

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:49

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

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

### Synthesis and characterization of two- and three-dimensional coordination polymers built with 3,5-bis(4'-carboxy-phenyl)-1,2,4-triazole and/or 1,4-bis(imidazol-1-ylmethyl)benzene

Xiang-Yang Hou<sup>a</sup>, Xiao Wang, Feng Fu<sup>a</sup>, Ji-Jiang Wang<sup>a</sup> & Long Tang<sup>a</sup>

<sup>a</sup> Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an University, Yan'an, China

Accepted author version posted online: 22 Jul 2013. Published online: 14 Aug 2013.

To cite this article: Xiang-Yang Hou, Xiao Wang, Feng Fu, Ji-Jiang Wang & Long Tang (2013) Synthesis and characterization of two- and three-dimensional coordination polymers built with 3,5-bis(4'-carboxy-phenyl)-1,2,4-triazole and/or 1,4-bis(imidazol-1-ylmethyl)benzene, Journal of Coordination Chemistry, 66:17, 3126-3136, DOI: [10.1080/00958972.2013.827178](https://doi.org/10.1080/00958972.2013.827178)

To link to this article: <http://dx.doi.org/10.1080/00958972.2013.827178>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Synthesis and characterization of two- and three-dimensional coordination polymers built with 3,5-bis(4'-carboxy-phenyl)-1,2,4-triazole and/or 1,4-bis(imidazol-1-ylmethyl)benzene

XIANG-YANG HOU, XIAO WANG, FENG FU\*, JI-JIANG WANG and LONG TANG

Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an University, Yan'an, China

(Received 7 October 2012; in final form 2 July 2013)

Two new coordination polymers,  $[\text{Cd}(\text{bct})(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})$  (**1**) and  $[\text{Zn}(\text{bct})(\text{bip})] \cdot 2(\text{H}_2\text{O})$  (**2**) ( $\text{H}_2\text{bct} = 3,5\text{-bis}(4'\text{-carboxy-phenyl})\text{-}1,2,4\text{-triazole}$ ,  $\text{bip} = 1,4\text{-bis}(\text{imidazol-}1\text{-ylmethyl})\text{benzene}$ ), have been synthesized. Their structures have been determined by single-crystal X-ray diffraction analysis and further characterized by elemental analysis, IR spectroscopy, and thermogravimetric analysis. Compound **1** is a two-dimensional structure with double-layered network, where bct ligands adopt a  $\mu_4\text{-}k^1, k^1, k^1, k^1$  bridging mode linking four five-coordinate Cd ions. Compound **2** exhibits a three-dimensional framework consisting of double-layered helical chains with the bct and bip adopting  $\mu_3\text{-}k^1, k^1, k^1$  and  $\mu_2\text{-}k^1, k^1$  bridging mode, respectively. Complexes **1** and **2** exhibit intense emissions at 399 and 441 nm, respectively.

*Keywords:* Cadmium; Zinc; Coordination polymer; Crystal structure; Fluorescence

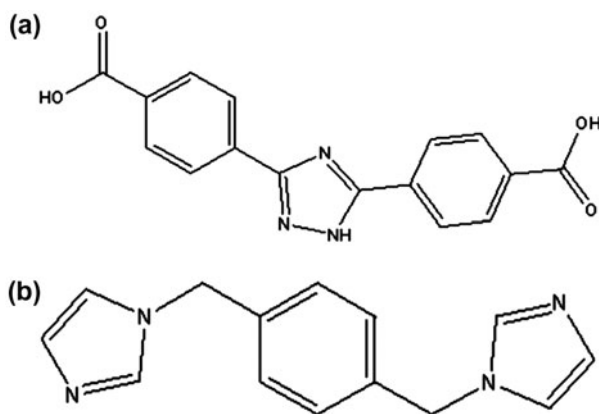
### 1. Introduction

Design and synthesis of coordination polymers (CPs), which are also known as metal–organic frameworks (MOFs), represent a growing subject because of their interesting structures [1] and potential applications in luminescence [2], adsorption [3], catalysis [4], gas storage [5], magnetism [1a, 6], etc. The effective approach to the design of these MOFs is usually the fabrication of metal ion as nodes and multidentate ligands as bridges or terminal groups. In general, there are many parameters to influence structures and properties of the CPs including the central metal ion coordination geometry, Lewis acidity [7], the shapes, lengths, symmetries, flexibilities, and substituent groups of the organic ligands [8], as well as the reaction conditions such as temperature, ligand to metal salt ratio, solvent, etc. [9]. Explorations on the factors that contribute to a given structure are important to prepare the desired MOFs. Many carboxylates are selected as multifunctional linkers because of their abundant coordination modes allowing for various structures and properties [10]. Moreover, nonrigid ligands are multifunctional linkers in multidimensional networks [11].

\*Corresponding author. Email: wx2248@126.com

The conformational freedom of the flexible ligands may provide more possibility for the construction of unusual structures and functional materials [12].

N-heterocyclic carboxylates of  $H_2bct$  has been investigated for the synthesis of MOFs with a range of structures and applications. Such as, twofold interpenetrating 2-D framework  $[Cd_2(L)(bpa)]_2 \cdot 2(H_2O) \cdot 2(CH_3OH)$  [13a] ( $L = 3,5$ -bis(3-carboxyphenyl)-1,2,4-triazole),  $bpa = 4,4$ -bis(4-pyridyl)ethane), with  $L \mu_4-k^1, k^1, k^1, k^1$  and seven-coordinate  $Cd^{2+}$ ; 3-D CPs  $[Ni_3(OH)-(L)_3] \cdot n(solv)$  [13c] ( $H_2L =$  pyridine-3,5-bis(phenyl-4-carboxylic acid),  $L_1$  with  $\mu_5-k^1, k^1, k^1, k^1, k^1$  mode and seven-coordinate  $Ni^{2+}$ ; and 3-D framework  $[Mg_3(\mu_3-OH)(L)_3]$  [13b] ( $H_2L =$  pyridine-3,5-bis(phenyl-4-carboxylic acid),  $L \mu_5-k^1, k^1, k^1, k^1, k^1$  and six-coordinate  $Ni^{2+}$ ). The flexible and long  $H_2bct$  is an excellent candidate for the preparation of functional MOFs, with three obvious characteristics: first,  $H_2bct$  (scheme 1) adopts various coordination modes when it coordinates to metals owing to carboxylate and triazole arms; second, it can partially or completely deprotonate and act not only as a hydrogen bond acceptor but also as a hydrogen bond donor; and third, the introduction of a second bridging ligand to extend the metal carboxylate system is a way to obtain higher dimensional networks, and bisimidazole donors of  $bip$  as neutral ligands have been used for this purpose. Interrelated  $bip$  has been frequently used as linker of metal ions because of good complexing ability and also the capability of N to bridge metal ions. Examples are  $[Zn(CH_3O-ip)(bib)]$  with three-fold interpenetrated 3-D framework ( $CH_3O-H_2ip = 5$ -methoxyisophthalate,  $bib = 1,4$ -bis(2-methyl-imidazol-1-yl)butane) [14a], with four-coordinate  $Zn^{2+}$ ;  $Cd(CH_3O-ip)(btb)_{0.5}(H_2O) \cdot 2H_2O$  has a (3,5)-connected 2-D layer framework [14b] ( $btb = 1,4$ -bis(1,2,4-triazol-1-yl)butane), with six-coordinate  $Cd^{2+}$ ; 2-D layer framework  $[Cd_2(L)_2(L_1)_2] \cdot 2H_2O$  [14c] ( $L =$  bis(N-imidazolyl)methane,  $H_2L_1 = 4,4'$ -oxybis(benzoic acid), with six-coordinate  $Cd^{2+}$ ;  $[Cd(L)^2(ClO_4)] \cdot ClO_4$  [14d] ( $L = 1,3$ -bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene) is 1-D beaded chains further assembled by intermolecular  $C-H \cdots O$  hydrogen bonds to form a 2-D layer, with five-coordinate  $Cd^{2+}$ ;  $[Cu(L_2)(cnic)_2] \cdot H_2O$  [14e] ( $adip =$  adipate,  $L = 1,4$ -bis(N-imidazolyl)butane) as a 3-D framework structure with a number of non-conventional weak interactions, and five-coordinate  $Cu^{2+}$ ; and  $[CdBr_2(L)]$  contains a 1-D helical chain with  $CdBr_2$  units linked by  $L$  [14f] ( $L = 1,3$ -bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene). As an extension of our recent efforts to explore coordination chemistry and crystal engineering of triazole-based dicarboxylates, the new  $H_2bct$  and/or  $bip$  co-ligands are



Scheme 1. (a) Structure of  $H_2bct$ ; (b) structure of  $bip$  ligands.

selected to investigate new functional CP materials. Herein, we report the synthesis and crystal structures of **1** and **2**, [Cd(bct)(H<sub>2</sub>O)]·(H<sub>2</sub>O) (**1**) and [Zn(bct)(bip)]·2(H<sub>2</sub>O) (**2**). The thermal properties and luminescent behavior of these materials are also discussed. To the best of our knowledge, this is the first report of systematic investigation into the coordination chemistry of a transition metal in the system with H<sub>2</sub>bct and/or bip.

## 2. Experimental

### 2.1. Materials and methods

All solvents and starting materials of analytical grade in the experiments except H<sub>2</sub>bct bought from Jinan Camolai Trading Company were obtained from commercial sources and used without purification. Elemental analyses (C, H, and N) were determined on a Perkin–Elmer 2400 type elemental analyzer. Infrared spectra were recorded from 400 to 4000 cm<sup>-1</sup> on a Bruker EQUINOX-55 spectrophotometer using KBr pellets. PXRD patterns were recorded using Cu K<sub>α</sub> radiation on a PANalytical X'Pert PRO diffractometer. The thermogravimetric analyses were performed on a NETZSCH STA 449C thermogravimetric analyzer. Photoluminescence analyses of the solid samples were performed on an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

### 2.2. Syntheses of [Cd(bct)(H<sub>2</sub>O)]·(H<sub>2</sub>O) (**1**)

Compound **1** was synthesized from a mixture of cadmium acetate, 3,5-bis(4'-carboxy-phenyl) 1,2,4-triazole, ethanol, and water. A mixture of H<sub>2</sub>bct (0.4 mM, 0.1238 g), Cd (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.4 mM, 0.1066 g) in a solution of water (10 mL) and ethanol (5 mL) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure heated at 130 °C for three days and cooled to 20 °C at 3 °C h<sup>-1</sup>; colorless prismatic single crystals suitable for X-ray analyses were obtained. The crystals were collected by filtration, washed with distilled water and ethanol, and dried at room temperature. Yield: 0.0820 g (45%, based on Cd). Elemental analysis for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>Cd (%): Calcd: C, 42.07; H, 2.84; N, 9.27. Found: C, 42.17; H, 2.88; N, 9.22. IR (KBr pellet, cm<sup>-1</sup>): 3437(vs), 1677(s), ν<sub>1633</sub>(s), 1589(s), 1507(s), 1369(s), 1543(w), 1446(w), 1225(w), 1163(w), 1077(w), 1036(m), 842(m), 798(s), 752(m), 550(w), 424(w).

### 2.3. Syntheses of [Zn(bct)(bip)]·2(H<sub>2</sub>O) (**2**)

Compound **2** was synthesized from a mixture of zinc acetate, H<sub>2</sub>bct, bip, triethylamine, and water. A mixture of H<sub>2</sub>bct (0.2 mM, 0.0619 g), bip (0.2 mM, 0.0476 g), Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.2 mM, 0.0439 g) in a solution of water (12 mL), ethanol (3 mL), and triethylamine (three drops) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure heated at 160 °C for four days and cooled to 20 °C at 5 °C h<sup>-1</sup>; light colorless block single crystals suitable for X-ray analyses were obtained. Yield: 0.0647 g (50%, based on Zn). Elemental analysis for C<sub>30</sub>H<sub>27</sub>N<sub>7</sub>O<sub>6</sub>Zn (%): Calcd: C, 55.68; H, 4.27; N, 15.19. Found: C, 55.70; H, 4.21; N, 15.15. IR (KBr pellet, cm<sup>-1</sup>): 3443(vs), 1689(s), ν<sub>1646</sub>(s), 1613(s), 1516(s), 1359(s), 1544(w), 1473(w), 1236(w), 1179(w), 1065(w), 1032(m), 841(m), 787(s), 756(m), 553(w), 428(w).

## 2.4. Crystal structure determination

Crystal data for the compounds were collected using a Bruker Smart-1000 CCD diffractometer with graphite monochromated  $\text{MoK}_\alpha$  ( $\lambda = 0.71075 \text{ \AA}$ ) radiation. The single crystal structure of the compounds was solved by direct methods using SHELXS-97 and refined on  $F^2$  by full-matrix least-squares methods using SHELXL-97 [15]. All non-hydrogen atoms were refined anisotropically by full matrix least squares. The C–H hydrogens were calculated in idealized geometry riding on carbon; the protic O–H were found and refined. The crystal data and refinement details of the compounds are summarized in table 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 904705 and 904706 for **1** and **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 <http://www.ccdc.cam.ac.uk>).

## 3. Results and discussion

### 3.1. Structure description of **1**

Compound **1** crystallizes in triclinic system, space group P-1. The structure of **1** is a two-dimensional framework, which via hydrogen bonds forms three-dimensional supramolecules. As shown in figure 1(a), its asymmetric unit consists of one Cd1, one bct anion, one coordinated, and one lattice water. The Cd1 is five-coordinate by one water (O1w) and three carboxylate oxygens (O2, O3#1, O4#3) of three bct ligands, and a nitrogen (N3#2) from btc to generate a distorted square pyramid coordination geometry with  $\text{NO}_4$

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

Compound	<b>1</b>	<b>2</b>
Measurement temperature/K	296(2)	293(2)
Empirical formula	$\text{CdC}_{16}\text{H}_{13}\text{N}_3\text{O}_6$	$\text{ZnC}_{30}\text{H}_{27}\text{O}_6\text{N}_7$
Formula weight	455.71	645.13
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
<i>a</i> (Å)	9.1911(14)	26.712(10)
<i>b</i> (Å)	10.0208(16)	12.445(5)
<i>c</i> (Å)	10.2252(16)	17.903(6)
$\alpha$ (°)	74.732(2)	90.00
$\beta$ (°)	88.994(3)	101.851(11)
$\gamma$ (°)	64.725(2)	90.00
$V/\text{\AA}^3$	816.7(2)	5825(4)
$D_c/\text{Mg m}^{-3}$	1.853	1.473
$\theta$ range for data collection (°)	2.34 to 24.99	3.1 to 25.3
Indices range ( <i>h, k, l</i> )	$-9 \leq h \leq 10, -11 \leq k \leq 11, -12 \leq l \leq 9$	$-27 \leq h \leq 32, -12 \leq k \leq 14, -18 \leq l \leq 20$
Reflections collected	8082	12,724
Data/restraints/parameters	2792/0/238	5149/2/404
$F(0\ 0\ 0)$	452	2664
Final <i>R</i>	$R_1 = 0.0511, wR_2 = 0.1548$	$R_1 = 0.0819, wR_2 = 0.2263$
<i>R</i> indices (all data)	$R_1 = 0.0544, wR_2 = 0.1624$	$R_1 = 0.1115, wR_2 = 0.2517$
<i>Z</i>	2	8

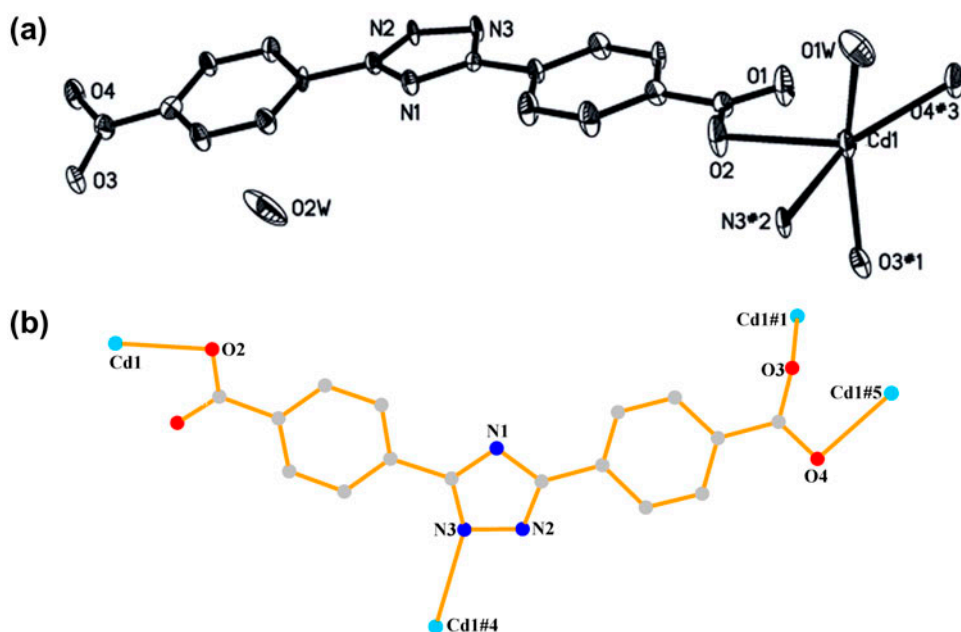


Figure 1. (a) The coordination environment of Cd1 in **1** at 30% probability level; (b) the coordination environment of bct in **1**. Hydrogens are omitted for clarity. Symmetry codes: #1  $2-x, -y, 1-z$ ; #2  $1+x, -1+y, z$ ; #3  $1+x, -2+y, 1+z$ ; #4  $-1+x, 1+y, z$ ; #5  $-1+x, 2+y, -1+z$ .

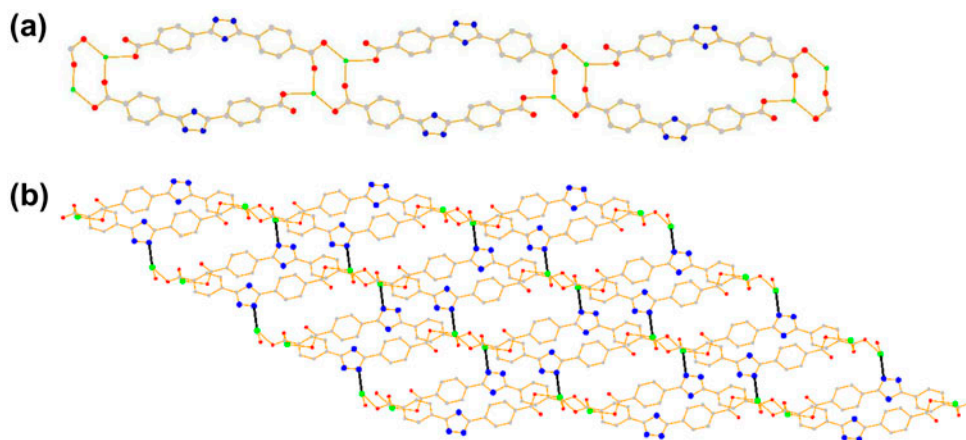
donor set. O1w, N3#2, O4#3, and O3#1 make up the plane, with O2 apical. The Cd1–O bond lengths are 2.254(7)–2.364(6) Å and Cd1–N3 bond length is 2.641(6) Å. Selected interatomic distances and angles for **1** and **2** are listed in table 2; they are similar to those found in other cadmium complexes [16]. From figure 1(b), there is one kind of crystallographically unique bct anion in the structure, with N3 of bct directly bridging cadmium, and two coordination modes of carboxylate to Cd1 including  $\mu_1$ (O2)-monodentate mode and  $\mu_2$ (O3, O4)-bridging bidentate mode. One carboxylate (O2) of bct binds monodentate to one cadmium and the other carboxylate (O3, O4) binds to two cadmium ions through bridging bidentate mode. Thus, each bct has the same coordination environment by coordinating to four cadmium ions with two carboxylates and one nitrogen.

As shown in figure 2(a), Cd1 are connected by bct to form a double-layered chain along the *a* direction. In the double-layered chain, the nearest adjacent Cd1 are bridged by carboxyl oxygens (O3, O4) to form a dinuclear unit  $[\text{CdCO}_2]_2$  with Cd1 $\cdots$ Cd1 distance of 3.809 Å. The dinuclear unit is at a center of symmetry, with Cd1, O3, Cd1, and O3 on the same plane. The Cd1 $\cdots$ O3 length is 2.343 Å and the two angles are 101.229(O3–Cd1–O4) and 119.604(O3–C12–O4), respectively. In contrast to  $\{[\text{Cd}(\text{bpbz})(\text{hfipbb})] \cdot (\text{H}_2\text{O})_3\}_n$ ,  $\text{H}_2\text{hfipbb} = 4,4'$ -(hexafluoroisopropylidene)bis(benzoic acid),  $\text{bpbz} = 1,4$ -bis(4-pyridyl)benzene] with the dinuclear unit  $[\text{CdCO}_2]_2$  [17], in which the dinuclear unit Cd $\cdots$ Cd and Cd $\cdots$ O distances are 4.115 Å and 2.228 Å and the two angles are 119.38(O–Cd–O) and 126.11(O–C–O) angle, respectively. A second building unit  $[\text{Cd}_4(\text{bct})_2]$  has been formed with Cd1 $\cdots$ Cd1 distance of 18.132 Å. The angle of three adjacent Cd1 is 180.0° in each monolayer chain showing Cd1 formed a straight linear double chain. The centroid $\cdots$ centroid distances between two neighboring benzene rings (C2–C3–C4–C5–C6–C7) and



Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

Compound <b>1</b>					
Cd1–O1W	2.254(7)	Cd1–O2	2.283(6)	Cd1–O3#1	2.343(6)
Cd1–O4#2	2.364(6)	Cd1–N3#3	2.641(6)	O1W–Cd1–N3#3	80.7(2)
O1W–Cd1–O1	105.3(3)	O1–Cd1–O2	54.1(2)	O2–Cd1–N3#3	74.89(19)
N3#3–Cd1–O3#1	85.12(19)	O3#1–Cd1–O3#2	74.7(2)	O1W–Cd1–O4#2	82.8(2)
O1W–Cd1–O2	96.8(3)	O1W–Cd1–O3#1	157.8(2)	O2–Cd1–O3#1	95.8(3)
O2–Cd1–O4#2	135.3(2)	O3#1–Cd1–O4#2	101.2(2)	O1W–Cd1–O3#2	90.2(2)
O2–Cd1–O3#2	168.5(2)				
Symmetry codes: #1: 2–x, –y, 1–z; #2: 1+x, –1+y, z; #3: 1+x, –2+y, 1+z					
Compound <b>2</b>					
Zn1–O1	2.237(4)	Zn1–O4#1	2.157(4)	Zn1–O3#2	2.226(4)
Zn1–N4	2.213(5)	Zn1–N9#3	2.219(5)	O4#1–Zn1–N9#3	88.78(16)
O1–Zn1–O2	54.64(13)	N4–Zn1–O2	83.15(15)	N4–Zn1–O3#2	94.38(17)
O3#2–Zn1–N9#3	84.81(17)	O4#1–Zn1–N9#3	89.00(18)	O1–Zn1–O4#1	95.35(17)
O4#1–Zn1–N4	92.98(15)	N9#3–Zn1–N4	178.13(15)	O4#1–Zn1–O3#2	126.88(13)
Symmetry codes: #1: 1–x, –1–y, 0.5–z; #2: 0.5+x, 0.5–y, –0.5+z; #3: 0.5+x, –0.5+y, z					

Figure 2. (a) The double layer chain in **1**; (b) the 2-D structure of **2** formed by bridging bct ligands between neighboring layers; blue lines indicate the links between the chains.

(C10–C11–C12–C13–C14–C15) is 5.875 Å indicating no  $\pi$ – $\pi$  interactions between aromatic rings in the double-layered chain. The bct furnishes N3 binding sites extending Cd1 of adjacent layers giving staggered ladder 2-D framework in the *ab* plane (figure 2(b)). Neighboring double-layered chains are related with shifting a half unit along the *a* axis. Coordinated waters, lattice waters, carboxylate oxygens, and uncoordinated nitrogen (N1) of **1** are engaged in hydrogen bonds between the 2-D framework leading to 3-D supramolecules. The geometrical parameters of the hydrogen bonds are summarized in table 3.

### 3.2. Structure description of **2**

As illustrated in figure 3(a), single crystal X-ray diffraction analysis reveals that **2** crystallizes in monoclinic *C2/c* space group. The asymmetric unit contains a Zn(II), one bct, one bip, and two guest H<sub>2</sub>O molecules. Zn1 is five-coordinate by three carboxylate oxygens (O1, O3#2, O4#1) from three bct and two nitrogens (N4, N9#3) provided by two different



Table 3. Hydrogen bonds of **1**.

D–H···A	<i>d</i> (D–H)/Å	<i>d</i> (H···A)/Å	<i>d</i> (D···A)/Å	∠DHA/°
O5–H···N1#1	0.85(1)	2.34(4)	2.919(6)	125(4)
O5–H···O6#1	0.85(1)	1.82(9)	2.660(1)	165(1)
O6–H#1···O1#2	0.85(1)	2.08(1)	2.851(3)	149(9)
O6–H#1···O4#3	0.85(2)	2.23(8)	3.016(1)	152(2)

Symmetry codes: #1: 2–*x*, –1–*y*, 1–*z*; #2: 2–*x*, –2–*y*, 2–*z*; #3: 1–*x*, –*y*, 1–*z*.

bip to generate a distorted trigonal bipyramid coordination geometry. O1, O3#2, and O4#1 are almost coplanar with mean deviation of 0.0046 Å, while N4 and N9#3 occupy vertices of the trigonal bipyramid. The Zn–O bond lengths are 2.157(4)–2.237(4) Å and Zn–N bond lengths are 2.219(5) and 2.213(5) Å. The Zn–O2 bond length is 2.544(3) Å, slightly longer than normal Zn–O bond distance; it can be regarded as a weak Zn–O interaction. Selected interatomic distances and angles for **1** and **2** are listed in table 2; they fall in the usual range for similar compounds [18]. The two carboxylates of bct show two coordination modes to Zn<sup>2+</sup> in **2**, one carboxylate (O1) of bct binds monodentate to one zinc, another (O3, O4) binds bridging bidentate to two zinc ions. Thus, each bct shares the same coordination environment by coordinating to three zinc ions with two carboxylates (figure 3(b)) and each bip binds to two Zn ions via its two N atoms (N1, N1#6) through bis-monodentate mode (figure 3(c)).

Two nearest Zn1 ions are bridged via carboxyl oxygens (O3, O4) to form a dimer unit [ZnCO<sub>2</sub>]<sub>2</sub> with zinc···zinc separation of 3.849 Å. The dinuclear unit is a center of symmetry, with OCO and OZnO angles of 120.88 and 126.88, respectively. In contrast to known [Zn<sub>2</sub>(L)(nba)<sub>2</sub>·2-DMF], L = 1,4-bis(imidazol-1-yl)benzene, H<sub>2</sub>nba = 1,4-naphthalenedicarboxylic acid with the dimer unit [ZnCO<sub>2</sub>]<sub>2</sub> [19], in which the dinuclear unit has zinc···zinc distance of 3.652 Å, and OCO and OZnO angles are 124.29 and 124.09. The dimer units are connected through monodentate (O1) and bridging bidentate (O3, O4) modes leading to a double left-handed helix chain structure along the *a* direction, as illustrated in figure 4 (a), which contains a second building unit [Zn<sub>4</sub>(bct)<sub>2</sub>] with a pitch of 17.548 Å. The bip provides N4 and N9 as binding sites to link [ZnCO<sub>2</sub>]<sub>2</sub> units of adjacent double helical chains giving a 2-D layered undulating framework in the *ac* plane (figure 4(a)). The bip in identical method links the remaining [ZnCO<sub>2</sub>]<sub>2</sub> unit of adjacent double helical chains in the *b*-axis, changing to a 3-D framework (figure 4(b)). An interesting feature of **2** is that bip binds to [ZnCO<sub>2</sub>]<sub>2</sub> to form two right-handed helical chains (figure 4(a)) along the *b* and *c* directions. The right-handed helices have second building units [Zn<sub>4</sub>(bip)<sub>2</sub>], with a pitch of 14.737 Å and Zn1 ions line up in two parallel columns along the *b* and *c* axes. Because left- and right-handed helical chains coexist in the crystal structure, the whole crystal is not chiral [20]. This suggests that bip and bct play a role in increasing the dimension and sustaining and stabilizing the structure. The coordinated water and unbonded carboxylate oxygens point toward the channels forming hydrophilic cavities filled with guest waters. The void volume of the channels without the guest molecules, calculated by PLATON, is 6.7%.

### 3.3. X-ray powder diffraction and thermogravimetric analyses

The PXRD experimental and computer-simulated patterns of **1** and **2** are shown in Supplementary material (figures S1 and S2), in which the main peaks of the experimental spectra of **1** and **2** are consistent with simulated spectra.

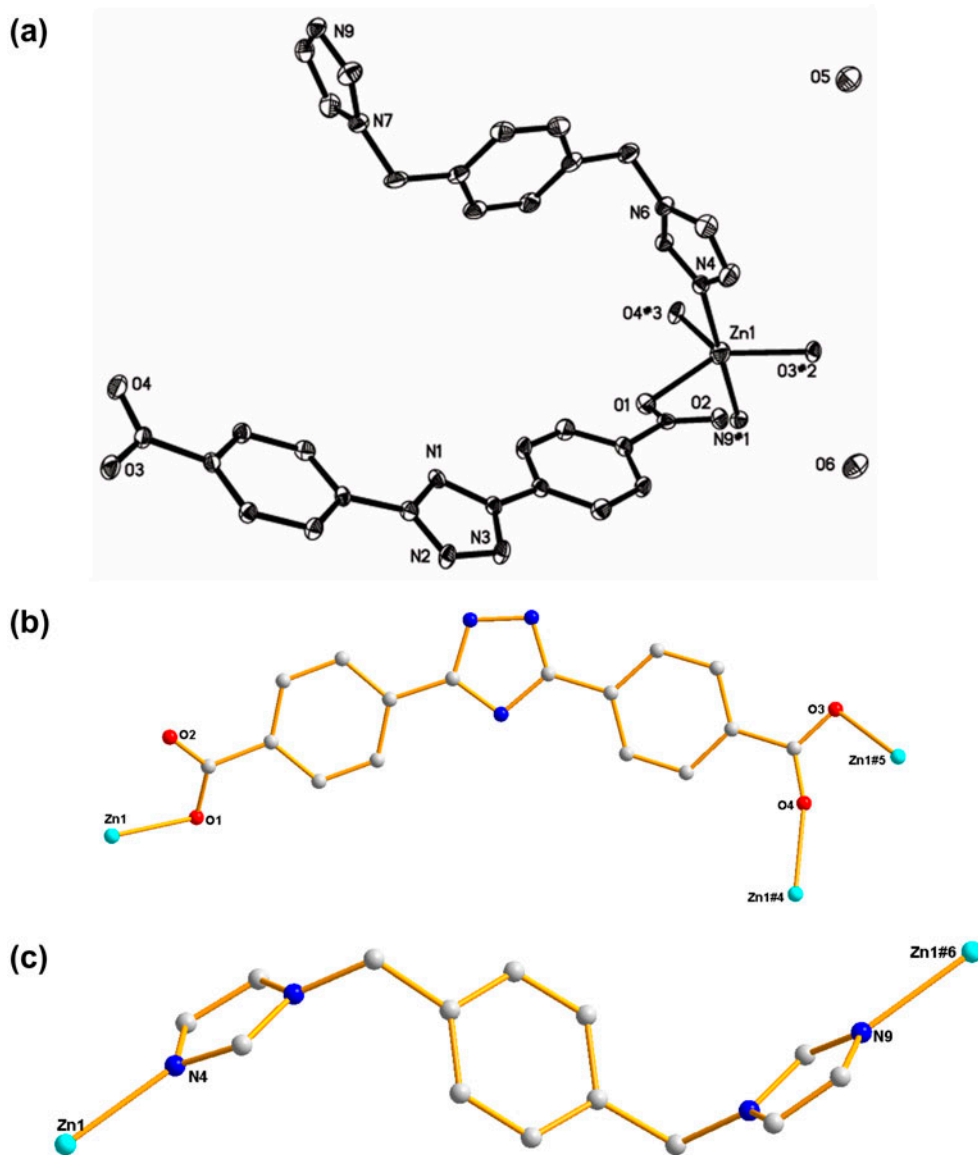


Figure 3. (a) The coordination environment of Zn1 at 30% probability level; (b) the coordination environment of bct in **2**; (c) the coordination environment of bip in **2**. Hydrogens are omitted for clarity. Symmetry codes: #1  $0.5+x, -0.5+y, z$ ; #2  $0.5+x, 0.5-y, 0.5+z$ ; #3  $1-x, -y, 0.5-z$ ; #4  $1-x, y, 0.5-z$ ; #5  $-0.5+x, 0.5-y, 0.5+z$ ; #6  $0.5+x, 0.5+y, z$ .

To estimate the stability of **1** and **2**, thermal behaviors were studied by TGA (Supplementary material, figures S3 and S4). Crystalline samples were heated from 40 to 900 °C in air at a heating rate of 10 °C/min. An initial weight loss of 8.1% from 130 to 220 °C was observed for **1**, attributed to loss of two waters per formula unit (calculated 7.9%). A further sharp weight loss was observed from 330 to 610 °C implying that bct decomposes; the final residual mass corresponds to CdO supported by the expected value of 28.7% (Calcd 28.2%). The thermogravimetric analysis data show that **2** undergo three weight

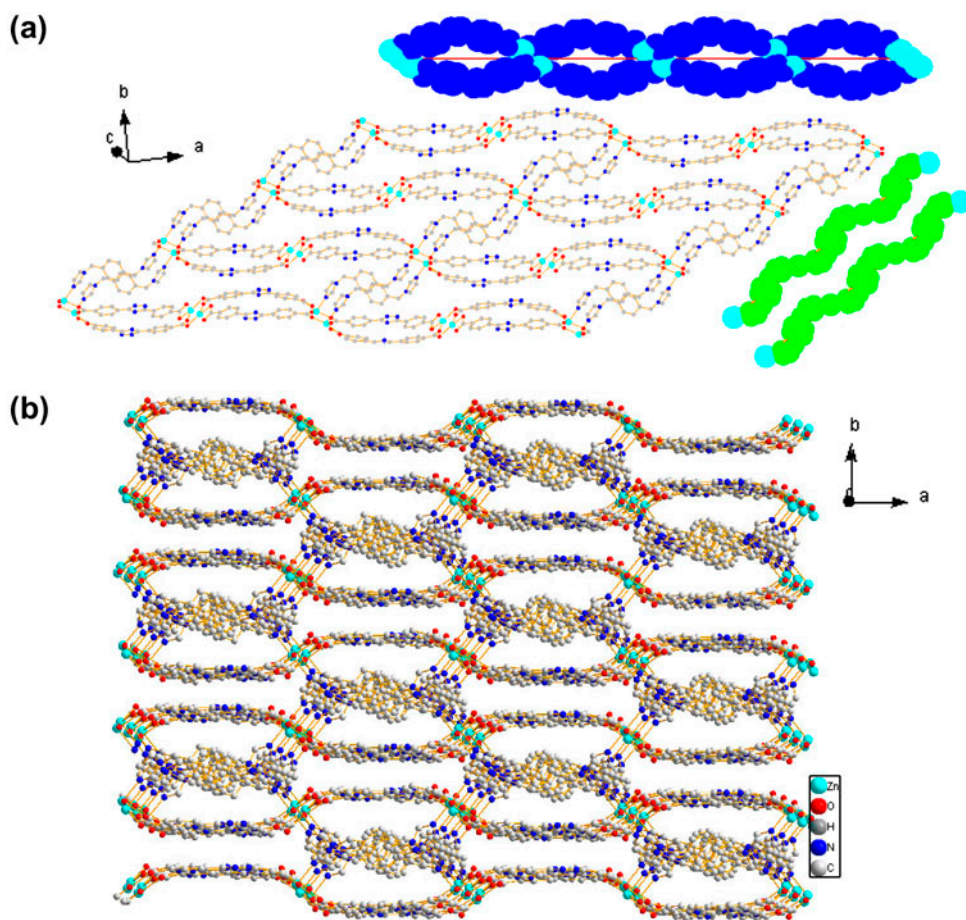


Figure 4. (a) 2-D framework of **2**, including double left-handed helical chains along the *a* axis and two right-handed helical chains along the *c* axis; (b) 3-D framework of **2**.

losses. Water molecules are removed in a single step at 120–200 °C, with weight loss of 5.8% (Calcd: 5.6%). The second stage is attributed to the removal of bip from 290 to 410 °C, with a weight loss of 36.6% (Calcd: 36.9%). A further sharp weight loss was observed from 460 to 620 °C implying that *bct* decomposes; the final residual mass corresponds to ZnO supported by the expected value of 12.7% (Calcd: 12.6%).

### 3.4. Luminescence

As reported previously, metal-organic compounds have the ability to affect the emission wavelength and intensity of organic material through metal coordination. We have examined the photoluminescent properties of **1** and **2** in the solid state at room temperature (figure 5). Pure H<sub>2</sub>bct and bip have emissions of 423 and 430 nm upon being excited at 353 and 356 nm, respectively. Complex **1** exhibits an intense emission at 399 nm upon being excited at 337 nm and has a slight blue-shift compared with that of pure H<sub>2</sub>bct and bip ligands. Different from **1**, **2** excited at 363 nm produces an intense emission with a maximum at 441 nm, compared with the emission spectra of H<sub>2</sub>bct and bip, a red shift was observed.

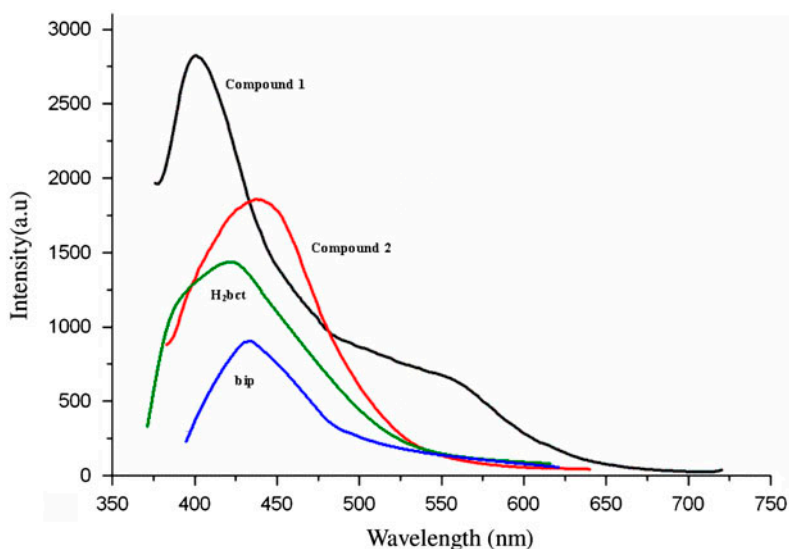


Figure 5. Emission spectra of **1** (black), **2** (red), bip (blue) and H<sub>2</sub>bct (green) in the solid state at room temperature (see <http://dx.doi.org/10.1080/00958972.2013.827178> for color version).

Apparently, emission spectra of **1** and **2** resemble that of H<sub>2</sub>bct except for the emission intensity and peak positions, indicating that the fluorescence of the complexes is ligand-based emission [21]. The different locations and profiles of their emission peaks may result from different metal centers, structures, and ligands as well as weak interactions in the network lattice, which may affect the rigidity of the whole network and further the energy transfer involved in luminescence [22]. The compounds show enhanced luminescence and may be considered as good candidates for luminescent applications, especially for **1**.

#### 4. Conclusion

Two polymers, [Cd(bct)(H<sub>2</sub>O)]·(H<sub>2</sub>O) (**1**) and [Zn(bct)(bip)]·2(H<sub>2</sub>O) (**2**), were synthesized by self-assembly of bct anion, bip ligands, and Cd(CH<sub>3</sub>COO)<sub>2</sub>·2(H<sub>2</sub>O) or Zn(CH<sub>3</sub>COO)<sub>2</sub>·2(H<sub>2</sub>O). The work proves that H<sub>2</sub>bct and bip are good candidates in assembling MOFs with various double-layered subunits, such as double-layered straight-chains and double-layered helical-chains. H<sub>2</sub>bct ligands adopt a  $\mu_4-k^1, k^1, k^1, k^1$  and  $\mu_3-k^1, k^1, k^1$  modes for **1** and **2**, respectively. The diversities of structures result from the different geometries, coordination abilities, and sizes inducing the different coordination spheres. **1** and **2** display two- and three-dimensional structures in the solid state, which is quite different. Polymers **1** and **2** exhibit intense emissions, which appear to be potential luminescent materials. Subsequent work will focus on the structures and properties of a series of CPs constructed by the present ligand with copper, cobalt, manganese, silver, and rare earth metals, to enrich the family of CPs.

#### Acknowledgement

This project is supported by the Natural Scientific Research Foundation of Shaanxi Provincial Education Office of China (No. 11JK0583), and science and technology research and development projects of Shaanxi Provincial (No. 2013JM2015).

## References

- [1] (a) F. Blank, C. Janiak. *Coord. Chem. Rev.*, **253**, 827 (2009); (b) X.-H. Bu, M.-L. Tong, Y.-B. Xie, J.-R. Li, H.-C. Chang, S. Kitagawa, J. Ribas. *Inorg. Chem.*, **44**, 9837 (2005); (c) D.-S. Li, L. Tang, F. Fu, M. Du, J. Zhao, N. Wang, P. Zhang. *Inorg. Chem. Commun.*, **13**, 1126 (2010); (d) X. Feng, Y.-F. Wang, Z.-Q. Shi, J.-J. Shang, L.-Y. Wang. *Inorg. Chem. Commun.*, **22**, 131 (2012).
- [2] (a) S.-Y. Liao, W. Gu, L.-Y. Yang, T.-H. Li, J.-L. Tian, L. Wang, M. Zhang, X. Liu. *Cryst. Growth Des.*, **12**, 3927 (2012); (b) W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu. *Inorg. Chem. Commun.*, **24**, 209 (2012).
- [3] D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Glaser, G. Kalies, K.A. Cychosz, M. Thommes, R. Staudt, H. Krautscheid. *Angew. Chem. Int. Ed.*, **50**, 10344 (2011).
- [4] K.-S. Jeong, Y.-B. Go, S.-M. Shin, S.-J. Lee, J. Kim, O.-M. Yaghi, N. Jeong. *Chem. Sci.*, **2**, 877 (2011).
- [5] C. Wang, Z.-G. Xie, K.-E. DeKrafft, W.-B. Lin. *J. Am. Chem. Soc.*, **133**, 13445 (2011).
- [6] H.-B. Zhou, J. Wang, H.-S. Wang, Y.-L. Xu, X.-J. Song, Y. Song, X.-Z. You. *Inorg. Chem.*, **50**, 6868 (2011).
- [7] Y. Zuo, M. Fang, G. Xiong, P.-F. Shi, B. Zhao, J.-Z. Cui, P. Cheng. *Cryst. Growth Des.*, **12**, 3917 (2012).
- [8] B. Zhao, P. Cheng, X.-Y. Chen, C. Cheng, W. Shi, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang. *J. Am. Chem. Soc.*, **126**, 3012 (2004).
- [9] (a) Z. Chen, B. Zhao, Y. Zhang, W. Shi, P. Cheng. *Cryst. Growth Des.*, **8**, 2291 (2008); (b) F. Hung-Low, A. Renz, K.K. Klausmeyer. *Polyhedron*, **28**, 407 (2009); (c) S.K. Ghosh, S. Kitagawa. *CrystEngComm.*, **10**, 1739 (2008); (d) G. Férey. *Chem. Soc. Rev.*, **37**, 191 (2008); (e) H.-C. Fang, J.-Q. Zhu, L.-J. Zhou, H.-Y. Jia, S.-S. Li, X. Gong, S.-B. Li, Y.-P. Cai, P.-K. Thallapally, J. Liu, G.-J. Exarhos. *Cryst. Growth Des.*, **10**, 3277 (2010).
- [10] (a) Y.-G. Sun, M.-Y. Guo, G. Xiong, F. Ding, L. Wang, B. Jiang, M.-C. Zhu, E.-J. Gao, F. Verpoort. *J. Coord. Chem.*, **63**, 4188 (2010); (b) H.-A. Tsai, M.-C. Suen, P.-N. Wang, Y.-F. Hsu, J.-C. Wang. *J. Coord. Chem.*, **64**, 2658 (2011); (c) X.-F. Zheng, L.-G. Zhu. *Polyhedron*, **30**, 666 (2011); (d) W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu. *Chem. Commun.*, **47**, 3834 (2011).
- [11] (a) W.-T. Yang, M. Guo, F.-Y. Yi, Z.-M. Sun. *Cryst. Growth Des.*, **12**, 5529 (2012); (b) L. Qin, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng. *Cryst. Growth Des.*, **12**, 5783 (2012).
- [12] (a) R.-B. Fu, S.-M. Hu, X.-T. Wu. *CrystEngComm.*, **14**, 3478 (2012); (b) L. Croitor, E.B. Coropceanu, A.V. Siminel, O. Kulikova, V.I. Zelentsov, T. Datsko, M.S. Fonari. *CrystEngComm.*, **14**, 3750 (2012); (c) L.-Y. Xin, G.-Z. Liu, X.-L. Li, L.-Y. Wang. *Cryst. Growth Des.*, **12**, 147 (2012).
- [13] (a) C.-X. Chen, Q.-K. Liu, J.-P. Ma, Y.-B. Dong. *J. Mater. Chem.*, **22**, 9027 (2012); (b) Q.-G. Zhai, Q.-P. Lin, T. Wu, S.-T. Zheng, X.-H. Bu, P.-Y. Feng. *Discuss. Faraday Soc.*, **41**, 2866 (2012); (c) J.-H. Jia, X. Lin, C. Wilson, A.J. Blake, N.R. Champness, P. Hubberstey, G. Walker, E.J. Cussen, M. Schröder. *Chem. Commun.*, **8**, 840 (2007).
- [14] (a) J.-H. Qin, L.-F. Ma, Y. Hu, L.-Y. Wang. *CrystEngComm.*, **14**, 2891 (2012); (b) M.-L. Han, J.-G. Wang, L.-F. Ma, H. Guo, L.-Y. Wang. *CrystEngComm.*, **14**, 2691 (2012); (c) X.-F. Feng, W.-C. Song, Q. Yang, X.-H. Bu. *Discuss. Faraday Soc.*, **41**, 4217 (2012); (d) C.-H. He, C.-H. Jiao, J.-C. Geng, G.-H. Cui. *J. Coord. Chem.*, **65**, 2294 (2012); (e) S.-W. Jin, D.-Q. Wang, Y.-C. Xu. *J. Coord. Chem.*, **65**, 1953 (2012); (f) C.-H. Jiao, C.-H. He, J.-C. Geng, G.-H. Cui. *J. Coord. Chem.*, **65**, 2852 (2012).
- [15] (a) G.M. Sheldrick. *SHELXS 97, Program for Crystal Structure Solution*, University of Gottingen, Germany (1997); (b) G.M. Sheldrick. *SHELXS 97, Program for Refinement of Crystal Structure*, University of Gottingen, Germany (1997).
- [16] (a) B. Liu, L.-J. Fan, Y.-Y. Liu, J. Yang, J.-F. Ma. *J. Coord. Chem.*, **64**, 413 (2011); (b) H.-Y. Xia, X.-C. Zha, G.-X. Liu, Y. Wang, X.-M. Ren. *Chin. J. Inorg. Chem.*, **27**, 1441 (2011); (c) D.-S. Li, P. Zhang, J. Zhao, Z.-F. Fang, M. Du, K. Zou, Y.-Q. Mu. *Cryst. Growth Des.*, **12**, 1697 (2012).
- [17] L. Qin, J.-S. Hu, Y.-Z. Li, H.-G. Zheng. *Cryst. Growth Des.*, **12**, 403 (2012).
- [18] (a) H.-W. Kuai, J. Fan, Q. Liu, W.-Y. Sun. *CrystEngComm.*, **14**, 3708 (2012); (b) L.-W. Kong, M.-L. Ma, L.-C. Wu, X.-L. Zhao, F. Guo, B. Jiang, K. Wen. *Discuss. Faraday Soc.*, **41**, 5625 (2012).
- [19] Y.-W. Li, H. Ma, Y.-Q. Chen, K.-H. He, Z.-X. Li, X.-H. Cryst. *Growth Des.*, **12**, 189 (2012).
- [20] (a) S. Hu, Z.-S. Meng, M.-L. Tong. *Cryst. Growth Des.*, **10**, 1742 (2010); (b) J.-K. Sun, Q.-X. Yao, Z.-F. Ju, J. Zhang. *CrystEngComm.*, **12**, 1709 (2010).
- [21] (a) D.M. Ciurtin, N.G. Pschirer, M.D. Smith, U.H.F. Bunz, H.-C. zur Loye. *Chem. Mater.*, **13**, 2743 (2001); (b) M.-F. Wang, X.-J. Hong, Q.-G. Zhan, Y.-T. Liu, H.-G. Jin, Z.-P. Zheng, S.-H. Xu, Y.-P. Cai. *Dalton Trans.*, 11898 (2012).
- [22] (a) S. Wang, H. Xing, Y. Li, J. Bai, Y. Pan, M. Scheer, X. You. *Eur. J. Inorg. Chem.*, **15**, 3041 (2006). (b) X.-L. Sun, Z.-J. Wang, S.-Q. Zang, W.-C. Song, C.-X. Du. *Cryst. Growth Des.*, **24**, 4431 (2012).