

Supporting Information

Two novel POM-based inorganic-organic hybrid compounds: synthesis, structures, magnetic properties, photodegradation and selective absorption of organic dyes†

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Experiments

Optical band gaps

The UV-vis absorption spectra of compounds **1** and **2** were performed in the crystalline state at room temperature (Figure S1a). Some inorganic-organic hybrid materials based on inorganic polyoxometalates units have been testified to be good semiconductors.¹ So we investigated the conductivities of compounds **1** and **2**. The measurements of diffuse reflectivity for powder samples were carried out to obtain their band gaps (E_g). The E_g values are determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka-Kunk function F versus energy $E(F=(1-R)^2/2R)$.² As shown in Figure S1b, the E_g value of both complexes are about 2.9 eV, indicating that both **1** and **2** are underlying semi-conducting materials.

Methylene blue (MB) Adsorption experiments

Adsorption equilibrium experiments were carried out by adding 5mg or 10mg as-synthesized crystals of complex **1** into 100ml MB solution with different concentration (5-100 mg L⁻¹) at room temperature in dark under stirring. After several days, the concentration was not changed and the final value was defined by UV-vis spectrometer at 664 nm.

The specific adsorbed amount of MB was calculated according to the equation:

$Q_e=V(C_0-C_e)/m$, where C_0 and C_e are the initial and the equilibrium liquid-phase concentration of MB (mg L⁻¹), m is the amount of adsorbent (g), and V is the volume of the solution (L). The results are shown in Figure 5a in text.

Adsorption kinetic experiments

As-synthesized crystals (5.0 mg) of complex **1** were dispersed into the MB solution (10 mg L⁻¹, 100 mL) with stirring or without any disturbance (no stirring). At given time intervals, the change of the concentration of the MB solution was monitored using UV-vis spectra at 664 nm. The results are shown in Figure 5b in text.

Dye adsorption selective kinetic experiments.

As-synthesized crystals of complex **1** (50mg) was added into the aqueous solution (10 mg L⁻¹, 100 mL) of MB, methy violet (MV), MO and RhB, respectively, at room temperature under stirring. At given time intervals, the change of the concentration of dye solutions were monitors using UV-vis spectra at the maximum absorbance of each dye (664nm, 464nm, 554nm, 581nm for MB, MO, RhB and methyl violet, respectively). The results are shown in Figure 6 in text.

Similarly, crystalline solid (100 mg) of **1** was added into 100 mL a binary mixture of MB/MO or MB/RhB at room temperature under stirring. The starting concentration of each dye component in the binary mixture is 10 mg L⁻¹. At given time intervals, the change of the concentration of each dye component was monitored using UV-vis spectra. The results are shown in Figure 7 in text.

Photodegradation experiments of MO or MB.

Crystals (80 mg) of **1** was dispensed into a solution (20.0 mg L⁻¹, 100 mL) MO or MB under stirring. After adding 2.0 mL hydrogen peroxide (30%), the reaction mixture was irradiated with 300W Xe lamp as the visible light source. At given time intervals, the concentration of dyes was measured with UV-vis spectra at the maximum absorbance of the MO or MB dye. Here 2.0 ml peroxide is enough for degradation of dyes and the finally solid obtained by filtration after reaction is green, as the origin color of the as-synthesized crystals of **1**. In comparison, blank experiments were also carried out without catalyst **1** but in the presence of peroxide (2.0 mL). The results are shown in Figure 4a-c in text.

Owing to that complex **1** significantly absorbs MB, different volumes of peroxide were used to evaluate such effects on the degradation of MB. Crystalline solid (80 mg) of **1** was added into 100 mL 20mg L⁻¹ MB solution under stirring, and then different amounts (i. e. 0, 1.0, 1.5 and 2.0 mL) of peroxide was added to the solution under visible light irradiation, respectively. At given time intervals, the concentrations of MB were measured by UV-vis spectrometer. After three hours irradiation, the concentrations of MB were almost closed to zero expect the experiment in the absence peroxide. However, when the amount peroxide used is less than 2.0 mL, the finally solid obtained by filtration was blue. The results are shown in Figure 4d in text.

Release and photodegradation experiments of absorbed MB on **1**.

20 mg crystalline solid of **1** was dispersed into 300 mL 100 mg L⁻¹ MB at room temperature under stirring. After several days, the concentration of MB was not changed and the absorbance was 2.5. The loading of MB was calculated to be 1168 mg g⁻¹. The deep blue solid recycled by filtration was added into 300 mL water under stirring, and at given time intervals, the concentration of the resulting MB solution was measured by UV-vis spectrometer. The results were shown in Figure 8a in text.

Similar photodegradation experiments of absorbed MB were carried out in the presence of different amounts of peroxide. Crystalline solid of **1** (80mg) was added to 100 mL 20mg L⁻¹ MB solution under stirring. After 24 hours, the concentration of MB solution was approaching zero, indicating MB are already absorbed completely on **1**, and the solid became blue. The blue solid obtained by filtration was immersed into deionized water, and after adding different amounts of peroxide (2-10mL) under stirring, the reaction mixture was irradiated with 300W Xe lamp as the visible light source. At given time intervals, the concentration of MB solution was measured by UV-vis spectrometer. The results are shown in Figure 8b.

References:

- 1 W. J. Chang, Y. C. Jiang, S. L. Wang and K. H. Li, *Inorg.Chem.*, 2006, **45**, 6586.
- 2 X. Xiao, W. W. Ju, W. T. Hou, D. R. Zhu and Y. Xu, *CrystEngComm.*, 2014, **16**, 82.

Table S1. Selected bonds (Å) and angles(°) for **1**

1					
Bonds	Dis. (Å)	Bonds	Dis. (Å)	Bonds	Dis. (Å)
Mo(1)-O(6)	1.687(9)	Mo(2)-O(15)	2.062(9)	Mo(4)-O(12)	1.965(10)
Mo(1)-O(7)	1.746(9)	Mo(3)-O(4)	1.689(11)	Mo(4)-Mo(2)#2	3.203(2)
Mo(1)-O(8)#1	1.931(9)	Mo(3)-O(3)	1.727(9)	Cu(1)-N(4)#3	1.981(8)
Mo(1)-O(8)	2.148(9)	Mo(3)-O(5)	1.925(9)	Cu(1)-N(1)	1.985(11)
Mo(2)-O(11)	1.681(11)	Mo(3)-O(8)	2.128(8)	Cu(1)-O(2)	2.147(10)
Mo(2)-O(10)	1.743(9)	Mo(4)-O(13)	1.707(11)	Cu(1)-O(3)	2.161(9)
Mo(2)-O(9)	1.860(10)	Mo(4)-O(14)	1.730(11)	Cu(1)-O(10)#4	2.197(9)
Mo(2)-O(12)	2.046(9)	Mo(4)-O(15)#2	1.879(9)	N(4)-Cu(1)#3	1.981(8)
Bond angles		(°)	Bond angles		(°)
O(6)-Mo(1)-O(7)		104.4(4)	O(4)-Mo(3)-O(8)		102.6(4)
O(6)-Mo(1)-O(5)		102.5(4)	O(13)-Mo(4)-O(12)		103.0(4)
O(7)-Mo(1)-O(5)		99.1(4)	O(14)-Mo(4)-O(12)		99.2(5)
O(11)-Mo(2)-O(10)		105.5(5)	N(4)#3-Cu(1)-N(1)		171.9(4)
O(11)-Mo(2)-O(15)		106.6(5)	N(4)#3-Cu(1)-O(2)		92.3(4)
O(9)-Mo(2)-O(15)		84.4(4)	N(1)-Cu(1)-O(2)		92.8(4)
O(4)-Mo(3)-O(3)		104.4(5)	N(1)-Cu(1)-O(3)		87.3(4)
O(4)-Mo(3)-O(9)		100.7(5)	O(7)#3-Cu(1)-O(3)		105.3(3)
Symmetry codes: #1 -x, -y+1, -z+1 #2 -x, -y+1, -z #3 -x, -y+2, -z+1 #4 x, y+1, z					

2					
Bonds	Dis. (Å)	Bonds	Dis. (Å)	Bonds	Dis. (Å)
Mo(1)-O(6)	1.707(4)	Mo(2)-O(4)#2	1.927(4)	Cu(1)-O(7)	1.984(4)
Mo(1)-O(5)	1.734(4)	Mo(2)-O(9)	2.114(3)	Cu(1)-N(1)	2.008(4)
Mo(1)-O(7)#1	1.776(4)	Mo(3)-O(10)	1.688(4)	Cu(1)-N(4)#3	2.010(4)
Mo(1)-O(4)	1.856(4)	Mo(3)-O(11)	1.724(4)	Cu(1)-O(5)	2.326(4)
Mo(2)-O(3)	1.679(4)	Mo(3)-O(8)#3	1.920(4)	Cu(1)-O(11)	2.415(4)
Mo(2)-O(2)	1.747(4)	Mo(3)-O(9)#4	1.941(3)	O(9)-Mo(3)#5	1.941(3)
Mo(2)-O(8)	1.907(4)	Cu(1)-O(2)	1.981(4)	N(4)-Cu(1)#3	2.010(4)
Bond angles		(°)	Bond angles		(°)
O(6)-Mo(1)-O(5)		107.4(2)	O(8)#3-Mo(3)-O(9)#4		142.86(15)
O(6)-Mo(1)-O(7)#1		110.04(19)	O(2)-Cu(1)-O(7)		175.49(17)
O(5)-Mo(1)-O(4)		109.05(19)	O(2)-Cu(1)-N(1)		86.64(17)
O(3)-Mo(2)-O(2)		103.92(19)	O(7)-Cu(1)-N(1)		94.58(17)
O(2)-Mo(2)-O(8)		94.88(17)	N(1)-Cu(1)-N(4)#3		170.11(18)
O(2)-Mo(2)-O(9)		154.22(16)	O(7)-Cu(1)-O(5)		89.85(15)
O(10)-Mo(3)-O(11)		104.3(2)	O(7)-Cu(1)-O(11)		80.55(15)
O(10)-Mo(3)-O(8)#3		102.25(18)	N(1)-Cu(1)-O(11)		87.01(15)
Symmetric codes: #1 -x+1, -y+1, -z+1; #2 -x+1, -y+2, -z+1; #3 -x+1, -y+1, -z; #4 x, y-1, z #5					

Additional Figures

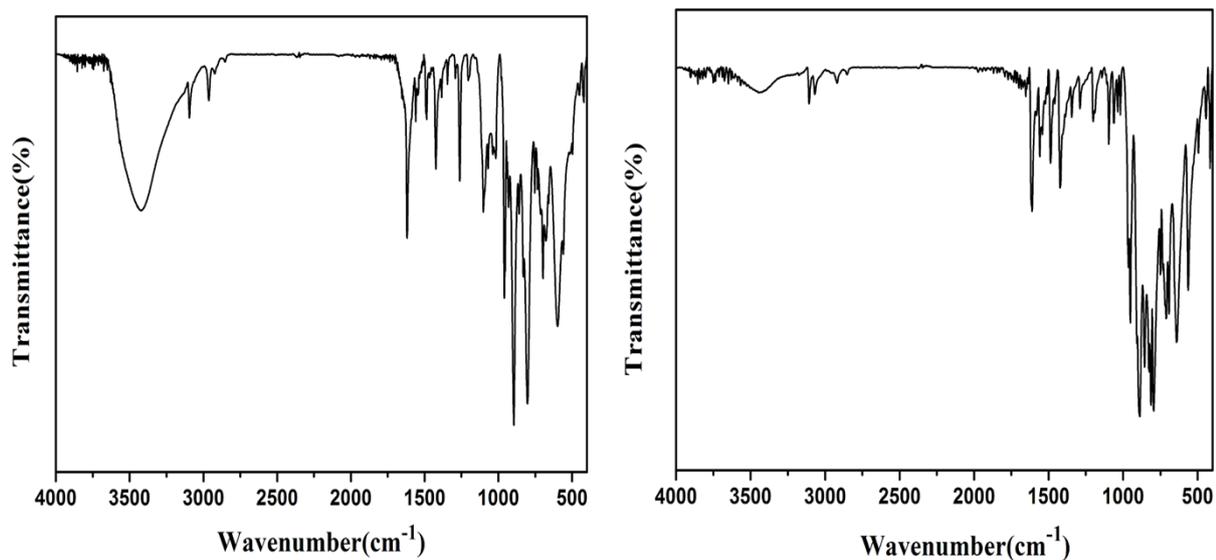


Figure S1. The IR Spectra of complexes **1** (left) and **2** (right).

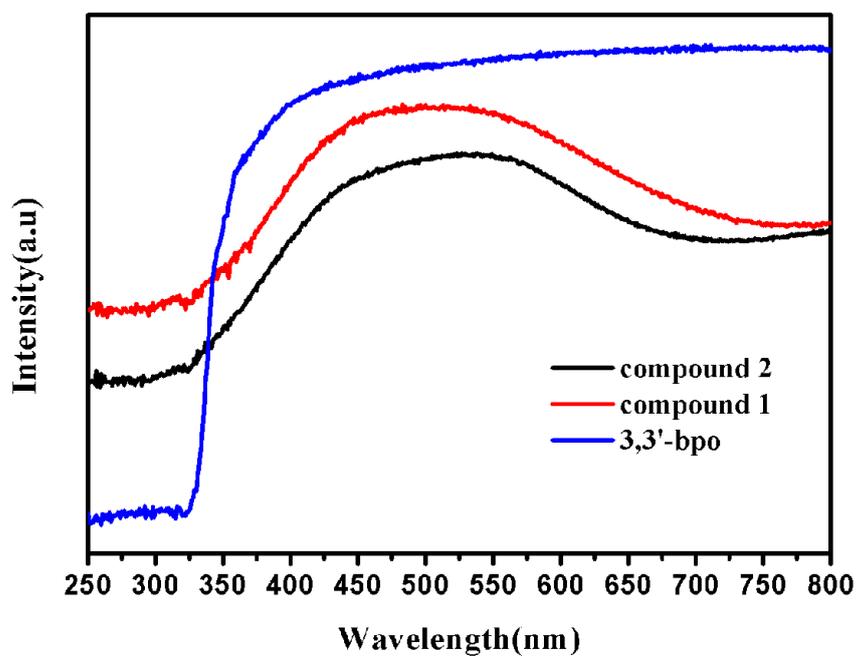


Figure S2. Solid-state emission spectra of the 3, 3'-bpo ligand and complexes **1** and **2** at room temperature.

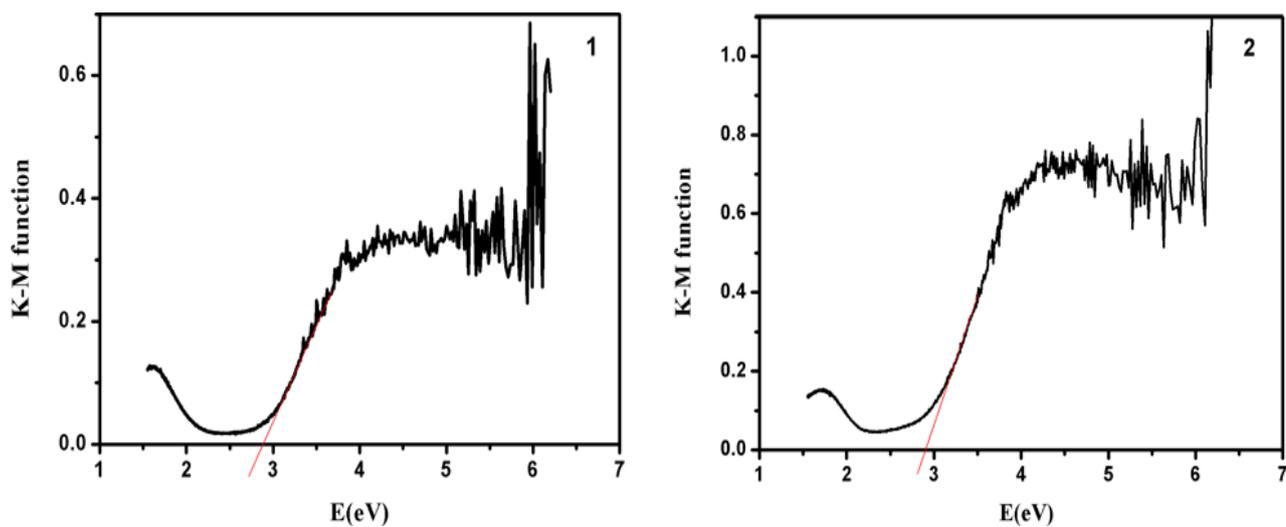


Figure S3. Diffuse reflectance UV-VIS-NIR spectra of K-M functions versus energy (eV) of complexes **1** and **2**.

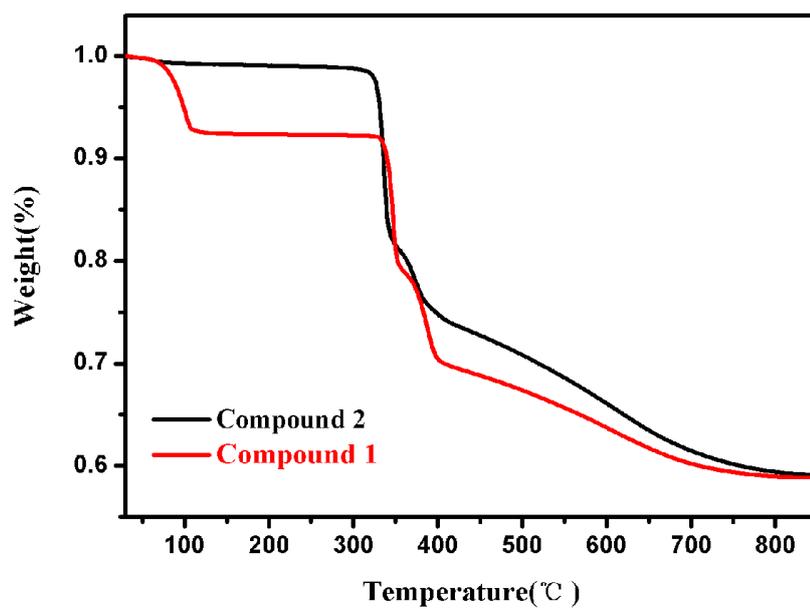


Figure S4. The TGA curves of complexes **1** and **2**.

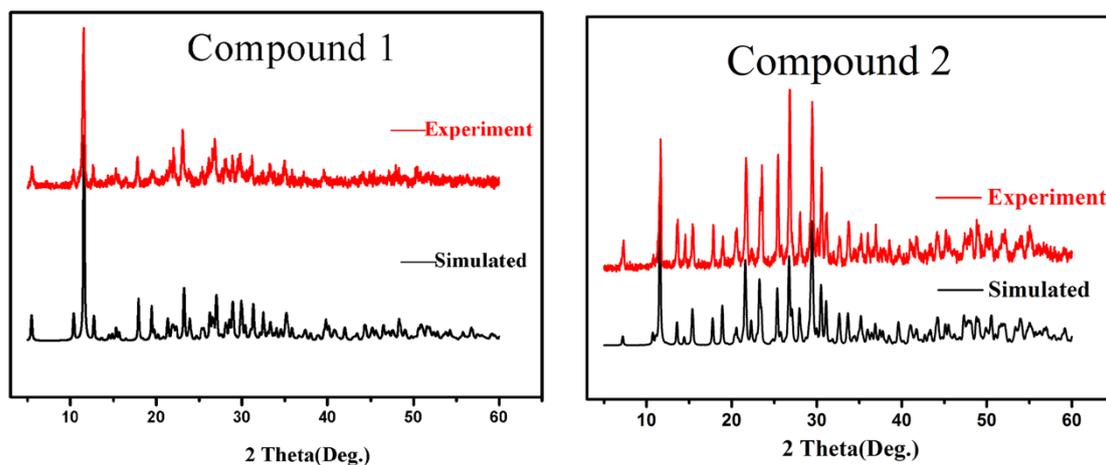


Figure S5. Simulated (black) and experimental (red) PXRD patterns of complexes **1** and **2**.

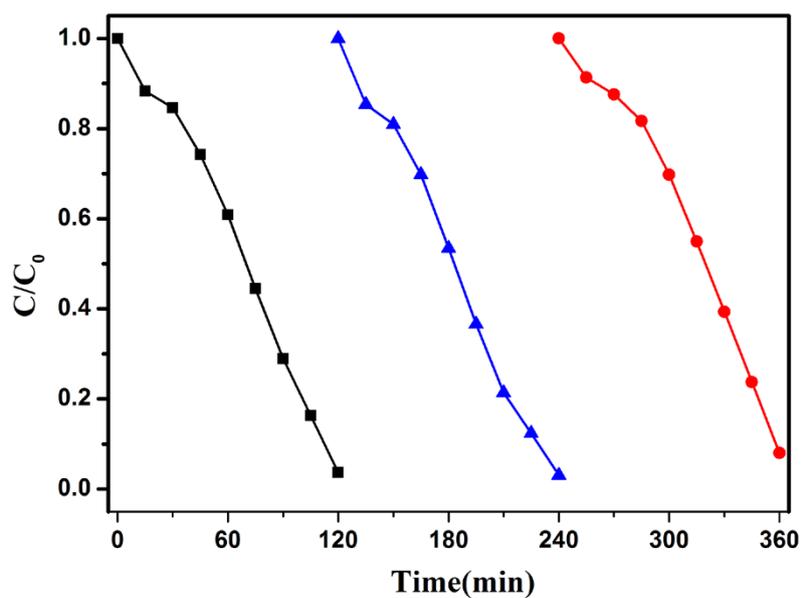


Figure S6. MO photodegradation recyclability test on complex **1** under visible light irradiation.

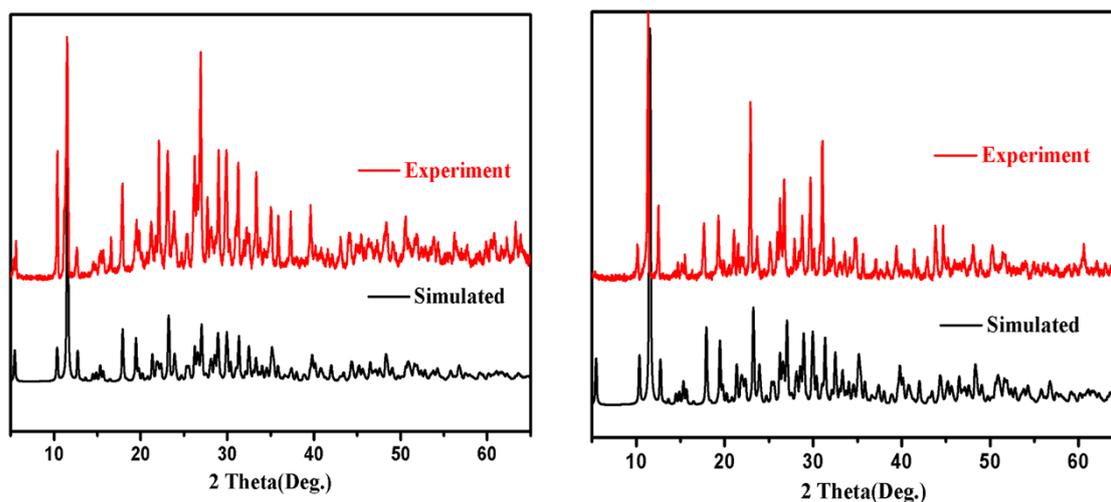


Figure S7. Simulated (black) and experimental (red) PXRD patterns of **1** after MO (left) and MB (right) degradation.

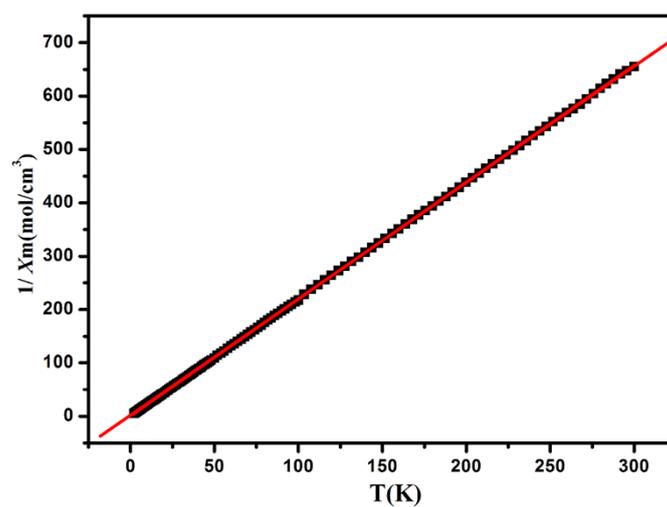


Figure S8. The temperature dependences of χ_m^{-1} for complex **1**.

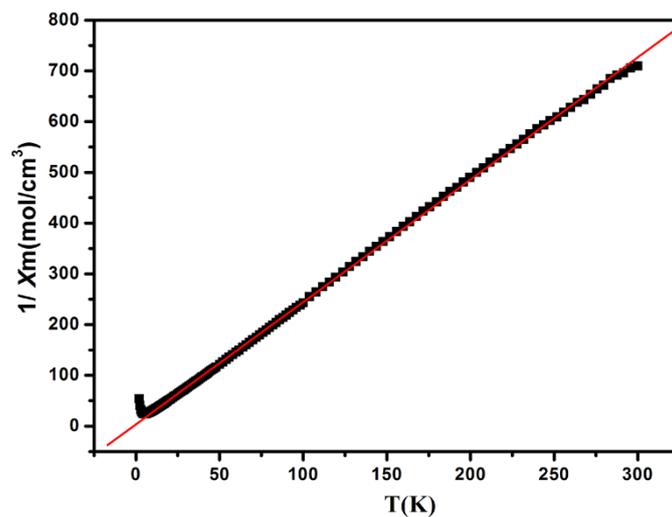


Figure S9. The temperature dependences of χ_m^{-1} for complex **2**.

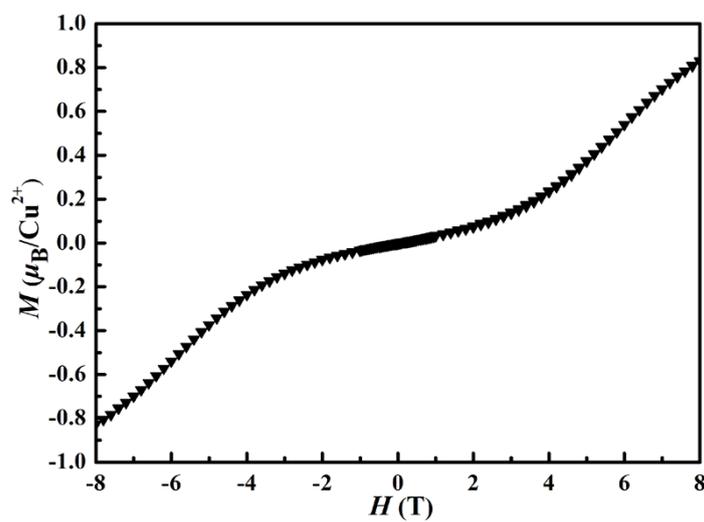


Figure S10. The field dependence (-8 to 8T) of magnetization of **2** at 2K

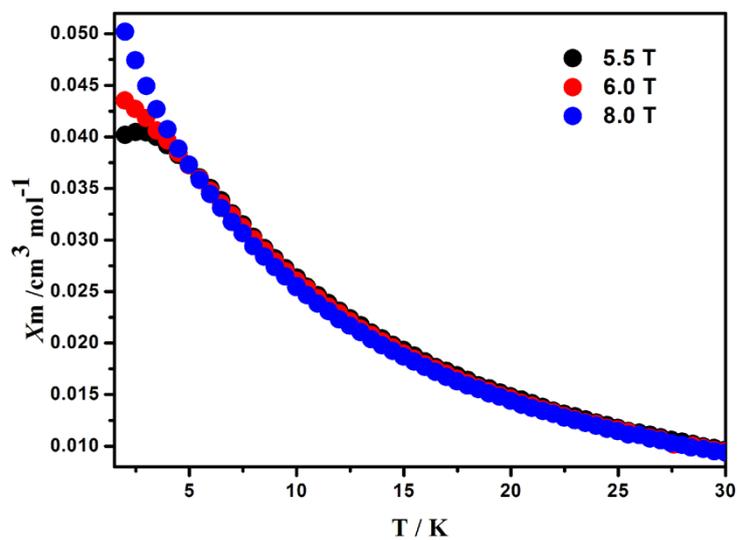


Figure S11. The magnetic susceptibility of **2** at 2-30K in different field