<Supporting Information>

Three novel polyoxometalate-based inorganic-organic hybrid materials based on 2,6-bis(1,2,4-triazol-1-yl)pyridine

Yingying Wu, Xuefei Li, Ying Liu, Ge Xiao, Yijiao Huang, Yamin Li *, Dongbin Dang, Yan Bai **

(*Henan Key Laboratory of Polyoxometalate*, *Institute of Molecular and Crystal Engineering*, *College of Chemistry and Chemical Engineering*, *Henan University*, *Kaifeng, Henan 475004*, *PR China*)

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* Corresponding author. Key Laboratory of polyoxometalate Chemistry of Henan Province, majoring in the structure and property of functional materials. School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, PR China.
** Corresponding author.
E-mail addresses: liyamin@henu.edu.cn.

Table S1. Crystal data and refinement for the compounds **1–3**

Compound	**1**	**2**	**3**
Empirical fomula	$CoW_5C_{18}H_{16}N_{14}O_{17}$	$Cd_3P_2W_{24}C_{54}H_{66}N_{42}O_{92}$	$Ag_3PMo_{12}C_{18}H_{17}N_{14}O_{41.5}$
Formula weight	1678.63	7587.02	2599.32
Crystal size (mm^3)	0.17×0.15×0.11	0.20×0.20×0.20	0.20×0.20×0.20
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Cubic	Monoclinic
Space group	*Cccm*	*Ia-3*	$P2_1/n$
a (Å)	13.0024(8)	30.375(4)	11.861(3)
b (Å)	21.9573(13)	30.375(4)	20.437(6)
c (Å)	22.2526(14)	30.375(4)	22.536(6)
β (°)	90.00	90.00	93.471(4)
Volume ($Å^3$)	6353.1(7)	28026(6)	5453(2)
Temperature (K)	296(2)	293(2)	296(2)
Z	8	8	4
D_{calcd} ($g\ cm^{-3}$)	3.510	3.591	3.166
μ (mm^{-1})	18.643	20.188	3.853
F(000)	6024	26864	4860
θ range for date collection (°)	1.82 to 25.00	2.51 to 24.99	2.07 to 25.00
R_{int}	0.0547	0.0675	0.0306
Index ranges, *hkl*	$-15 \le h \le 15, -20 \le k \le 26, -26 \le l \le 26$	$-36 \le h \le 34, -36 \le k \le 36, -36 \le l \le 35$	$-14 \le h \le 11, -23 \le k \le 24, -26 \le l \le 26$
Reflections collected	2897	4114	9456
Independent reflections	2359	4113	8979
R_1, wR_2 ($I>2\sigma(I)$)	R_1=0.0305, wR_2=0.0621	R_1=0.0920, wR_2=0.1887	R_1=0.0329, wR_2=0.0757
R_1, wR_2 (all data)	R_1=0.0428,	R_1=0.0920,	R_1=0.0384,

	wR_2=0.0651	wR_2=0.1887	wR_2=0.0778
GOOF on F^2	1.055	1.232	1.148
Largest diff. peak and hole (e Å^{-3})	1.46/–1.822	4.667/–3.057	1.345/–1.009

$R = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(ap)^2+bP]$, $P = (F_o^2+2F_c^2)/3]$. **1**: a = 0.0277, b = 31.3472; **2**: a = 0.0328, b = 5173.3159; **3**: a = 0.0284, b = 21.5563.

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

Bond	(Å)	Bond	(Å)	Bond	(Å)
W2–O7 #6	1.898(5)	W4–O10 #6	1.895(8)	W3–O7#7	1.913(6)
W1–O4#7	1.899(5)	W4–O8#7	1.924(6)	W2–O8#7	1.970(6)
Co1–N1#1	2.066(7)	Co1–N1#4	2.066(7)	Co1–O1W	2.320(10)
Co1–N1#2	2.066(7)	Co1–N1	2.066(7)	Co1–O1W #4	2.320(10)
O1–Co2	2.127(7)	W2–O4#7	1.938(5)	W3–O2#6	2.370(7)
N8–C8 #5	1.337(10)	O6–W2#3	1.8993(5)	O7–W2#6	1.898(5)
O8–W2#7	1.970(6)	O10–W4 #6	1.895(8)	Co2–N2#7	2.099(7)
Co2–N2#5	2.099(7)	Co2–N2#8	2.099(7)	Co2–O1#8	2.127(7)
Angles	(°)	Angles	(°)	Angles	(°)
N1#1–Co1–N1#4	176.7(4)	N1#1–Co1–N1#2	88.6(4)	N1#4–Co1–N1	88.6(4)
N1#4–Co1–N1#2	91.5(4)	N1#1–Co1–N1	91.5(4)	N1#1–Co1–O1W	91.6(2)
N1#2–Co1–O1W	88.4(2)	N1#2–Co1–N1	176.7(4)	N1–Co1–O1W	88.4(2)
N1#1–Co1–O1W#4	88.4(2)	N1#4–Co1–O1W	91.6(2)	N1#4–Co1–O1W#4	88.4(2)
N1#2–Co1–O1W#4	91.6(2)	N1–Co1–O1W#4	91.6(2)	O1W–Co1–O1W#4	180.000(1)
C4–N2–Co2	135.4(6)	C3–N2–Co2	121.7(6)	N2#7–Co2–N2#8	88.0(4)
C9#5–C10–H10A	121.2	N2#7–Co2–N2#5	180.0(5)	N2#5–Co2–N2#8	92.0(4)
N2#8–Co2–N2	180.0(3)	N2#7–Co2–N2	92.0(4)	N2#5–Co2–N2	88.0(4)
N2#5–Co2–O1	88.6(2)	N2#8–Co2–O1	88.6(2)	N2#7–Co2–O1	91.4(2)
N2–Co2–O1	91.4(2)	N2#7–Co2–O1#8	88.6(2)	N2#5–Co2–O1#8	91.4(2)
N2–Co2–O1#8	88.6(2)	N2#8–Co2–O1#8	91.4(2)		

Symmetry code for **1**: #1: *x*, −*y*+1/2, −*z*+1/2; #2: −*x*, −*y*+1, +*z*; #3: −*x*, −*y*, *z*; #4: −*x*, *y*, −*z*+1/2; #5: −*x*+1/2, −*y*+1/2, *z*; #6: −*x*, −*y*, −*z*; #7: *x*, *y*, −*z*; #8: −*x*+1/2, −*y*+1/2.

Table S3. Selected bond lengths (Å) and bond angles (°) for compound **2**

Bond	(Å)	Bond	(Å)	Bond	(Å)
Cd1–N2#3	2.30(2)	Cd1–N2	2.30(2)	Cd1–O1W	2.44(3)
Cd1–N7#7	2.35(3)	Cd1–N7#12	2.35(3)	Cd1–O1W#3	2.44(3)
W2–O13#5	2.48(3)	W1–O14#4	2.52(3)	W1–O4#2	1.938(18)
W1–O8#8	1.88(2)	W2–O7#8	1.95(2)	W3–O11#10	1.87(4)
W4–O1#2	2.043(11)	W3–O10#10	1.91(2)	O16–O2#10	1.54(4)
O1–W4#1	2.043(11)	O2–O16#9	1.54(4)	O7–W2#5	1.95(2)
O10–W3#11	1.91(2)	O4–W1#1	1.938(18)	O11–W3#11	1.87(4)
O16–O2#9	1.54(4)	O14–W1#4	2.52(3)	O13–O14#4	1.67(4)
N7–Cd1#6	2.35(3)	O14–W1#5	2.52(3)	O16–O2#11	1.54(4)
Angles	(°)	Angles	(°)	Angles	(°)
N2#3–Cd1–N2	96.1(11)	N2#3–Cd1–N7#7	98.2(8)	N2–Cd1–N7#12	98.2(8)
N2–Cd1–N7#7	94.8(8)	N2#3–Cd1–N7#12	94.8(8)	N2#3–Cd1–O1W	174.7(10)
N7#7–Cd1–O1W	84.1(10)	N7#7–Cd1–N7#12	160.5(13)	N7#12–Cd1–O1W	81.8(10)

N2#3–Cd1–O1W#3	88.4(10)	N2–Cd1–O1W	88.4(10)	N2–Cd1–O1W#3	174.7(10)
N7#7–Cd1–O1W#3	81.8(10)	N7#12–Cd1–O1W#3	84.1(10)	C5–N7–Cd1#6	123(2)
O8#8–W1–O14#4	91.8(13)	W3–O10–W3#11	140.9(13)	O6–W2–O13#5	95.3(12)
O3–W3–O10	100.9(12)	O15–W4–O1#2	106.5(11)	O12–W3–O11#10	153.9(17)
O11#10–W3–O10	86.9(17)	O1–W4–O1#2	113.2(6)	O16#9–O2–P2	48(2)
W1–O4–W1#1	139.3(11)	O13#8–O14–O13#5	97(3)	P2–O2–W4	133(2)

Symmetry code for **1**: #1: −*z*−1/2, −*x*, *y*−1/2; #2: −*y*, *z*+1/2, −*x*−1/2; #3: *x*+1, −*y*−1/2, *z*; #4: −*x*, −*y*, −*z*−1; #5: *z*+1/2, *x*, −*y*−1/2; #6: *z*+3/2, *x*−1, −*y*−3/2; #7: *y*+1, −*z*−3/2, *x*−3/2; #8: *y*, −*z*−1/2, *x*−1/2; #9: −*x*+1/2, −*y*−1/2, −*z*−3/2; #10: *z*+1, *x*−1/2, −*y*−1; #11: *y*+1/2, −*z*−1, *x*−1; #12: −*y*, *z*+1, *x*−3/2.

Table S4. Selected bond lengths (Å) and bond angles (°) for compound **3**

Bond	(Å)	Bond	(Å)	Bond	(Å)
Ag1–N11	2.161(5)	Ag1–N11#4	2.161(5)	Ag2–N3	2.528(5)
Ag2–N14#1	2.222(5)	Ag2–N2	2.315(5)	Ag2–N4	2.564(6)
Ag3–N1#3	2.143(5)	Ag4–N5	2.251(5)	Ag4–N9	2.305(5)
Ag4–N8	2.514(5)	N14–Ag2#2	2.222(5)	Mo1–O33	1.858(4)
Angles	(°)	Angles	(°)	Angles	(°)
N11–Ag1–N11#4	180.0	N14#1–Ag2–N2	129.96(19)	N14#1–Ag2–N4	90.3(2)
N11#1–Ag2–N3	134.44(17)	N2–Ag2–N3	67.25(17)	N3–Ag2–N4	62.42(16)
N5–Ag4–N9	129.62(19)	N5–Ag4–N8	130.75(18)	N2–Ag2–N4	129.53(17)
N9–Ag4–N8	67.47(16)	C1–N4–Ag2	135.1(5)	N1#3–Ag3–N1	179.998(1)
C2–N1–Ag3	138.7(4)	N7–N4–Ag2	118.6(4)	C9–N2–Ag2	137.1(4)
N6–N2–Ag2	120.0(4)	C1–N1–Ag3	118.2(4)	C8–N5–Ag4	130.6(4)
C3–N3–Ag2	124.9(4)	C7–N3–Ag2	117.4(4)	C8–N6–N2	108.9(5)
C10–N8–Ag4	125.5(4)	C9–N5–Ag4	125.8(4)	C14–N8–Ag4	117.2(4)
C18–N9–Ag4	137.4(5)	N13–N9–Ag4	119.1(4)	C18–N14–Ag2#2	126.5(4)
C16–N11–Ag1	135.4(4)	C17–N11–Ag1	121.6(4)	C15–N14–Ag2#2	129.7(4)

Symmetry code for **1**: #1: *x*−1, *y*, *z*; #2: *x*+1, *y*, *z*; #3: −*x*−1, −*y*+2, −*z*−1; #4: −*x*, −*y*+3, −*z*−1.

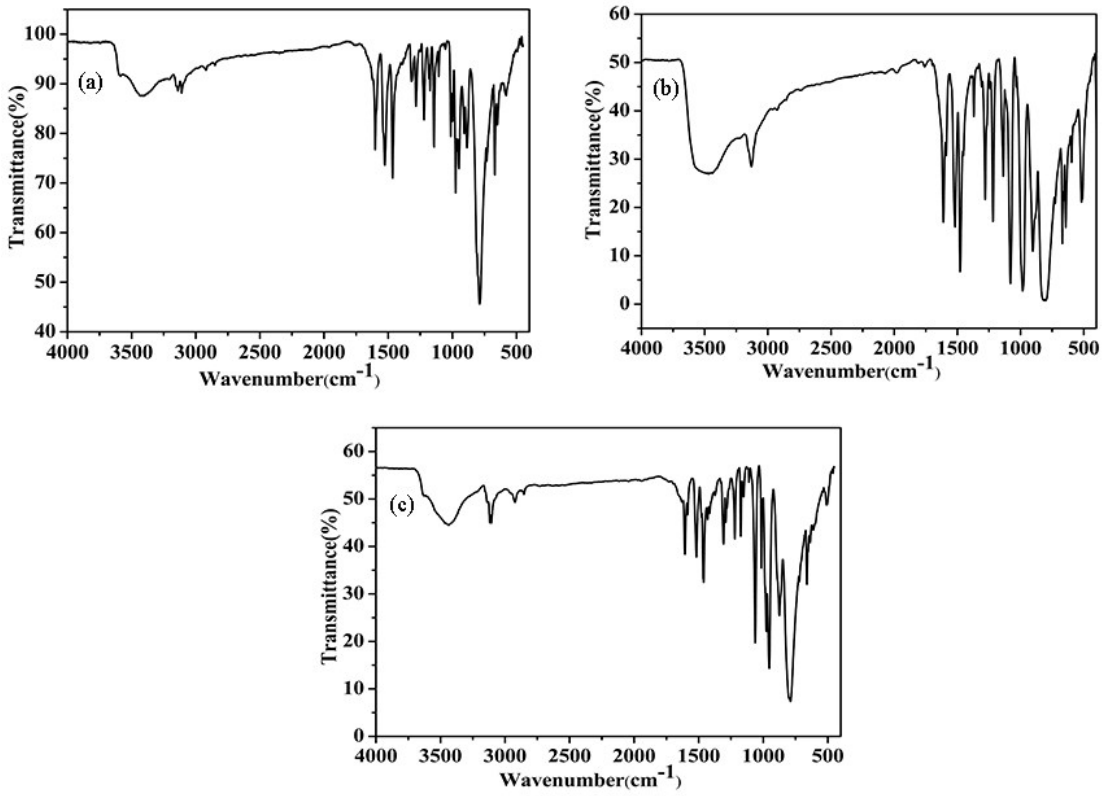

Fig. S1 IR spectra of compounds **1–3** (a–c).

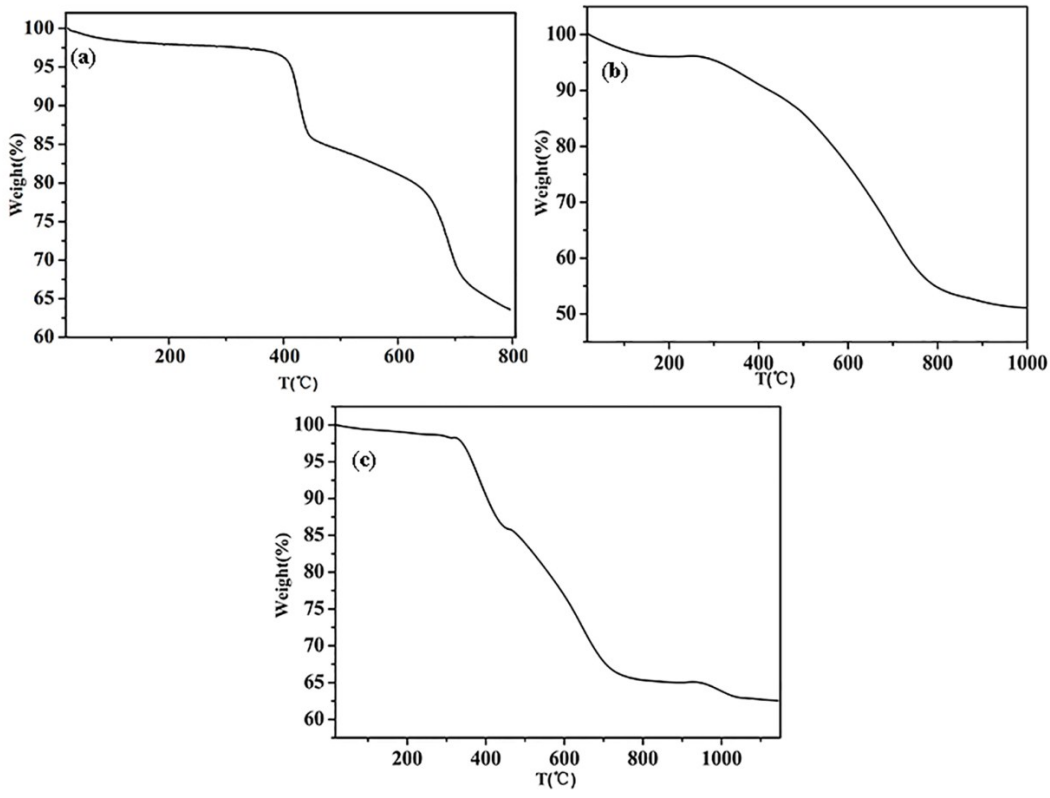

Fig. S2 TGA curves of compounds **1–3** (a–c).

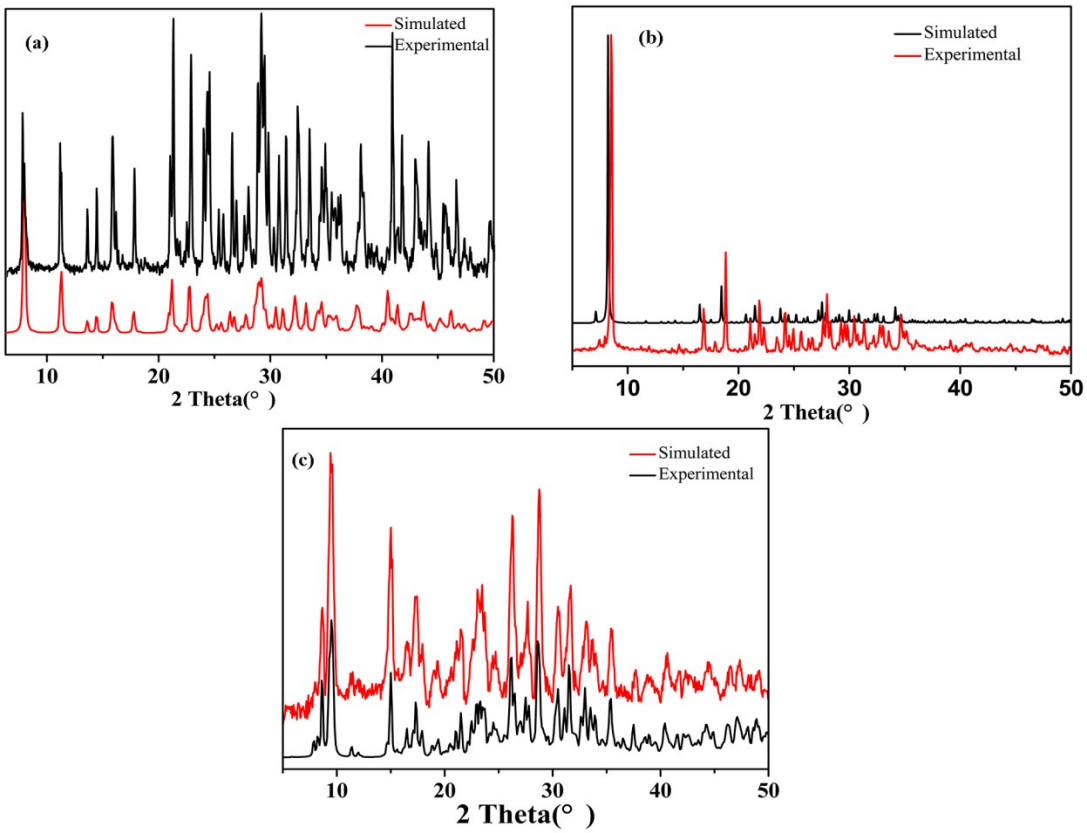

Fig. S3 PXRD patterns of compounds **1–3** (a–c).

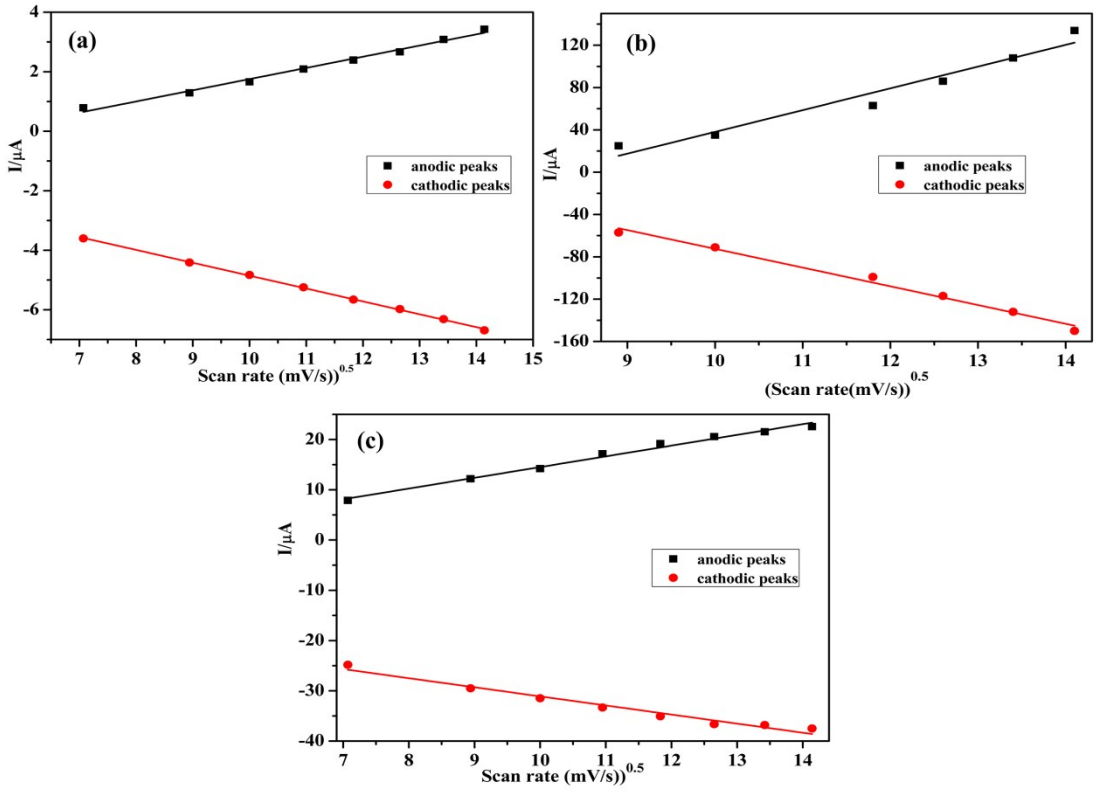

Fig. S4 (a), (b), (c) The plots of the anodic and the cathodic peak II–II' currents for **1**–GCE, I–I' currents for **2**–GCE, II–II' currents for **3**–GCE against scan rates.

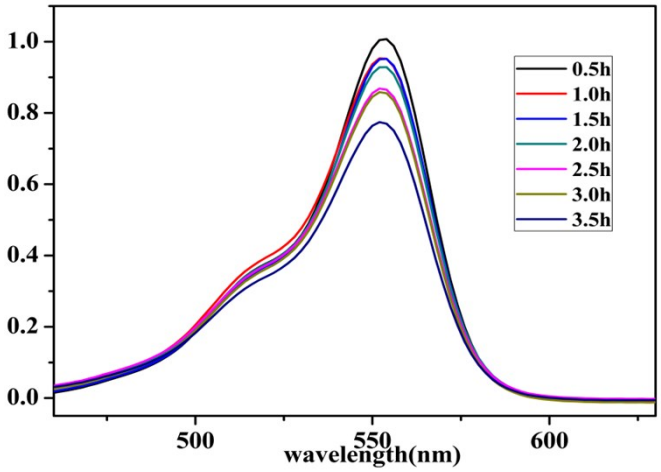

Fig. S5 Absorption spectra of the RhB solutions during the decomposition reaction without catalyst.

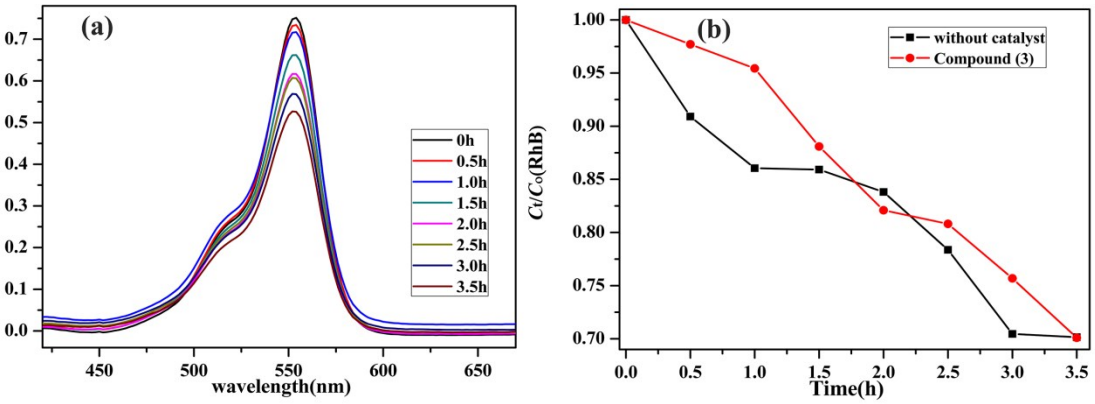

Fig. S6 (a) Absorption spectra of the RhB (10 mg L^{-1}) solution during the decomposition reaction under UV light irradiation with the use of compound **3**. (b) The comparison of the compound and no crystal decomposition rate of RhB in the same conditions.

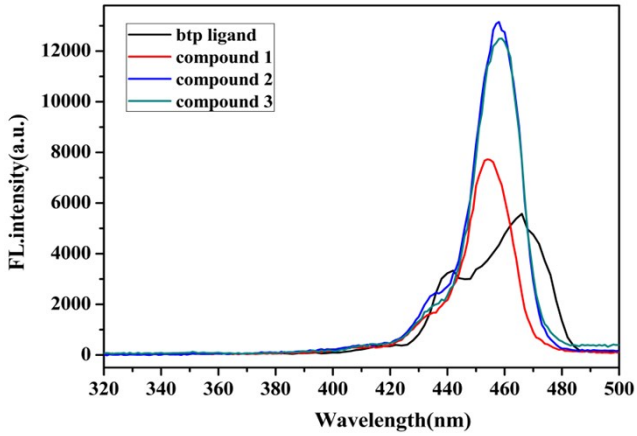

Fig. S7 Solid-state photoluminescence spectra of compounds **1–3** and the btp ligand at the room temperature.

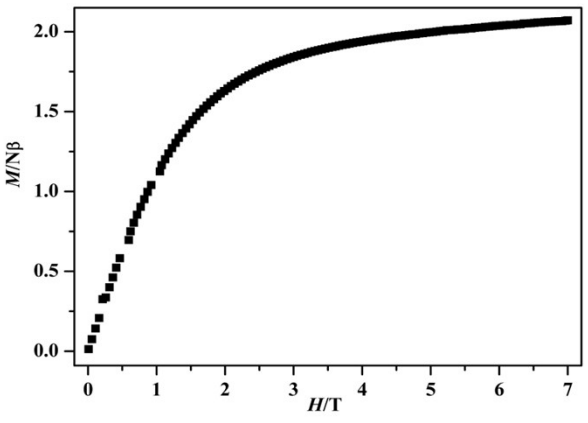

Fig. S8 The plot of *M vs*. *H*.