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Diverse polyoxometalates-based metal–organic complexes constructed by a tetrazole- and pyridyl-containing asymmetric amide ligand or its *in-situ* transformed ligand †

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Table S1 Selected bond distances (Å) and angles (°) for compounds **1–4**.

		Compound **1**	
Cu(1)-N(2)#1	2.036(6)	N(3)#1-Cu(1)-N(3)	87.3(3)
Cu(1)-N(2)	2.036(6)	N(2)#1-Cu(1)-O(1W)	89.8(2)
Cu(1)-N(3)#1	2.037(6)	N(2)-Cu(1)-O(1W)	89.8(2)
Cu(1)-N(3)	2.037(6)	N(3)#1-Cu(1)-O(1W)	90.2(2)
Cu(1)-O(1W)	2.341(7)	N(3)-Cu(1)-O(1W)	90.2(2)
N(1)-Cu(2)	2.053(6)	N(11)#2-Cu(2)-N(11)#3	179.996(1)
Cu(2)-N(11)#2	2.024(6)	N(11)#2-Cu(2)-N(1)#4	88.1(2)
Cu(2)-N(11)#3	2.024(6)	N(11)#3-Cu(2)-N(1)#4	91.9(2)
Cu(2)-N(1)#4	2.053(6)	N(11)#2-Cu(2)-N(1)	91.9(2)
Cu(2)-N(11)#2	2.024(6)	N(11)#3-Cu(2)-N(1)	88.1(2)
N(2)#1-Cu(1)-N(2)	94.2(4)	N(1)#4-Cu(2)-N(1)	179.998(1)
N(2)#1-Cu(1)-N(3)#1	176.6(2)	N(11)#2-Cu(2)-N(11)#3	179.996(1)
N(2)-Cu(1)-N(3)#1	89.3(2)	N(11)#2-Cu(2)-N(1)#4	88.1(2)
N(2)#1-Cu(1)-N(3)	89.3(2)	N(1)#4-Cu(2)-N(1)	179.998(1)
N(2)-Cu(1)-N(3)	176.6(2)		

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

		Compound **2**	
Co(1)-N(1)	2.132(5)	N(7)#1-Co(1)-N(7)	96.3(3)
Co(1)-N(1)#1	2.132(5)	N(1)-Co(1)-O(2W)	88.99(18)
Co(1)-O(1W)	2.135(7)	N(1)#1-Co(1)-O(2W)	88.99(18)
Co(1)-N(7)#1	2.142(5)	O(1W)-Co(1)-O(2W)	175.6(3)
Co(1)-N(7)	2.142(5)	N(7)#1-Co(1)-O(2W)	89.07(18)
Co(1)-O(2W)	2.162(6)	N(7)-Co(1)-O(2W)	89.08(18)
Co(2)-N(12)	2.125(5)	N(12)-Co(2)-N(12)#2	179.998(1)
Co(2)-N(12)#2	2.125(5)	N(12)-Co(2)-N(6)#3	88.5(2)
Co(2)-N(6)#3	2.131(5)	N(12)#2-Co(2)-N(6)#3	91.47(19)
Co(2)-N(6)#4	2.131(5)	N(12)-Co(2)-N(6)#4	91.5(2)
Co(2)-O(3W)	2.212(7)	N(12)#2-Co(2)-N(6)#4	88.5(2)
Co(2)-O(3W)#2	2.212(7)	N(6)#3-Co(2)-N(6)#4	180.0(2)
N(1)-Co(1)-N(1)#1	85.8(3)	N(12)-Co(2)-O(3W)	91.2(2)
N(1)-Co(1)-O(1W)	87.8(2)	N(12)#2-Co(2)-O(3W)	88.8(2)

N(1)#1-Co(1)-O(1W)	87.8(2)	N(6)#3-Co(2)-O(3W)	85.8(3)
N(1)-Co(1)-N(7)#1	89.0(2)	N(6)#4-Co(2)-O(3W)	94.2(3)
N(1)#1-Co(1)-N(7)#1	174.4(2)	N(12)-Co(2)-O(3W)#2	88.8(2)
O(1W)-Co(1)-N(7)#1	93.8(2)	N(12)#2-Co(2)-O(3W)#2	91.2(2)
N(1)-Co(1)-N(7)	174.4(2)	N(6)#3-Co(2)-O(3W)#2	94.2(3)
N(1)#1-Co(1)-N(7)	89.0(2)	N(6)#4-Co(2)-O(3W)#2	85.8(3)
O(1W)-Co(1)-N(7)	93.8(2)	O(3W)-Co(2)-O(3W)#2	180.0(4)
N(1)-Co(1)-N(7)	174.4(2)		

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

Compound **3**

Ag(1)-N(9)	2.127(8)	N(8)#1-Ag(2)-O(5)	107.7(3)
Ag(1)-N(1)	2.153(8)	N(8)#1-Ag(2)-O(2W)	88.92(3)
Ag(1)-O(5)	2.819(8)	N(3)-Ag(2) -O(41)	81.23(2)
Ag(2)-N(8)#1	2.283(8)	N(3)-Ag(2)-O(2W)	82.95(2)
Ag(2)-N(3)	2.343(8)	N(3)-Ag(2)-O(5)	90.2(3)
Ag(2)-O(5)	2.449(8)	N(8)#1-Ag(2)-N(3)	157.3(3)
Ag(2)-O(41)	2.643(8)	O(41)-Ag(2)-O(5)	91.16(3)
Ag(2)-O(2W)	2.612(8)	O(2W)-Ag(2)-O(5)	147.08(3)
N(9)-Ag(1)-N(1)	170.7(3)	O(41)-Ag(2)-O(2W)	119.23(3)
N(1)-Ag(1)-O(5)	101.52(3)	N(8)#1-Ag(2)-O(41)	84.38(2)
N(9)-Ag(1)-O(5)	87.56(3)		

Symmetry code for **3** #1–x, –y – 1, –z.

Compound **4**

Ag(1)-N(2)	2.165(19)	N(2)-Ag(1)-N(1)	142.8(7)
Ag(1)-N(1)	2.22(2)	N(2)-Ag(1)-O(18)	118.16(3)
Ag(1)-O(18)	2.876(2)	O(26)#2-Ag(1)-O(18)	81.59(2)
Ag(1)-O(19)	2.703(2)	N(2)-Ag(1)-O(14)#1	81.63(2)
Ag(1)-O(14)#1	2.819(2)	N(2)-Ag(1)-O(26)#2	88.61(2)
Ag(1)-O(26)#2	2.873(2)	N(1)-Ag(1)-O(14)#1	89.67(3)
N(1)-Ag(1)-O(18)	93.51(3)	N(1)-Ag(1)-O(26)#2	76.62(3)
N(1)-Ag(1)-O(19)	97.59(3)	O(26)#2-Ag(1)-O(14)#1	142.55(7)
O(26)#2-Ag(1)-O(19)	137.95(7)	O(18)-Ag(1)-O(14)#1	134.61(7)
O(19)-Ag(1)-O(18)	56.94(3)	O(19)-Ag(1)-O(14)#1	77.74(2)
N(2)-Ag(1)-O(19)	115.43(7)		

Symmetry code for **4** #1 –x + 1, –1–y,1–z.

Table S2. Selected hydrogen–bonding geometry (Å, º) for compounds **1** and **2**.

	D–H···A	D–H	H···A	D···A	D–H···A
Compound **3**	C(15)–H(15A)···O(23)	0.93	2.25	3.100	152
Compound **4**	C(17)–H(17A)···O(3)	0.93	2.41	3.169	138

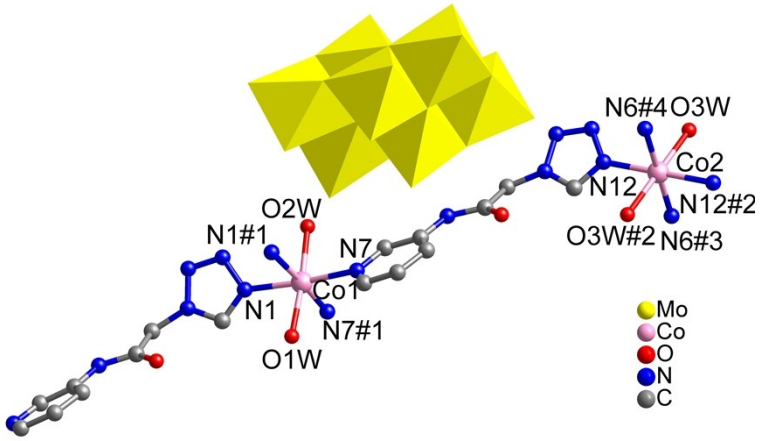

Fig. S1 The coordination environment of the Co^{II} ions in **2**. All H atoms and lattice water molecules are omitted for clarity. Symmetry code for **2** #1 –x + 1, y, z; #2 –x + 3/2, –y + 3/2, –z + 1; #3 –x + 1, y + 1/2, –z + 1/2.

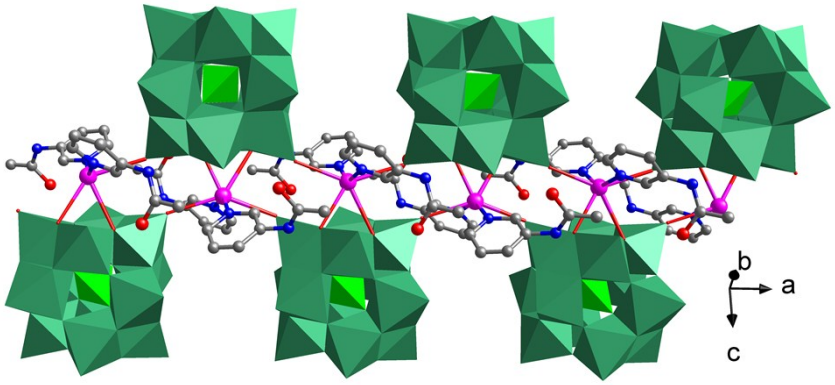

Fig.S2 The 1D chain in **4**.

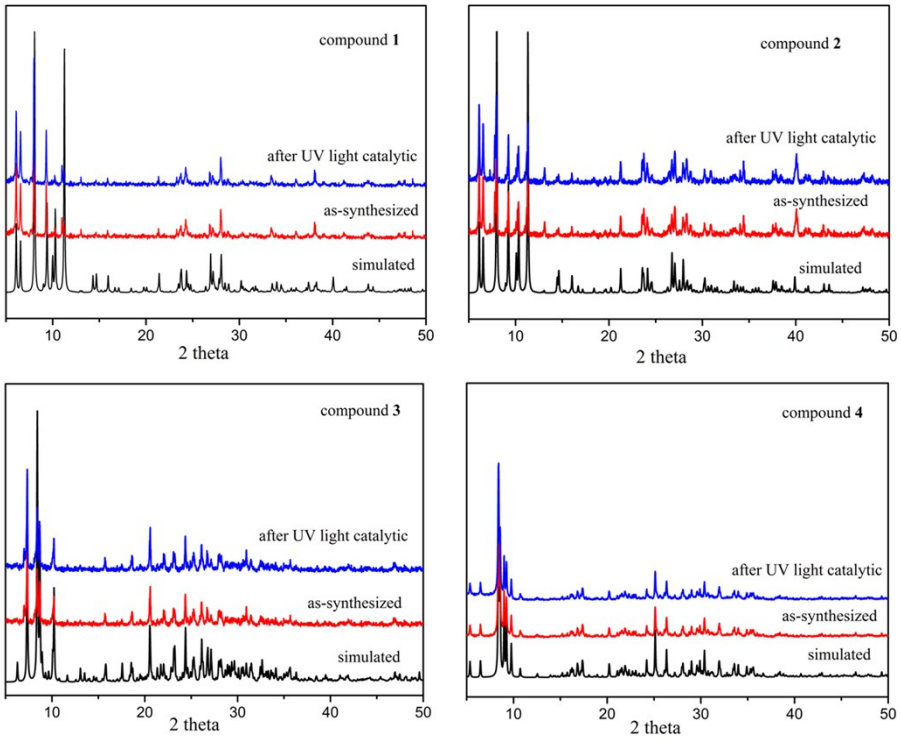

Fig. S3 The PXRD of compounds **1-4**.

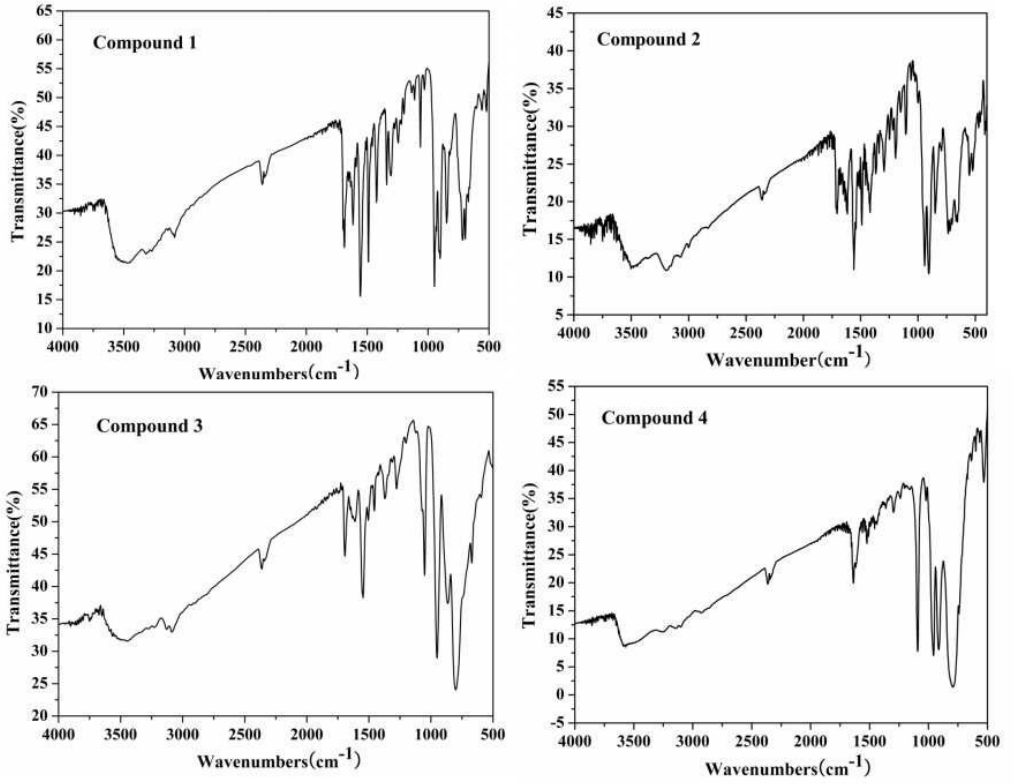

Fig. S4. The IR spectra of compounds **1-4**.

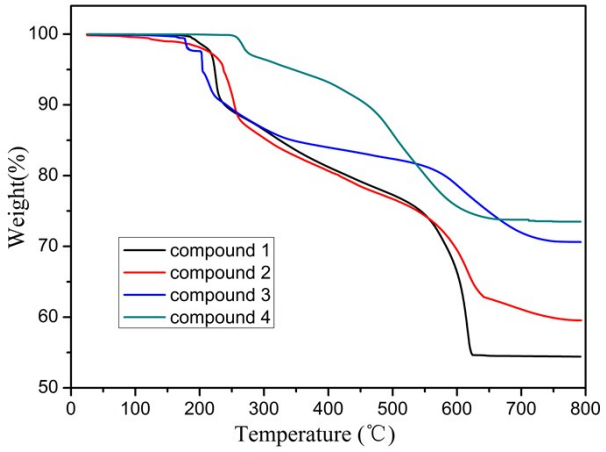

Fig. S5. The TGA curves of compounds **1-4**.

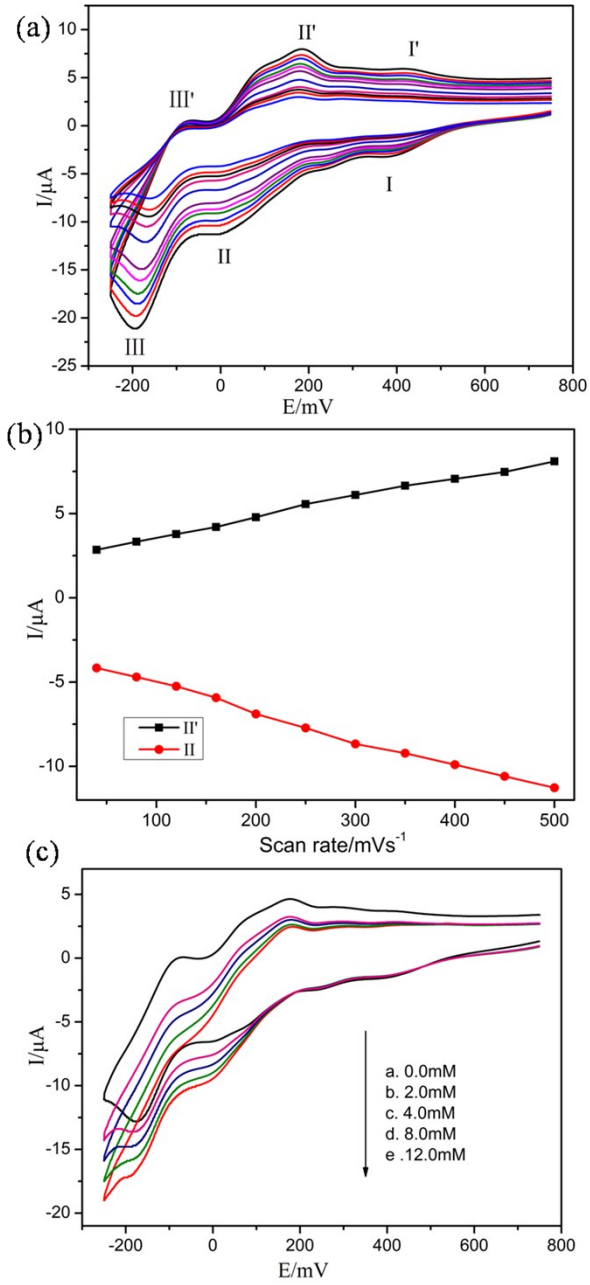

Fig. S6. (a) Cyclic voltammograms of the **3**–CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 80, 120, 160, 200, 250, 300, 350, 400, 450, 500 mVs^{-1}); (b) The dependence of anodic peak (II) and cathodic peak (II') currents on scan rates for **3**–CPE; (c) Cyclic voltammograms of **3**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 solution containing 0.0–12.0 mM H_2O_2.

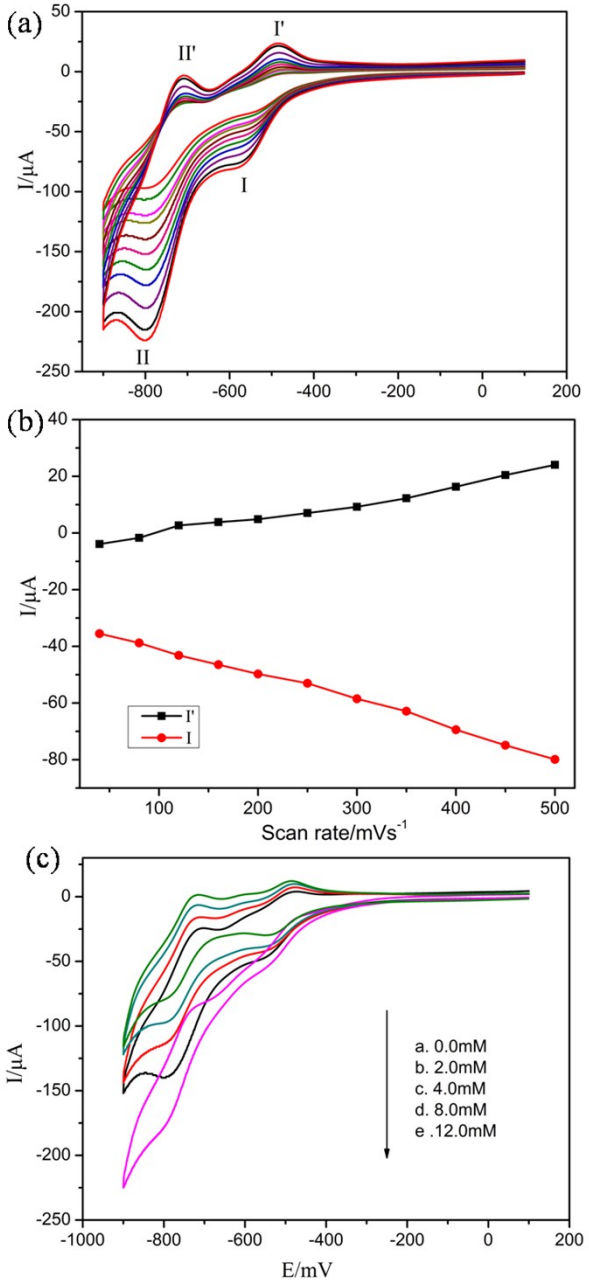

Fig. S7. (a) Cyclic voltammograms of the **4**–CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 80, 120, 160, 200, 250, 300, 350, 400, 450, 500 mVs^{-1}); (b) The dependence of anodic peak (I) and cathodic peak (I') currents on the scan rates for **4**–CPE; (c) Cyclic voltammograms of **4**–CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 solution containing 0.0–12.0 mM H_2O_2.

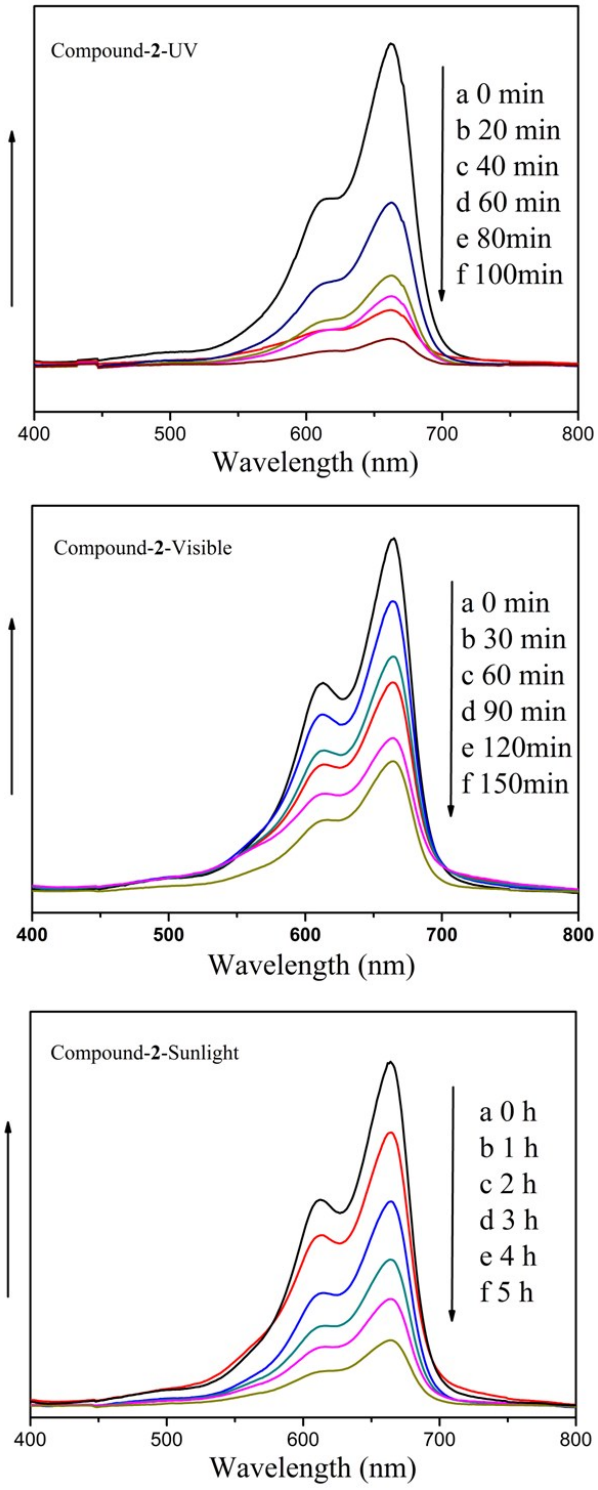

Fig. S8. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **2**.

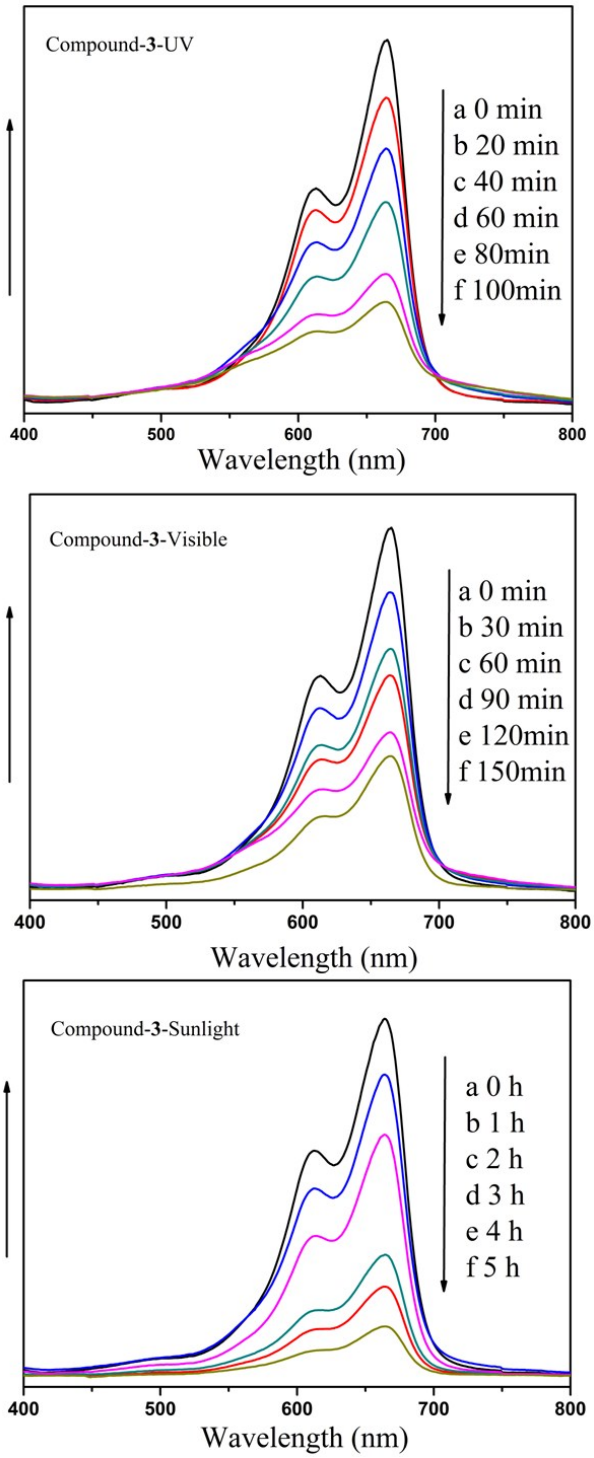

Fig. S9. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **3**.

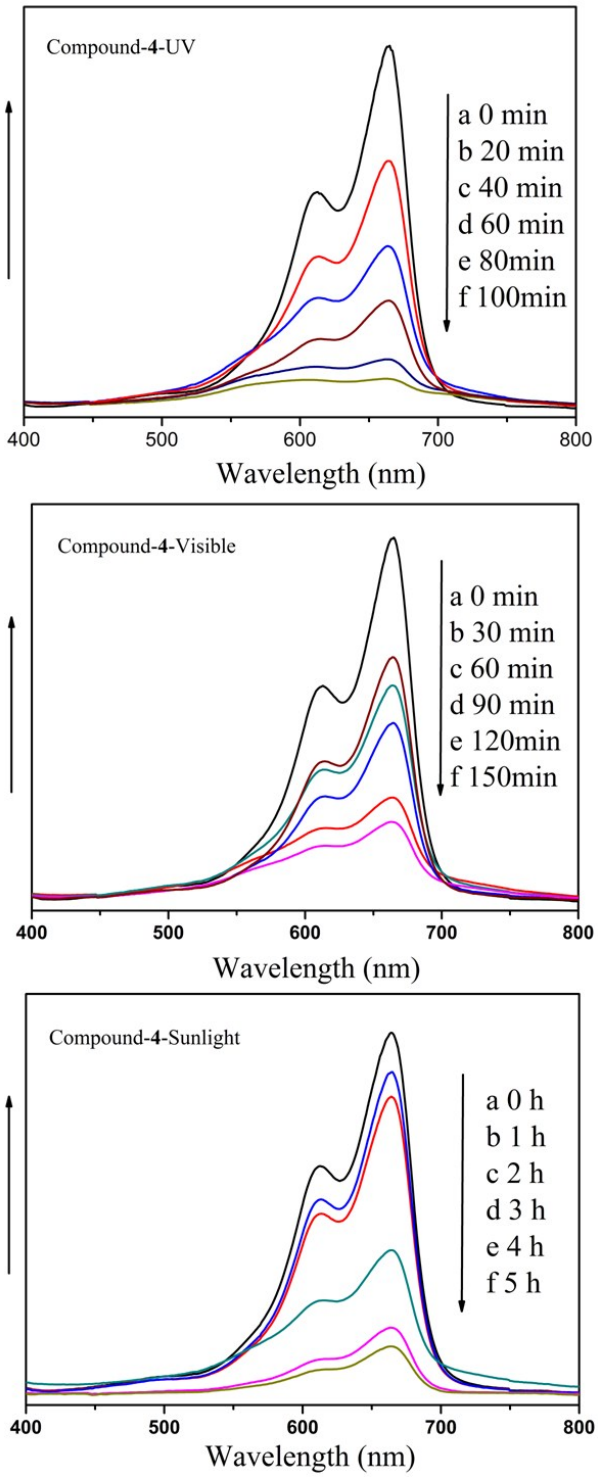

Fig. S10. Absorption spectra of the MB solution during the decomposition reaction under UV (a), visible (b) and sunlight (c) irradiation in the presence of the compound **4**.

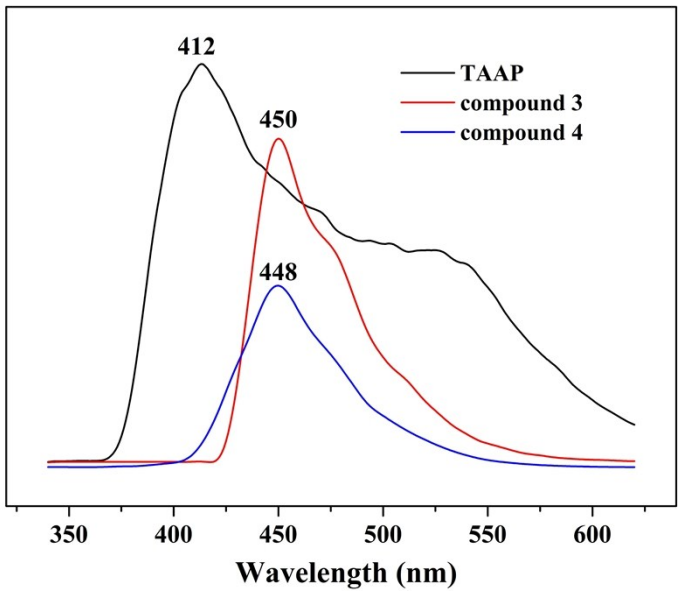

Fig. S11. Emission spectra of the TAPP ligand and compounds **3-4** in the solid state at room temperature.