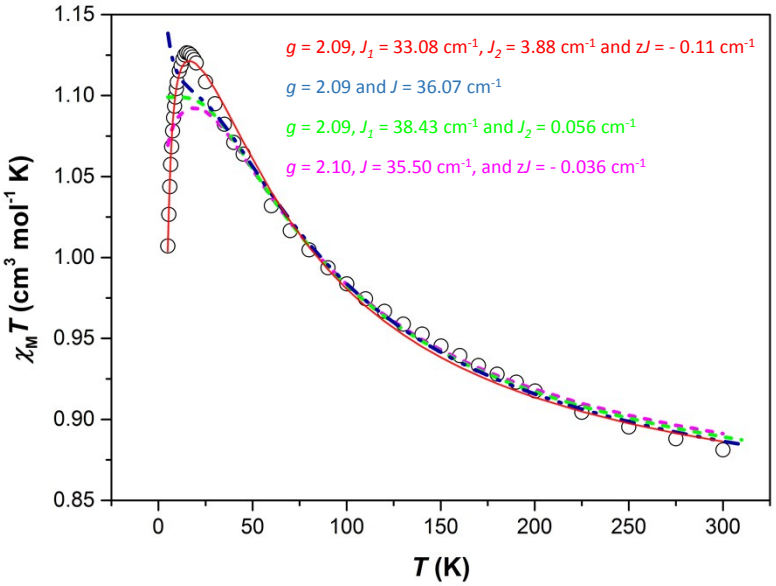

Fig. S26. $\chi_M T$ (○) vs. T plot for complex **1** (values are normalized for [Cu_2]). The red line and values represent the best fit of the experimental data in the 300-5K temperature range by using a ring model comprising 12 Cu^{II} ions. The rest of the methods can fit the experimental data satisfactorily in the 300-30K temperature range. The dashed green line and values represent the best fit of the experimental data by using the Bleaney-Bowers equation, the dashed magenta line and values represent the best fit of the experimental data by considering magnetically isolated [Cu_2] dimers (fitting with PHI) and the dashed blue line and values represent the best fit of the experimental data by using the equation that considers equally spaced magnetic centers (Cu^{II} dimers) with local spins S =1.

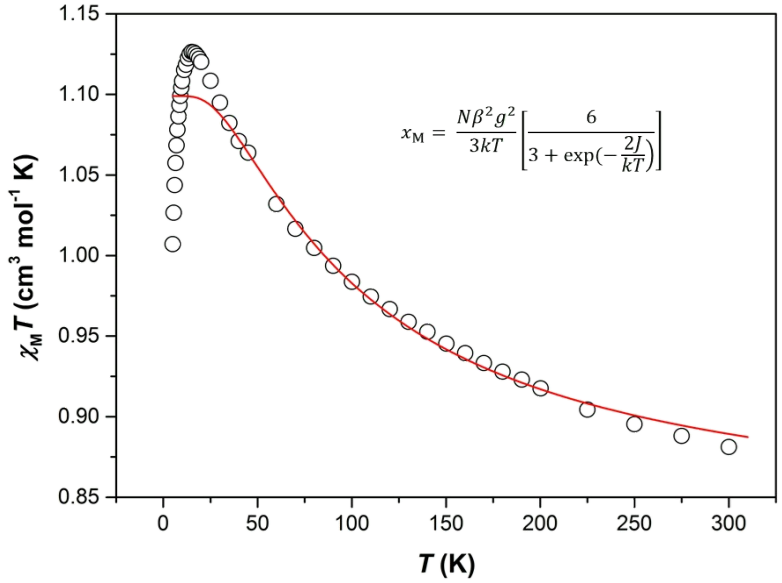

Fig. S27. $\chi_M T$ (○) vs. T plot for complex **1** (values are normalized for [Cu_2]). The red line represent the best fit of the experimental data by using the Bleaney-Bowers equation (inset). Best fit parameters: g = 2.09 and J = 36.07 cm^{-1}.

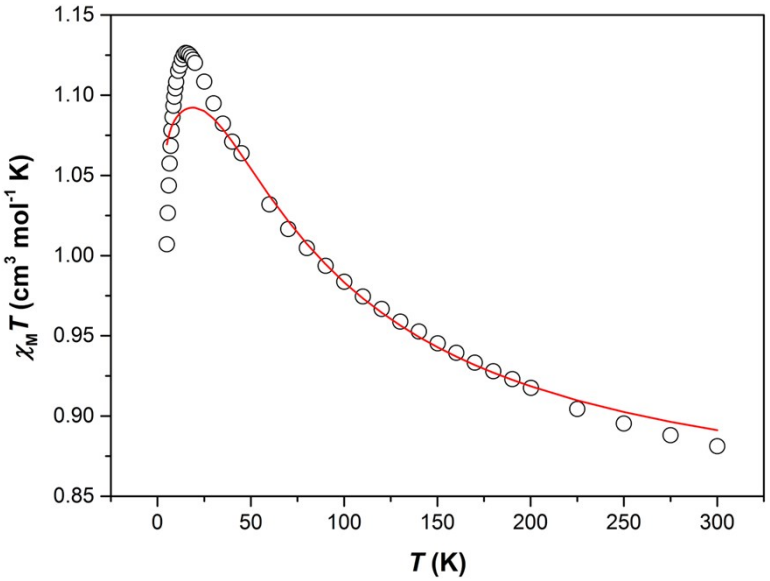

Fig. S28. $\chi_M T$ (○) vs. T plot for complex **1** (values are normalized for [Cu_2]). The red line represent the best fit of the experimental data by considering magnetically isolated [Cu_2] dimers (fitting with PHI). Best fit parameters: g = 2.10, J = 35.50 cm^{-1}, and zJ = - 0.036 cm^{-1}.

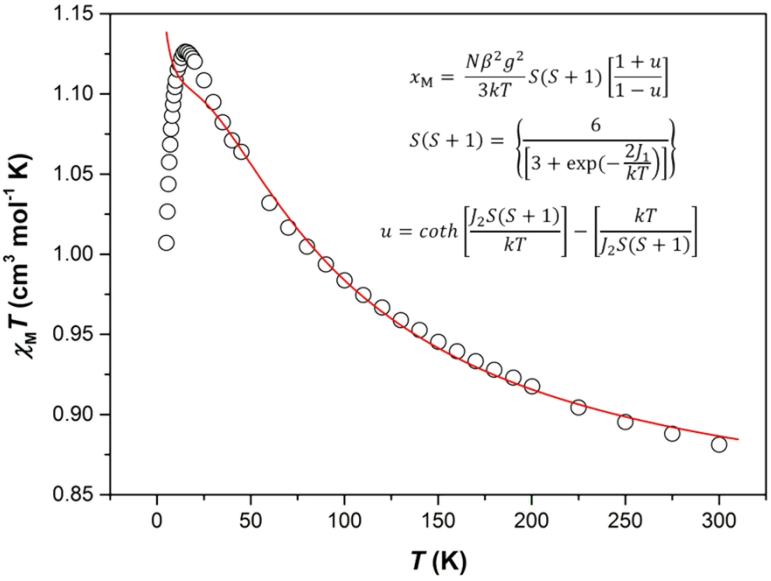

Fig. S29. $\chi_M T$ (○) vs. T plot for complex **1** (values are normalized for [Cu_2]). The red line represent the best fit of the experimental data by using the equation shown in the inset. Best fit parameters: g = 2.09, J_1 = 38.43 cm^{-1} (intra-dimer) and J_2 = 0.056 cm^{-1} (inter-dimer).

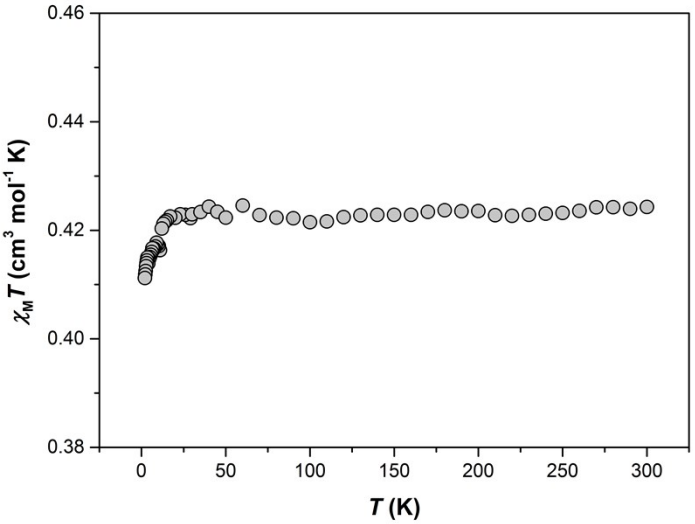

Fig. S30. $\chi_M T$ (○) vs. T plot for complex **2** consistent with magnetically isolated Cu^{II} ions.