

由氢键连接的三个金属-有机网状化合物的合成、结构及半导体性质

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摘要: 以 2,4,6-三(1-吡唑基)-1,3,5-三嗪(TPTz)与不同金属离子进行溶剂热反应,得到了 3 个氢键连接的金属-有机网状化合物。实验发现 TPTz 的水解产物 6-(1-吡唑基)-1,3,5-三嗪-2,4-二酚(H_2L)在反应中起到了实际的配位作用。单晶结构分析表明,它们是同构化合物,分子式为 $[M(HL)_2] \cdot 2H_2O$ ($M=Zn, 1; Co, 2; Mn, 3$)。每个中心金属原子分别与 2 个吡唑基上的 N、2 个吡嗪环上的 N 和 2 个水分子中的 O 形成六配位的结构。2 个 HL^- 与 1 个中心金属配位形成一个零维的金属-有机配合物小分子,这些小分子通过氢键连接进一步拓展为二维层状结构。紫外-可见漫反射(UV-Vis DRS)分析结果表明,这 3 种化合物都是宽禁带半导体材料,其带隙宽度分别为 3.80(Zn), 3.30(Co), 3.27(Mn) eV, 其半导体性质同中心金属原子表现出明显的相关性。

关键词: 金属-有机网状化合物; 氢键; 2,4,6-三(1-吡唑基)-1,3,5-三嗪

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Three Hydrogen-Bonded Metal-Organic Networks with Tunable Semiconductor Properties

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Abstract: Solvothermal reaction of 2,4,6-tris(pyrazole-1-yl)-1,3,5-s-triazine (TPTz) and three metal ions resulted in the formation of three hydrogen-bonded metal-organic networks. It's found that 6-(pyrazole-1-yl)-1,3,5-triazine-2,4-diol (H_2L) hydrolyzed from TPTz acts as the ligand in reality. Single-crystal structure analysis shows that the three compounds are isomorphous with the formula of $[M(HL)_2] \cdot 2H_2O$ ($M=Zn, 1; Co, 2; Mn, 3$). The center metal ion is six-coordinated by two N atoms from pyrazolyl, two N atoms from triazine ring and two O atoms from waters, respectively. Two HL^- coordinate to one center metal ion forming a zero-dimensional metal-organic molecular, which was linked by the hydrogen bond, and then extended to a two-dimensional layer network. UV-Vis DRS analysis shows that they are all wide band semiconductors with a band-gap of 3.80 (Zn), 3.30 (Co), 3.27 (Mn) eV, respectively, showing an obvious dependence on their center metal ions. CCDC: 904985, **1**; 904986, **2**; 904987, **3**.

Keywords: metal-organic networks; hydrogen-bond; 2,4,6-tris(pyrazole-1-yl)-1,3,5-s-triazine

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0 Introduction

During the past two decades, metal-organic frameworks (MOFs) have attracted more and more attention not only because of their high porosity and regularity structures but also due to that they usually showed versatile excellent properties such as in catalysis^[1], gas adsorption and separation^[2], chemical sensor^[3], magnetism^[4] and luminescence^[5]. Among which, it is recently clearly pointed out that MOFs can take potential important usage as semiconductors^[6]. The most-studied such MOFs were focused on materials assembled by carboxylates and d^{10} metals, MOF-5 is a typical example, it is a wide band-gap semiconductor with a band gap of 3.4 eV which was estimated by its UV-Vis diffuse reflectance spectrum^[6a] (usually materials with a band-gap over 2.0 eV were defined as wide band semiconductors, such as GaN, $E_g=3.4$ eV, SiC, $E_g=2.86$ eV and ZnO, $E_g=3.4$ eV). These materials are widely used in ultraviolet optoelectronic devices, field emission devices and electronic devices undergo conditions of high temperature, high frequency and high power^[7].

Although basically proposed during the same period around the early 1990s with MOFs, research on the hydrogen-bonded organic frameworks (HOFs) has been significantly lagging behind, as their hydrogen-bonding interactions are typically too weak to stabilize the framework, thus is more fragile and usually without any permanent porosities^[8]. Recently, there has been a renewed interest in the exploration of porous HOFs, since some progress has been made to stabilize HOFs and thus to establish permanent porosities, which exemplifying the bright promise of HOFs as new category of functional materials^[9]. However, as to our knowledge, most research of their functional properties are focused on their gas separation behavior, semiconductor properties of HOFs are still rarely mentioned in the literature^[10]. Thus hydrogen-bonded metal-organic networks which simultaneously possess two distinct properties of MOFs and HOFs, is still out of the public attention^[11].

For a category of materials, taking potential

usage as semiconductors, flexible modulating of their band-gap and thus with different semiconductor properties should be necessary^[12]. Both experimental and theoretical studies showed that for MOFs assembled by carboxylates, their unique structures together with the organic ligands play important roles in their band-gap values, while isomorphous complexes with different center metal ions just show tiny difference^[7,13]. On tuning of their semiconductor properties, the common experimental method involved: (1) To regulate the size of their secondary building units (SBUs), since enlargement of SBU brings with a decrement on their band gap values^[14]; (2) to modify various substituents or change the size on the ligands, one can also tune their band-gap^[12-13].

In conflict with that of MOFs formed by carboxylates, herein, we will show that by using a N-donor ligand, the center metal ions of three isomorphous hydrogen-bonded metal-organic networks make great impact on their semiconductor properties, which has guiding significance for the synthesis of some novel compounds with tunable semiconductor properties.

1 Experimental

1.1 Materials and methods

Elemental analyses of C, H, N were performed on an Elementar Vario MICRO Elemental Analyzer. Fourier Transform Infrared (FT-IR) spectra were obtained on a Bruker Vector 22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of $5^{\circ}\sim 50^{\circ}$ on a Bruker D8 advance instrument using $\text{Cu K}\alpha$ ($\lambda=0.154\text{ }178\text{ nm}$) radiation at room temperature. Ultraviolet visible diffused reflection spectra (UV-Vis DRS) were recorded on Varian Cary 5000 UV-Vis-NIR, corrected by BaSO_4 . Reagents and solvents were commercially available and used as received without further purification. The ligand 2,4,6-tris(pyrazole-1-yl)-1,3,5-s-triazine (TPTz) was prepared according to the reported procedure^[15].

1.2 Synthesis of compounds 1~3

Compounds **1~3** was synthesized by a solvothermal reaction of TPTz with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the mixture of *N,N*-dimethyl formamide (DMF) and H_2O solvent, respectively. Details were shown below.

Synthesis of $[\text{Zn}(\text{HL})_2] \cdot 2\text{H}_2\text{O}$ (**1**): $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (59.4 mg, 0.2 mmol) and TPTz (27.9 mg, 0.1 mmol) were dissolved in the mixture of DMF (3 mL) and H_2O (1 mL), then the solution was transferred into a vial, sealed and heated at 100 °C for 2 days. The vial was then allowed to cool down to room temperature. Colorless crystals (33 mg) were obtained by filtration and washed with DMF and ether, respectively. Yield: 73% (based on TPTz). Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Zn}$ (%): C, 31.49; H, 2.64; N, 30.60; Found(%): C, 31.60; H, 2.14; N, 30.68. FTIR (KBr, cm^{-1}): 3 310(w), 3 160(s), 3 040(s), 2 810(s), 1 700(w), 1 480(s), 1 390(s), 1 210(m), 1 090(m), 1 050(s), 970(m), 924(s), 795(m), 640(s), 471(m).

Synthesis of $[\text{Co}(\text{HL})_2] \cdot 2\text{H}_2\text{O}$ (**2**): Orange rhombic crystals of **2** were obtained following the same procedure as **1** with the replacement of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Yield: 83% (based on TPTz). Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Co}$ (%): C, 31.94; H, 2.68; N, 31.04; Found (%): C, 32.01; H, 2.18; N, 31.24. FTIR (KBr, cm^{-1}): 3 300(w), 3 160(s), 3 030(s), 2 800(s), 1 700(w), 1 560(s), 1 480(m), 1 390(m), 1 210(m), 1 090(s), 1 050(m), 966(m), 922(s), 796(s), 644(s), 471(m).

Synthesis of $[\text{Mn}(\text{HL})_2] \cdot 2\text{H}_2\text{O}$ (**3**): The preparation of **3** was similar to that of **1**, but $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (59.4 mg, 0.2 mmol) was substituted by $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50.2 mg, 0.2 mmol), colorless crystals of **3** were isolated with a yield of 65% (based on TPTz). Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Mn}$ (%): C, 32.23; H, 2.70; N, 31.32%; Found(%): C, 31.72; H, 2.26; N, 30.74. FTIR (KBr, cm^{-1}): 3 280(w), 3 160(s), 3 040(s), 2 810(s), 1 700(w), 1 560(s), 1 480(m), 1 400(m), 1 210(m), 1 090(s), 1 050(m), 970(m), 924(s), 872(s), 653(s), 471(m).

1.3 Single-crystal X-ray crystallography

The suitable crystals of compounds **1~3** were selected for single-crystal X-ray diffraction. The data collections were carried out on a Bruker Smart APEX II CCD diffractometer at 296 K, using graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Data reductions and absorption corrections were performed using the SAINT and SADABS programs^[16], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on F^2 using the SHELXL-97 program^[17]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. Details of the crystal parameters, data collection and refinements for compounds **1~3** are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

CCDC: 904985, **1**; 904986, **2**; 904987, **3**.

Table 1 Crystallographic data for compounds 1~3

Compound reference	1	2	3
Chemical formula	$\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Zn}$	$\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Co}$	$\text{C}_{12}\text{H}_{12}\text{N}_{10}\text{O}_6\text{Mn}$
Formula weight	457.69	451.25	447.26
Crystal system	Triclinic	Triclinic	Triclinic
<i>a</i> / nm	0.722 81(9)	0.721 5(6)	0.724 28(10)
<i>b</i> / nm	0.740 15(9)	0.738 9(6)	0.751 82(10)
<i>c</i> / nm	0.826 15(10)	0.830 1(7)	0.830 76(11)
α / (°)	104.862 0(10)	104.474(8)	105.172 0(10)
β / (°)	97.825 0(10)	97.988(9)	98.313(2)
γ / (°)	104.022 0(10)	104.253(8)	104.432(2)
Volume / nm ³	0.405 09(9)	0.405 7(6)	0.412 04(10)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>Z</i>	1	1	1

Continued Table 1

Reflections measured	2 922	2 930	2 949
Independent reflections	1 446	1 449	1 447
R_1 ($I > 2\sigma(I)$)	0.026 8	0.040 3	0.038 9
wR (F^2) ($I > 2\sigma(I)$)	0.081 5	0.109 1	0.115 7
R_1 (all data)	0.027 1	0.050 4	0.042 0
wR (F^2) (all data)	0.081 7	0.129 1	0.117 9
Goodness of fit on F^2	0.990	1.065	1.038

Table 2 Selected bond lengths (nm) and angles ($^\circ$) of compounds 1-3

1					
Zn(1)-O(1W) ⁱ	0.213 76(18)	Zn(1)-N(5) ⁱ	0.218 26(19)	Zn(1)-N(1)	0.219 67(19)
Zn(1)-O(1W)	0.213 76(18)	Zn(1)-N(1) ⁱ	0.219 67(19)	Zn(1)-N(5)	0.218 26(19)
O(1W) ⁱ -Zn(1)-O(1W)	180.000(1)	N(5) ⁱ -Zn(1)-N(5)	180.00(5)	N(5) ⁱ -Zn(1)-N(1) ⁱ	74.26(7)
O(1W) ⁱ -Zn(1)-N(5) ⁱ	90.58(7)	O(1W) ⁱ -Zn(1)-N(1)	90.47(7)	O(1W)-Zn(1)-N(1) ⁱ	90.51(7)
O(1W)-Zn(1)-N(5) ⁱ	89.42(7)	O(1W)-Zn(1)-N(1)	89.53(7)	O(1W) ⁱ -Zn(1)-N(1) ⁱ	89.49(7)
O(1W) ⁱ -Zn(1)-N(5)	89.42(7)	N(1)-Zn(1)-N(1) ⁱ	180	N(5)-Zn(1)-N(1)	74.26(7)
O(1W)-Zn(1)-N(5)	90.58(7)	N(5)-Zn(1)-N(1) ⁱ	105.74(7)	N(5) ⁱ -Zn(1)-N(1)	105.74(7)
2					
Co(1)-O(1W)	0.204 8(3)	Co(1)-N(5) ⁱ	0.217 3(3)	Co(1)-N(1) ⁱ	0.219 9(3)
Co(1)-O(1W) ⁱ	0.204 8(3)	Co(1)-N(1)	0.219 9(3)	Co(1)-N(5)	0.217 3(3)
O(1W)-Co(1)-O(1W) ⁱ	180.000(1)	N(5)-Co(1)-N(1) ⁱ	105.00(11)	N(1) ⁱ -Co(1)-N(1)	180
O(1W)-Co(1)-N(5) ⁱ	89.59(11)	O(1W)-Co(1)-N(1)	89.86(12)	O(1W) ⁱ -Co(1)-N(1)	90.17(12)
O(1W) ⁱ -Co(1)-N(5) ⁱ	90.41(11)	O(1W)-Co(1)-N(5)	90.41(11)	N(5) ⁱ -Co(1)-N(1)	105.99(11)
O(1W) ⁱ -Co(1)-N(1) ⁱ	89.86(12)	O(1W) ⁱ -Co(1)-N(5)	89.59(11)	N(5)-Co(1)-N(1)	74.01(11)
N(5) ⁱ -Co(1)-N(1) ⁱ	74.01(11)	N(5) ⁱ -Co(1)-N(5)	180.000(1)		
3					
Mn(1)-O(1W) ⁱ	0.220 8(2)	Mn(1)-N(1)	0.225 7(2)	Mn(1)-N(5) ⁱ	0.225 7(2)
Mn(1)-O(1W)	0.220 8(2)	Mn(1)-N(5)	0.225 7(2)	Mn(1)-N(1) ⁱ	0.225 7(2)
O(1W) ⁱ -Mn(1)-O(1W)	180.000(1)	N(1) ⁱ -Mn(1)-N(5) ⁱ	71.03(7)	O(1W)-Mn(1)-N(5) ⁱ	89.77(8)
O(1W) ⁱ -Mn(1)-N(1)	90.01(8)	N(1)-Mn(1)-N(5)	71.03(7)	N(1)-Mn(1)-N(5) ⁱ	108.98(7)
O(1W)-Mn(1)-N(1)	89.99(8)	N(1) ⁱ -Mn(1)-N(5)	108.97(7)	O(1W) ⁱ -Mn(1)-N(5)	89.83(8)
O(1W) ⁱ -Mn(1)-N(1) ⁱ	89.99(8)	N(1)-Mn(1)-N(1) ⁱ	180.00(1)	O(1W)-Mn(1)-N(5)	90.17(8)
O(1W)-Mn(1)-N(1) ⁱ	90.01(8)	O(1W) ⁱ -Mn(1)-N(5) ⁱ	90.23(8)	N(5) ⁱ -Mn(1)-N(5)	180.00(6)

Symmetry codes: ⁱ $-x+1, -y+2, -z+1$

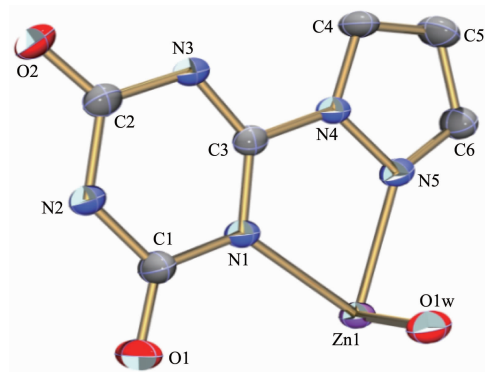
2 Results and discussion

2.1 Crystal structures of compounds 1-3

Single-crystal X-ray diffraction analysis reveal that **1**, **2** and **3** are isomorphous, so compound **1** is chosen to describe the crystal structure. The minimum asymmetric unit of **1** is shown in Fig.1, from which we

can see that TPTz was hydrolyzed in the coordination reaction, with two pyrazolyl substituted by oxygen atoms, while the remaining unhydrolyzed pyrazolyl coordinates with metal ions. Hydrolysis of triazine ligands was previously reported by Manzur et al.^[18], where Cu²⁺ can catalyze TPTz hydrolyzed into the same product as we got in methanol system, while Zhou et al.

found that in methanol system TPTz hydrolyzed to 2,4,6-trimethoxy-1,3,5-triazine catalyzed by Zn^{2+} , elsewhere Hg^{2+} can't catalyze the hydrolysis process of TPTz^[19].



H atoms are omitted for clarity

Fig.1 ORTEP drawings of the minimum asymmetric unit of **1** with the thermal ellipsoids drawn at 50% probability

As shown in Fig.2, it is clear to see that the center Zn atom is six-coordinated by two N atoms from pyrazolyl, two N atoms from triazine ring and two O atoms from water, respectively. While two HL^- ligands coordinate to one center metal forming a simple zero-dimensional compound.

PLATON simulation shows that there are plenty of hydrogen bonds in compound **1**, as shown in Fig.3, H1W^i and H1W^{ii} formed hydrogen bonds with N3 and O2 atoms of the adjacent compound, respectively.

Table 3 Hydrogen bond lengths (nm) and bond angles ($^\circ$) in compound **1**

D-H \cdots A	d(D-H) / nm	d(H \cdots A) / nm	d(D \cdots A) / nm	$\angle(\text{DHA}) / (^\circ)$
O1W-H1W ⁱ \cdots N3	0.082(3)	0.214(3)	0.292 0(3)	160(3)
O1W-H1W ⁱⁱ \cdots O2	0.083(3)	0.191(3)	0.272 0(3)	167(3)
C6-H6 ⁱⁱⁱ \cdots O1 (intramolecular)	0.093	0.221	0.291 7(4)	133

Symmetry codes: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $x+1, y+1, z$; ⁱⁱⁱ $-x+1, -y+2, -z+1$

While H6^{iii} and O1 formed intramolecular hydrogen bond in the complex. The hydrogen bond lengths and bond angles are listed in Table 3. The hydrogen bond linked the simple zero-dimensional complex, and then extended to a two-dimensional layer system along the *c*-axis (Fig.4). As viewed along the *b*-axis orientation,

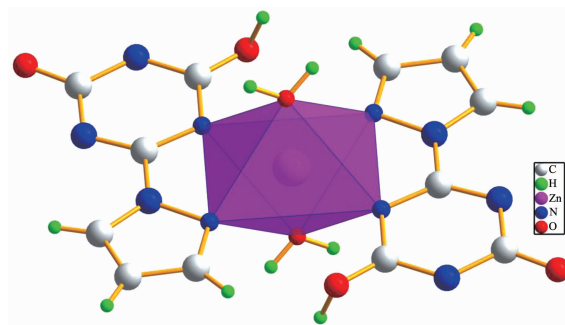


Fig.2 Zero-dimensional complex formed by HL^- and the metal ion

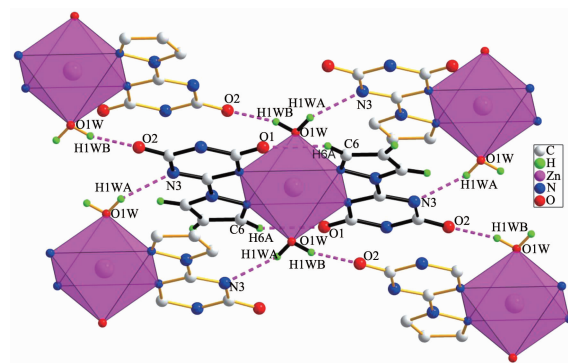


Fig.3 Hydrogen bonds formed in compound **1**

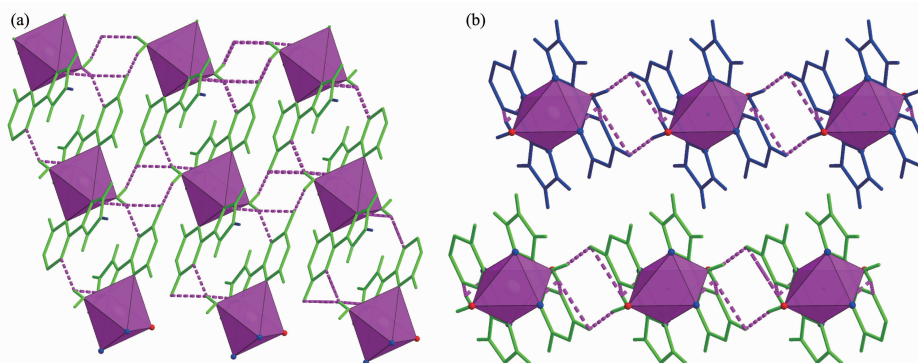


Fig.4 Layers formed by hydrogen bonds viewed along the *c*-axis orientation (a) and *b*-axis orientation (b)

the layer is isolated by an interval of 0.245 nm, without formation of any hydrogen bond.

2.2 PXRD and thermogravimetric (TG) analysis

The powder X-ray diffraction (PXRD) pattern calculated from the single-crystal structure data of compound **1** is in good agreement with those observed for the as-synthesized compounds **1**~**3**, as shown in Fig.5.

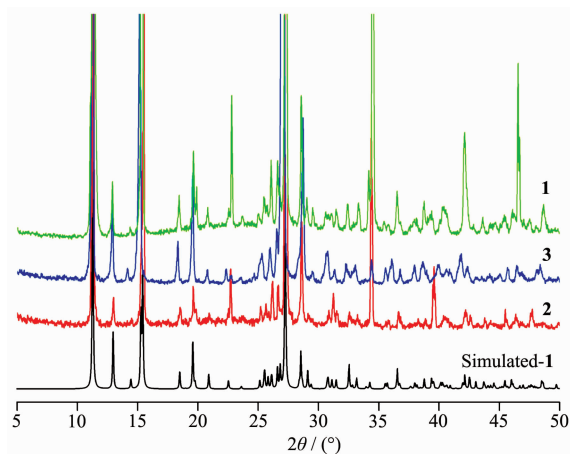


Fig.5 Simulated PXRD pattern of compound **1** and experimental patterns of **1**~**3**

To study the thermal stability of compounds **1**~**3**, thermogravimetric analyses (TGA) were carried out. As shown in Fig.6, compound **2** exhibits obviously weight loss at about 220 °C, while it appears at 260 °C for **1** and **3**, which indicates that compounds **1** and **3** are much more stable than **2**. This difference may be due to their different center metal ions. From 260 to 325 °C, there was a distinct platform in compound **1**, with a weight loss of 7.75% corresponding to the loss of the coordinated water molecules (Calcd. 7.91%), which was not too clear in the curves of **2**

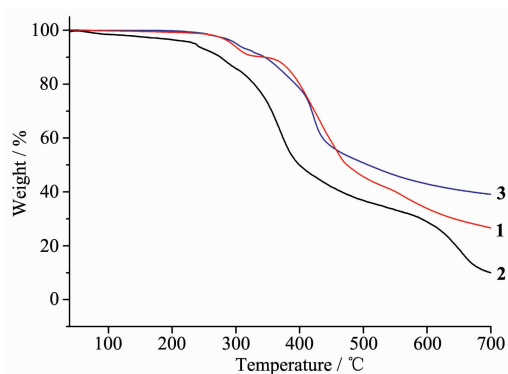


Fig.6 TG curves of compounds **1**~**3**

and **3**. After that, the continuous weight loss without any platform indicates that the ligand decomposed gradually as the temperature increasing.

2.3 UV-Vis DRS analysis and semi-conductive properties

The solid UV-Vis DRS spectra (Fig.7a) clearly shows that the maximum absorption peaks of compounds **1**~**3** locate at 280, 290 and 320 nm, respectively. Besides, there was a broad absorption peak around 470 nm for compound **2** which attributed to the transition energy decrease of π - π^* following the coordination bond formation between Co ion and electro-donating N atom^[5b].

The absorption peak falls sharply from 300 to 400 nm, which implies that the materials may have semiconductor properties. The band gap of material can be calculated from its UV-Vis DRS spectrum by Kubelka-Munk method^[13]: $(\alpha h\nu)^2 = A(h\nu - E_g)$, where h is Planck constant; ν is the frequency; α is the absorption coefficient; A is the proportionality constant; E_g is the band gap. As shown in Fig.7b, the band gap of compound **1** is 3.80 eV, while that for **2** and **3** to be

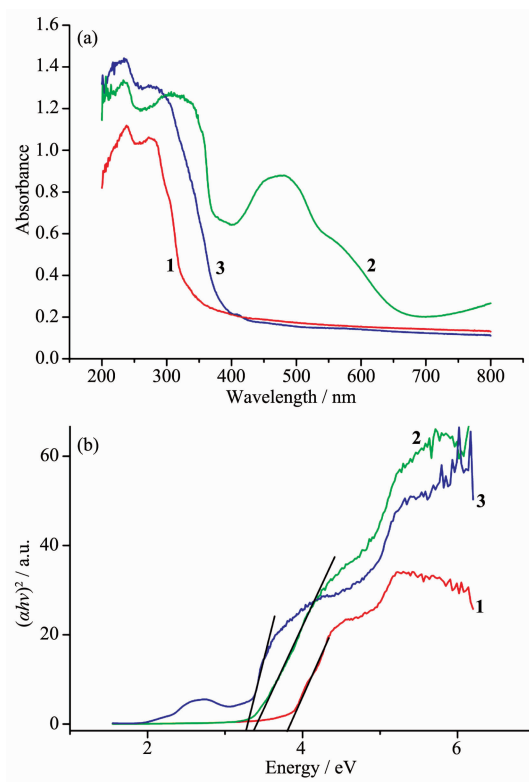


Fig.7 UV-Vis DRS spectra of compounds **1**~**3** (a) and band gaps of **1**~**3** (b)

3.30 and 3.27 eV, respectively. In consideration that **1~3** are isomorphous, it is clear to see that semiconductor properties of these complexes formed from N-donor ligand have important relationship with the center metal ions which is different from the carboxylates. Although the mechanism is still unclear, there is guiding significance for the synthesis of some novel coordination compounds based on N-donor ligands with tunable semiconductor properties.

3 Conclusions

In summary, we have successfully synthesized three isomorphous coordination compounds $[M(HL)_2] \cdot 2H_2O$ ($M=Zn$, **1**; Co , **2**; Mn , **3**) with 6-(pyrezole-1-yl)-1,3,5-triazine-2,4-diol (H_2L) hydrolyzed from TPTz. Two HL^- coordinate to one center metal ion forming a simple zero-dimensional complex, which was linked by the hydrogen bonds, and then extended to a two-dimensional layer system. They are all wide band semiconductors with a band-gap of 3.80 (Zn), 3.30 (Co) and 3.27 (Mn) eV, respectively. The result shows that the center metal ions have significant effect on their semiconductor properties, which has guiding significance for the synthesis of some novel coordination compounds based on N-donor ligands with tunable semiconductor properties.

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