Supporting Information

Triazolate-based 3D frameworks and 2D layer with centrosymmetric Cu^{II}_7, Cu^{II}_5, Cu^{II}_4 clusters and tunable interlayer/interchain compactness: Hydrothermal syntheses, crystal structures and magnetic properties

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Table S1 Selected bond lengths (Å) and angles (º) for **1**[a]

Cu(1)–O(10)	1.922(4)	Cu(2)–O(2)$^{\#5}$	2.294(4)
Cu(1)–O(1)	1.937(4)	Cu(3)–O(10)	1.898(4)
Cu(1)–O(7)$^{\#1}$	1.968(4)	Cu(3)–N(2)	1.983(5)
Cu(1)–N(1)	1.974(5)	Cu(3)–N(6)	1.986(5)
Cu(1)–O(7)$^{\#2}$	2.352(4)	Cu(3)–O(9)$^{\#3}$	2.008(4)
Cu(2)–N(3)$^{\#3}$	1.959(4)	Cu(4)–N(5)	1.931(5)
Cu(2)–O(4)$^{\#4}$	1.963(4)	Cu(4)–O(9)	1.968(4)
Cu(2)–N(4)	1.986(4)	Cu(5)–O(5)$^{\#6}$	1.908(4)
Cu(2)–O(9)	2.040(4)	Cu(5)–O(3)$^{\#7}$	1.969(4)
O(10)–Cu(1)–O(7)$^{\#2}$	98.46(16)	N(3)$^{\#3}$–Cu(2)–O(2)$^{\#5}$	93.21(16)
O(10)–Cu(1)–O(7)$^{\#1}$	88.02(16)	O(4)$^{\#4}$–Cu(2)–O(2)$^{\#5}$	90.61(16)
O(1)–Cu(1)–O(7)$^{\#1}$	88.35(15)	N(4)–Cu(2)–O(2)$^{\#5}$	83.85(16)
O(10)–Cu(1)–N(1)	86.65(17)	O(9)–Cu(2)–O(2)$^{\#5}$	118.96(16)
O(1)–Cu(1)–N(1)	97.02(17)	O(10)–Cu(3)–N(2)	84.87(17)
O(1)–Cu(1)–O(7)$^{\#2}$	80.10(15)	O(10)–Cu(3)–N(6)	96.71(17)
O(7)$^{\#1}$–Cu(1)–O(7)$^{\#2}$	77.93(15)	N(2)–Cu(3)–O(9)$^{\#3}$	86.12(16)
N(1)–Cu(1)–O(7)$^{\#2}$	107.12(16)	N(6)$^{\#5}$–Cu(3)–O(9)$^{\#3}$	91.99(17)
N(3)$^{\#3}$–Cu(2)–O(4)$^{\#4}$	96.59(17)	N(5)–Cu(4)–O(9)	89.35(17)
N(4)–Cu(2)–O(9)	88.95(16)	N(5)$^{\#3}$–Cu(4)–O(9)	90.65(17)
O(4)$^{\#4}$–Cu(2)–N(4)	89.14(18)	O(5)$^{\#6}$–Cu(5)–O(3)	91.38(17)
N(3)$^{\#3}$–Cu(2)–O(9)	87.50(16)	O(5)$^{\#2}$–Cu(5)–O(3)	88.62(17)
O(4)$^{\#4}$–Cu(2)–O(9)	149.96(17)	O(5)$^{\#2}$–Cu(5)–O(3)$^{\#7}$	91.37(17)

[a] Symmetry codes: $^{\#1}$ $1-x, 1-y, 2-z$; $^{\#2}$ $x+1, y, z$; $^{\#3}$ $3-x, 2-y, 2-z$; $^{\#4}$ $1+x, y, 1+z$. $^{\#5}$ $2-x, 2-y, 2-z$; $^{\#6}$ $1-x, 1-y, 1-z$; $^{\#7}$ $2-x, 1-y, 1-z$.

Table S2 Selected bond lengths (Å) and angles (º) for **2** [a]

Cu(1)–N(5)	1.978(4)	Cu(2)–N(6)	2.012(4)
Cu(1)–N(1)	1.980(4)	Cu(2)–N(8)	2.166(3)
Cu(1)–N(11)	1.987(5)	Cu(3)–N(2)	1.920(4)
Cu(1)–O(1)	2.030(3)	Cu(3)–O(1)	1.964(3)
Cu(1)–O(2)	2.190(9)	Cu(3)–N(9)	2.459(4)
Cu(2)–N(7)$^{\#1}$	1.917(2)	Cu(4)–N(12)	1.979(5)
Cu(2)–O(1)	1.995(3)	Cu(4)–N(4)	2.011(4)
Cu(2)–N(3)$^{\#2}$	2.008(4)	Cu(4)–O(3)	2.418(7)
N(5)–Cu(1)–N(11)	90.96(19)	O(1)$^{\#2}$–Cu(3)–N(9)	101.43(16)
N(1)–Cu(1)–N(11)	91.01(19)	N(2)$^{\#2}$–Cu(3)–O(1)	89.13(15)
N(5)–Cu(1)–O(1)	86.03(16)	N(2)–Cu(3)–O(1)	90.87(15)
N(1)–Cu(1)–O(1)	91.11(16)	N(2)$^{\#2}$–Cu(3)–N(9)$^{\#2}$	89.6(5)
O(1)–Cu(1)–O(2)	81.3(2)	N(2)–Cu(3)–N(9)$^{\#2}$	90.4(5)
N(5)–Cu(1)–O(2)	91.6(3)	O(1)–Cu(3)–N(9)$^{\#2}$	101.4(4)
N(1)–Cu(1)–O(2)	89.5(3)	O(1)$^{\#2}$–Cu(3)–N(9)$^{\#2}$	78.6(4)
N(11)–Cu(1)–O(2)	123.3(2)	N(2)$^{\#2}$–Cu(3)–N(9)	90.44(18)
N(3)$^{\#2}$–Cu(2)–N(8)	86.56(19)	N(2)–Cu(3)–N(9)	89.56(18)
O(1)–Cu(2)–N(8)	84.91(13)	O(1)–Cu(3)–N(9)	78.57(16)
N(7)$^{\#1}$–Cu(2)–N(3)$^{\#2}$	90.22(16)	N(4)–Cu(4)–O(3)	94.0(2)
O(1)–Cu(2)–N(3)$^{\#2}$	90.02(15)	N(12)–Cu(4)–N(4)	90.07(19)
N(7)$^{\#1}$–Cu(2)–N(6)	90.25(16)	N(12)–Cu(4)–N(4)$^{\#3}$	89.93(19)
O(1)–Cu(2)–N(6)	87.71(15)	N(12)–Cu(4)–O(3)$^{\#3}$	84.9(2)
N(7)$^{\#1}$–Cu(2)–N(8)	108.42(9)	N(4)–Cu(4)–O(3)$^{\#3}$	86.0(2)
N(6)–Cu(2)–N(8)	100.71(19)	N(12)–Cu(4)–O(3)	95.1(2)

[a] Symmetry codes: $^{\#1}$ $-x, 1-y, -z$; $^{\#2}$ $1-x, 1-y, -z$; $^{\#3}$ $-x, 1-y, 1-z$.

Table S3 Selected bond lengths (Å) and angles (º) for **3** [a]

Cu(1)–N(2)	1.974(5)	Cu(4)–O(10)	1.953(3)
Cu(1)–O(9)	1.977(3)	Cu(4)–O(1)	1.968(3)
Cu(1)–N(7)	2.006(5)	Cu(4)–N(5)	1.984(4)
Cu(1)–N(4)	2.047(4)	Cu(4)–N(12)$^{\#3}$	2.002(4)
Cu(1)–O(1)	2.366(4)	Cu(4)–N(3)	2.322(5)
Cu(2)–O(6)	1.949(4)	Cu(5)–N(11)	1.942(4)
Cu(2)–O(7)$^{\#1}$	1.988(4)	Cu(5)–O(10)	1.949(3)
Cu(2)–N(1)	1.989(4)	Cu(6)–O(3)$^{\#4}$	1.965(5)
Cu(2)–N(9)$^{\#2}$	2.017(4)	Cu(6)–N(6)	1.980(4)
Cu(2)–O(9)	2.304(4)	Cu(6)–N(10)	1.994(4)
Cu(3)–N(8)	1.947(5)	Cu(6)–O(8)$^{\#5}$	2.044(4)
Cu(3)–O(9)	1.987(3)	Cu(6)–O(10)	2.230(3)
Cu(3)–O(5)	2.420(3)		
N(2)–Cu(1)–O(9)	88.75(17)	O(9)–Cu(3)–O(5)	78.03(13)
O(9)–Cu(1)–N(7)	90.22(16)	N(8)$^{\#2}$–Cu(3)–O(5)$^{\#2}$	87.21(15)
N(2)–Cu(1)–N(4)	90.35(19)	O(10)–Cu(4)–N(5)	89.39(14)
O(9)–Cu(1)–O(1)	123.26(13)	O(1)–Cu(4)–N(5)	90.15(15)
N(7)–Cu(1)–N(4)	93.08(19)	O(10)–Cu(4)–N(12)$^{\#3}$	88.99(14)
N(2)–Cu(1)–O(1)	83.14(17)	O(1)–Cu(4)–N(12)$^{\#3}$	90.49(15)
N(7)–Cu(1)–O(1)	92.70(16)	O(10)–Cu(4)–N(3)	100.52(16)
N(4)–Cu(1)–O(1)	82.72(15)	O(1)–Cu(4)–N(3)	85.05(16)
O(6)–Cu(2)–N(1)	90.52(17)	N(12)$^{\#3}$–Cu(4)–N(3)	105.79(19)
O(7)$^{\#1}$–Cu(2)–N(1)	92.76(17)	N(11)–Cu(5)–O(10)$^{\#3}$	88.84(15)
O(6)–Cu(2)–N(9)$^{\#2}$	88.56(16)	N(11)–Cu(5)–O(10)	91.16(15)
O(7)$^{\#1}$–Cu(2)–N(9)$^{\#2}$	89.82(17)	O(3)$^{\#4}$–Cu(6)–N(6)	93.03(19)
O(6)–Cu(2)–O(9)	105.66(16)	O(3)$^{\#4}$–Cu(6)–N(10)	87.16(19)
O(7)$^{\#1}$–Cu(2)–O(9)	97.72(15)	O(3)$^{\#4}$–Cu(6)–O(8)$^{\#5}$	143.91(17)
N(1)–Cu(2)–O(9)	86.98(17)	N(6)–Cu(6)–O(8)$^{\#5}$	92.98(18)
N(9)$^{\#2}$–Cu(2)–O(9)	89.04(16)	N(10)–Cu(6)–O(8)$^{\#5}$	90.29(17)
N(8)–Cu(3)–O(9)$^{\#2}$	91.01(16)	O(3)$^{\#4}$–Cu(6)–O(10)	121.80(16)
N(8)–Cu(3)–O(9)	88.99(16)	N(6)–Cu(6)–O(10)	87.09(15)
N(8)–Cu(3)–O(5)	87.22(15)	N(10)–Cu(6)–O(10)	87.83(15)
N(8)$^{\#2}$–Cu(3)–O(5)	92.79(15)	O(8)$^{\#5}$–Cu(6)–O(10)	94.03(15)
O(9)$^{\#2}$–Cu(3)–O(5)	101.97(13)	N(5)–Cu(4)–N(3)	84.18(18)

[a] Symmetry codes: $^{\#1}$ $-x, 2-y, -z$; $^{\#2}$ $-x, 1-y, -z$; $^{\#3}$ $1-x, 1-y, 1-z$; $^{\#4}$ $x+1, y, z$; $^{\#5}$ $1-x, 2-y, -z$.

Table S4 Selected bond lengths (Å) and angles (º) for **4** [a]

Cu(1)–O(5)	1.8872(18)	Cu(2)–O(3)$^{\#2}$	1.9722(17)
Cu(1)–O(6)	1.9353(17)	Cu(2)–N(3)$^{\#1}$	1.984(2)
Cu(1)–O(2)	1.9353(18)	Cu(2)–O(6)	2.2555(18)
Cu(1)–O(3)$^{\#2}$	2.6166(2)	Cu(2)–O(6)$^{\#1}$	1.9588(18)
Cu(1)–N(2)	1.957(2)	Cu(2)–O(1)	1.9516(18)
Cu(3)–O(5)	1.9019(19)	Cu(3)–N(1)	1.997(2)
O(5)–Cu(1)–O(2)	89.66(8)	O(6)$^{\#1}$–Cu(2)–N(3)$^{\#1}$	88.69(8)
O(6)–Cu(1)–O(2)	97.45(7)	O(1)–Cu(2)–N(3)$^{\#1}$	89.01(8)
O(5)–Cu(1)–N(2)	86.80(8)	O(6)$^{\#1}$–Cu(2)–O(3)$^{\#2}$	92.71(7)
O(6)–Cu(1)–N(2)	86.81(8)	O(1)–Cu(2)–O(6)	97.47(7)
O(3)$^{\#2}$–Cu(2)–O(6)	89.04(7)	O(6)$^{\#1}$–Cu(2)–O(6)	81.79(7)
N(3)$^{\#1}$–Cu(2)–O(6)	103.24(8)	O(5)–Cu(3)–N(1)$^{\#3}$	91.69(8)
O(1)–Cu(2)–O(3)$^{\#2}$	89.82(8)	O(5)–Cu(3)–N(1)	88.31(8)

[a] Symmetry codes: $^{\#1}$ $-x, -y, 1-z$; $^{\#2}$ $1-x, -y, 1-z$; $^{\#3}$ $1-x, 1-y, 1-z$.

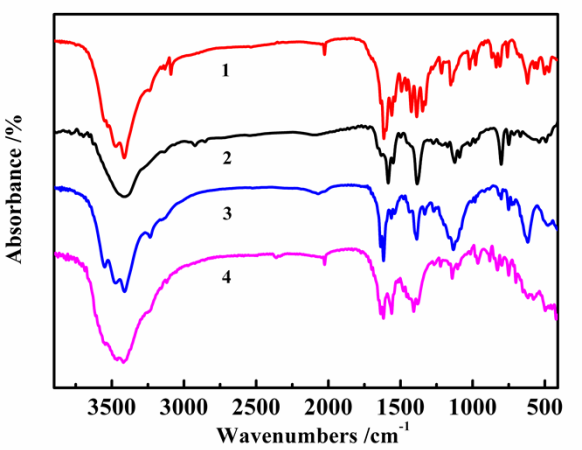

Fig. S1 FT-IR spectra of **1**–**4**.

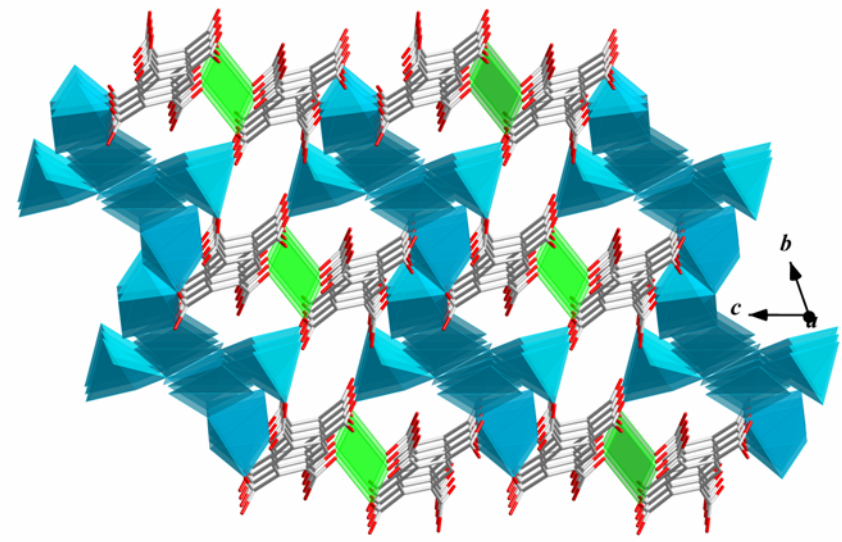

Fig. S2 3D framework of **1**.

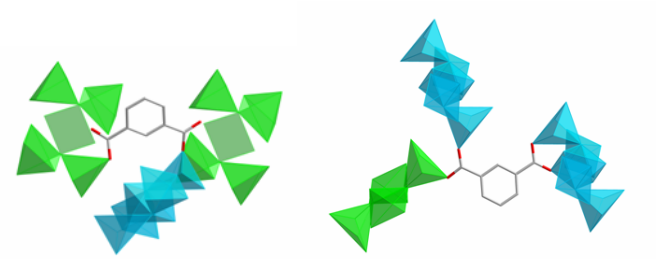

Fig. S3 Connectivity of Cu^{II}_5 cluster and ip^{2-} ligand in **3**.

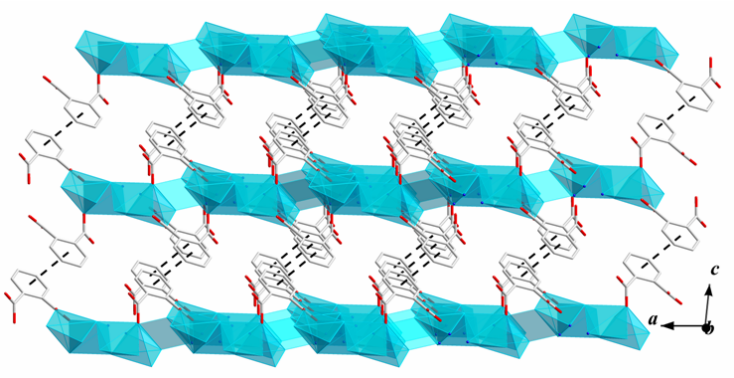

Fig. S4 3D supramolecular structure for **4**.

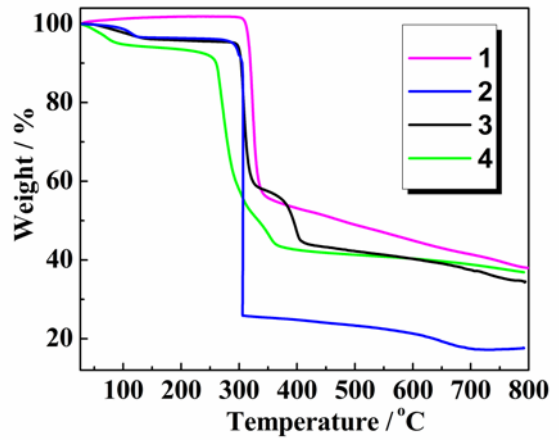

Fig. S5 TGA of **1**–**4**.

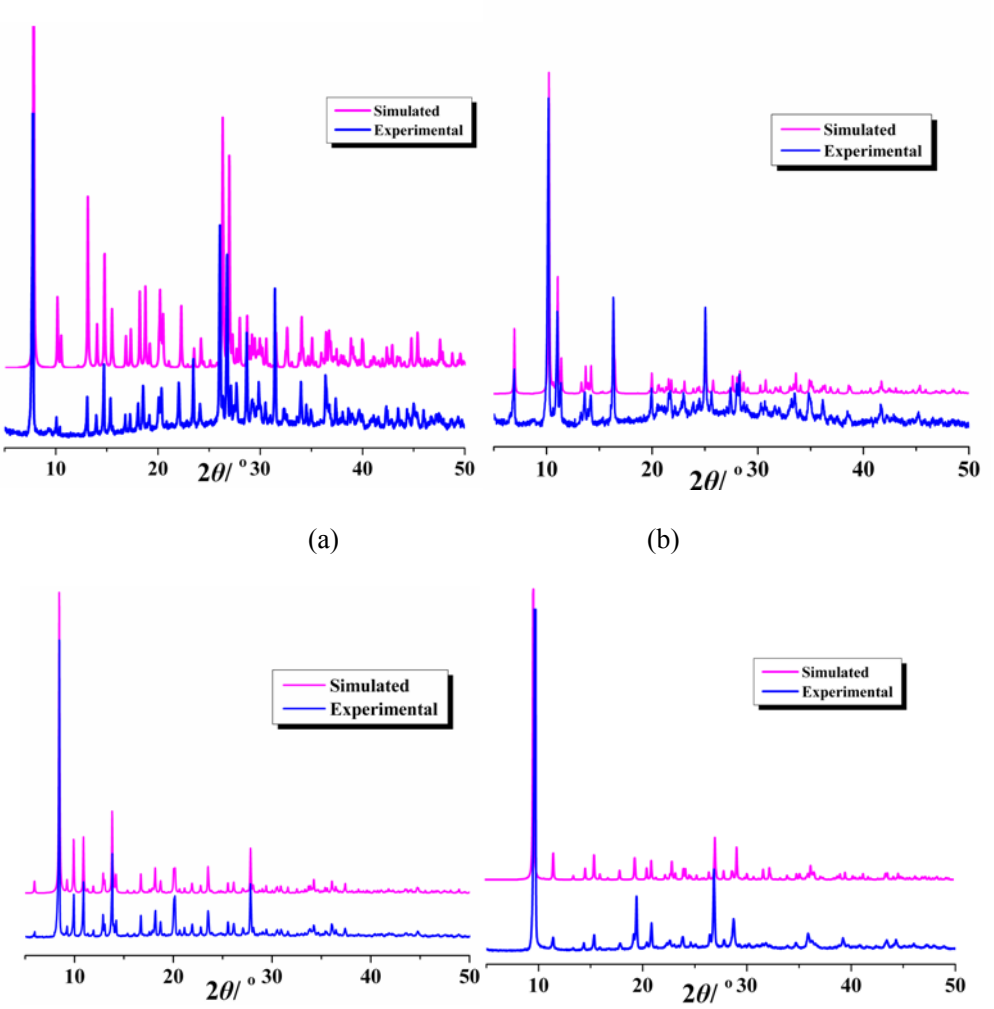

Fig. S6 Simulated (purple) and experimental (blue) PXRD patterns for **1**(a)–**4**(d).

Table S5 Magnetostructural parameters for **1**

Coupling constant	Pathway	$r_{Cu\cdots Cu}$/ (Å)	θ / °	∠CuOCu / °	∠CuNN / °
J_1	Cu1···Cu3	3.3935(5)	2.744	125.319(12)	123.750(14) 118.709(15)
	Cu2A···Cu3	3.4231(5)	15.423	115.499(12)	125.028(15) 118.780(16)
	Cu2A···Cu4	3.3599(8)	16.576	113.910(11)	125.050(16) 117.331(15)
	Cu3···Cu4	3.2215(6)	31.450	108.251(12)	124.092(17) 113.494(14)
J_2	Cu1···Cu2A	5.6892(10)	12.693		
	Cu2···Cu3	5.6229(9)	15.423		

*θ represents the dihedral angle of two Cu^{II} ion-generated planes.

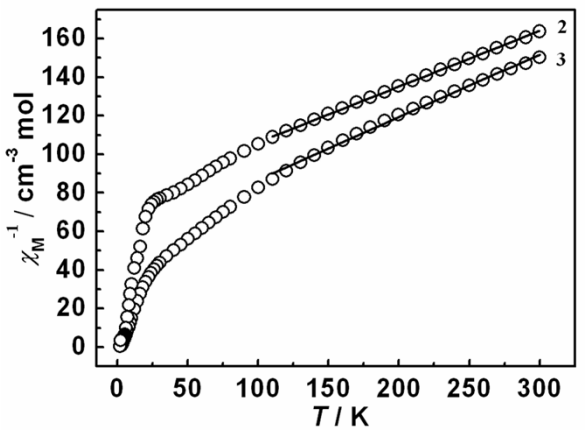

Fig. S7 Temperature dependence of $\chi_M T$ for **2** and **3** (The solid line represents the best fit to Curie-Weiss law).

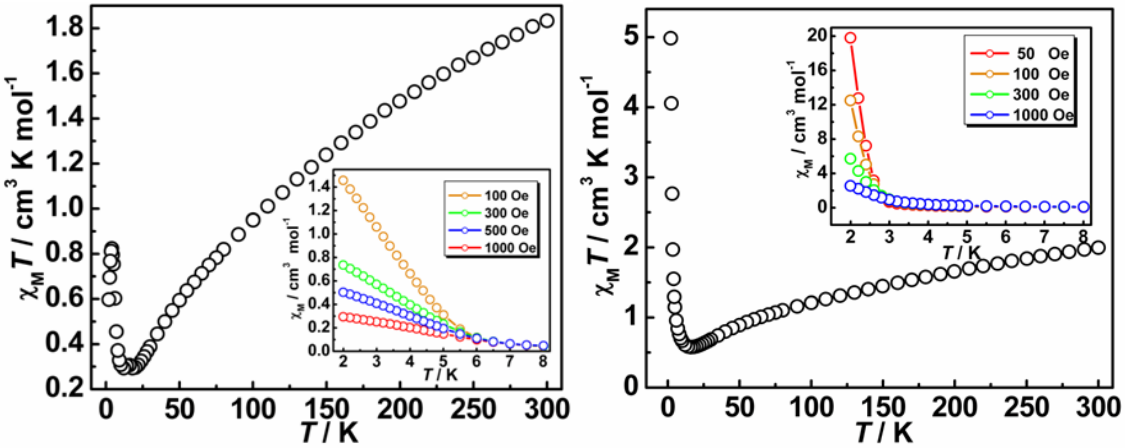

Fig. S8 Temperature dependence of $\chi_M T$ for **2** and **3** (inset: temperature-dependence of the field-cooled magnetic susceptibility at various magnetic fields).