

基于柔性三齿配体的镉(II)和锌(II)配合物的合成、结构和荧光性质

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摘要: 柔性三齿配体 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB) 和 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) 与金属镉(II)和锌(II)分别反应, 合成了配合物 $[\text{Cd}_3(\text{SO}_4)_4(\text{TITMB})_2(\text{H}_2\text{O})_4][\text{Cd}(\text{H}_2\text{O})_6] \cdot 2\text{CH}_3\text{OH}]_n$ (**1**) 和 $[\text{Zn}(\text{TITMB})(\text{HCOO})_2] \cdot \text{CH}_3\text{OH}]_n$ (**2**)。配合物 **1** 和 **2** 均采用单晶 X 射线衍射、红外光谱、固态荧光、热重分析和元素分析进行了表征。在配合物 **1** 中, 存在着由硫酸根离子和 Cd(II) 构成的一维链, 其再与配体 TITMB 配位形成二维层状结构, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ 位于层与层中间平衡电荷。配合物 **2** 具有典型的 6³ 二维蜂窝状拓扑结构。配合物 **1** 和 **2** 中的二维层状结构, 均通过氢键作用延伸成为三维结构。配合物 **1** 和 **2** 均具有较高的热稳定性, 并且在固态下释放蓝色荧光。

关键词: 柔性三齿配体; 配位聚合物; 荧光性质

中图分类号: O614.24²; O614.24¹

文献标识码: A

文章编号: 1001-4861(2017)10-1889-07

DOI: 10.11862/CJIC.2017.196

Syntheses, Crystal Structures and Fluorescence of Cadmium (II) and Zinc (II) Complexes Based on Flexible Tripodal Ligands

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Abstract: Two new coordination polymers, $[\text{Cd}_3(\text{SO}_4)_4(\text{TITMB})_2(\text{H}_2\text{O})_4][\text{Cd}(\text{H}_2\text{O})_6] \cdot 2\text{CH}_3\text{OH}]_n$ (**1**) and $[\text{Zn}(\text{TITMB})(\text{HCOO})_2] \cdot \text{CH}_3\text{OH}]_n$ (**2**), based on the flexible tripodal ligands 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB) and 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB), have been synthesized and characterized by single-crystal XRD analyses, IR spectra, solid state photoluminescence studies, thermogravimetric analyses, and elemental analyses. Single-crystal X-ray diffraction reveals that both complexes **1** and **2** are two-dimensional layers, and extended to three-dimensional structure by hydrogen bonds. In complex **1**, inorganic chains constructed by SO_4^{2-} and Cd(II) are linked by ligand TITMB to the 2D networks, where the $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ units locate in the cavity between two adjacent 2D layers by hydrogen bonds to neutralize the charge. Complex **2** owns typical 6³ 2D topological networks. The thermal stability and photoluminescence property were also studied. Both complexes show high thermal stabilities and display blue fluorescent emissions in the solid state at room temperature. CCDC: 808063, **1**; 808067, **2**.

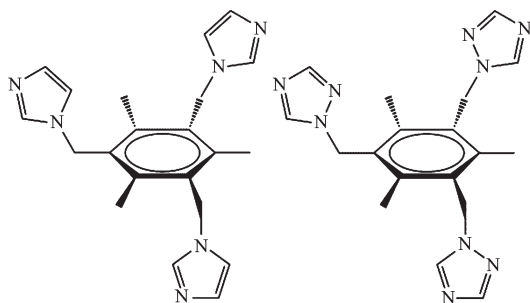
Keywords: flexible tripodal ligand; coordination polymers; luminescence property

收稿日期: 2017-05-02。收修改稿日期: 2017-06-08。

国家自然科学基金国际合作重点项目(No.21420102002)和国家自然科学基金(No.21601088, 21401105)资助。

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In recent years, the rational design and assembly of metal organic frameworks (MOFs) have attracted great attention due to their intriguing framework structures and potential applications in optical, gas storage, catalysis, and so on^[1-8]. In general, the resulted structures of MOFs could be influenced by several factors, such as the selection of metal centers, organic ligands and the reaction pathways^[9]. In contrast to the rigid ligands with fixed conformations, flexible ligands may adopt variable conformations to satisfy the requirement of the center metal ions^[10-11]. In previous work, the utilization of flexible tripodal nitrogen-including ligands have been proved to be effective candidates to build MOF structures, such as 1,3,5-tris(4-pyridylmethyl)benzene^[12], 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene^[13], 1,3,5-tris(1,2,4-triazol-1-ylmethyl)benzene^[14], and 1,3,5-tris(benzimidazole-1-ylmethyl)-2,4,6-trimethylbenzene^[15]. Herein, the structures and properties of two two-dimensional (2D) coordination polymers based on the 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB) and 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) have been synthesized and characterized, where both TITMB and TTTMB ligands have adopted *cis, cis, trans*-configuration (Scheme 1)^[16-18].



Scheme 1 Schematic showing of the *cis, cis, trans*-configuration of ligands TITMB and TTTMB

1 Experimental

1.1 Materials and measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. TITMB and TTTMB were prepared according to the literature methods^[19]. The C,

H and N analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded on a NEXUS 670 spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer instruments Diamond Thermogravimetric/Differential Thermal Analyzer under nitrogen with a heating rate of 10 °C·min⁻¹. The luminescence spectra were measured at room temperature on PEKIN ELMER Luminescence Spectrometer LS50B.

1.2 Synthesis of complex {[Cd₃(SO₄)₄(TITMB)₂(H₂O)₄][Cd(H₂O)₆·2CH₃OH]_n (1)

A mixture of CdSO₄·8/3H₂O (8.54 mg, 0.041 mmol), ligand TITMB (16.6 mg, 0.046 mmol), and 1,4-bis(triazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (*p*-BTMB) (12.4 mg, 0.042 mmol) was suspended in 4 mL mixed solvents of methanol and H₂O (1:3, V/V), and heated in a Teflon-lined steel bomb at 120 °C for 2 d. After the mixture was slowly cooled to room temperature, colorless crystals of **1** were obtained. Anal. Calcd. for C₄₄H₇₆Cd₄N₁₂O₂₈S₄(%): C, 29.37; H, 4.25; N, 9.34. Found (%): C, 29.28; H, 3.88; N, 9.00. IR (KBr, cm⁻¹): 3 381(s), 1 621(m), 1 520(m), 1 457(w), 1 400(w), 1 319(m), 1 246(m), 1 237(m), 1 118(s), 980(w), 935(w), 760(m), 660(m).

1.3 Synthesis of {[Zn(TTTMB)(HCOO)₂]_n·CH₃OH]_n (2)

A mixture of Zn(CH₃COO)₂·2H₂O (87.2 mg, 0.4 mmol), TTTMB (145.6 mg, 0.4 mmol), 1,3-bis(1-imidazo-1-ylmethyl)-2,4,6-trimethylbenzene (*m*-BITMB) (112.0 mg, 0.4 mmol), 3 mL methanol and 1 mL ethanol was placed in a 10 mL glass vial and dissolved by ultrasound. Methanoic acid was added to adjust pH value to 4. The glass vial was transferred into a 30 mL Teflon-lined stainless steel vessel and heated at 80 °C for 3 d. After the mixture was slowly cooled to the room temperature, colorless crystals of **2** were obtained. Anal. Calcd. for C₂₁H₂₇N₉O₅Zn(%): C, 45.74; H, 4.90; N, 22.87. Found (%): C, 45.00; H, 4.80; N, 22.58. IR (KBr, cm⁻¹): 3 398(m), 3 087(m), 3 005(m), 2 821(m), 2 744(w), 1 712(w), 1 611(s), 1 524(m), 1 448(m), 1 339(s), 1 280(s), 1 221(w), 1 201(w), 1 132(s), 1 033(w), 1 013(w), 1 005(w), 994(s), 875(w), 773(m),

674(s).

1.4 X-ray crystal structure determinations

The single crystals of both complexes **1** and **2** were mounted onto thin glass fibers by epoxy glue in air for data collection. And the diffraction data for complexes **1** and **2** were collected on a Bruker Apex 2 CCD with Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) using ω - 2θ scan method at 298 K. An empirical absorption correction was applied. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic molecule were refined in calculated positions, assigned isotropic thermal parameters, and allowed to

ride their parent atoms, while the H atoms for water are located from different map. All calculations were performed using the SHELX-97 program package^[20]. In complex **1**, the sulfate oxygen atoms (O1, O2, O4 and O6, O7, O8) split to two parts with the occupation of 0.66(2) and 0.34(2), 0.59(3) and 0.41(3), respectively. Details of the crystal parameters, data collections and refinements for **1** and **2** are summarized in Table 1. Selected bond lengths and angles, and hydrogen bonds for **1** and **2** are listed in Table 2 and Table 3, respectively.

CCDC: 808063, **1**; 808067, **2**.

Table 1 Crystal data and structural refinement of complexes **1** and **2**

Complex	1	2
Empirical formula	C ₄₄ H ₇₆ Cd ₄ N ₁₂ O ₂₈ S ₄	C ₂₁ H ₂₇ N ₉ O ₅ Zn
Formula weight	1 799.01	550.89
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.027 61(11)	0.914 93(9)
b / nm	1.233 42(15)	1.259 85(13)
c / nm	1.469 65(16)	1.291 34(15)
α / (°)	68.646(1)	61.093(1)
β / (°)	84.642(2)	84.690(2)
γ / (°)	69.495(1)	68.873(1)
V / nm ³	1.623 7(3)	1.209 4(2)
Z	1	2
D_c / (g·cm ⁻³)	1.846	1.513
μ / mm ⁻¹	1.51	1.07
$F(000)$	904	572
GOF	1.028	1.047
Collected reflection	8 251	6 403
Unique reflection	5 587	4 186
R_1	0.060	0.093
wR_2	0.184	0.235

Table 2 Selected bond lengths (nm) and angles (°) for complexes **1** and **2**

Complex 1					
Cd1-N9	0.221 4(7)	Cd2-N6	0.225 1(7)	Cd1-O1	0.257(2)
Cd1-N3	0.224 0(6)	Cd2-O5	0.234 3(6)	Cd1-O9	0.262 0(10)
Cd1-O2C	0.225 0(12)	Cd2-O10	0.239 1(8)	Cd3-O12	0.230 8(5)
Cd1-O6B	0.239 7(18)	Cd3-O13	0.223 4(8)	Cd3-O11	0.232 2(6)
Cd1-O2	0.262 8(12)				
N9-Cd1-N3	173.7(3)	O6B-Cd1-O2	162.1(5)	N3-Cd1-O6B	80.9(5)
N9-Cd1-O2C	94.4(4)	O6B-Cd1-O1	142.7(7)	N3-Cd1-O2C	91.9(4)

Continued Table 1

N9-Cd1-O2	91.6(3)	O9-Cd1-O2	119.7(4)	N3-Cd1-O9	84.2(3)
N9-Cd1-O6B	97.3(5)	O9-Cd1-O1	67.0(7)	N3-Cd1-O1	90.2(7)
N9-Cd1-O9	89.5(3)	O9-Cd1-O6B	76.1(5)	N3-Cd1-O2	91.8(3)
N9-Cd1-O1	87.7(7)	O1-Cd1-O2	52.8(7)	O2C-Cd1-O6B	104.3(5)
O2C-Cd1-O9	176.0(4)	O2C-Cd1-O1	112.2(7)	O2C-Cd1-O2	59.4(5)
N6-Cd2-O5	89.0(2)	O13-Cd3-O12	91.9(3)	N6-Cd2-O10	84.6(3)
O5D-Cd2-O5	180	O13-Cd3-O12A	88.1(3)	N6D-Cd2-N6	180
N6-Cd2-O10D	95.4(3)	O12-Cd3-O12A	180	N6-Cd2-O5D	91.0(2)
O5-Cd2-O10D	90.2(2)	O12-Cd3-O11A	92.9(2)	O5-Cd2-O10	89.8(2)
O12-Cd3-O11	87.1(2)	O13A-Cd3-O11	89.2(3)	O10D-Cd2-O10	180
O13A-Cd3-O13	180	O13-Cd3-O11	90.8(3)	O11A-Cd3-O11	180
Complex 2					
Zn1-O3	0.207 2(6)	Zn1-N6	0.207 5(6)	Zn1-O2	0.217 2(8)
Zn1-N3	0.209 3(6)	Zn1-N9	0.226 1(6)	Zn1-O1	0.238 9(8)
O3-Zn1-N6	91.1(2)	O3-Zn1-N3	91.9(2)	O3-Zn1-O1	92.9(3)
N6-Zn1-N3	108.0(2)	O3-Zn1-O2	91.6(3)	N3-Zn1-O1	99.1(3)
N6-Zn1-O2	94.8(3)	N3-Zn1-O2	156.9(3)	N9-Zn1-O1	83.4(2)
O3-Zn1-N9	176.2(2)	N6-Zn1-N9	91.9(2)	N6-Zn1-O1	152.4(3)
N3-Zn1-N9	89.5(2)	O2-Zn1-N9	85.8(2)	O2-Zn1-O1	57.8(3)

Symmetry codes: A: 2-x, -y, -z; B: x, 1+y, z; C: 1-x, 2-y, -z; D: -x+2, -y+2, -z+1 for **1**.Table 3 Hydrogen bond lengths (nm) and angles (°) for complexes **1**~**2**

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠ D-H...A / (°)
1				
O9-H9A...O5A	0.085 0	0.195 7	0.278 7(14)	165
O9-H9B...O14	0.095 0	0.229 1	0.300(2)	141
O10-H10A...O8	0.084 9	0.257 6	0.270(2)	123
O11-H11A...O7A	0.085 0	0.214 9	0.299 6(13)	174
O11-H11B...O4B	0.085 0	0.204 7	0.277 5(19)	143
O12-H12A...O3B	0.085 0	0.191 2	0.274 6(12)	167
O12-H12B...O6A	0.085 1	0.212 3	0.296(2)	167
O13-H13C...O8A	0.085 0	0.207 9	0.271(2)	130
O14-H14...O1	0.082 0	0.223 0	0.284(3)	131
2				
O5-H5...O1	0.081 6	0.196 2	0.276(2)	166
C6-H6...O1	0.093 0	0.253 5	0.308 4(12)	118
C2-H2...O4	0.093 0	0.217 3	0.309 5(11)	171

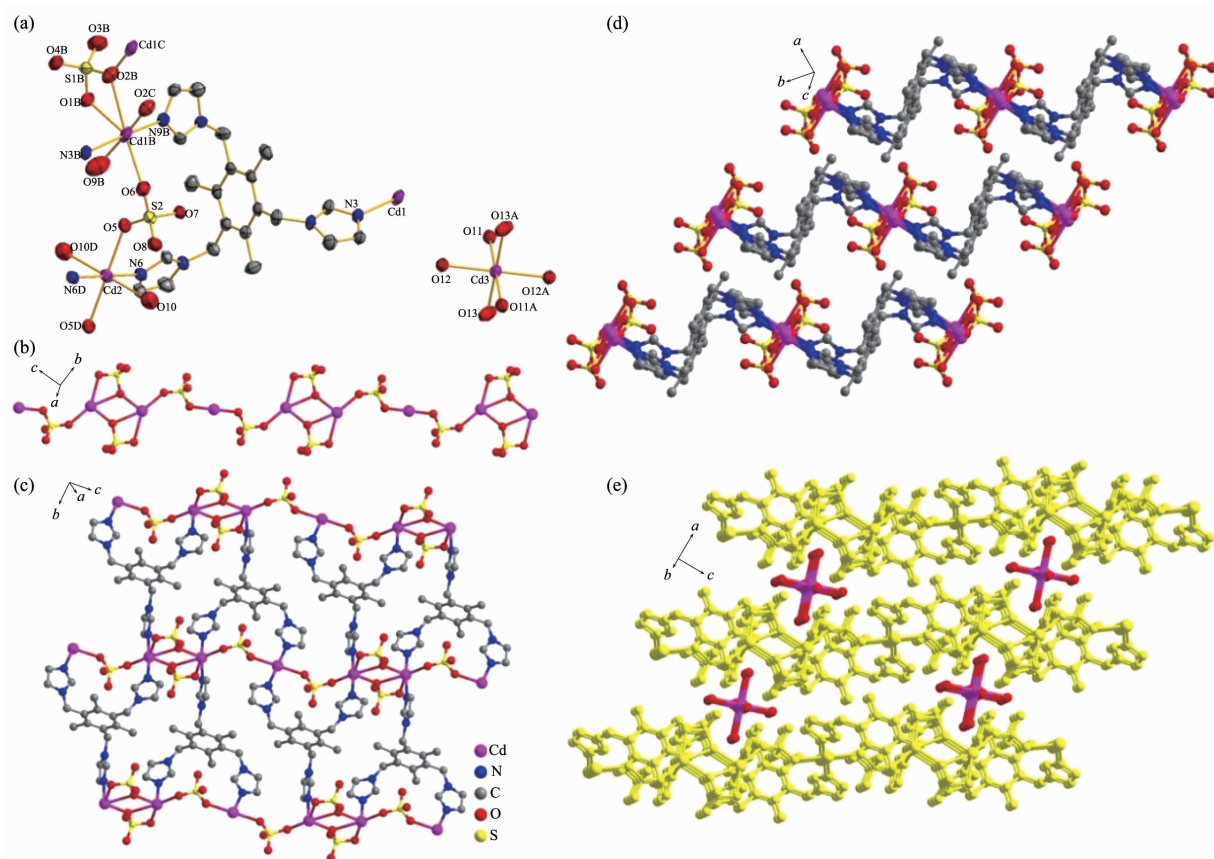
Symmetry codes: A: x, -1+y, z; B: 1-x, 1-y, -z for **1**.

2 Results and discussion

2.1 Crystal structure of complex **1**

Single crystal X-ray diffraction reveals that complex **1** crystallizes in the triclinic $P\bar{1}$ space group. There are two independent units in complex **1**:

$[\text{Cd}_3(\text{SO}_4)_4(\text{TITMB})_2(\text{H}_2\text{O})_4]^{2-}$ and $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$. In complex **1**, three crystallographic distinct Cd(II) ions exist (Fig.1): one seven coordinated Cd1 with bipyramidal geometry and two six coordinated Cd2 and Cd3 with distorted octahedral geometry (Fig.1a). Each Cd1 is coordinated by two nitrogen atoms (N9B and N3B)



Hydrogen atoms and methanol molecules are omitted for clarity; Symmetry codes: A: $2-x, -y, -z$; B: $x, 1+y, z$; C: $1-x, 2-y, -z$; D: $2-x, 2-y, 1-z$

Fig.1 (a) View of ORTEP drawing of complex **1** with 30% ellipsoid; (b) One dimensional inorganic chain formed by bridging sulfate anion and Cd(II); (c) Two dimensional network constructed by TITMB ligands with 1D inorganic chain; (d) AAA stacking modes in complex **1**; (e) Cd(H₂O)₆ units located between the 2D networks further extending the 2D network to 3D framework through hydrogen bonds

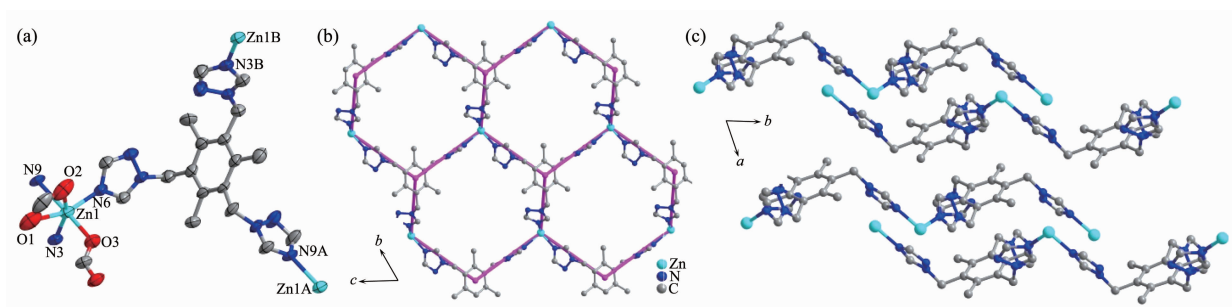
from imidazole rings, four oxygen atoms (O1B, O2B, O2C and O6) from three distinct sulfate anions and one terminated water molecule (O9B). Each Cd2 sitting at symmetric center is coordinated by two nitrogen atoms (N6 and N6D) from two imidazole rings, two oxygen atoms (O5 and O5D) from two different sulfate anions and two terminal water molecules (O10 and O10D). Each Cd3 was coordinated by six water molecules and independently located in complex **1**. The average bond length of Cd-N and Cd-O is comparable to previously reported^[21].

Each sulfate anion in complex **1** coordinates two Cd(II) ions through adopting two different bridging modes (η^1 - η^1 - η^0 - η^0 - and η^1 - η^2 - η^0 - η^0 -coordination mode for the four oxygen atoms, respectively), which extends to one dimensional (1D) inorganic chain (Fig.1b). The 1D chains are further linked by the TITMB ligand

with *cis*, *cis*, *trans*-configuration to two dimensional (2D) network (Fig.1c), where each TITMB ligand coordinates to three Cd(II) centers. The 2D networks stack in an AAA sequence along the *b* axis (Fig.1d), where the [Cd(H₂O)₆]²⁺ units locate in the cavity between two adjacent 2D layers by hydrogen bonds to neutralize the charge (Fig.1e). The strong O-H...O hydrogen bonds between the Cd(H₂O)₆ units and the sulfate anions facilitated the formation of the 3D structure of complex **1**, where the distance between the donor oxygen atom to the acceptor oxygen atom was in the range of 0.270(2)~0.300(2) nm (Table 3).

2.2 Crystal structure of complex 2

As shown in Fig.2, the asymmetric unit of complex **2** contains one zinc(II), one TITMB ligand and two methanoic acid, and one methanol molecular. Single crystal X-ray crystallographic analyses reveal



Methanol molecule and the hydrogen atoms are omitted for clarity; Symmetry codes: A: $x, -1+y, 1+z$; B: $x, -1+y, z$

Fig.2 (a) View of ORTEP of complex **2** with 30% ellipsoid; (b) Two dimensional honeycomb 6^3 network built by TTTMB ligand with Zn(II) centers; (c) ABAB packing mode of 2D layers along a axis in complex **2**

that each zinc(II) is six-coordinated with a distorted octahedral geometry by three nitrogen atoms (N3, N6 and N9) from three different TTTMB ligands and three oxygen atoms (O1, O2, O3) from two methanoic acid (Fig.2a). Two methanoic acids present two different coordination modes, chelate and monodentate, respectively^[17]. The Zn-O bond distances vary from 0.207 2(6) to 0.238 9(8) nm, and the Zn-N distances are in the range of 0.207 5(6)~0.226 1(6) nm.

A typical 6^3 2D topological network is found in complex **2**, where each TTTMB ligand coordinates to three Zn(II) centers and is considered as a 3-connected nodes. The 2D networks stack in an ABAB packing sequence and further extend to a 3D structure by hydrogen bonds between the methanoic acid and methanol molecules (Table 3).

2.3 Thermal stability analyses

Thermogravimetric analyses were performed on grounded samples of **1** and **2** to evaluate their thermal robustness and decomposition behavior and the results are shown in Fig.3a. Up to 350 °C, complex **1** undergoes continuous weight loss of 13.1% due to the release of

two free methanol and ten coordinated water molecules (Calcd. 13.6%). Obvious rapid weight loss is observed after heating over 350 °C, which suggests the structure decomposition of complex **1**. For complex **2**, the first weight loss (11.1%) under 90 °C may be assigned to the loss of methanol molecule (5.8%) and partially release of methanoic acid, and the structure could be maintained up to 250 °C.

2.4 Photoluminescence property

The photoluminescence of ligands TITMB, TTTMB, complexes **1** and **2** was studied in the solid state at room temperature. The excitation wavelength for TITMB and **1**, TTTMB and **2** is 330 and 280 nm, respectively. The results were depicted in Fig.3b and 3c.

Complex **1** shows a weak emission band at 400 nm and a strong peak at 450 nm upon the excitation (Fig.3b). Since free ligand TITMB displays an emission band at 402 nm upon the excitation, the emission band of complex **1** at 400 nm should be due to the ligand-to-ligand ($\pi-\pi^*$) charge transfer (LLCT)^[22-24]. The 450 nm band should be ascribed to the ligand-to-

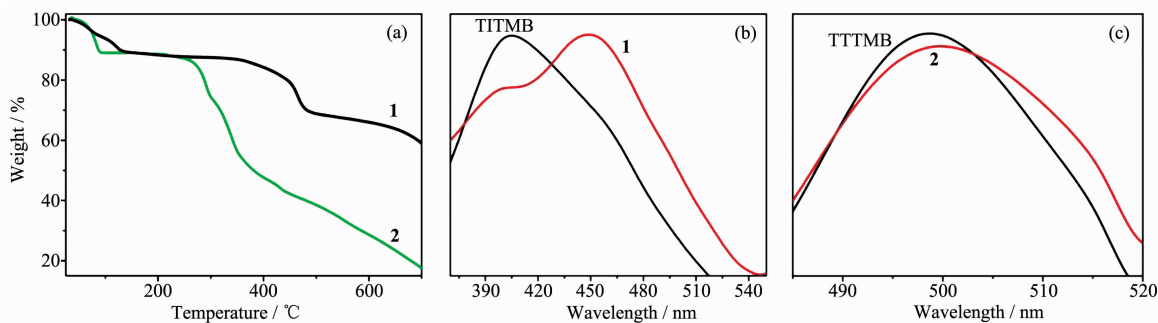


Fig.3 TGA curves of complexes **1** and **2** (a), solid state photoluminescence emission spectra of ligand TITMB and complex **1** with 330 nm excitation (b), ligand TTTMB and complexes **2** with 280 nm excitation (c), respectively

metal charge transfer (LMCT)^[25-27]. Complex **2** exhibits very similar emission band at 498 nm comparing to the free TTTMB ligand (Fig.3c). Thus, the emission of complex **2** is assigned to be ligand-based (LLCT)^[28-29].

3 Conclusions

Two new 2D coordination polymers based on flexible tripodal ligands of TITMB and TTTMB have been synthesized and characterized. In both complexes, the TITMB and TTTMB adopt *cis*, *cis*, *trans*-configuration. The counter anions play an important role in the construction of coordination polymer in consideration of their different coordination ability, size and so on. In this work, sulfate anions participate in the coordination of the resulted structure of complex **1** as the bridging ligand, while in complex **2**, act as terminal coordination ligand only. In addition, complexes **1** and **2** display blue fluorescent emissions in the solid state at room temperature.

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