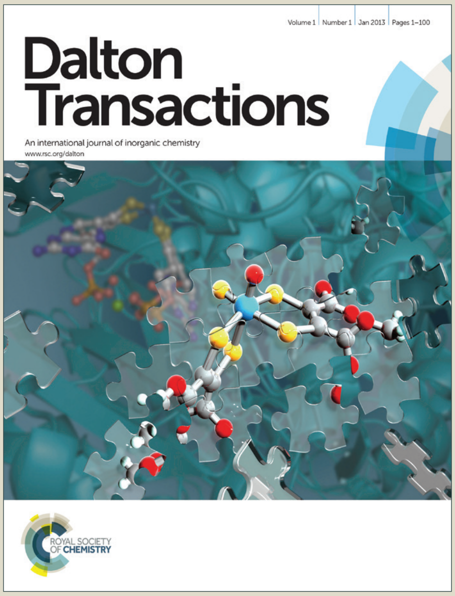
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Structural Diversity and Photoluminescent Properties of Cadmium Thiophenedicarboxylate Coordination Polymers

Li-Ping Xue,[†] Xin-Hong Chang,[†] Shi-Hui Li,[†] Lu-Fang Ma,*[,†] and Li-Ya Wang*[,†,‡]

[†]*College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, P. R. China.*

[‡]*College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, P. R. China*

Received (in XXX, XXX) Xth XXXXXXXXX 2014, Accepted Xth XXXXXXXXX 2014

First published on the web Xth XXXXXXXXX 2014

DOI: 10.1039/b000000x

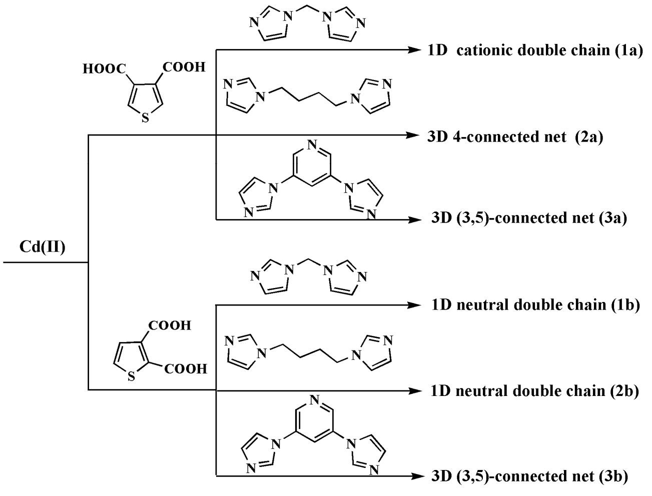
Two series of Cd(II) coordination polymers (CPs) , $\{[Cd(bimm)_2(H_2O)_2][(3,4\text{-}tdc)_2][H_2O]_2\}_n$ (**1a**), $[Cd(3,4\text{-}tdc)(bimb)]_n$ (**2a**), $[Cd(3,4\text{-}tdc)(bimpy)(H_2O)]_n$ (**3a**) and $[Cd(2,3\text{-}Htdc)_2(bimm)_2]_n$ (**1b**), $\{[Cd(2,3\text{-}tdc)(bimb)](H_2O)\}_n$ (**2b**), $[Cd(2,3\text{-}tdc)(bimpy)(H_2O)]_n$ (**3b**) where H_2tdc= thiophenedicarboxylic acid, bimm = 1,2-bis(imidazol-1′-yl)methane, bimb = 1,2-bis(imidazol-1′-yl)butane and bimpy = 3,5-bis(imidazol-1′-yl)pyridine, have been synthesized by using Cd(II) acetate with H_2tdc and N-donor ligands under hydrothermal conditions. Two related isomeric thiophenedicarboxylic acids were chosen to examine the positional isomeric effect on the construction of these CPs with distinct dimensionality and connectivity. The structure of **1a** is a one-dimensional (1D) cationic double chain further forming a two-dimensional (2D) supramolecular network *via* hydrogen-bonding interactions, while **1b** exhibits a neutral double chain structure. Interestingly, a three-dimensional (3D) 4-connected **cds** network for **2a** as well as a 1D neutral double chain structure for **2b** were obtained in the presence of bimb. When the rigid tripodal bimpy was introduced, isomorphous **3a** and **3b** with 3D (3,5)-connected $(6^2.8)$ $(6^7.8^3)$ nets were constructed. Structural diversity of **1a−2b** mainly stems from positional isomeric effect of thiophenedicarboxylate, while **3a** and **3b** are well regulated by rigid bimpy. Moreover, thermal stability and photoluminescence of **1a−3b** are investigated.

Introduction

By virtue of a feasible synthesizing strategy of crystal engineering, a great many coordination polymers (CPs) have been rationally designed and constructed.[1] Although rapid progress in this flourishing field has been made, it still remains a great challenge to rationally prepare such crystalline materials with desired fascinating structures and potential functions in crystal engineering. It has been recognized that the assembly of CPs can be tuned by altering synthetic parameters such as the coordination preferences of ion, various coordination modes of the organic ligands, the metal/ligand ratio, solvent, and temperature, etc. These factors may result in the complexity and uncertainty of the CPs, and great contributions have been focused on this field to investigat the effects and guide the syntheses. [2] In this regard, the appropriate design of suitable organic ligands is a key element to adjust the topologies of CPs. Currently, rigid multicarboxylates such as benzenepolycarboxylate and N-heterocyclic ligands have been widely employed for their various coordination modes and strong affinities for metal ions. Nevertheless, less attention has been paid to the role of positional isomeric effect of rigid multicarboxylates on the structural assemblies with d^{10} metal ions.[3] In this sense, an investigation for understanding the relationship between the positional isomeric effect and the structural diversification of heterocyclic aromatic ligands is still challenging.

As is well known, thiophenes and their derivatives possess unique physical and chemical properties due to its lone pair of electrons from sulfur atoms can be more easily delocalized within thiophene ring, and such ligands usually show good charge-transfer abilities. Recently, thiophenes and their derivatives have been extensively and thoroughly studied for their structural diversities and potential applications as functional materials. Commercially available 2,5-thiophenedicarboxylic acid (2,5-H_2tdc) has been extensively employed to prepare CPs.[4] However, research on 3,4-thiophenedicarboxylic acid (3,4-H_2tdc) and 2,3-thiophenedicarboxylic acid (2,3-H_2tdc) in the construction of CPs is still very limited so far.[5] 3,4-H_2tdc and 2,3-H_2tdc are a pair of isomers of thiophenedicarboxylic acid, which differ in the position of the dicarboxylic acid at the substituted thiophene ring, and may afford various supramolecular assemblies in view of their isomeric effect.

Our group has previously investigated positional isomeric effect of isomeric benzene–dicarboxylates and the results show that isomeric benzene–dicarboxylates play crucial roles in modulating diverse structures of CPs.[6] Here we report six Cd-CPs based on two positional isomeric thiophenedicarboxylic acids with N-donor auxiliary ligands. Structural diversity of these CPs reveal positional isomeric organic thiophenedicarboxylate and N-donor ligands play dominating roles in modulating the final structures (Scheme **1**). Solid-state properties for these crystalline materials, such as thermal and luminescence properties, have also been investigated.



Scheme 1 Syntheses of compounds **1a**–**3b**.

Experimental section

Materials and methods

3,4-thiophenedicarboxylic acid,[7] 2,3-thiophenedicarboxylic acid,[8] bimm[9] and bimb[10] were synthesized in accordance with the procedure reported, repectively. $Cd(OAc)_2·2H_2O$ and bimpy were purchased commercially and used without further purification. The hydrothermal reaction was performed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000 to 400 cm^{-1}. Elemental analyses for C, H, and N were carried out on a Flash 2000 elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analyses were carried out on a SDT Q600 thermogravimetric analyzer. A platinum pan was used for heating the sample with a heating rate of 10 °C/min under a N_2 atmosphere. Luminescent spectra were recorded with a Hitachi F4500 fluorescence spectrophotometer.

Synthesis of $\{[Cd(bimm)_2(H_2O)_2][(3,4\text{-tdc})_2][H_2O]_2\}_n$ (1a)

A mixture of 3,4-H_2tdc (0.017 g, 0.10 mmol), $Cd(OAc)_2·2H_2O$ (0.027 g, 0.10 mmol), bimm (0.030 g, 0.20 mmol), and 8 mL deionized water was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 ºC for 5 days under autogenous pressure, followed by cooling to room temperature at a rate of 5 $^{o}C\ h^{-1}$.Yellow block crystals of **1a** were obtained (yield: 13% based on Cd). Elemental analysis calcd (%) for $C_{26}H_{28}CdN_8O_{12}S_2$: C, 38.00; H, 3.41; N, 13.64. Found: C, 38.09; H, 3.48; N, 13.59. IR (KBr pellet, ν/cm^{-1}): 3102 (m), 1687(m), 1544 (s), 1505 (s), 1466 (m), 1438(m), 1374 (vs), 1282 (m), 1231 (s), 1107 (m), 1088 (m), 1035 (m), 932 (m), 886 (w), 846 (s), 793 (m), 756 (s), 730 (s).

Synthesis of $[Cd(2,3\text{-Htdc})_2(bimm)_2]_n$ (1b)

Compound **1b** was synthesized by a procedure similar to that of **1a**, except 2,3-H_2tdc (0.017 g, 0.10 mmol) replaced 3,4-H_2tdc. Colourless block crystals of **1b** were obtained (yield: 21% based on Cd). Elemental analysis calcd (%) for $C_{26}H_{22}CdN_8O_8S_2$: C, 41.54; H, 2.93; N, 14.91. Found: C, 41.49; H, 2.96; N, 14.93. IR (KBr pellet, ν/cm^{-1}): 1682 (m), 1602 (m), 1581 (s), 1453 (m), 1419 (m), 1323 (vs), 1288 (m), 1186 (m), 1126 (m), 1071 (m), 1026 (m), 933 (m), 860 (s), 802 (m), 683 (s), 666 (m).

Synthesis of $[Cd(3,4\text{-tdc})(bimb)]_n$ (2a)

Compound **2a** was synthesized by a procedure similar to that of **1a**, except bimb (0.038g, 0.20 mmol) replaced bimm. Light-yellow block crystals of **2a** were obtained (yield: 25% based on Cd). Elemental analysis calcd (%) for $C_{16}H_{16}CdN_4O_4S$: C, 40.61; H, 3.38; N, 11.85. Found: C, 40.68; H, 3.43; N, 11.87. IR (KBr pellet, ν/cm^{-1}): 1542 (s), 1465 (m), 1441 (m), 1384 (vs), 1339(s), 1251(m), 1106 (s), 1087(m), 1034(m), 1005 (w), 941 (m), 907 (w), 844 (vs), 822 (s), 774 (s), 750 (s), 729 (m), 680 (m).

Synthesis of $\{[Cd(2,3\text{-tdc})(bimb)](H_2O)\}_n$ (2b)

Compound **2b** was synthesized by a procedure similar to that of **2a**, except bimb (0.038 g, 0.20 mmol) replaced bimm. Colourless block crystals of **2b** were obtained (yield: 33% based on Cd). Elemental analysis calcd (%) for $C_{16}H_{18}CdN_4O_5S$: C, 39.12; H, 3.67; N, 11.41. Found: C, 39.49; H, 3.70; N, 11.51. IR (KBr pellet, ν/cm^{-1}): 3403 (br), 1543 (s), 1466 (m), 1440 (m), 1384 (vs), 1340 (s), 1252 (m), 1106 (s), 1087 (m), 1034 (m), 1005 (w), 941 (m), 907 (w), 845 (vs), 774 (s), 751 (s), 732 (m), 682 (m).

Synthesis of $\{[Cd(3,4\text{-tdc})(bimpy)](H_2O)\}_n$ (3a)

Compound **3a** was synthesized by a procedure similar to that of **1a**, except bimpy (0.042 g, 0.20 mmol) replaced bimm. Yellow block crystals of **3a** were obtained (yield: 43% based on Cd). Elemental analysis calcd (%) for $C_{17}H_{13}CdN_5O_5S$: C, 39.86; H, 2.54; N, 13.21. Found: C, 39.76; H, 2.60; N, 13.11. IR (KBr pellet, ν/cm^{-1}): 3200 (br), 1557 (s), 1396 (m), 1343 (m), 1288 (m), 1191 (m), 1084 (m), 1020 (m), 988 (w), 930 (m), 826 (m), 766 (m), 713 (w), 683 (m).

Synthesis of $\{[Cd(2,3\text{-tdc})(bimpy)](H_2O)\}_n$ (3b)

Compound **3b** was synthesized by a procedure similar to that of **1b**, except bimpy (0.042 g, 0.20 mmol) replaced bimm. Colourless block crystals of **3b** were obtained (yield: 32% based on Cd). Elemental analysis calcd (%) for $C_{17}H_{13}CdN_5O_5S$: C, 38.50; H, 2.83; N, 13.68. Found: C, 38.86; H, 2.90; N, 13.49. IR (KBr pellet, ν/cm^{-1}): 3200 (br), 1557 (s), 1396 (m), 1344 (m), 1288 (m), 1191(m), 1084 (m), 1020 (m), 932 (m), 826 (m), 766 (m), 713 (w), 682 (m).

X-ray crystallography

The crystal structure data of **1a**−**3b** were collected on Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation using an ω scan mode at 293 K. An empirical absorption correction was applied using the SADABS program.[11] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model. Other hydrogen atoms were placed at the calculation positions. S atoms of compound **3b** are in positional disorder, and has been resolved in terms of their occupancy. A summary of the crystallographic data of **1a**–**3b** is listed in Table S1 of ESI.† Selected bond lengths of **1a**–**3b** are listed in Table S2 of ESI.†

Results and discussions

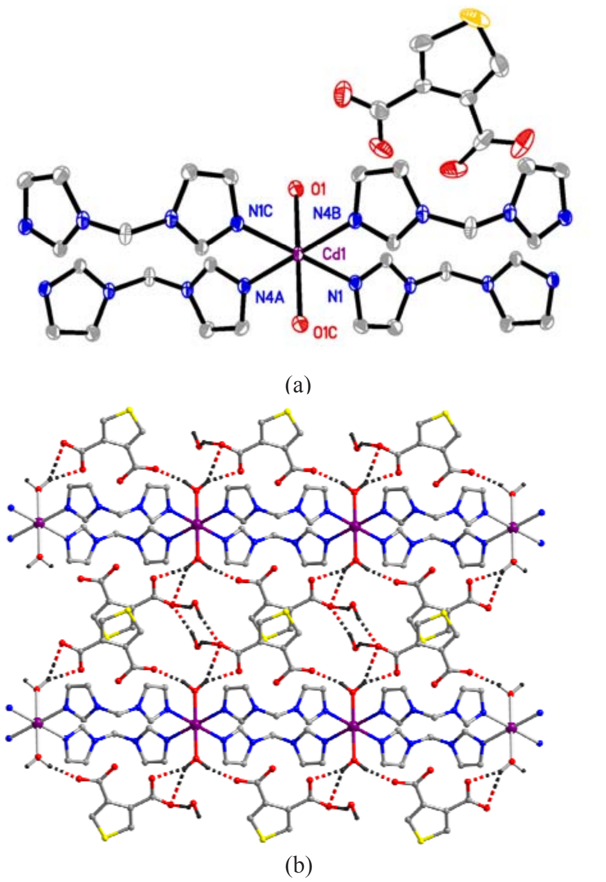
Synthesis

According to our experimental results, the direct combination of the cadmium acetate dihydrate, H_2tdc and auxiliary co-ligands resulted in formation of unknown precipitates by common methods. Therefore, the hydrothermal method was employed in this work for the syntheses of **1a**–**3b**. Compounds **1a**–**3b** are stable at room temperature and not soluble in water and common organic solvents. The elemental analysis results match well with the composition of crystal structure determination.

Description of crystal structures

$\{[Cd(bimm)_2(H_2O)_2][(3,4\text{-}tdc)_2][H_2O]_2\}_n$ (1a) and $[Cd(2,3\text{-}Htdc)_2(bimm)_2]_n$ (1b)

X-ray crystallographic data show that compound **1a** crystallizes in triclinic space group $P\bar{1}$. The structure of **1a** consists of 1D $\{[Cd(bimm)_2(H_2O)_2]^{2+}\}_n$ cationic double chains, 3,4-tdc^{2-} anions and lattice water molecules. Each Cd^{2+} ion is six-coordinated by four nitrogen atoms from different bimm and two water molecules to form a slightly distorted octahedral geometry. Four nitrogen atoms lie in the equatorial plane and two coordinated water molecules are in the apical positions (Fig. 1a). In **1a**, two Cd^{2+} ions are bridged by two bimm to form a 16-membered macrometallacycle with a Cd···Cd separation of 9.310 Å. Each bimm coordinates to two Cd^{2+} ions, acting as a bridging ligand to link Cd^{2+} ions to form an infinite 1D cationic double chain. It is noted that tdc^{2-} anion does not coordinate to the Cd^{2+} ion while acts as a counteranion, and participates in an extensive hydrogen bonding network with coordinated water molecules, leading to a 2D supramolecular structure (Fig. 1b). When 2,3-H_2tdc ligand was used, a structurally different framework **1b** was formed. **1b** crystallizes in monoclinic space group $C2/c$ and consists of a 1D neutral polymeric chain in which the octahedral Cd^{2+} ion is coordinated to four bimm ligands and two individual 2,3-Htdc$^-$ ligands (Fig. 2a). In **1b**, two Cd^{2+} ions are also bridged by two bimm to form a 16-membered metallomacrocycle with a Cd···Cd separation of 8.764 Å, which is shorter than that observed in **1a**. Each bimm connects Cd^{2+} ions to form a 1D linear neutral polymeric double chain (Fig. 2b). The H_2tdc ligand is just partially deprotonated, one carboxylate group participates in bonding while the other one remains free to satisfy the charge of Cd^{2+} ion.



(a)

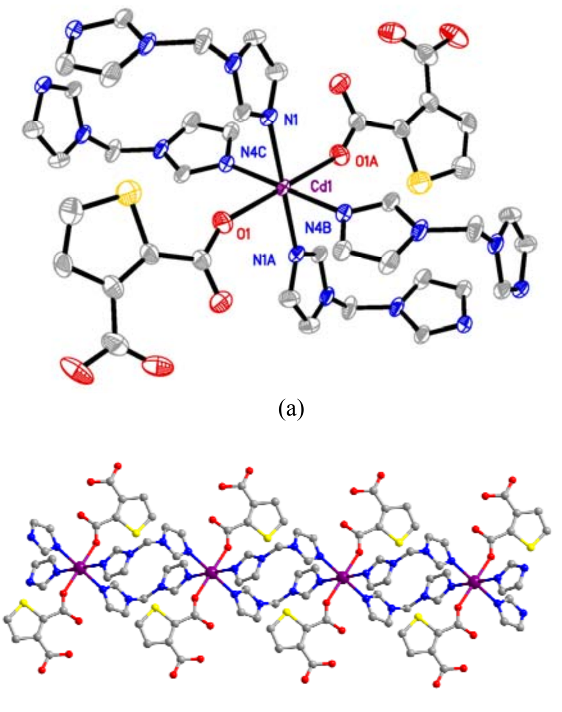
(b)

Fig. 1. (a) Coordination environment of the Cd(II) ion in **1a**, The hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: A: $x-1, y+1, z$; B: $-x+1, -y+1, -z+1$; C: $-x, -y+2, -z+1$. (b) View of the 2D supramolecular layer.

$[Cd(3,4\text{-}tdc)(bimb)]_n$ (2a) and $\{[Cd(2,3\text{-}tdc)(bimb)](H_2O)\}_n$ (2b)

When a long sized bimb was used instead of bimm, pure crystalline **2a** and **2b** with monoclinic space group $C2/c$ were formed under similar reaction conditions. As shown in Fig. 3a, the fundamental building unit of **2a** contains half a Cd^{2+} ion, a tdc^{2-} anion in a general position and half a bimb lying about inversion centres. The Cd^{2+} ion is six-coordinated to four oxygen atoms from two different tdc^{2-} anions and two nitrogen atoms from two bimb to finish a distorted octahedral coordination environment. In **2a**, each tdc^{2-} anion serves as a μ_2-bridge linking two adjacent Cd^{2+} ions in the bis(chelating) mode to give rise to an infinite $[Cd(tdc)]_n$ zigzag chain along the [001] direction with Cd···Cd diatance of 6.53 Å (Fig. 3b). These chains are further extended by the connection between the Cd^{2+} ion and bimb to form a 3D **cds**-type framework with a $6^5.8$ topology (Fig. 3c).

In contrast, the asymmetric unit of **2b** consists of one crystallographically independent Cd^{2+} ion, one bimp, one tdc^{2-}



(a)

(b)

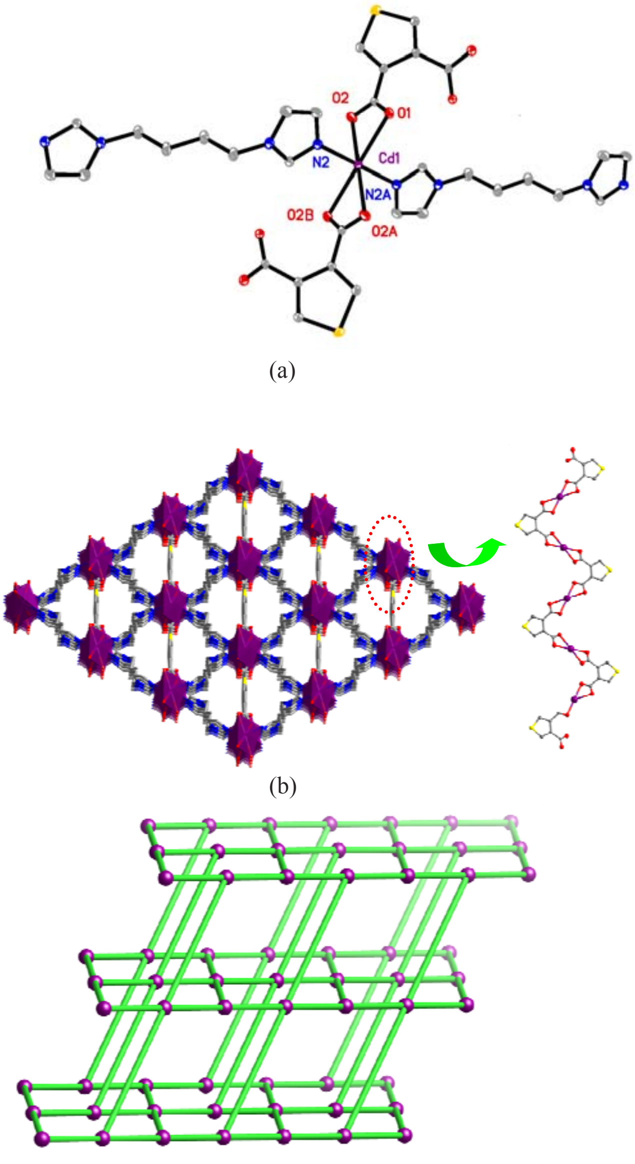
Fig. 2. (a) Coordination environment of the Cd(II) ion in **1b**, Symmetry codes: A: –*x* + 1/2, –*y* – 1/2, –*z* + 1; B: –*x* + 1/2, –*y* + 1/2, –*z* + 1; C: *x*, *y* – 1, *z*. (b) View of the 1D double chain.

anion, and one free water molecule (Fig. 4a). Each Cd^{2+} ion lies in a distorted octahedral coordination environment completed by four oxygen atoms from two μ-κ^2 carboxylate groups and two N atoms from two bimp ligands. As shown in Fig. 4b, a pair of oppositely arranged μ_2-bimb in **2b** bind two Cd^{2+} ions to form a $[Cd_2(bimb)_2]$ 24-membered metallomacrocycle ring subunit. On the other hand, a pair of oppositely arranged tdc^{2-} anions adopting μ_2-κ^2, κ^2 coordination mode bind two Cd^{2+} ions to form another kind of subunit. These two kinds of subunits link each other by sharing the Cd^{2+} ions with the adjacent subunits, to form a no-planar 1D double chain. Furthermore, the free water molecules are hydrogen bonded to three oxygen atoms from tdc^{2-} anions of intra- and interchain, respectively (O6−H2W···O1^i, O6−H2W···O3^i and O6−H1W···O4, Symmetry codes: (i) −x +1/2, −y +1/2, −z +1), together with the C−H···π interaction between the rings of imidazole and thiophene ring of tdc^{2-} anions with an edge-to-face orientation (d = 2.720 Å; A = 170°; d and A stand for H···π separation and C−H···π angle in the C−H···π pattern, respectively) to extend the 1D chains into a 2D network (Fig. 4c).

$\{[Cd(3,4\text{-}tdc)(bimpy)](H_2O)\}_n$ (3a) and $\{[Cd(2,3\text{-}tdc)(bimpy)](H_2O)\}_n$ (3b)

When rigid tridentate 3,5-bis(imidazol-1′-yl)pyridine was used, **3a** and **3b** were obtained. Single crystal X-ray structural analysis reveal both complexes are isomorphous and crystallize in the non-centrosymmetrical tetragonal space group *I*(-4)2*d*. Thus, only the structure of **3a** is described representatively. In the asymmetrical unit, there exist a half Cd^{2+} ion, a half tdc^{2-} anion, a half bimpy and one lattice water molecule. As depicted in Fig. 5a, each Cd^{2+} ion is located in seven-coordinated pentagonal bipyramid environment: four O atoms (Cd−O: 2.342(4) and 2.517(4) Å) from two tdc^{2-} anions, and three N atoms (Cd−N: 2.345(4) and 2.439(5) Å) from bimpy ligands, respectively.

In **3a**, each bimpy connects three Cd^{2+} ions using its pyridyl and imidazole groups. If the coordination bonds between Cd^{2+} ions and tdc^{2-} anions are neglected, the Cd^{2+} centers are bridged by bimpy to give rise to a double-layered 2D network parallel to the *ab* plane, as illustrated in Fig. 5b. The layers are further linked together by full deprotonated tdc^{2-} anions to generate a 3D framework (Fig. 5c). From the topological view, each bimpy can be defined as a 3-connected node, each

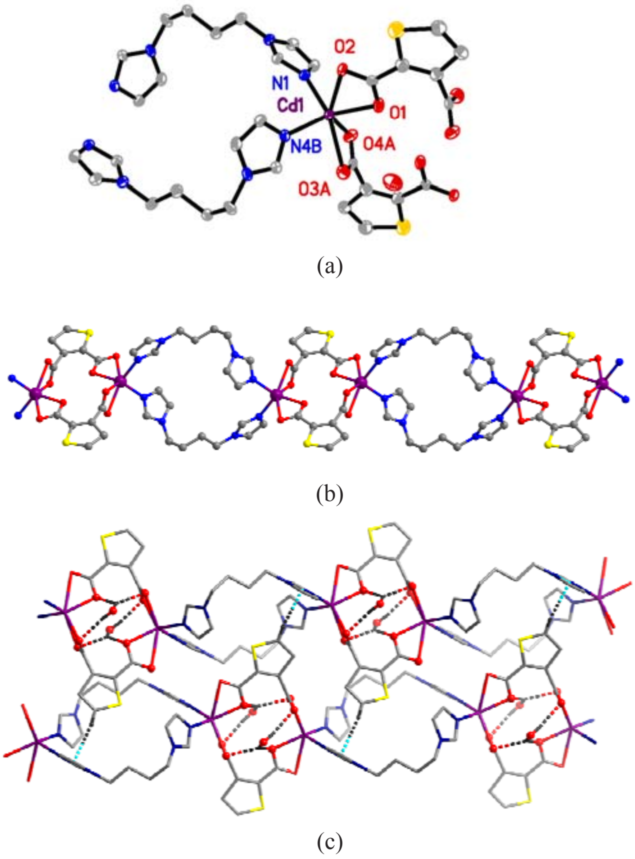


(a)

(b)

(c)

Fig. 3. (a) Coordination environment of the Cd(II) ion in **2a**, Symmetry codes: A: –*x* + 1, –*y*, –*z*. (b) View of the 3D network and $[Cd(tdc)]_n$ zigzag chain. (c) Schematic view of the **cds** net.



(a)

(b)

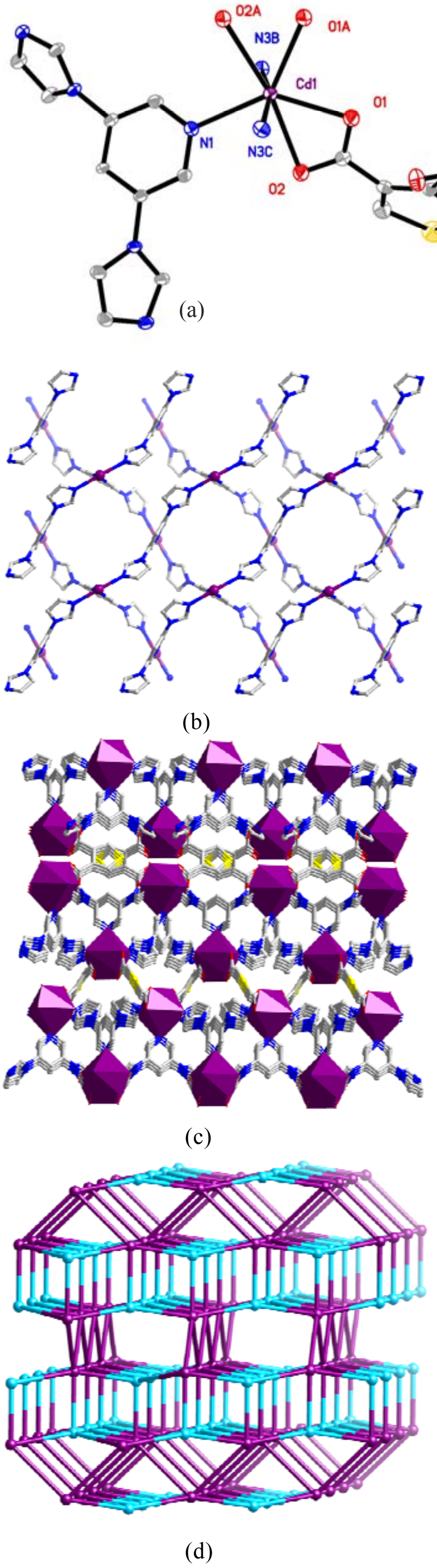
(c)

Fig. 4. (a) Coordination environment of the Cd(II) ion in **2b**, The hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: A: *–x* + 1/2, *–y* + 1/2, *–z* + 1; B: *–x* + 3/2, *–y* – 1/2, *–z* + 1. (b) View of the 1D double chain. (c) View of the 2D supramolecular layer.

Cd^{2+} ion is a 5-connected node and the μ_2-bridging tdc^{2-} anion acts as a linker between two 5-connected nodes, the structure of **3a** can be described as a binodal (3,5)-connected net with a Schläfli symbol of $\{6^2.8\}\{6^7.8^3\}$ (Fig. 5d). In addition, hydrogen bonds among the lattice water molecules and carboxylate groups of tdc^{2-} are formed: O(3)–H(1W)···O(2) [2.670(8) Å, 177.6(9)°] and O(3)–H(2W)···O(3) [2.863(12) Å, 178.8(2)°].

Effects of isomeric thiophene skeleton of H$_2$tdc on the frameworks incorporating N-Donor auxiliary ligands

As aforementioned, it can be seen that N-donor ligands have a significant effect on the structures of these compounds. Similar results can be found in the literatures.[13] In the present study, it is interesting to notice that 1D cationic double chains in **1a** are extended into a 2D supramolecular motif through intermolecular hydrogen bonds, whereas only neutral double chain structure is formed in **1b**. When flexible bimb was introduced, distinct net structures (3D **cds**-type net vs 1D neutral double chain) was obtained, although the coordination mode of tdc^{2-} anions in **2a** is similar to that in **2b**. As well known, the flexible nature of bis-imidazole ligands could be tuned by changing the length of the spacer between the two terminal imidazole groups, the different conformational bis-



(a)

(b)

(c)

(d)

Fig. 5. (a) Coordination environment of the Cd(II) ion in **3a**, The hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: A: *–y* + 1/2, *x* + 3/2, *–z* + 3/2; B: *y* + 1/2, *–x* + 1/2, *–z* + 3/2; C: *–x*, *–y* + 2, *z*. (b) View of the 2D double-layered structure. (c) View of the 3D network. (d) Schematic view of the (3,5)-connected net.

imidazole ligands with distinct torsion angles play an important role in determining the relutling structure. For **1a** and **1b**, bimm ligand shows *cis* conformation and the dihedral angle between two imidazole rings in one ligand is 68.4° for **1a** and 73.3° for **1b**, respectively. In **2a**, bimb ligand adopts the *TTT* conformation with a N···N distance of 10.259 Å and two imidazole rings are coplanar. However, in **2b**, the bimb ligand adopts the *GTT* conformation with a N···N distance of 8.287 Å and a dihedral angle of 60.25° between two imidazole rings, which is unsimilar to that of bimb in **2a.** In other words, flexible nature of bis-imidazole ligands can adopt various conformations together with the thiophene carboxylate group to meet the requirement of coordination geometries of metal ions in the assembly process, which result in the diversified structures of CPs. So structural diversities of **1a**–**1b** or **2a**–**2b** should be mainly attributed to the positional isomeric effect of isomeric thiophenedicarboxylic acids. In comparison with flexible bimm and bimb, rigid bimpy ligand has a larger conjugated backbone and can adopt a tridentate mode using its pyridyl and two imidazole groups. Here, when bimpy was applied as the auxiliary coligand, two isostructural complexes **3a** and **3b** were obtained, showing a 3D (3,5)-connected net. This may originate from the main government of rigid bimpy.

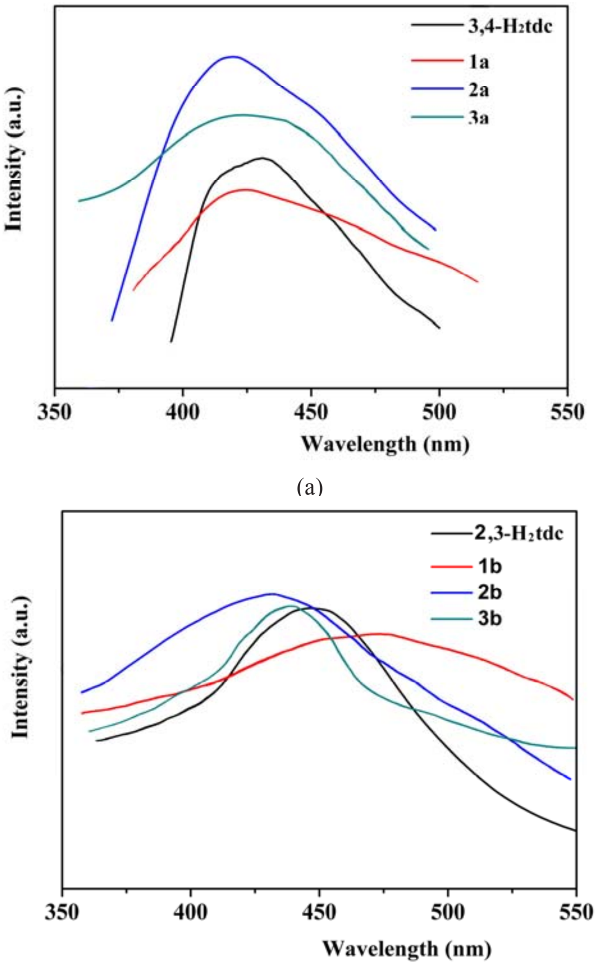
PXRD and TGA results

Powder X-ray diffraction (PXRD) experiments for compounds **1a–3b** have been carried out to characterize their purity of the bulky samples in the solid state. The experimental and simulated PXRD patterns of the corresponding compounds are shown in in Fig. S1, ESI.† The measured PXRD patterns closely match the simulated patterns generated from the results of single-crystal diffraction data, indicative of pure products. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

To examine the thermal stability of complexes **1a–3b**, thermogravimetric analyses (TGA) experiments were carried out performed on powder samples with a heating rate of 10°C min^{-1} (Fig. S2, ESI†). Compound **1a** begins to decompose at 130 °C. For **1b**, the departure of organic components occurs at 240 °C. Compound **2a** begins to decompose at 289 °C. For **2b**, it releases its water molecules from 50 to 145 °C (calcd/found 3.67/3.72%), and the anhydrous compound begins to decompose at 234 °C. Compounds **3a** and **3b** show similar thermal behaviors. In the temperature range of 60 to 125 °C, weight loss of water molecules is observed at 3.35% for **3a,** 3.29% for **3b** (calcd 3.40% for **3a** and **3b**), respectively. Above 290 °C, the backbones start to collapse.

Photoluminescence studies

At present, luminescent CPs with d^{10} metal centers are promising candidates for photoactive materials with potential applications, in particular in structures where the organic ligand itself is luminescent, as it is possible to realize an enhancement in the intensity and a shift in the emission maxima when the ligand is incorporated into a framework structure. Therefore, the photoluminescence properties of complexes **1a–3b** together with 3,4-H$_2$tdc, 2,3-H$_2$tdc were studied in the solid state at room temperature.



(a)

(b)

Fig. 6. Solid-state emission spectra of **1a–3b**, 3,4-H$_2$tdc and 2,3-H$_2$tdc at room temperature.

As depicted in Fig. 6a, 3,4-H$_2$tdc shows one intense emission peak at 436 nm (λ_{ex} = 305 nm), which may be ascribed to the $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ transitions. Compounds **1a**, **2a** and **3a** display similar emission peaks in the range of 350- 500 nm at 425 nm (λ_{ex} = 320 nm), 419 nm (λ_{ex} = 300 nm) and 423 nm (λ_{ex} = 340 nm), respectively. As shown in Fig. 6b, 2,3-H$_2$tdc shows blue photoluminescence property and it exhibits intense emission with maxima at 448 nm upon excitation at 398 nm. Compounds **1b**, **2b** and **3b** also exhibit similar emission at 476 nm (λ_{ex} = 318 nm), 430 nm (λ_{ex} = 310 nm) and 438 nm (λ_{ex} = 330 nm), respectively. Considering that the 3d^{10} valence electron configuration of Cd(II) ion, the emission band of the Cd(II) compounds may be assigned to the ligand-to-ligand change-transfer transition (LLCT), admixing with the LMCT as previously reported.[14]

CONCLUSION

In summary, two different series of Cd(II) CPs based on two positional isomeric thiophenedicarboxylic acids (3,4-H_2tdc and 2,3-H_2tdc) and N-donor auxiliary ligands have been synthesized. The structural diversities indicate that N-donor auxiliary ligands and the isomeric effect of thiophene-based dicarboxylate tectons play dominating roles in modulating the formation of structures of these crystalline materials. Accordingly, this work will enrich the crystal engineering strategy and offer the possibility of controlling the formation of the desired network structures. Meanwhile, it will provide new perspectives for the design and synthesis of novel CPs with isomeric thiophenedicarboxylic acids.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21371089 and 21271098), and sponsored by Program for New Century Excellent Talents in University (NCET-11-0947) and Innovation Scientists and Technicians Troop Construction Projects of Henan Province (134100510011).

Notes and references

[a] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan 471022, P. R. China, E-mail: mazhuxp@126.com; wlya@lynu.edu.cn*

†Electronic Supplementary Information (ESI) available: CCDC: 945060-945063 for complexes 1-4. CCDC: 975442-975443 for complexes 5-6 For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/b000000x/

1 (*a*) O. R. Evans and W. Lin, *Acc. Chem. Res*., 2002, **35**, 511; (*b*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev*., 2003, **246**, 247; (*c*) X.-M. Chen and M.-L. Tong, *Acc. Chem. Res*., 2007, **40**, 162; (*d*) S. Qiu and G. Zhu, *Coord. Chem. Rev*., 2009, **253**, 2891; (*e*) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res*., 2010, **43**, 1115; (*f*) O. K. Farha and J. T. Hupp, *Acc. Chem. Res*., 2010, **43**, 1166; (*g*) D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res*., 2011, **44**, 123.

2 (*a*) H. W. Roesky and M. Andruh, *Coord. Chem. Rev*., 2003, **236**, 91; (*b*) S. A. Barnett and N. R. Chempness, *Coord. Chem. Rev*., 2003, **246**, 145; (*c*) X. C. Huang, J. P. Zhang, Y. Y. Lin, X. L. Yu and X. M. Chen, *Chem. Commun*., 2004, 1100; (*d*) X. L. Wang, C. Qin, E. B. Wang, Y. G. Li, Z. M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed*., 2005, **44**, 5824; (*e*) Y.-H. Wang, K.-L. Chu, H.-C. Chen, C.-W. Yeh, Z.-K. Chan, M.-C. Suen and J.-D. Chen, *CrystEngComm*, 2006, **8**, 84; (*f*) J. R. Li, Q. Yu, C. Sanudo, Y. Tao and X. H. Bu, *Chem. Commun*., 2007, 2602; (*g*) J. Heo, Y. Jeon and C. A. Mirkin, *J. Am. Chem. Soc*., 2007, **129**, 7712; (*h*) H.-J. Hao, F.-J. Liu, H.-F. Su, Z.-H. Wang, D.-F. Wang, R.-B. Huang and L.-S. Zheng, *CrystEngComm*, 2012, **14**, 6726; (*i*) H. Ma, H. Ren, S. Meng, Z. Yan, H. Zhao, F. Sun and G. Zhu, *Chem. Commun*., 2013, **49**, 9773.

3 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O.M. Yaghi, *Science*, 2002, **295**, 469; (*b*) C. A. Williams, A. J. Blake, P. Hubberstey and M. Schröder, *Chem. Commun*., 2005, 5435; (*c*) F. Guo, F. Wang, H. Yang, X. Zhang and J. Zhang, *Inorg. Chem*., 2012, **51**, 9677; (*d*) Y.-P. Wu, D.-S. Li, J. Zhao, Z.-F. Fang, W.-W. Dong, G.-P. Yang and Y.-Y. Wang, *CrystEngComm*, 2012, **14**, 4745; (*e*) F.-J. Liu, H.-J. Hao, C.-J. Sun, X.-H. Lin, H.-P. Chen, R.-B. Huang and L.-S. Zheng, *Cryst. Growth Des*. 2012, **12**, 2004; (*f*) T. Liu, S. Wang, J. Lu, J. Dou, M. Niu, D. Li and J. Bai, *CrystEngComm*, 2013, **15**, 5476.

4. (*a*) B. L. Chen, K. F. Mok, S. C. Ng and M. G. B. Drew, *Polyhedron*, 1999, **18**, 1211; (*b*) B. L. Chen, K. F. Mok, S. C. Ng and M. G. B. Drew, *New J. Chem*., 1999, **23**, 877; (c) X.-Z. Sun, Z.-L. Huang, H.-Z. Wang, B.-H. Ye and X.-M. Chen, *Z. Anorg. Allg. Chem*., 2005, **631**, 919; (*d*) Z.-P. Deng, S. Gao, L.-H. Huo and H. Zhao, *Acta Crystallogr., Sect. E: Struct.,* 2006, **62**, m87; (*e*) A. Demessence, G. Rogez, R. Welter and P. Rabu, *Inorg. Chem*., 2007, **46**, 3423; (*f*) Z. Chen, Y. Zuo, X.-H. Li, H. Wang, B. Zhao, W. Shi and P. Cheng, *J. Mol. Struct*., 2008, **888**, 360; (*g*) J. Zhang, S. Chen, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc*., 2008, **130**, 12882; (*h*) J.-G. Wang, C.-C. Huang, X.-H. Huang and D.-S. Liu, *Cryst. Growth Des*., 2008, **8**, 795; (*i*) W. Huang, D. Wu, P. Zhou, W. Yan, D. Guo, C. Duan and Q. Meng, *Cryst. Growth Des*., 2009, **9**, 1361; (*j*) Z. Chen, B. Zhao, P. Cheng, X.-Q. Zhao, W. Shi and Y. Song, *Inorg. Chem*., 2009, **48**, 3493; (*k*) Z. Zhang, S. Xiang, Y.-S. Chen, S. Ma, Y. Lee, T. Phely-Bobin and B. Chen, *Inorg. Chem*., 2010, **49**, 8444; (*l*) J. Zhang, J. Bu, S. Chen, T. Wu, S. Zheng, Y. Chen, R. Nieto, P. Feng and X. Bu, *Angew. Chem., Int. Ed*., 2010, **49**, 8876; (*m*) P. J. Calderone, D. Banerjeea, A.C. Santulli, S. S. Wong and John B. Parise, *Inorg. Chim. Acta*., 2011, **378**, 109; (*n*) H.-H. Zou, Y.-P. He, L.-C. Gui and F.-P. Liang, *CrystEngComm*, 2011, **13**, 3325; (*o*) Y.-g. Sun, B. Jiang, T.-F. Cui, G. Xiong, P. F. Smet, F. Ding, E.-J. Gao, T.-Y. Lv, K. V. d. Eeckhout, D. Poelman and F. Verpoortc, *Dalton Trans*., 2011, **40**, 11581; (*p*) R. E. Osta, M. Frigoli, J. Marrot, M. E. Medina, R. I. Walton and F. Millange, *Cryst. Growth Des*., 2012, **12**, 1531.

5. (*a*) Z.-H. Li, L-P. Xue, S.-H. Li, J.-G. Wang, B.-T. Zhao, J. Kan and W.-P. Su, *CrystEngComm*, 2013, **15**, 2745; (*b*) Z.-H. Li, T. Zhang, L-P. Xue, S.-B. Miao, B.-T. Zhao, J. Kan and W.-P. Su, *CrystEngComm*, 2013, **15**, 7423; (*c*) L.-P. Xue, X.-H. Chen, T. Zhang and Z.-H. Li, *J Inorg. Organomet Polym*., 2013, **23**, 1122; (*d*) L-P. Xue, Z.-H. Li, S.-H. Li and J.-G. Wang, *Chinese J. Struct. Chem*., 2013, **32**, 704; (*e*) T. Zhang, X.-H. Chen, Z.-H. Li and L.-P, Xue, *Chinese J. Struct. Chem*., 2013, **32**, 1854.

6. (*a*) L.-F. Ma, L.-Y. Wang, S.-H. Chen, H.-W. Hou and S. R. Batten, Polyhedron, 2009, **28**, 2494; (*b*) L.-F. Ma, X.-Q. Li, Q.-L. Meng, L.-Y. Wang, M. Du, and H.-W. Hou, *Cryst. Growth Des*., 2011, **11**, 175.

7. K.-Y. Tserng and L. Bauer, *J. Org. Chem*., 1975, **40**, 172.

8. Y.-H. Chao, S.-C. Kuo, K. Ku, I-P. Chiu, C.-H. Wu, A. Mauger, H.-K. Wang and K.-H. Lee, *Bioorg. Med. Chem*., 1999, **7**, 1025.

9. E. Díez-Barra, A. de la Hoz, A. Sánchez-Migallón and J. Tejeda, Heterocycles 1992, **34**, 1365.

10. J.-F. Ma, J. Yang, G.-L. Zheng, L. Li, and J.-F. Liu, *Inorg. Chem*., 2003, **42**, 7531.

11 G. M. Sheldrick, SADABS, Program for Siemens Area Detector Absorption Corrections, University of Göttingen, Germany, 1997.

12 (*a*) G.M. Sheldrick, SHELXTL Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1998; (*b*) G. M. Sheldrick, SHELXL-97, *Program for the Refinement of Crystal Structure*; University of Göttingen, Germany, 1997.

13 (*a*) A. Absmeier, M. Bartel, C. Carbonera, G. N. Jameson, P. Weinberger, A. Caneschi, K. Mereiter, J. F. Letard and W. Linert, *Chem.–Eur. J*., 2006, **12**, 2235; (*b*) X. H. Bu, W. H. Hou, M. Du, W. Chen and R. H. Zhang, *Cryst. Growth Des*., 2002, **2**, 303; (*c*) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Chem.–Eur. J*., 2006, **12**, 2680; (*d*) J. Fan, G. T. Yee, G. B. Wang and B. E. Hanson, *Inorg. Chem*., 2006, **45**, 599; (*e*) Y. Q. Lan, S. L. Li, X. L. Wang, K. Z. Shao, D. Y. Du, Z. M. Su and E. B. Wang, *Chem.–Eur. J*., 2008, **14**, 9999; (*f*) X. Li, R. Cao, W. Bi, Y. Wang, Y. Wang, X. Li and Z. Guo, *Cryst. Growth Des*., 2005, **5**, 1651; (*g*) G. H. Cui, J. R. Li, J. L. Tian, X. H. Bu and S. R. Batten, *Cryst.Growth Des*., 2005, **5**, 1775.

14 (*a*) L. L. Wen, D. B. Dang, C. Y. Duan, Y. Z. Li, Z. F. Tian and Q. J. Meng, *Inorg. Chem*., 2005, **44**, 7161; (*b*) L.-Y. Zhang, J.-P. Zhang, Y.-Y. Lin, and X.-M. Chen, *Cryst. Growth Des*., 2006, **6**, 1684; (*c*) B. Y. Li, F. Yang, G. H. Li, D. Liu, Q. Zhou, Z. Shi and S. H. Feng, *Cryst. Growth Des*., 2011, **11**, 1475.