Inorganic-organic hybrid compounds based on the coexistence of different isomers or forms of polymolybdate

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Table S1. Selected bond lengths [Å] and angles [deg] for **1**.

Ni(1)-N(1)	2.049(5)
Ni(1)-O(1)	2.015(4)
Ni(1)-O(1W)	2.105(5)
O(1)-Ni(1)-N(1)	89.19(17)
O(1)-Ni(1)-N(1)#1	90.81(17)
O(1)-Ni(1)-O(1W)#1	95.94(19)
O(1)-Ni(1)-O(1W)	84.06(19)
N(1)-Ni(1)-O(1W)	90.6(2)
N(1)-Ni(1)-O(1W)#1	89.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y, -z+1

Table S2. Hydrogen bonds for **1** [Å and deg].

D-H...A	d(D-H)	d(D...A)	<(DHA)
N(8)-H(17)...O(7)#2	0.86	2.707(6)	147.8
N(6)-H(6A)...O(19)	0.86	2.939(8)	153.7
N(7)-H(7)...O(25)#4	0.86	3.012(7)	135.2
N(7)-H(7)...O(18)	0.86	2.865(7)	114
O(2W)-H(2B)...O(2)#1	0.80(9)	2.935(8)	140(9)
O(2W)-H(2B)...O(25)#6	0.80(9)	3.160(7)	124(8)
O(2W)-H(2A)...O(14)#1	0.87(9)	2.853(7)	125(7)
O(2W)-H(2A)...O(23)#6	0.87(9)	3.072(7)	142(8)
O(1W)-H(1A)...O(2W)	0.72(7)	2.705(7)	170(8)

O(1W)-H(1B)...O(4)#2	0.90(8)	2.967(7)	172(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 ; #2 -x,-y+1,-z+1 ; #4 -x+2,-y,-z+2 ; #6 x, y, z-1

Table S3. Selected bond lengths [Å] and angles [deg] for **2**.

Co(1)-O(26)#3	2.051(4)
Co(1)-N(3)	2.092(5)
Co(1)-O(1W)#3	2.089(5)
Co(2)-O(6W)#4	2.110(7)
Co(2)-O(7W)#4	2.056(7)
Co(2)-O(8W)#4	2.102(6)
O(26)-Co(1)-O(1W)	94.97(18)
O(26)-Co(1)-O(1W)#3	85.03(18)
O(26)-Co(1)-N(3)	88.65(19)
O(26)-Co(1)-N(3)#3	91.35(19)
O(1W)-Co(1)-N(3)	88.1(2)
O(1W)-Co(1)-N(3)#3	91.9(2)
O(7W)-Co(2)-O(6W)	95.3(4)
O(7W)#4-Co(2)-O(6W)	84.7(4)
O(7W)-Co(2)-O(8W)	89.0(3)
O(7W)-Co(2)-O(8W)#4	91.0(3)
O(8W)-Co(2)-O(6W)	88.1(3)
O(8W)-Co(2)-O(6W)#4	91.9(3)

Symmetry transformations used to generate equivalent atoms:
#3 -x+2,-y+1,-z+1; #4 -x+1,-y+2,-z+2.

Table S4. Selected bond lengths [Å] and angles [deg] for **3**.

Cu(1)-N(3)	1.932(10)
Cu(1)-N(7)	1.949(10)
Cu(1)-O(13)#1	2.270(8)
Cu(1)-O(22)#2	2.437(9)
Cu(2)-N(4)	1.930(9)
Cu(2)-N(1)	1.935(10)
Cu(2)-O(21)	2.299(8)
Cu(3)-N(8)	1.895(10)
Cu(3)-N(5)#3	1.905(11)
N(3)-Cu(1)-N(7)	149.6(4)
N(3)-Cu(1)-O(13)#1	114.1(4)
N(7)-Cu(1)-O(13)#1	88.2(3)
N(3)-Cu(1)-O(22)#2	91.6(4)
N(7)-Cu(1)-O(22)#2	111.6(4)
O(13)#1-Cu(1)-O(22)#2	85.1(3)
N(4)-Cu(2)-N(1)	164.8(4)

N(4)-Cu(2)-O(21)	96.7(4)
N(1)-Cu(2)-O(21)	95.9(4)
N(8)-Cu(3)-N(5)#3	176.7(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z; #2 -x+1,-y,-z; #3 x-1, y, z.

Table S5. Thermodynamic data of the involved polyanions: entropy and enthalpy

Polyanion	ΔH_{298} (kcal mol^{-1})	ΔS_{298} (kcal K^{-1} mol^{-1})
β-$[Mo_8O_{26}]^{4-}$	79.58	0.2418
$[Mo_6O_{19}]^{2-}$	56.82	0.1763
$[Mo_2O_7]^{2-}$	19.06	0.1064

The following reaction[4a] was studied and exploited through quantum chemical calculations:

$$[Mo_8O_{26}]^{4-}(aq) \overset{\Delta_R G}{=\!=} [Mo_6O_{19}]^{2-}(aq) + [Mo_2O_7]^{2-}(aq) \quad (1)$$

The optimized calculations were first performed at the polyanions β-$[Mo_8O_{26}]^{4-}$, $[Mo_6O_{19}]^{2-}$ and $[Mo_2O_7]^{2-}$ in order to find the structure with the lowest energy for each studied polyanion. Three optimized structures are shown in Fig. S7. Then, the entropy and enthalpy for the reaction depicted in Equation (1) can be obtained through the corresponding frequency calculations. These values are summarized in Table S5. According to the second law of thermodynamics, the Gibbs free energy ΔG is defined as:

$$\Delta_R G = \Delta_R H - T\Delta_R S \quad (2)$$

which could tell us about the spontaneity of the reaction. Taking into account the known thermodynamic data for Equation (1), $\Delta_R H$ = -3.70 kcal mol^{-1}, $\Delta_R S$ = 0.0409 kcal K^{-1} mol^{-1}. Then the obtained Gibbs free energy is $\Delta_R G$ = -15.89 kcal mol^{-1}, which indicates Equation (1) is a favored reaction, and $[Mo_6O_{19}]^{2-}$ polyanion is a spontaneous product.

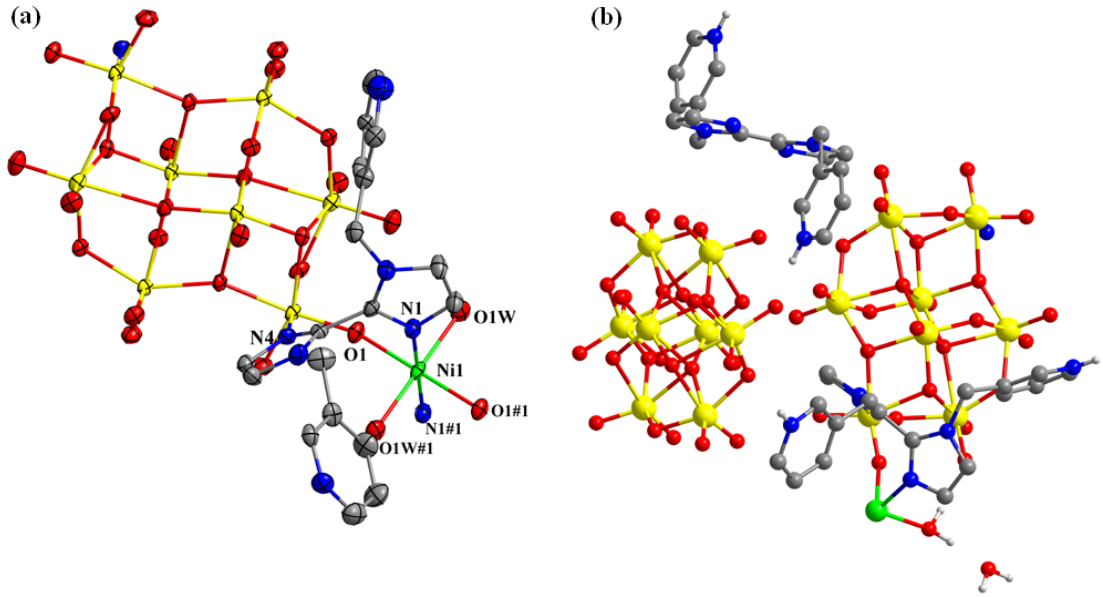

Fig. S1. (a) Coordination mode of Ni atom in compound **1** with 50% thermal ellipsoids. (b) The asymmetric unit in compound **1**.

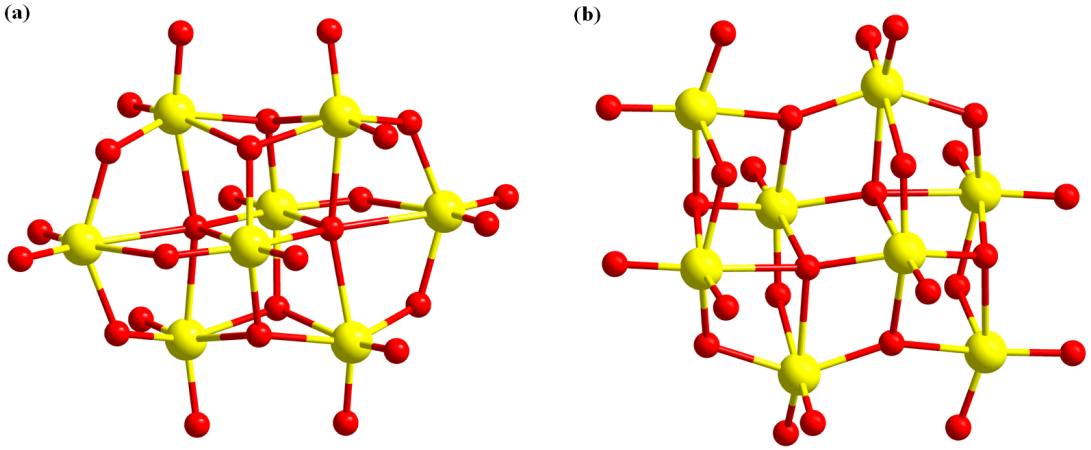

Fig. S2. (a) The configuration of β-$[Mo_8O_{26}]^{4-}$ anion. (b) The configuration of γ-$[Mo_8O_{26}]^{4-}$ anion.

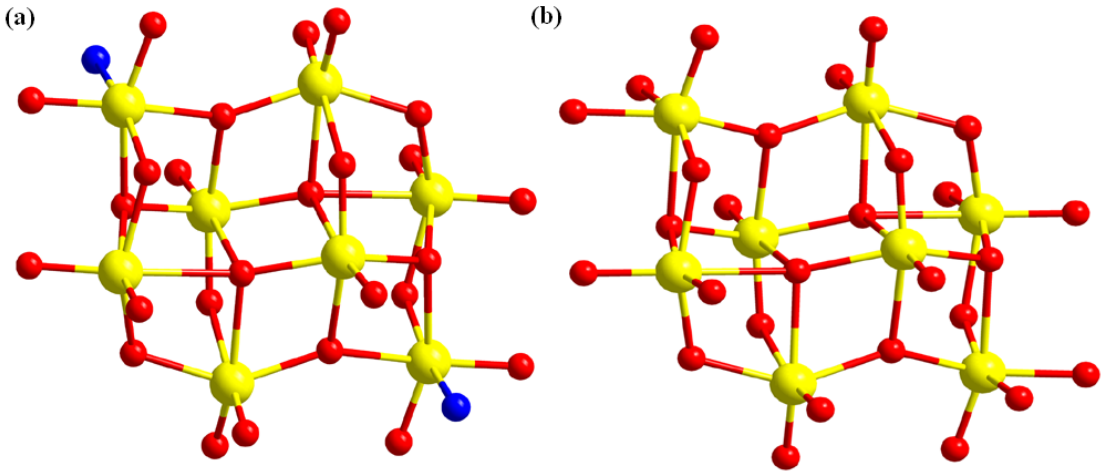

Fig. S3. Two kinds of occupied of γ-octamolybdate: (a) γ-[$Mo_8O_{26}N_2$] and (b) γ-[Mo_8O_{28}]

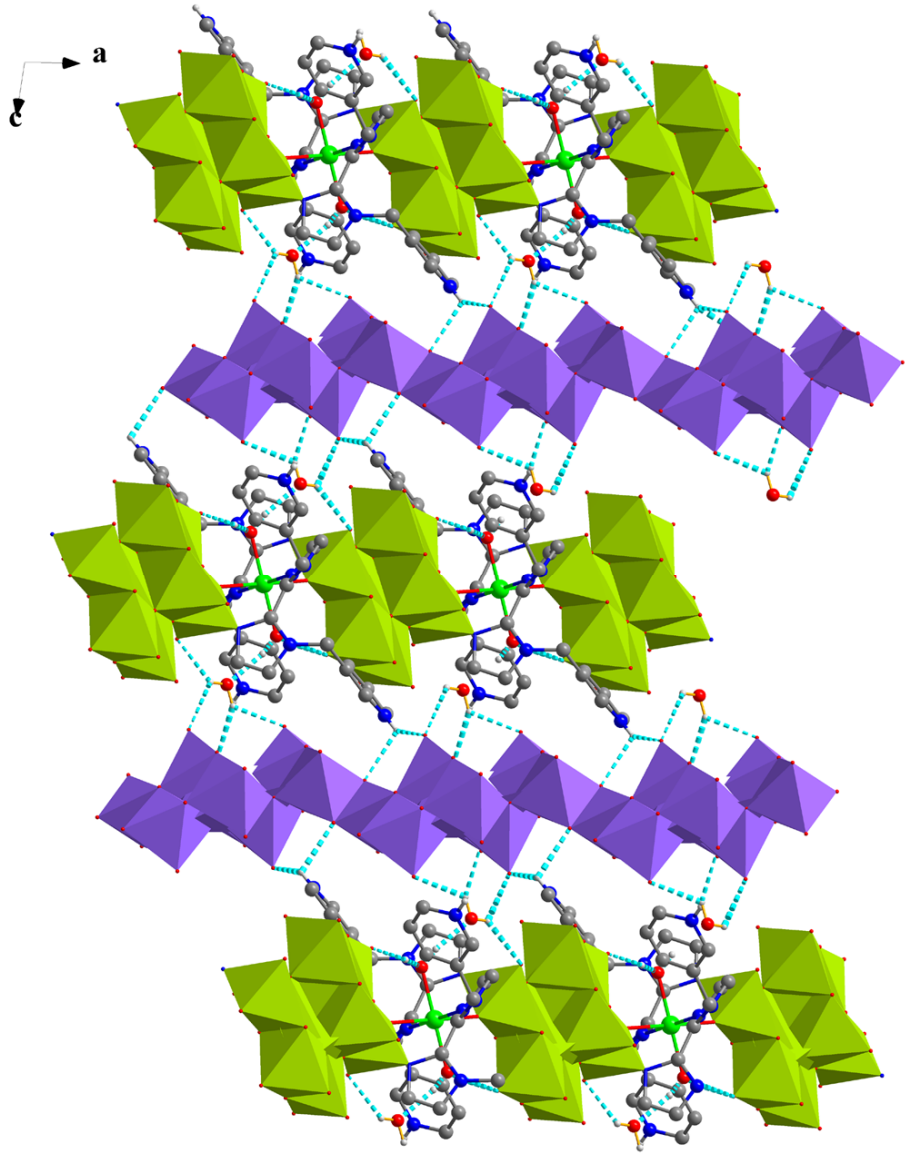

Fig. S4. View of the 3D supramolecular structure of compound **1** along *b* axis.

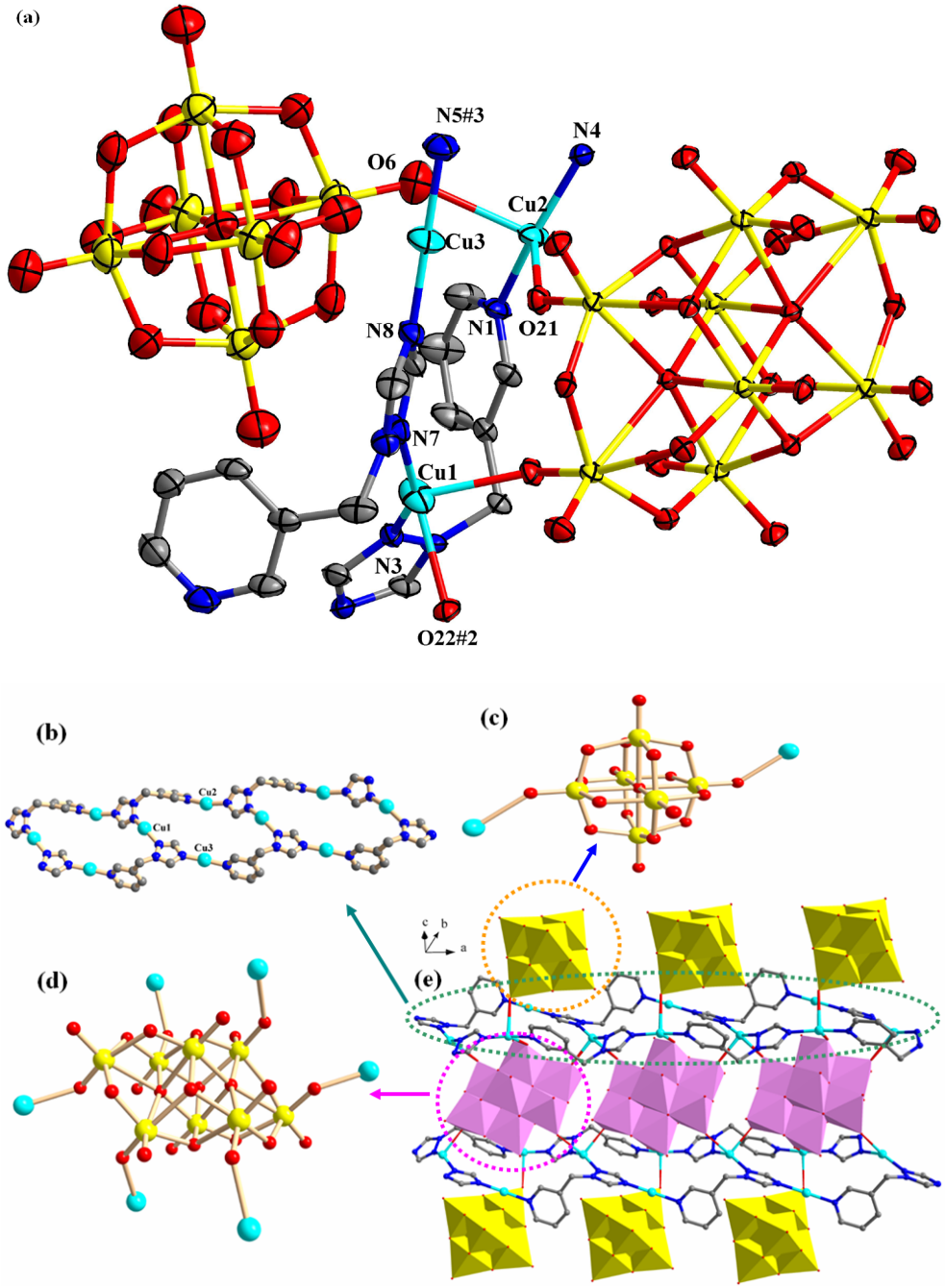

Fig. S5. (a) Coordination environment of the Cu^{I} center in compound **3** with 50% thermal ellipsoids (All the hydrogen atoms are omitted for clarity). (b) L^2 ligands connect Cu^{I} ions to generate a ladder-like metal-organic chain. (c) Coordination mode of $[Mo_6O_{19}]^{2-}$ anion. (d) Coordination mode of $[Mo_8O_{26}]^{4-}$ anion. (e) The linking modes of $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$ with metal-organic chains. Symmetry code:

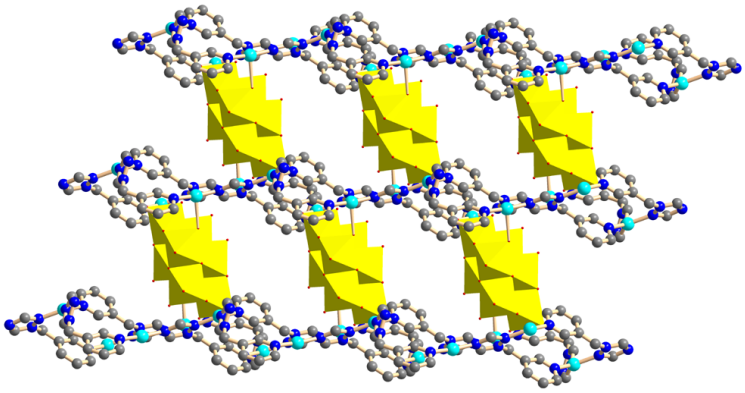

Fig. S6. The octamolybdate anions pillar the metal organic belts.[30c]

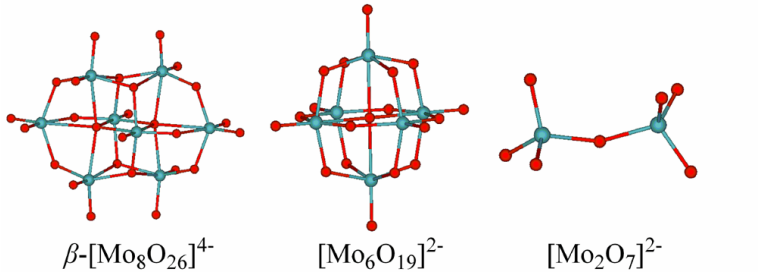

Fig. S7. Optimized structures for the polyanions β-$[Mo_8O_{26}]^{4-}$, $[Mo_6O_{19}]^{2-}$ and $[Mo_2O_7]^{2-}$.

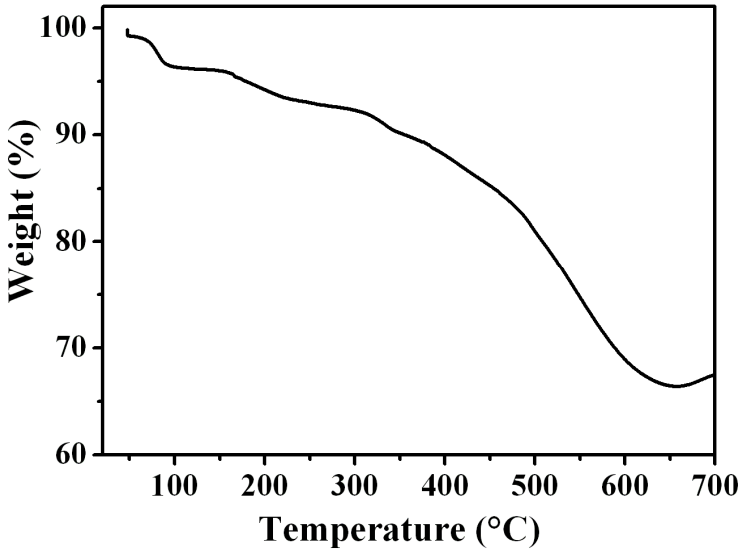

Fig. S8. The TG curve of compound **1**.

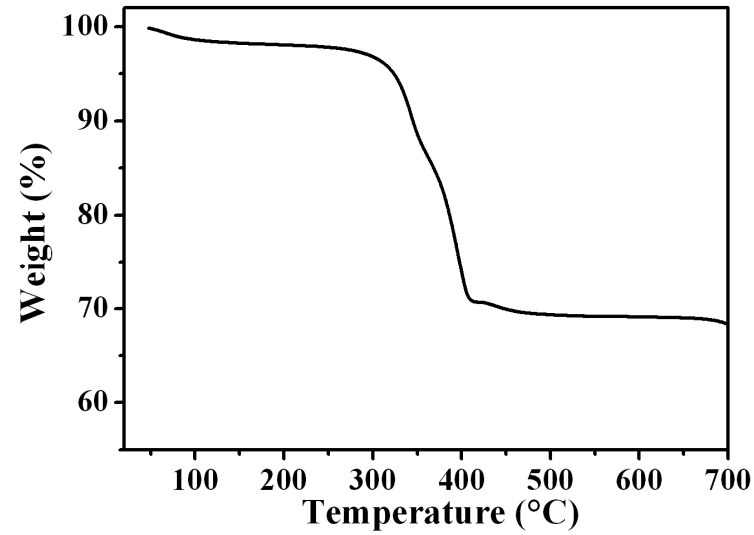

Fig. S9. The TG curve of compound **2**.

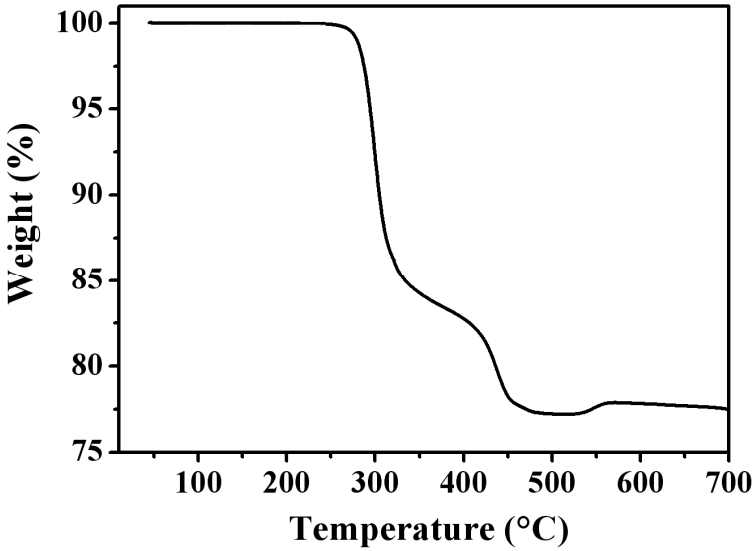

Fig. S10. The TG curve of compound **3**.

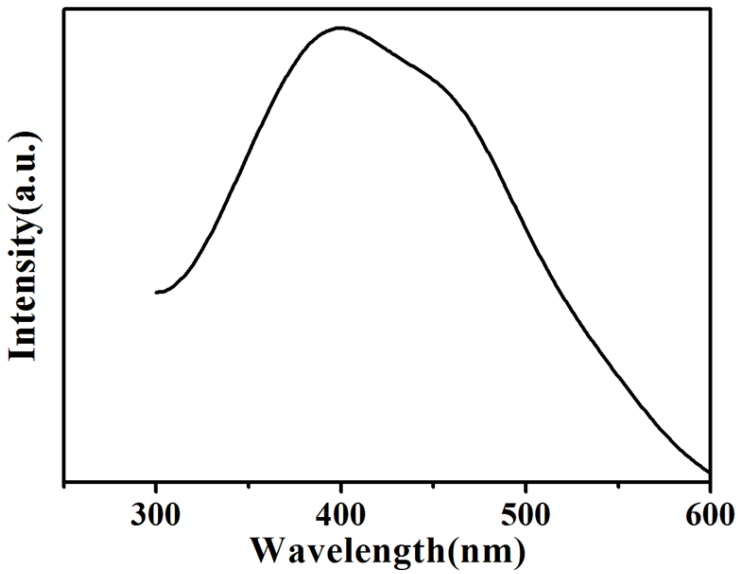

Fig. S11. Photoluminescent spectrum of compound **3**.