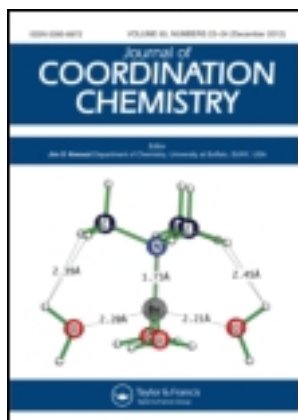


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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Syntheses, crystal structures, and luminescence of two new coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate

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Published online: 08 Apr 2011.

To cite this article: Lou-Jun Gao, Pei-Xiang Cao, Ji-Jiang Wang, Ya-Pan Wu, Feng Fu, Mei-Li Zhang, Yi-Xia Ren & Xiang-Yang Hou (2011) Syntheses, crystal structures, and luminescence of two new coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate, *Journal of Coordination Chemistry*, 64:8, 1299-1308, DOI: [10.1080/00958972.2011.567416](https://doi.org/10.1080/00958972.2011.567416)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.567416>

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Syntheses, crystal structures, and luminescence of two new coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate

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(Received 13 October 2010; in final form 15 February 2011)

Two new coordination polymers, $[\text{Zn}(\text{H}_2\text{btc})(4,4'\text{-bpy})_2]_n$ (**1**) and $\{[\text{Cd}(\text{H}_2\text{btc})(\text{terpy})] \cdot \text{H}_2\text{O}\}_n$ (**2**) (H_4btc = biphenyl-2,2',4,4'-tetracarboxylic acid, 4,4'-bpy = 4,4'-bipyridine, terpy = terpyridine), have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectra, and single-crystal X-ray diffraction. Complexes **1** and **2** are 1-D chains linked through partially deprotonated H_4btc . The adjacent 1-D chains of **1** are further formed into 2-D supramolecular architecture through inter-chain $\text{N-H} \cdots \text{O}$ hydrogen bonds. In contrast, due to a different auxiliary ligand, the 1-D chains of **2** are further extended into 3-D supramolecular framework through inter-chain $\text{O-H} \cdots \text{O}$ hydrogen bonds. Thermal stabilities and luminescence of **1** and **2** were also studied.

Keywords: Biphenyl-2,2',4,4'-tetracarboxylate; Synthesis; Crystal structure; Luminescence

1. Introduction

Metal–organic frameworks (MOFs) or coordination polymers [1–3] have received attention for their potential applications including materials for luminescence, gas storage and catalysis [4, 5], and also for rigid and open framework [6]. To obtain frameworks with desirable properties, an enormous amount of research is focused on versatile organic ligands as spacers and on metal ions or metal clusters as nodes. Carboxylic acids exhibit diverse coordination modes, especially for multi-carboxylic acids, such as biphenyl-tetracarboxylate, used in the preparation of various coordination polymers. Biphenyl-tetracarboxylate, depending on the number of deprotonated carboxylic groups, can be regarded as hydrogen-bond acceptors and also as hydrogen-bond donors. Coordination polymers based on biphenyl-tetracarboxylate have been studied extensively [7–10].

Porous coordination polymers with luminescent properties constructed by larger carboxylic acids, such as biphenyl-3,3',4,4'-tetracarboxylic acid and biphenyl-3,3',5,5'-tetracarboxylic acid, have been reported [11–18]. By comparison, complexes based on

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biphenyl-2,2',4,4'-tetracarboxylic acid are found to be less common [19, 20]. To understand the coordination chemistry of biphenyl-2,2',4,4'-tetracarboxylate and to study the influence of auxiliary ligands on the framework structures of their complexes, we are currently interested in the structures of such complexes. Herein, we report two new d^{10} metal coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate, $[\text{Zn}(\text{H}_2\text{btc})(4,4'\text{-bpy})_2]_n$ (**1**) and $\{[\text{Cd}(\text{H}_2\text{btc})(\text{terpy})] \cdot \text{H}_2\text{O}\}_n$ (**2**), where these two complexes contain $(\text{H}_2\text{btc})^{2-}$ spacers and 4,4'-bpy/terpy.

2. Experimental

2.1. Materials and methods

All chemicals are of analytical reagent grade and used as received. IR spectra were recorded from KBr pellets (4000 to 400 cm^{-1}) on a Bruker EQUINOX-55 spectrometer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of $10^\circ\text{C min}^{-1}$ using a NETZSCH STA 449C thermogravimetric analyzer.

2.2. Synthesis

2.2.1. Synthesis of $[\text{Zn}(\text{H}_2\text{btc})(4,4'\text{-bpy})_2]_n$ (1**).** A mixture of ZnO (0.2 mmol), H_4btc (0.1 mmol), 4,4'-bpy (0.1 mmol), and 10 mL H_2O was stirred for 30 min. The mixture was then placed in a 23 mL Teflon-lined stainless-steel vessel and heated at 160°C for 4d. Colorless crystals were obtained when the mixture was cooled to room temperature. Yield: *ca* 46% based on Zn. Calcd for $\text{C}_{36}\text{H}_{24}\text{N}_4\text{O}_8\text{Zn}$ (%): C, 61.2; H, 3.4; N, 7.9. Found (%): C, 61.4; H, 3.5; N, 7.8. IR (KBr pellet, cm^{-1}): 3431m, 1618vs, 1541s, 1421m, 1386s, 1225m, 1164m, 1098m, 816m, 787m, 644m, 460w (Supplementary material, figure S3).

2.2.2. Synthesis of $\{[\text{Cd}(\text{H}_2\text{btc})(\text{terpy})] \cdot \text{H}_2\text{O}\}_n$ (2**).** The same synthetic method as that of **1** was used except that ZnO was replaced by CdO and 4,4'-bpy was replaced by terpy. Yield: *ca* 49% based on Cd. Calcd for $\text{C}_{31}\text{H}_{21}\text{N}_3\text{O}_9\text{Cd}$ (%): C, 53.8; H, 3.0; N, 6.1. Found (%): C, 53.9; H, 3.2; N, 6.0. IR (KBr pellet, cm^{-1}): 3491m, 1707s, 1597s, 1543m, 1446w, 1369s, 1228w, 1161w, 802w, 773m, 680m, 424w (Supplementary material, figure S4).

2.3. X-ray crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at room temperature. The structure was solved by direct methods and successive Fourier difference synthesis (SHELXS-97) and refined by full-matrix least-squares on F^2 with anisotropic thermal

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	1	2
Empirical formula	C ₃₆ H ₂₄ N ₄ O ₈ Zn	C ₃₁ H ₂₁ N ₃ O ₉ Cd
Formula weight	705.96	691.41
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	P2(1)2(1)2(1)
Unit cell dimensions (Å, °)		
<i>a</i>	34.955(9)	7.431(18)
<i>b</i>	9.075(2)	17.13(4)
<i>c</i>	9.583(3)	20.92(5)
α	90	90
β	103.511(5)	90
γ	90	90
Volume (Å ³), <i>Z</i>	2955.8(14), 4	2664(11), 2
Calculated density (Mg cm ⁻³)	1.586	1.725
Absorption coefficient μ (mm ⁻¹)	0.897	0.886
<i>F</i> (000)	1448	1392
λ (Mo-K α) (Å)	0.71073	0.71073
Reflections collected	7242	13175
Independent reflections	2629	4819
S on <i>F</i> ²	1.033	1.002
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0476, 0.0975	0.0400, 0.0754
<i>R</i> ₁ , <i>wR</i> ₂ ^a (all data)	0.0728, 0.1030	0.0564, 0.0823

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}{F_c}$$

parameters for all non-hydrogen atoms (SHELX-97) [21]. All hydrogens were replaced in the located positions. The crystallographic data for **1** and **2** are summarized in table 1; selected bond lengths and angles are listed in tables 2 and 3.

3. Results and discussion

3.1. Crystal structure of **1** and **2**

The structures were determined by single-crystal X-ray diffraction analyses. Complex **1** belongs to the monoclinic system of *C2/c*. Complex **2** is the orthorhombic system of *P2(1)2(1)2(1)*.

Single-crystal X-ray diffraction analysis reveals that **1** is a 2-D supramolecular network based on hydrogen-bond interactions of the adjacent 1-D chains [Zn(H₂btc)(4,4'-bpy)₂]_n. Each Zn(II) is coordinated by four oxygens from two different (H₂btc)²⁻ anions and two nitrogens from two 4,4'-bpy ligands to give a distorted octahedral geometry (figure 1). The four Zn–O distances fall in the range 2.094(2)–2.121(2) Å and Zn–N bond lengths are 2.191(3) Å. The 2,2'-carboxylates adopt bis(bidentate) bridging mode (scheme 1a). On the basis of the connection mode, Zn(II) are linked by (H₂btc)²⁻ to form a 1-D chain (figure 2a); adjacent 1-D chains are further connected through N–H...O hydrogen bonds [O4...N2, 2.655(4) Å] (figure S1) to give a 2-D supramolecular network (figure 2b).

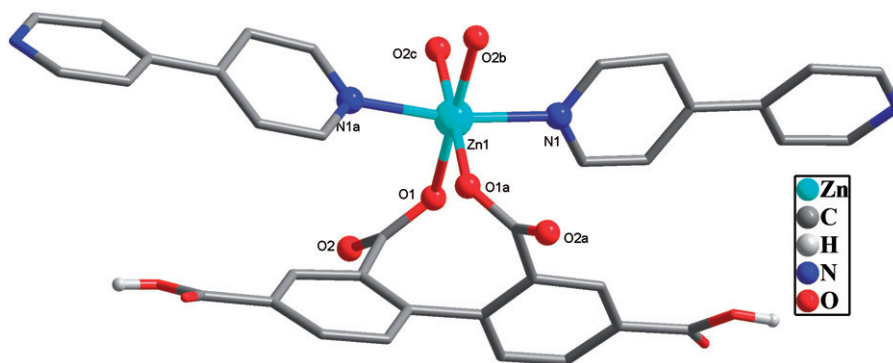
The crystal structure of **2** reveals that each Cd(II) is six coordinate, with three nitrogens from one terpyridine [Cd1–N1, 2.317(5) Å; Cd1–N2, 2.313(6) Å; Cd1–N3,

Table 2. Select bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(1)	2.121(2)	Zn(1)–O(2)b	2.094(2)
Zn(1)–O(1)a	2.121(2)	Zn(1)–O(2)c	2.094(2)
Zn(1)–N(1)	2.191(3)	Zn(1)–N(1)a	2.191(3)
O(2)c–Zn(1)–O(1)	178.42(8)	O(2)c–Zn(1)–O(2)b	91.31(12)
O(2)b–Zn(1)–O(1)	87.74(8)	N(1)a–Zn(1)–N(1)	169.50(15)

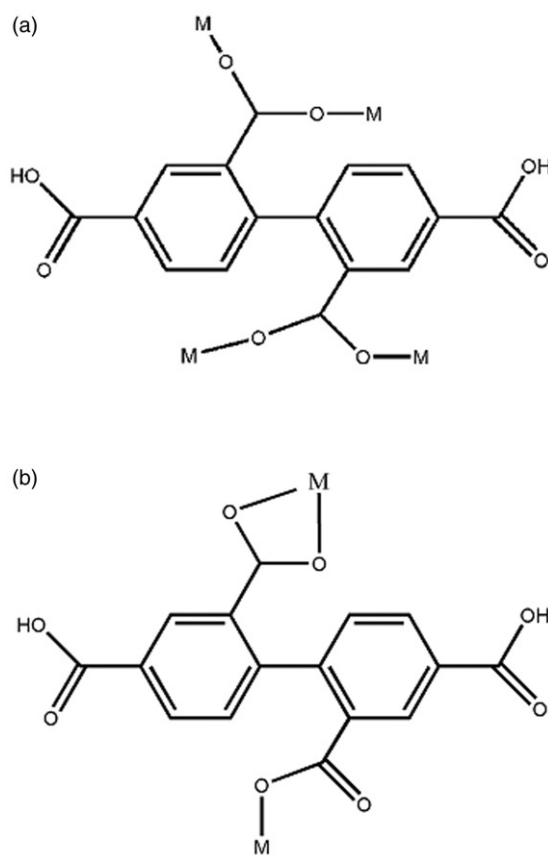
Symmetry code for **1**: (a) $-x, y, -z+1/2$, (b) $-x, -y, -z+1$, (c) $x, -y, z-1/2$.Table 3. Select bond lengths (Å) and angles (°) for **2**.

Cd(1)–N(1)	2.317(5)	Cd(1)–O(1)	2.228(5)
Cd(1)–N(2)	2.313(6)	Cd(1)–O(5)	2.360(5)
Cd(1)–N(3)	2.358(6)	Cd(1)–O(6)	2.491(6)
N(2)–Cd(1)–N(1)	70.6(2)	O(1)–Cd(1)–N(3)	93.74(17)
N(2)–Cd(1)–N(3)	69.50(17)	O(5)–Cd(1)–O(6)	53.00(16)
N(1)–Cd(1)–O(6)	98.4(2)	N(3)–Cd(1)–O(5)	122.44(15)
N(2)–Cd(1)–O(6)	90.59(17)	N(3)–Cd(1)–O(6)	85.66(19)
N(2)–Cd(1)–O(5)	136.20(17)	–	–

Figure 1. Coordination environment of Zn(II) in **1**. Hydrogens are omitted for clarity.

2.358(6) Å], two oxygens donated by one chelating bidentate $(\text{H}_2\text{btc})^{2-}$ and one from one bridging monodentate $(\text{H}_2\text{btc})^{2-}$ (scheme 1b) in a distorted octahedral geometry (figure 3). Cd(II) ions are linked by 2- or 2'-COO⁻ to form a 1-D chain (figure 4a). Cd(II)– $(\text{H}_2\text{btc})^{2-}$ chains are connected to form a 2-D grid (figure 4b) through O–H \cdots O hydrogen bonds [O2 \cdots O8, 2.701(9) Å] and further give a 3-D supramolecular network (figure 4c) by O–H \cdots O hydrogen bonds [O4 \cdots O6, 2.588(8) Å].

Comparing structures of **1** and **2**, **2** is significantly different showing that auxiliary ligands have significant effects on the formation and structure of the resulting complexes.



Scheme 1. (a) Coordination mode of $(\text{H}_2\text{btc})^{2-}$ in **1**; (b) coordination mode of $(\text{H}_2\text{btc})^{2-}$ in **2**.

3.2. IR spectra

IR spectra of **1** and **2** (figures S3 and S4) show characteristic vibration of carboxylic acids. The strong peaks of aromatic rings span over the range $1300\text{--}1628\text{ cm}^{-1}$ for **1** ($1254\text{--}1700\text{ cm}^{-1}$ for **2**). The spectrum of complexes **1** and **2** exhibit a strong band at $1690\text{--}1730\text{ cm}^{-1}$, assignable to the protonated carboxylate group of H_2btc ligand. IR spectra of **1** and **2** are in good agreement with crystal structure and charge balance consideration.

3.3. Spectroscopic properties

Luminescence of **1** and **2** were investigated showing intense fluorescent emission of **1** at 368 nm and of **2** at 405 nm. Compared to free biphenyl-2,2',4,4'-tetracarboxylic acid with maximum emission at 422 nm (figure 5), **2** results in a blue shift of 17 nm, whereas **1** displays a blue shift of 54 nm. Since Zn^{2+} and Cd^{2+} are difficult to oxidize or reduce due to their d^{10} configuration, emissions of **1** and **2** are not attributable to ligand-to-metal charge transfer bands (LMCT) and metal-to-ligand charge transfer bands

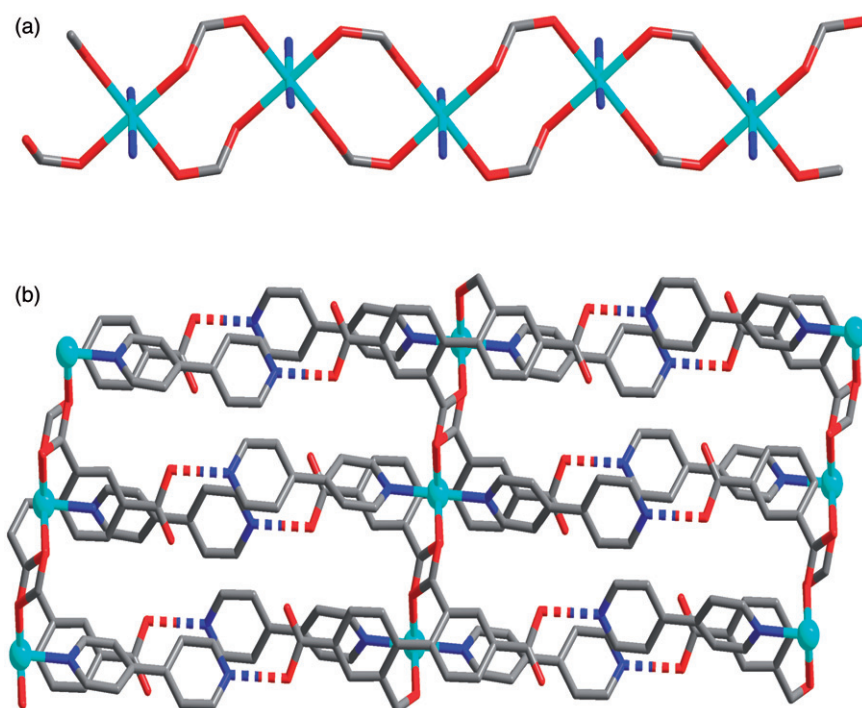


Figure 2. (a) 1-D chain structure of **1**; (b) 2-D structure of **1**. Benzene rings of 4,4'-bpy are omitted for clarity.

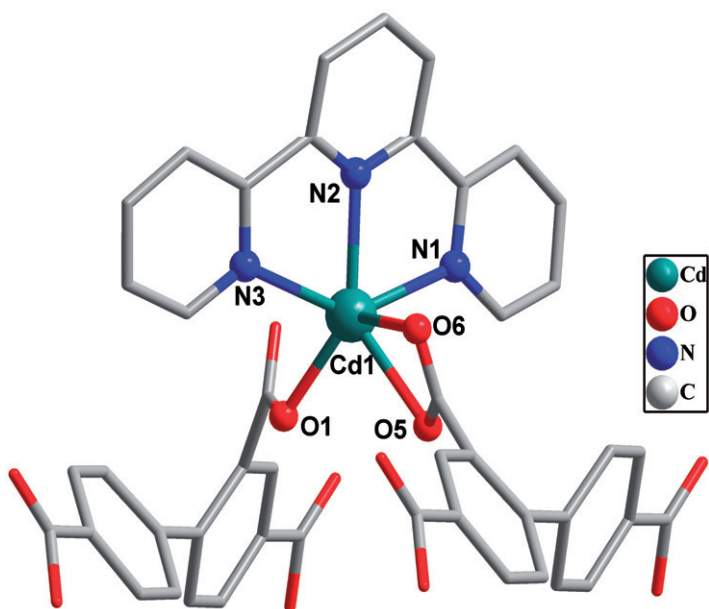


Figure 3. Coordination environment of Cd(II) in **2**. Hydrogens and water are omitted for clarity.

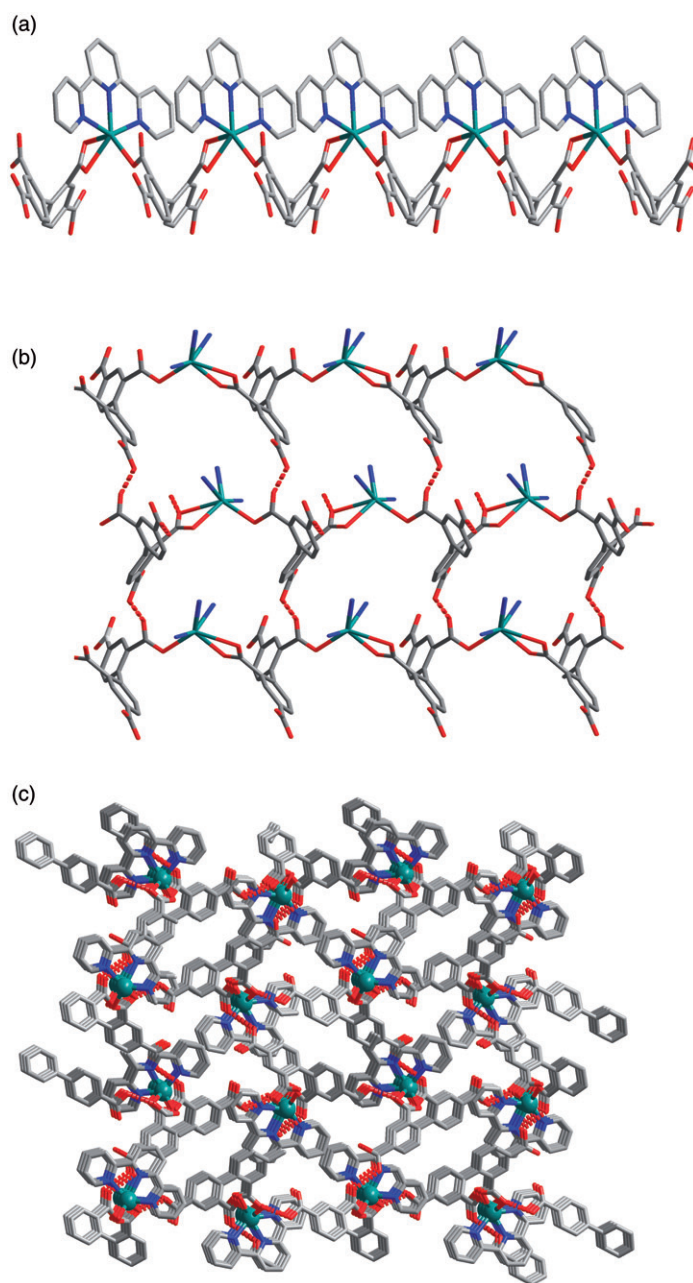


Figure 4. (a) 1-D chain structure of **2**; (b) 2-D structure of **2**. Benzene rings of terpyridine are omitted for clarity; (c) 3-D supermolecular structure of **2**.

(MLCT), but may be attributable to fluorescent emissions from an intraligand excited state [22]. The enhancement of luminescence may be attributed to ligand coordinated to the metal center, which effectively increases the rigidity of the ligand reducing the loss of energy by radiationless decay.

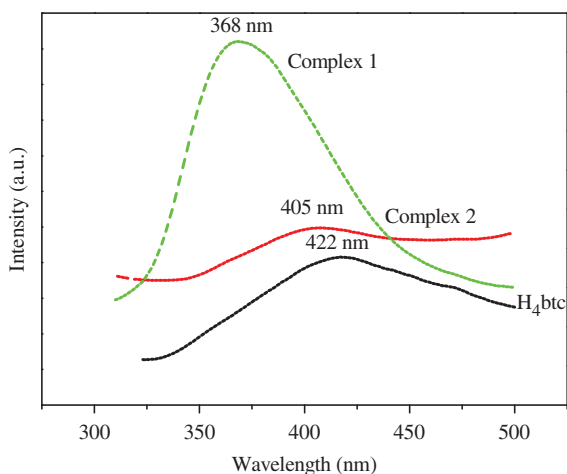


Figure 5. Emission spectra of H_4btc , **1** and **2** in the solid state at room temperature.

Structurally similar complexes based on biphenyl-2,2',4,4'-tetracarboxylic acid are constructed by the coordinate bond, and all have maximum emission at 420 nm [20]. In contrast, **1** displays shift of 62 nm and **2** produces shift of 15 nm, which likely result from the supramolecular effects of **1** and **2** [23–26].

3.4. Thermogravimetric analysis

The TGA trace (figure S5) illustrates that **1** decomposes at approximately 300°C and ends above 490°C. The final product is assumed to be ZnO (12.0%), which is supported by the expected value 11.49%. For **2**, the TGA trace (figure S6) shows two weight-loss steps: the first of 3.0% (Calcd 2.7%) is equivalent to the loss of uncoordinated water at 80–90°C. Then **2** is stable without loss from 150°C to 350°C, where decomposition begins, ending above 440°C. CdO is assumed to be the final residual product (20.2%), supported by the expected value of 19.07%. These results are well consistent with the X-ray structure.

4. Conclusion

Two new coordination polymers were constructed from H_4btc , Zn^{2+} , or Cd^{2+} in the presence of two auxiliary ligands under hydrothermal conditions. In **1** and **2**, biphenyl-tetracarboxylic acids possess different coordination modes and auxiliary ligands exert significant influence on the final supramolecular framework. The two complexes show intense emissions from intraligand fluorescence and may be potential

luminescent materials. We will continue our research on MOFs of fascinating structures and specific properties through the reaction of other related ligands and metals.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 794244 for **1** and CCDC 794245 for **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgments

This project was supported by the Natural Scientific Research Foundation of Shaanxi Provincial Education Office of China (Nos. 2010JK918, 2010JK903, 2010JK905, 2010JS061, and 2010JS062) and the Natural Scientific Research Foundation of Yan' an City Technology Division of China (Nos. 2009kg-01 and 2009ks-24).

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