

Sun, UV and X-ray triple photochromic properties of three coordination polymers based on 1,1'-bis(3-carboxylatobenzyl)-4,4'-bipyridinium ligand

Jinjian Liu*, Yiwei Lu, Wenbo Lu

Key Laboratory of Magnetic Molecules & Magnetic Information Materials Ministry of Education, The School of Chemical and Material Science, Shanxi Normal University, Linfen 041004, China.

liujj@sxnu.edu.cn (J. Liu)

S1. Experimental section

S1.1 Materials and methods

Zn(CH₃COO)₂·2H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, 4,4'-bipyridine, 3-(chloromethyl)benzoic acid, N,N-dimethylformamide, CH₃OH, NaOH, 1,2,4,5-benzenetetracarboxylic acid and 1,4-benzenedicarboxylic acid and acetonitrile were purchased commercially and used without further purification. The organic ligand 1,1'-bis((3-carboxylatobenzyl)-4,4'-bipyridinium)-dichloride (H₂bcbpyCl₂) was synthesized according to the same procedures reported in the literature [1]; X-ray powder diffraction (PXRD) pattern was collected using a Rigaku Ultima IV-185 diffractometer; using Vario EL III CHNOS elemental analyzer for elemental analysis of C, H and N; preparation of a Nicolet 5DX spectrometer using KBr pellets to obtain FT-IR spectra (4000–500 cm⁻¹); Solid-state UV–Vis diffuse reflectance spectra were recorded on a Varian Cary 500 UV–Vis spectrophotometer equipped with an integrating sphere at room temperature in the range of 200–750 nm; Electron paramagnetic resonance (EPR) spectroscopy at room temperature was recorded using a Bruker A300-10/12 spectrometer; HTG-3 equipment at 30–800 °C, 10 °C·min⁻¹ was used to perform thermogravimetric (TG) experiments in air; A ThermoFisher ESCALAB 250 X-ray photoelectron spectrometer (powered at 150 W) by Al K α radiation ($\lambda = 8.357 \text{ \AA}$; spot size, 500 μm) was used to perform X-ray photoelectron spectroscopy (XPS).

Preparation of 1 and 2

The general procedures for preparations of compounds **1** and **2** were as follows: A mixture of Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O (29.0 mg, 0.1 mmol) and H₂bcbpyCl₂ (50.0 mg, 0.1 mmol) was added into 15 mL water. Another mixture of NaOH (8.0 mg, 0.2 mmol) and *p*-H₂BDC (16.7 mg, 0.1 mmol) was heated to dissolve in a mixture of solvents dimethylformamide (5 mL, DMF), ethanol (5 mL, EtOH) and water (10 mL, H₂O). After putting the two kinds of solution together and stirring for 10 min, the residue was filtered. The filtrate was allowed to stand for several days to give block crystals.

Yield for orange **1**: 36% and light green **2**: 35%, based on H₂bc bpyCl₂. IR (KBr pellet, cm⁻¹): 3390, 3118, 3060, 2813, 2362, 2026, 1596, 1392, 1218, 1149, 1085, 1012, 852, 757, 696, 678, 511. Elemental analysis: Anal. Calcd for C₁₇H₁₈Co_{0.5}NO₇ (**1**, 377.79): C, 54.04; H, 4.81; N, 3.71%. Found: C, 53.87; H, 4.83; N, 3.77%. Anal. Calcd for C₃₄H₃₆NiN₂O₁₄ (**2**, 755.36): C, 54.06; H, 3.87; N, 3.71%. Found: C, 53.91; H, 4.82; N, 3.75%.

Synthesis of **3**

A mixture of Zn(CH₃COO)₂·2H₂O (44.0 mg, 0.2 mmol) and H₂bc bpyCl₂ (50.0 mg, 0.1 mmol) was added into 15 mL water and then stirred for 5 min. Another mixture of NaOH (16.0 mg, 0.4 mmol) and H₄BTEC (25.0 mg, 0.1 mmol) was heated to dissolve in a mixture of solvents dimethylformamide (5 mL, DMF), ethanol (5 mL, EtOH) and water (10 mL, H₂O), and filtrated. After putting the two kinds of solution together, the filtrate was left for slow evaporation in air at room temperature. After 10 days, colorless block crystals were collected by filtration, washed with water, and dried in the air (33% yield, based on H₂bc bpyCl₂). Elemental analysis: Anal. Calcd for C₃₆H₃₇Zn₂N₂O₂₀ (**3**, 948.41): C, 45.59; H, 3.94; N, 2.95 %. Found: C, 46.01; H, 3.98; N, 2.87 %. IR (KBr, cm⁻¹): 3386, 2026, 1613, 1380, 1216, 1147, 960, 811, 755, 673, 558.

In the meantime, powder X-ray diffraction (PXRD) is used to study their purities, and the results show that all crystal materials are pure phases (Fig. S1).

S1.2 X-ray crystallography

X-ray diffraction data of Compounds **1–3** was collected on an Oxford Gemini diffractometer at 293 K using graphite monochrome Mo-K α ($\lambda = 0.71073$). Using Olex2 [2], the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimization [3]. All non-hydrogen atoms were anisotropically refined. The crystallographic data of **1–3** are listed in Table S1, and the selected bond length and bond angle are listed in Table S2.

1. Li L, Tu ZM, Hua Y, Li XN, Wang HY, Zhang H, A novel multifunction photochromic metal–organic framework for rapid ultraviolet light detection, amine-selective sensing and inkless and erasable prints. *Inorg Chem Front* 2019; 6: 3077–3082.
2. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H, OLEX2: a complete structure solution, refinement and analysis program. *J Appl Cryst* 2009; 42: 339–341.
3. (a) Sheldrick GM. *Acta crystallogr. sect. A: Found. Crystallogr* 2008; A64: 112–122.
(b) Sheldrick GM, SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst* 2015; A71: 3–8.

Table S1. Crystal data and structure refinement for **1–3** at 293 K

Compound	1	2	3
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CCDC code	1974045	1953798	1967364
Empirical formula	C ₁₇ H ₁₈ Co _{0.5} NO ₇	C ₃₄ H ₃₆ NiN ₂ O ₁₄	C ₃₆ H ₃₇ Zn ₂ N ₂ O ₂₀
Formula weight	377.79	755.36	948.41
Crystal size (mm)	0.3×0.3×0.2	0.3×0.3×0.1	0.2×0.2×0.1
Crystal system,	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1
<i>a</i> (Å)	8.8697(5)	8.8566(5)	9.0976(6)
<i>b</i> (Å)	9.7658(6)	9.7807(6)	9.2250(6)
<i>c</i> (Å)	10.0805(6)	10.0500(6)	13.2980(9)
α (°)	69.1410(10)	68.9060(10)	76.768(2)
β (°)	84.8820(10)	84.7260(10)	80.206(2)
γ (°)	86.982(2)	87.0080(10)	62.4750(10)
Volume (Å ³)	812.48(8)	808.62(8)	960.76(11)
<i>Z</i>	2	1	1
<i>D_c</i> (g·cm ⁻³)	1.540	1.551	1.639
<i>F</i> (000)	391	394	487
<i>mμ</i> (mm ⁻¹)	0.605	0.677	1.337
<i>R</i> ₁ / <i>wR</i> ₂ , [<i>I</i> ≥2σ(<i>I</i>)] ^{a,b}	0.0456, 0.1280	0.0321, 0.0965	0.0327, 0.0980
<i>R</i> ₁ / <i>wR</i> ₂ , (all data)	0.0479, 0.1298	0.0355, 0.1087	0.0367, 0.1050

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

Table S2. Selected bond lengths (Å) and bond angles (°) for **1–3**

Compound 1

Co(1)–O(3)	2.1310(15)	Co(1)–O(1)	2.0865(14)
Co(1)–O(4)	2.0999 (16)		
O(3)–Co(1)–O(3)	180.0	O(1)–Co(1)–O(3)	94.68(6)
O(1)–Co(1)–O(3)	85.32(6)	O(1)–Co(1)–O(1)	180.0
O(1)–Co(1)–O(4)	91.50(7)	O(1)–Co(1)–O(4)	88.50(7)
O(4)–Co(1)–O(3)	92.19(6)	O(4)–Co(1)–O(3)	87.81(6)
O(4)–Co(1)–O(4)	180.0		
Compound 2			
Ni(1)–O(10)	2.103(4)	Ni(1)–O(11)	2.092(5)
Ni(1)–O(12)	2.077(5)	Ni(1)–O(9)	2.078(4)
Ni(1)–O(3)	2.048(5)	Ni(1)–O(2)	2.060(5)
O(11)–Ni(1)–O(10)	179.6(2)	O(12)–Ni(1)–O(10)	179.4(2)
O(9)–Ni(1)–O(10)	88.37(18)	O(9)–Ni(1)–O(11)	91.75(17)
O(3)–Ni(1)–O(10)	85.15(18)	O(3)–Ni(1)–O(11)	95.19(18)
O(3)–Ni(1)–O(12)	91.0(2)	O(3)–Ni(1)–O(9)	88.7(2)
O(3)–Ni(1)–O(2)	179.4(3)	O(2)–Ni(1)–O(10)	94.38(18)
O(2)–Ni(1)–O(11)	85.3(2)	O(2)–Ni(1)–O(12)	88.6(2)
O(2)–Ni(1)–O(9)	91.79(2)		
Compound 3			
Zn(1)–O(10)	1.945(7)	Zn(1)–O(12)	1.905(7)
Zn(1)–O(2)	2.021(6)	Zn(1)–O(14)	1.973(6)
Zn(2)–O(6)	1.923(6)	Zn(2)–O(13)	2.022(6)
Zn(2)–O(5)	1.931(6)	Zn(2)–O(3)	2.008(6)
O(10)–Zn(1)–O(2)	101.2(3)	O(10)–Zn(1)–O(14)	108.9(3)
O(12)–Zn(1)–O(10)	114.1(3)	O(12)–Zn(1)–O(2)	105.7(3)
O(12)–Zn(1)–O(14)	124.6(3)	O(14)–Zn(1)–O(2)	98.3(2)
O(6)–Zn(2)–O(13)	109.9(3)	O(6)–Zn(2)–O(5)	112.4(3)
O(6)–Zn(2)–O(3)	100.4(3)	O(5)–Zn(2)–O(13)	125.7(3)
O(5)–Zn(2)–O(3)	105.1(3)	O(3)–Zn(2)–O(13)	99.0(2)

Table S3. The hydrogen bond lengths (Å) in 1–3

Compound 1

O(7)–H···O(3)	1.973	O(3)–H···O(2)	2.037
C(10)–H···O(2)	2.258	O(4)–H···O(7)	1.940
C(9)–H···O(4)	2.433	C(8)–H···O(5)	2.685
O(7)–H···O(6)	1.858	C(11)–H···O(7)	2.380
C(12)–H···O(7)	2.636		
Compound 2			
C(18)–H···O(1)	2.256	O(13)–H···O(1)	2.014
O(14)–H···O(4)	1.975	O(11)–H···O(5)	1.787
C(19)–H···O(5)	2.655	O(12)–H···O(6)	1.750
O(13)–H···O(6)	1.819	O(9)–H···O(7)	1.762
C(17)–H···O(9)	2.455	O(9)–H···O(13)	2.346
O(8)–H···O(10)	1.865	C(8)–H···O(8)	2.657
C(10)–H···O(12)	2.385	C(16)–H···O(13)	2.378
C(12)–H···O(13)	2.594	C(15)–H···O(14)	2.652
C(11)–H···O(14)	2.375		
Compound 3			
O(17)–H···O(1)	2.012	O(15)–H···O(2)	2.176
O(18)–H···O(3)	2.581	O(20)–H···O(4)	2.179
O(15)–H···O(7)	1.894	O(20)–H···O(8)	2.619
O(18)–H···O(9)	1.915	O(17)–H···O(11)	2.011
C(8)–H···O(11)	2.699	O(14)–H···O(19)	1.796
C(18)–H···O(15)	2.447	O(19)–H···O(15)	2.051
O(16)–H···O(17)	1.888	C(31)–H···O(16)	2.716
O(16)–H···O(18)	1.908	C(11)–H···O(18)	2.695
C(10)–H···O(18)	2.485	C(36)–H···O(19)	2.681

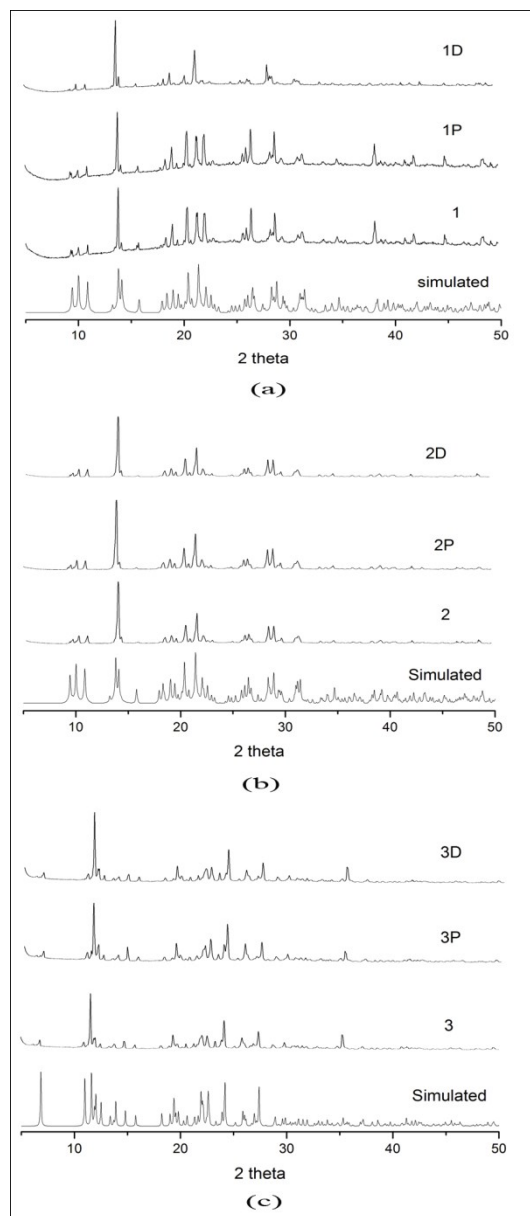


Fig. S1. The PXRD spectra before and after irradiation for **1** (a), **2** (b) and **3** (c).

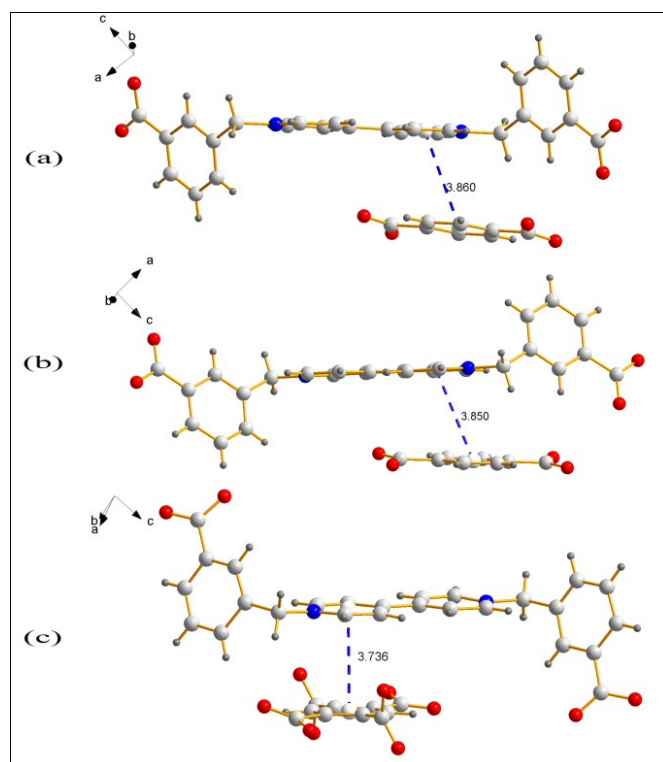


Fig.S2. π - π stacking interactions for **1** (a), **2** (b) and **3** (c).

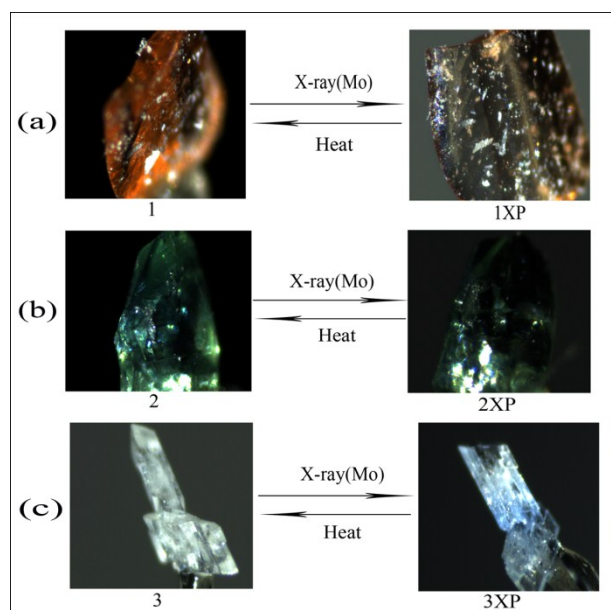


Fig.S3. Photographs of **1** (a), **2** (b) and **3** (c) subjected to irradiation by X-rays (Mo) and showing photochromism.

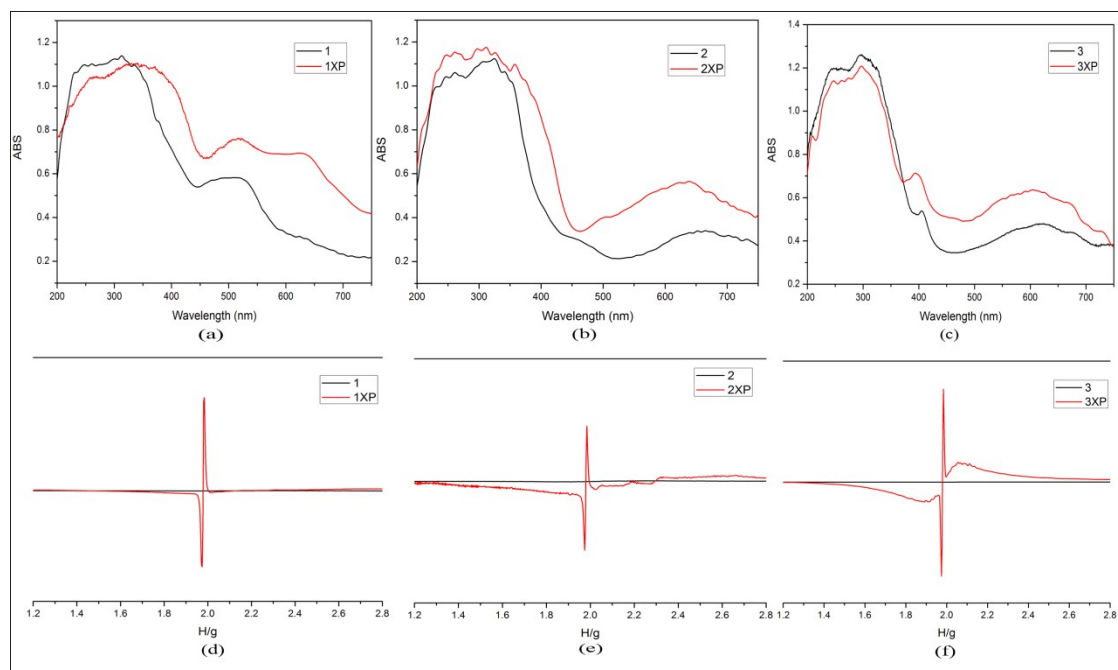


Fig. S4. UV-Vis spectra before and after X-ray-light irradiation for **1** (a), **2** (b) and **3** (c); The EPR spectra before and after X-ray-light irradiation for **1** (d), **2** (e) and **3** (f).

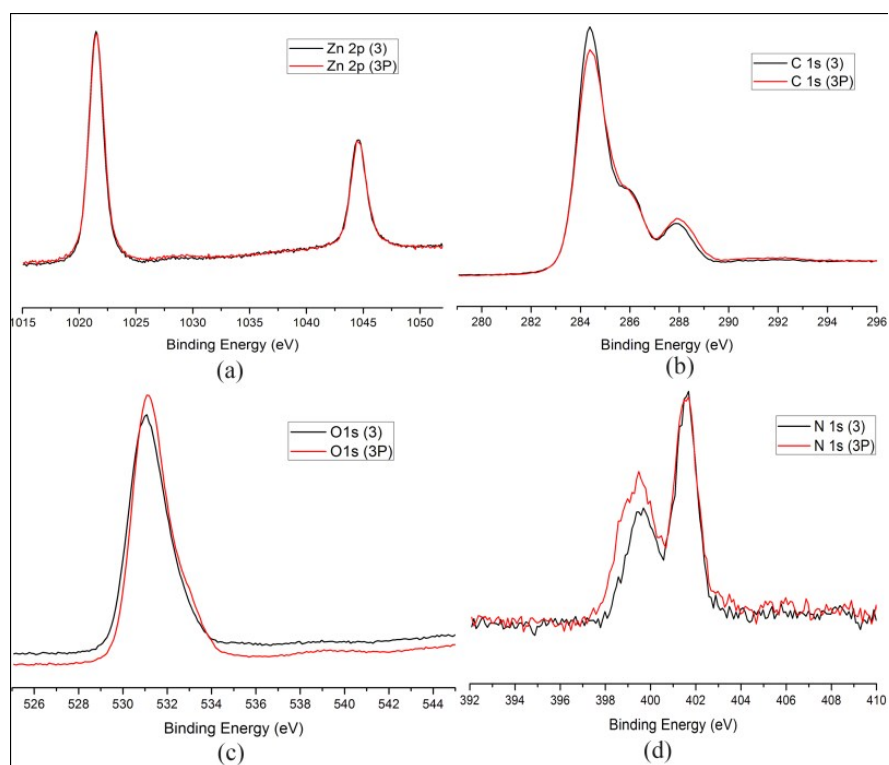


Fig.S5. XPS core-level spectra of **3** before (**3**, black line) and after UV-light irradiation (**3P**, red line).

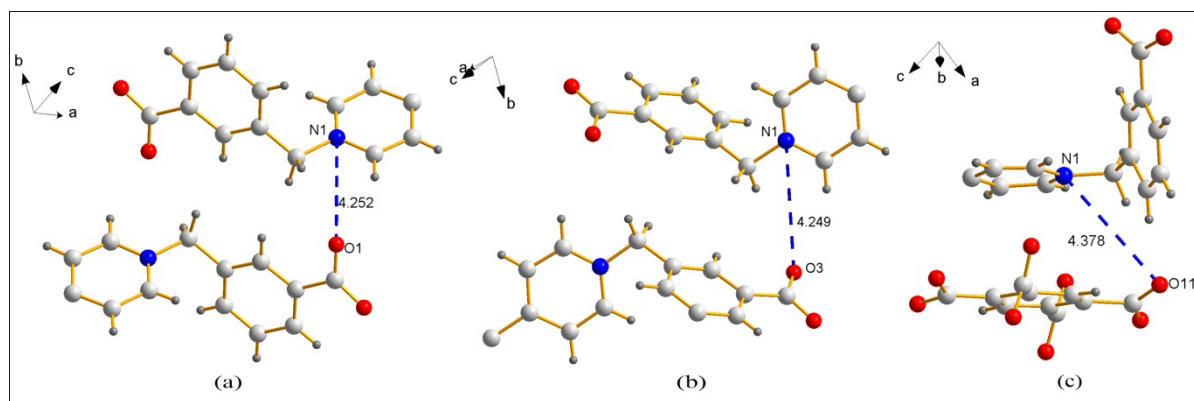


Fig. S6. ET distances of X-ray-induced photochromism for **1** (a), **2** (b) and **3** (c).

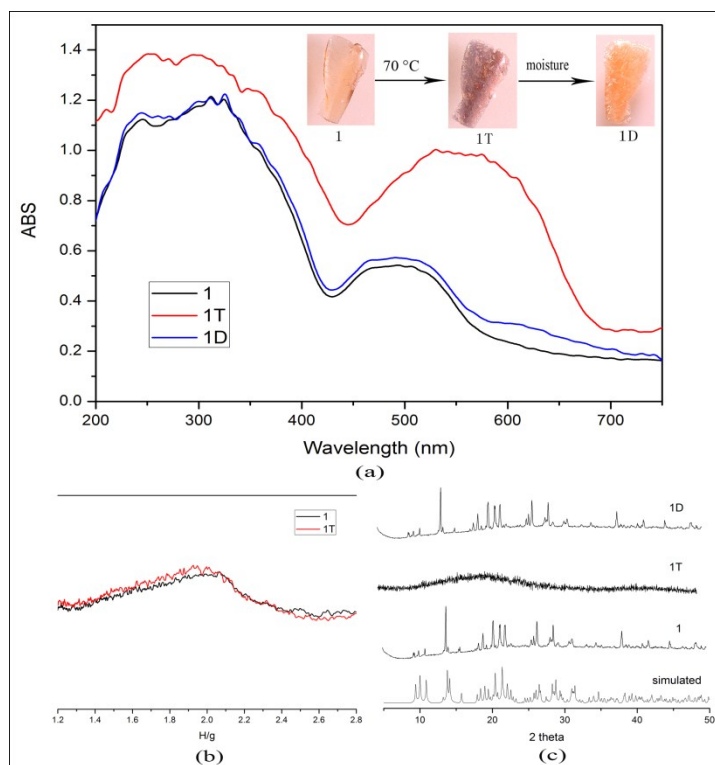


Fig. S7. Photographs and UV-Vis spectra before and after heating for **1** (a); The EPR spectra before and after heating for **1** (b); The PXRD spectra before and after heating for **1** (c).

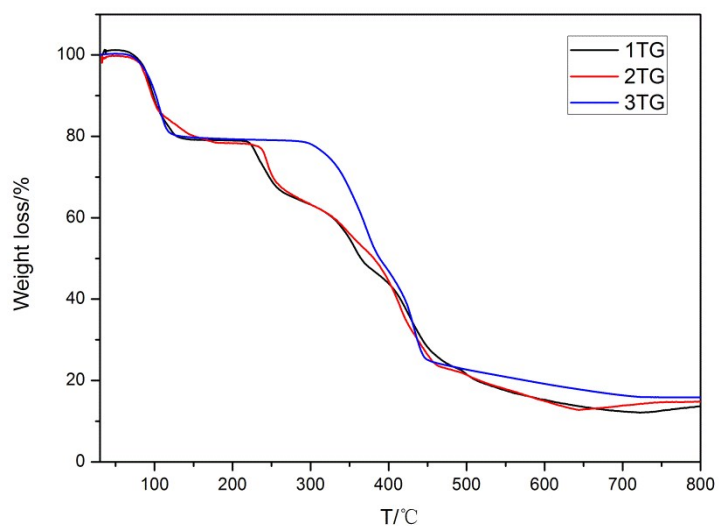


Fig. S8. TG tests of three compounds.

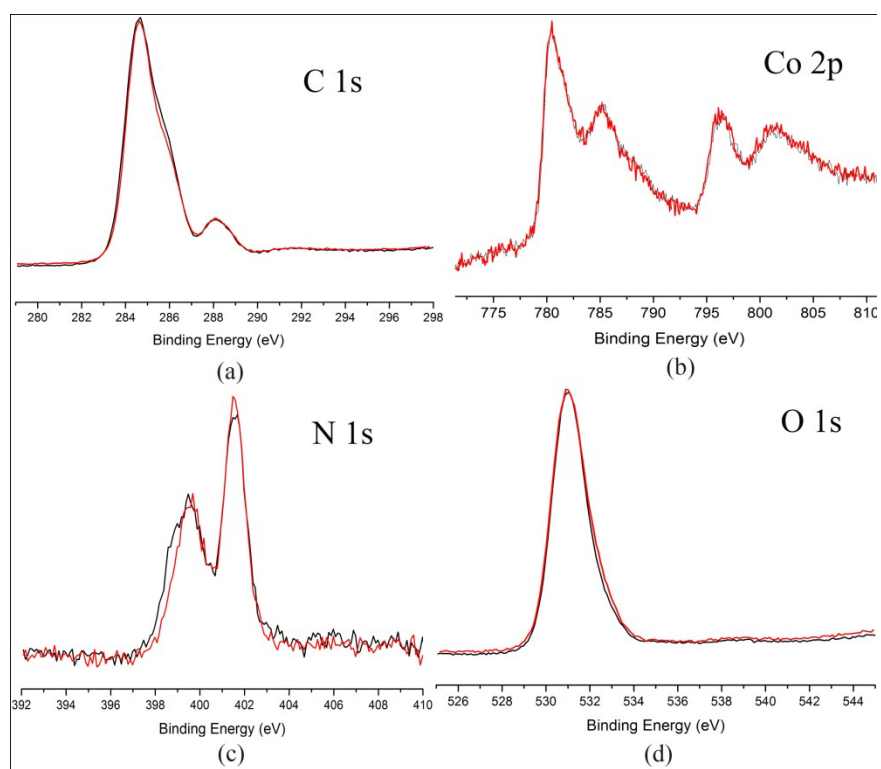


Fig.S9. XPS core-level spectra of **1** before (**1**, black line) and after heating (**1T**, red line).