Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary information

Crystal to crystal transformation induced a novel Cu(II)-MOF with zigzag $\cdots I_3^- \cdots I_3^- \cdots$ chains

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Materials and general procedures

Materials and Physical Measurements. All chemicals were commercially available and used as purchased. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400 – 4000 cm^{-1}. Elemental analyses (C, H and N) were carried out on a Flash EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using CuKα radiation on a PANalytical X'Pert PRO diffractometer. Energy-dispersive X-ray spectrometry (EDS) was conducted on a Burker ISMNM 761 scanning electron microscope.

Synthesis of TTTMB. 1,3,5-tris(triazol-1-ylmethyl)- 2,4,6-trimethylbenzene (TTTMB) was prepared according to the literature.[1] Trizole (0.63g, 9mmol) and KOH (2.2g, 40mmol) were dissolved in dimethylsulfoxide (25 mL) and then the mixture was stirred at room temperature. After two hours, 2,4,6 - (bromomethyl) -1,3,5 – trimethylbenzene was added to the mixture with stirring for three hours at room temperature. Then the solution was mixed with 25 mL H_2O, extracted with $CHCl_3$ (4×25 mL), dried with Na_2SO_4, filtered and evaporated in vacuo. After standing overnight at -18°C, the white powder was filtered, washed with diethyl ether and dried in a vacuum desiccator. Yield: 65%. ^1H NMR ($CDCl_3$): δ 2.43 (s, 9H), 5.48 (s, 6H), 7.86 (s, 3H), 7.96 (s, 3H). IR (KBr pellet, cm^{-1}): 3276s, 3085m, 1505s, 1443s, 1332m, 1276s, 1202w, 1135s, 1035w, 1013s, 961m, 880m, 824w, 778w, 682s, 645m. Anal. Calcd. for $C_{18}H_{21}N_9$: C, 59.65; H, 5.81; N, 34.71%. Found: C, 59.62; H, 5.71; N, 34.58%.

1 J. L. Du, T. L. Hu, S. M. Zhang, Y. F. Zeng, X. H. Bu, *CrystEngComm*, 2008, , 1866–1874.

Synthesis of complex $\{[Cd_3(TTTMB)_4I_2]\cdot I_4\}_n$ (1). CdI_2 (0.0370 g, 0.1 mmol), TTTMB (0.0370 g, 0.1 mmol), and H_2O (10 mL) were placed in a Teflon-lined autoclave, and the mixture was sealed and heated to 130°C for 72 h. The reaction system was cooled to room temperature. Big block yellowish crystals of **1** were obtained. Yield: 80%. Anal. Calcd. For **1** : C, 33.88%, N, 19.76%, H, 3.32%. Found:

C, 33.73%, N, 19.87%, H, 3.37%. IR (cm^{-1}, KBr): 3445(m), 3111(m), 1521(s), 1282(s), 1199(s), 1130(s), 1005(m), 983(m), 674(s).

Synthesis of $\{[Cu_4(TTTMB)_4(NO_3)_4(H_2O)_5]\cdot(NO_3)_2(I_3)_2H_2O\}_n$ (2) complex **1** was immersed into the aqueous solution of $Cu(NO_3)_2$ and left undisturbed at ambient temperature. Three weeks later, some new dark bule crystals **2** emerged. Yield: 80%. Anal. Calcd for $C_{72}H_{96}Cu_4I_6N_{42}O_{24:}$ C, 29.32%, N, 19.94% H, 3.28%. Found: C, 29.74%, N, 19.27%, H, 3.12%. IR (cm^{-1}, KBr): 3444(m), 3121(m), 1531(s), 1384(s), 1284(s), 1211(m), 1130(s), 1001(m), 882(m), 824(m), 672(s), 638(m).

Crystal Data Collection and Refinement. Single-crystal X-ray diffraction for crystal of **1** and **2** were performed using a Oxford Diffraction equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) and Rigaku CrystalClear-SM Expert 2.0 diffractometer equipped with graphite monochromatic Mo-K*α* radiation (λ = 0.71073 Å), respectively. The structures were solved by the direct method and refined by the full-matrix least-squares method on *F* with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located geometrically and refined isotropically.

Table S1. Crystallographic Data for **1** and **2**[a]

Complex	1	2
formula	$C_{72}H_{84}N_{36}I_6Cd_3$	$C_{72}H_{96}Cu_4I_6N_{42}O_{24}$
Formula mass	2552.35	2949.47
Temperature [K]	293(2)	383
Wavelength [Å]	0.71073	0.71073
Crystal system	Tetragonal	Triclinic
Space group	*I*4	P-1
a (Å)	17.232(2)	12.365(4)
b (Å)	17.232(2)	17.032(5)
c (Å)	16.444(3)	24.275(8)
α(°)	90	89.682(7)
β(°)	90	89.479(5)
γ(°)	90	88.829(7)
V (Å^3)	4882.7(14)	5111(3)
Z	2	2
D_{calcd}.(g·cm^{-3})	1.736	1.917
F(000)	2460	2896
θ (º)	2.92–24.99	1.46–25.00
GOF	1.050	0.986
R_1 (I>2sigma(I))	0.0840	0.0430
wR_2 (I>2sigma(I))	0.2200	0.0936

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}$.

Table S2. Selected bond lengths and bond angles

		1	
I(1)-Cd(1)	2.913(8)	I(2)-Cd(2)	2.902(3)
Cd(1)-N(1)	2.316(9)	Cd(1)-N(9)#5	2.414(11)
Cd(2)-N(6)#7	2.319(10)	N(1) #4-Cd(1)-N(1)	173.8(5)
N(1)-Cd(1)-N(9)#5	90.1(4)	N(1)-Cd(1)-N(9)#6	85.6(4)
N(9)#5-Cd(1)-N(9)#6	91.6(8)	N(1) #4-Cd(1)-I(1)	88.0(3)
N(1)-Cd(1)-I(1)	96.7(3)	N(9)#5-Cd(1)-I(1)#4	173.6(4)
N(9)#6-Cd(1)-I(1)#4	94.3(4)	I(1)#4-Cd(1)-I(1)	79.9(3)
N(6)#7-Cd(2)-N(6)#8	89.76(4)	N(6) #7-Cd(2)-N(6)	172.5(6)
N(6)-Cd(2)-N(6)#8	89.76(4)	N(6)#7-Cd(2)-I(2)	93.7(3)
		2	
Cu(1)-N(9)	1.976(4)	Cu(1)-N(10)	1.987(4)
Cu(1)-N(15)#1	2.065(4)	Cu(1)-O(2)	2.218(4)
Cu(1)-O(4)	2.270(4)	Cu(1)-O(1)	2.298(4)
Cu(2)-N(18)	1.980(4)	Cu(2)-N(3)#2	1.998(4)
Cu(2)-N(6)#3	2.013(4)	Cu(2)-O(25)	2.035(3)
Cu(2)-O(9)	2.418(4)	Cu(3)-N(33)#4	1.985(4)
Cu(3)-N(21)	2.004(4)	Cu(3)-N(24)#1	2.009(4)
Cu(3)-O(13)	2.088(3)	Cu(3)-O(23)	2.253(4)
Cu(4)-N(27)	1.997(4)	Cu(4)-N(30)	1.998(4)
Cu(4)-N(36)#1	2.015(4)	Cu(4)-O(24)	2.023(3)
Cu(4)-O(16)	2.411(4)	I(1)-I(2)	2.8988(10)
I(6)-I(5)	2.9292(8)	I(3)-I(2)	2.9757(11)
I(6)-I(5)-I(4)	177.570(16)	I(1)-I(2)-I(3)	178.582(16)

Symmetry transformations used to generate equivalent atoms for **1**: #4: -x+1, -y, z. #5: y+1/2, -x+1/2, z+1/2. #6: -y+1/2, x-1/2, z+1/2. #7: -x, -y, z. #8: -y, x, z. #9: y, -x, z; for **2**: #1 x+1, y, z. #2: x-1, y, z+1. #3: x, y, z+1. #4: x+1, y, z-1.

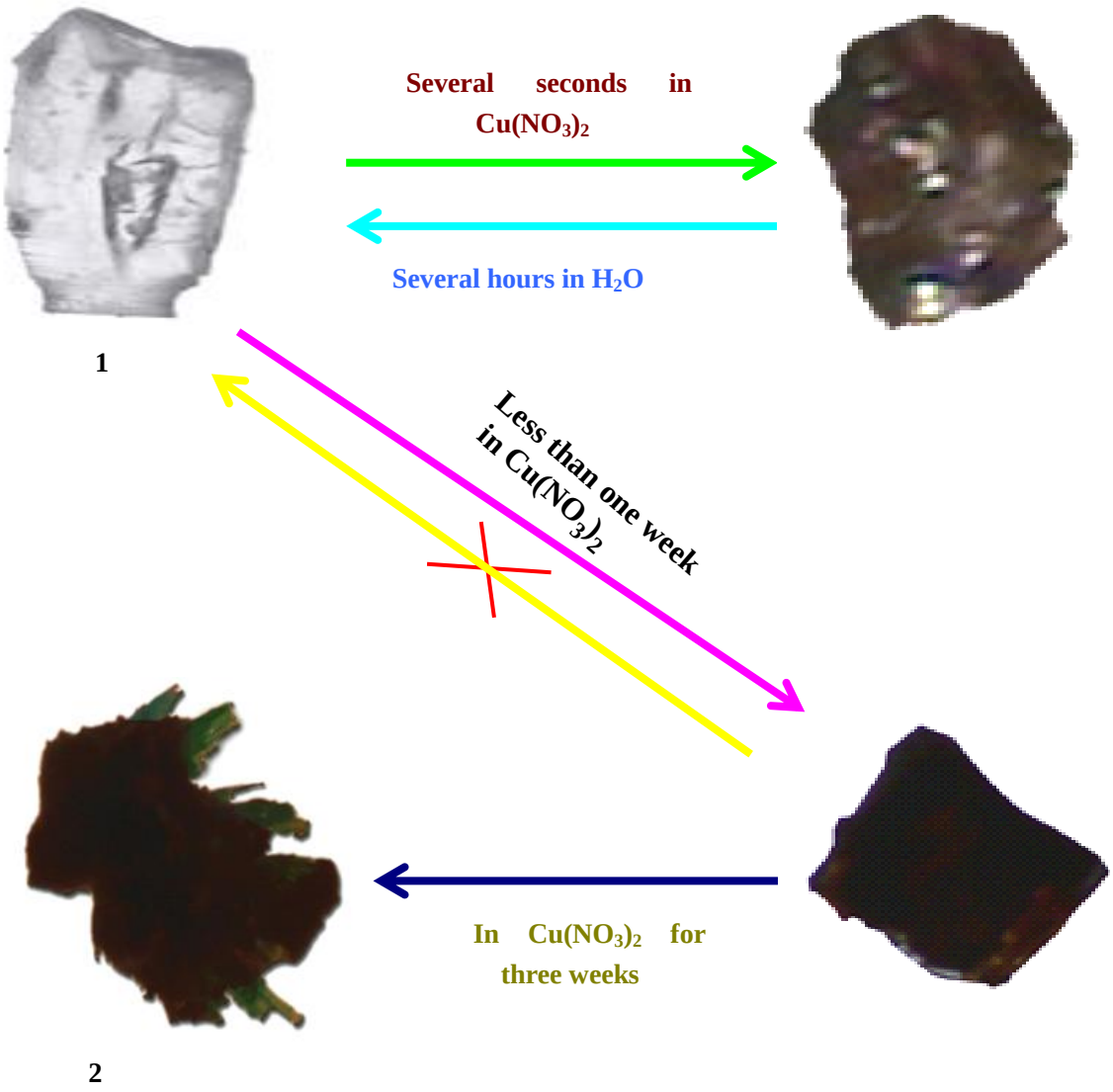

Fig. S1: Photographs of single crystals.

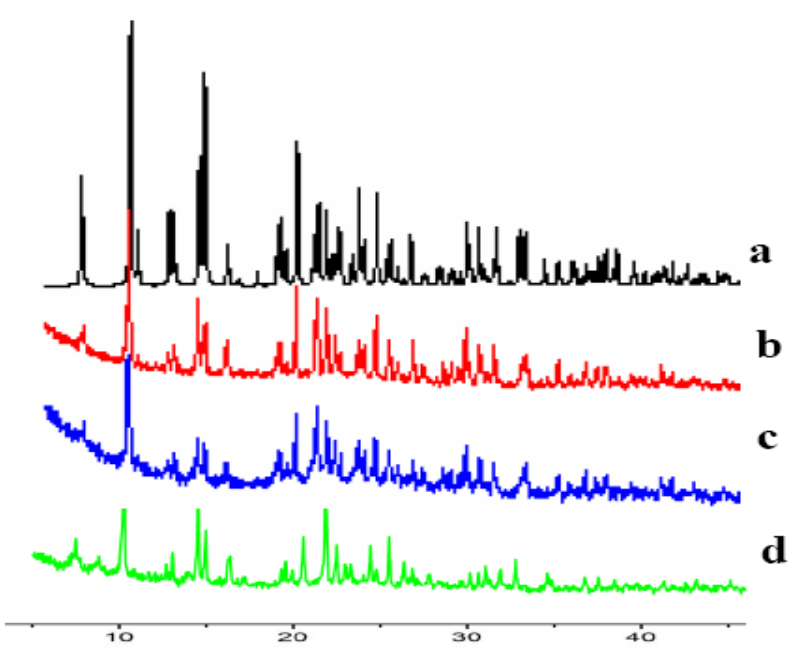

Fig. S2. Powder XRD patterns: (a) calculated pattern of **1** based on the structure determined by single-crystal XRD. (b) experimental pattern of **1**. (c) experimental pattern of the black crystals. (d) experimental pattern of the black crystals after soaking in water for several hours.

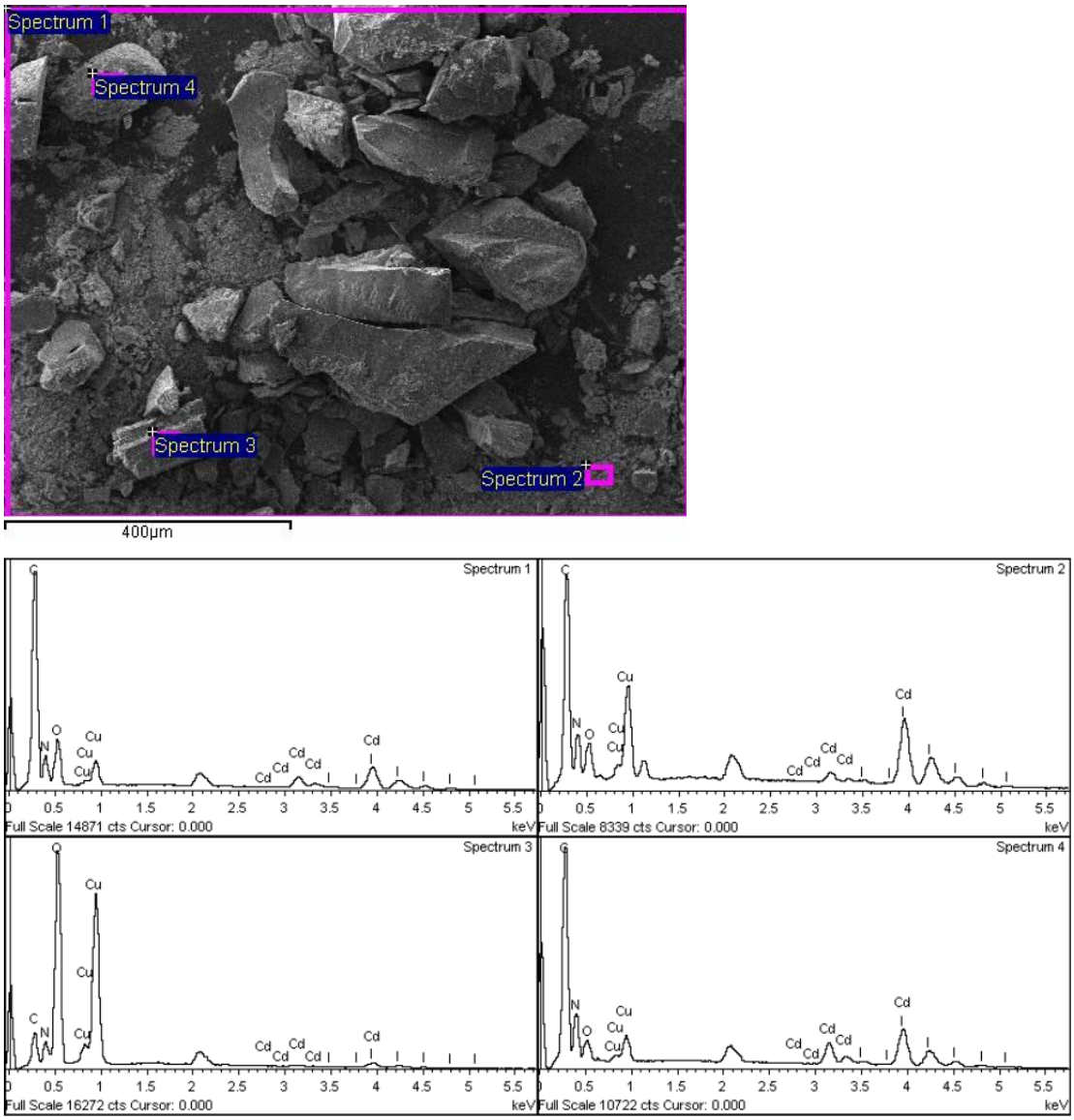

Fig. S3. SEM and EDS of the black crystals.

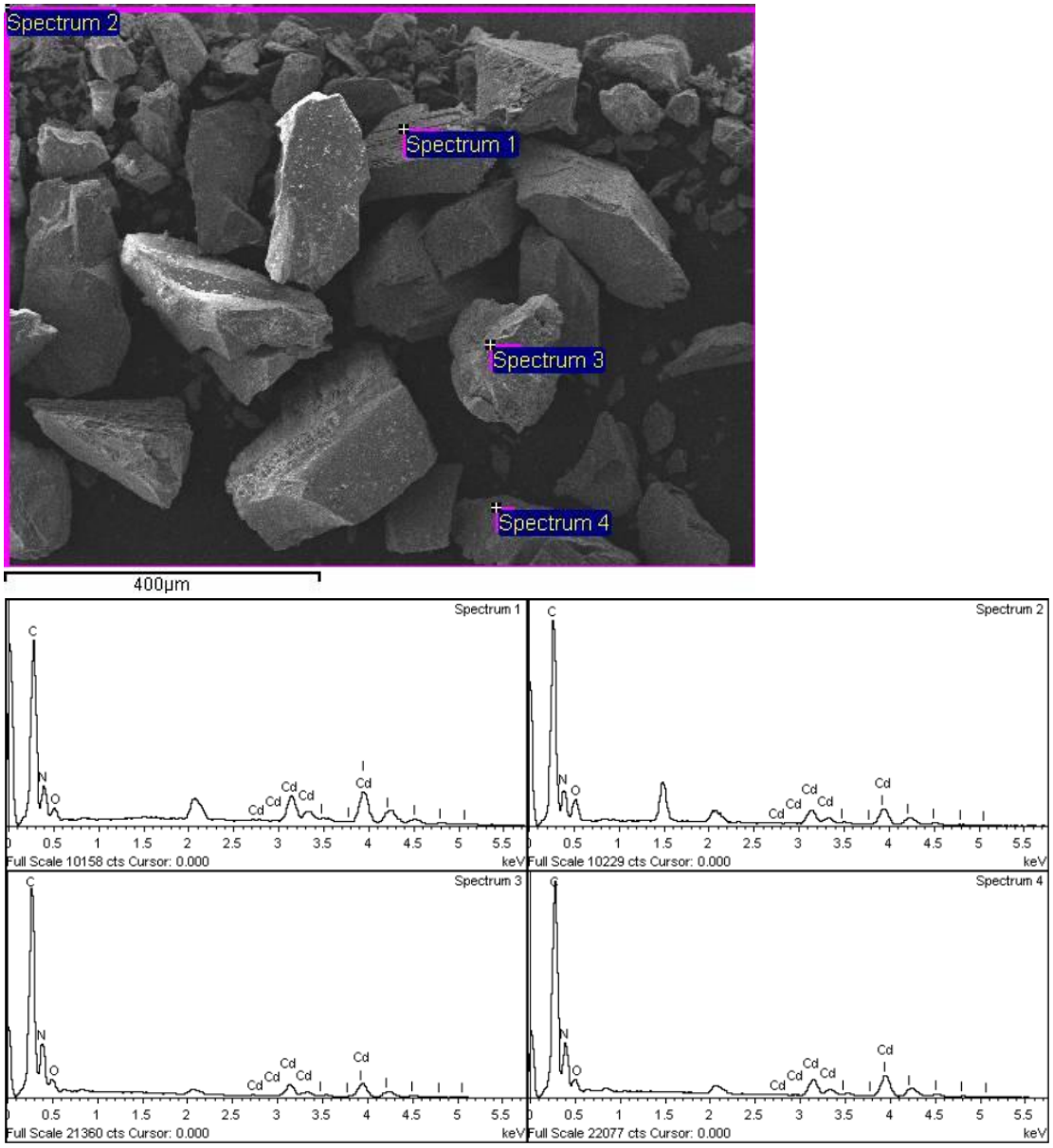

Fig. S4. SEM and EDS of the black crystals after soaking in water for several hours.

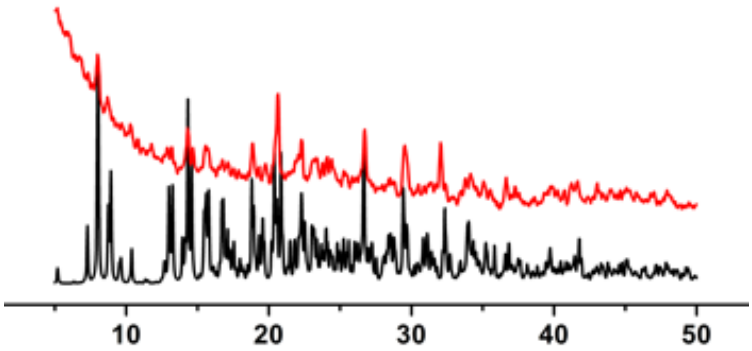

Fig. S5: Powder XRD patterns of **2** calculated based on the structure determined by single-crystal XRD (bottom) and experimental data (top).

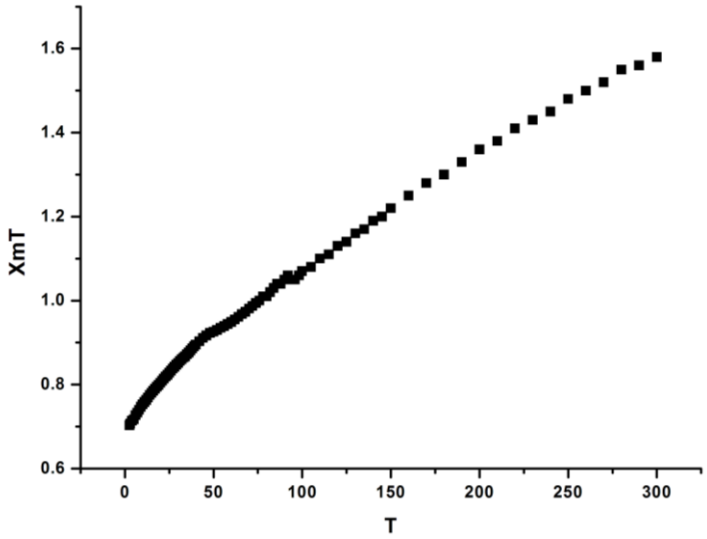

Fig. S6: Magnetic susceptibility of **2**.