



Synthesis, crystal structures and properties of lanthanide-organic frameworks based benzene carboxylates with two/three-dimensional structure

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ABSTRACT

A series of lanthanide coordination polymers, $\{[\text{Dy}_3(1,3\text{-BDC})_4(\text{NO}_3)(\text{phen})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Dy}_2(1,3\text{-BDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Ln}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ ($\text{Ln}=\text{Tb}$ (**3**), Ho (**4**), Er (**5**), $1,3\text{-H}_2\text{BDC}=1,3\text{-benzenedicarboxylate}$, $\text{phen}=1,10\text{-phenanthroline}$, $\text{DMF}=N,N\text{-dimethylformamide}$), have been synthesized and characterized. In coordination polymer **1**, each Dy^{3+} ion is connected to its neighboring Dy^{3+} ion through bridging carboxyl oxygen atoms of the $1,3\text{-BDC}^{2-}$ ligands to form a new three-dimensional open-framework structure which the Schläfli symbol of $\{6^4 \cdot 8^2\}_2\{6^6\}$. In coordination polymer **2**, center metal dysprosium ions are interlaced and connected through bridging carboxyl oxygen atoms to form an infinite helix chain. Two helix chains are linked through the $1,3\text{-BDC}^{2-}$ ligand to give rise to the two-dimensional layered structure. Coordination polymers **3–5** are isomorphous, which displays a (3,4)-connected net with the point symbol of $\{4^2 \cdot 6^3 \cdot 8\}\{4^2 \cdot 6\}$. The solid-state photoluminescence properties and lifetimes of the Dy (**1** and **2**) and Tb (**3**) coordination polymers have been measured at room temperature.

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1. Introduction

In recent years, crystal engineering of metal-organic frameworks (MOFs) has evoked increasing interests for chemists and material scientists due to their fascinating topologies and profuse potential applications, such as luminescence, catalysis, magnetic devices, ion exchange, gas storage and separation, etc [1–6]. Up to date, a variety of 4f and 4f–3d coordination polymers with interesting architectures and topologies have been successfully synthesized [7–10]. However, lanthanides, with high and variable coordination numbers ($6 \leq \text{CN} \leq 12$) and flexible coordination environments, showed very limited success in the design of predetermined molecular architectures [11]. In the field of coordination polymers constructed by carboxylate ligands, much work has been focused on lanthanide and transition metal coordination polymers constructed by multi-carboxylate ligands [12–18], especially, with the benzenedicarboxylate ligands [17,18]. A series of coordination polymers with 1,3-benzenedicarboxylate (1,3-H₂BDC) ligand were reported [18], and they exhibit strong fluorescence in the solid state at room temperature. The 1,3-H₂BDC ligand with diversiform coordination modes

possesses interesting features which are conducive to the formation of unusual coordination structures. The carboxylate groups on the molecules may be completely or partially deprotonated and could coordinate to the metal ions. As a result, the molecules may connect the metal ions in different directions, generating multidimensional architectures [19,20].

In this work, we report the syntheses, structures and luminescent properties of five novel lanthanide coordination polymers $\{[\text{Dy}_3(1,3\text{-BDC})_4(\text{NO}_3)(\text{phen})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Dy}_2(1,3\text{-BDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Ln}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ ($\text{Ln}=\text{Tb}$ (**3**), Ho (**4**), Er (**5**), $1,3\text{-H}_2\text{BDC}=1,3\text{-benzenedicarboxylate}$, $\text{phen}=1,10\text{-phenanthroline}$, $\text{DMF}=N,N\text{-dimethylformamide}$). All coordination polymers are characterized by X-ray crystallography, elemental analysis and IR spectrum. Furthermore, luminescent properties have been investigated for five coordination polymers.

2. Experimental

2.1. Materials and instrumentation

All reagents were commercially available and used without further purification. Infrared spectra were obtained from KBr

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pellets using a Nicolet Avatar-360 Infrared spectrometer in the 4000–400 cm^{-1} region. Elemental analyses were performed on a Perkin-Elmer 240c element analyzer. Nitrogen adsorption/desorption isotherms were measured at the liquid nitrogen temperature, using an ASAP2020 analyzer. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore size distributions were evaluated from the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 6–30° using $\text{Cu-K}\alpha$ radiation by Bruker D8 Advance. Luminescence spectra and fluorescence lifetimes were measured with an Edinburgh FLS920 Combined steady state Fluorescence and phosphorescence lifetime spectrometer using 375 nm laser as the excitation source (Continuum Surelite OPO).

2.2. Synthesis of the coordination polymers

2.2.1. $\{[\text{Dy}_3(1,3\text{-BDC})_4(\text{NO}_3)(\text{phen})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**)

A mixture of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (438 mg, 1 mmol), 1,3-benzenedicarboxylic acid (166 mg, 1 mmol), 1,10-phenanthroline (198 mg, 1 mmol), DMF (5.0 mL), distilled water (1.5 mL), and ethanol (1.0 mL) was stirred for 30 min, and the final pH is at ca. 6.5. The final straw yellow mixture was then sealed in a 15 mL Teflon-lined reactor and heated at 85 °C for 2 day. After being slowly cooled to room temperature, colorless well-shaped single crystals of coordination polymer **1** suitable for X-ray diffraction analysis were obtained (yield ca. 97%, based on 1,3- H_2BDC). Coordination polymer **1** is not soluble in common solvents, such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, CHCl_3 , DMSO or DMF. Elemental analysis for **1**: $\text{C}_{68}\text{H}_{44}\text{Dy}_3\text{N}_7\text{O}_{21}$ (Mr: 1782.60). Calcd: C, 45.82; N, 5.50; H, 2.49%. Found: C, 45.52; N, 5.32; H, 2.29%. IR (KBr, cm^{-1}): 3421 (s), 1641 (vs), 1543 (vs), 1480 (s), 1448 (s), 1393 (vs), 1299 (w), 1141 (w), 1103 (w), 845 (m), 826 (w), 731 (m), 705 (w), 656 (w), 572 (w), 432 (m), 419 (m).

2.2.2. $\{[\text{Dy}_2(1,3\text{-BDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**)

A mixture of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (43.8 mg, 0.1 mmol), and 1,3-benzenedicarboxylic acid (49.8 mg, 0.3 mmol), distilled water (5 mL) was stirred for 30 min, and the final pH is at ca. 4.0. Then the final mixture was sealed in a 15 mL Teflon-lined reactor, heated to 160 °C, and kept this temperature for 4 day. After being slowly cooled down to room temperature, colorless block-shaped single crystals of coordination polymer **2** suitable for X-ray diffraction analysis were obtained. The yield was ca. 52%, based on Dy. Elemental analysis for **2**: $\text{C}_{24}\text{H}_{18}\text{Dy}_2\text{O}_{15}$ (Mr: 871.38). Calcd: C, 33.08; H, 2.08%. Found: C, 33.34 H, 1.98%. IR (KBr, cm^{-1}): 3245 (s), 3404 (s), 1615 (vs), 1456 (vs), 1532 (vs), 1481 (vs), 1393 (vs), 1165 (m), 1077 (m), 922 (w), 834 (m), 806 (w), 746 (vs), 716 (vs), 656 (w), 542 (m), 418 (m).

2.2.3. $\{[\text{Tb}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (**3**)

A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (43.6 mg, 0.1 mmol), 1,3-benzenedicarboxylic acid (33.2 mg, 0.2 mmol), and distilled water (3 mL), DMF (5 mL) was stirred at pH 3.5 for 30 min, and the final pH is at ca. 5.5. The final white mixture was then sealed in a 15 mL Teflon-lined reactor and heated at 85 °C for 3 day. After being slowly cooled down to room temperature, colorless block-shaped single crystals of coordination polymer **3** suitable for X-ray diffraction analysis were obtained (yield ca. 67%, based on Tb). Coordination polymer **3** is not soluble in common solvents such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, CHCl_3 , DMSO, CH_3CN , CH_2Cl_2 or DMF. Elemental analysis of **3**: $\text{C}_{54}\text{H}_{50}\text{N}_2\text{O}_{32}\text{Tb}_4$ (Mr: 1874.64). Calcd: C, 34.60; N, 1.49; H, 2.69%. Found: C, 34.52; N, 1.20; H, 2.91%. IR (KBr, cm^{-1}): 3400 (s), 1667 (vs), 1612 (vs), 1551 (vs), 1480 (vs),

1451 (vs), 1396 (vs), 1164 (m), 1107 (m), 912 (m), 834 (m), 751 (s), 714 (s), 658 (w), 575 (w), 531 (w), 420 (m).

2.2.4. $\{[\text{Ho}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (**4**)

The procedure was similar to that for **3** except that $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was replaced by $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (44.0 mg, 0.1 mmol), and the solvent are distilled water (5.0 mL), DMF (3.0 mL). The final pH is at ca. 5.6. The final product, with a yield of 68% (based on Ho), is yellow and block-shaped single crystals, which can be used for X-ray diffraction analysis. Coordination polymer **4** is not soluble in common solvents such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, CHCl_3 , DMSO, CH_3CN , CH_2Cl_2 or DMF. Elemental analysis for **4**: $\text{C}_{54}\text{H}_{50}\text{N}_2\text{O}_{32}\text{Ho}_4$ (Mr: 1898.68). Calcd: C, 34.16; N, 1.48; H, 2.65%. Found: C, 34.42; N, 1.69; H, 2.87%. IR (KBr, cm^{-1}): 3403 (s), 1650 (m), 1613 (vs), 1551 (vs), 1528 (vs), 1480 (s), 1452 (vs), 1397 (vs), 1164 (m), 1107 (m), 1080 (w), 918 (w), 838 (m), 764 (s), 750 (s), 715 (s), 657 (m), 576 (w), 533 (w).

2.2.5. $\{[\text{Er}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (**5**)

The procedure was similar to that for **3** except that $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was replaced by $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (44.1 mg, 0.1 mmol), and the solvents are distilled water (5.0 mL), DMF (3.0 mL), and the final pH is at ca. 5.6. The mixture is heated at 85 °C for 24 h. The pink block-shaped single crystals of **1** were obtained, which can be used for X-ray diffraction analysis. The yield for coordination polymer **5** was 65% (based on Er). Coordination polymer **5** is not soluble in common solvents such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, CHCl_3 , DMSO, CH_3CN , CH_2Cl_2 or DMF. Elemental analysis for **5**: $\text{C}_{54}\text{H}_{50}\text{N}_2\text{O}_{32}\text{Er}_4$ (Mr: 1908.00). Calcd: C, 33.99; N, 1.47; H, 2.64%. Found: C, 34.22; N, 1.61; H, 2.42%. IR (KBr, cm^{-1}): 3401 (s), 1667 (m), 1614 (vs), 1552 (vs), 1534 (vs), 1481 (s), 1453 (vs), 1399 (vs), 1164 (m), 1106 (m), 1078 (w), 922 (w), 840 (m), 794 (s), 748 (s), 714 (s), 657 (m), 577 (w), 535 (w).

2.3. X-ray crystallographic studies

The X-ray diffraction data for coordination polymers **1–5** were collected at room temperature on a Rigaku R-Axis RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structures were resolved by direct method and refined by Semi-empirical formula from equivalents and full-matrix least squares based on F^2 using the SHELXTL 5.1 software package [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode except water molecules. The CCDC reference numbers for coordination polymers **1–5** are 842347, 842348, 842349, 842350, and 842351, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/deposit. Crystal structure data and details of the data collection and the structure refinement are given in Table 1. Selected bond lengths and hydrogen bonding data of coordination polymers **1–5** are listed in Table S1 and Table S2 of Supplementary information.

3. Results and discussion

3.1. Synthesis

Five lanthanide coordination polymers, $\{[\text{Dy}_3(1,3\text{-BDC})_4(\text{NO}_3)(\text{phen})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Dy}_2(1,3\text{-BDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Ln}_4(1,3\text{-BDC})_6(\text{DMF})(\text{H}_2\text{O})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (Ln = Tb (**3**), Ho (**4**), Er (**5**), 1,3- H_2BDC = 1,3-benzenedicarboxylate, phen = 1,10-phenanthroline, DMF = *N,N*-dimethylformamide), have been synthesized under hydrothermal or solvothermal conditions. Coordination polymer **1** displayed 3-D MOFs, coordination polymer **2** displayed

Table 1
Crystal data and structure refinements for coordination polymers **1–5**.

Data	1	2	3	4	5
Empirical formula	C ₆₈ H ₄₄ Dy ₃ N ₇ O ₂₁	C ₂₄ H ₁₈ Dy ₂ O ₁₅	C ₅₄ H ₅₀ N ₂ O ₃₂ Tb ₄	C ₅₄ H ₅₀ Ho ₄ N ₂ O ₃₂	C ₅₄ H ₅₀ Er ₄ N ₂ O ₃₂
Formula weight	1782.60	871.38	1874.64	1898.68	1908.00
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	10.286(2)	10.592(1)	10.855(2)	10.822(1)	10.822(1)
<i>b</i> (Å)	19.161(4)	14.206(1)	14.142(3)	14.074(1)	14.073(1)
<i>c</i> (Å)	19.787(4)	17.124(1)	20.078(4)	19.966(1)	19.965(1)
α (°)	77.52(3)	90.00	86.59(3)	86.53(1)	86.53(1)
β (°)	76.72(3)	97.93(1)	83.61	83.51(1)	83.51(1)
γ (°)	81.02(3)	90.00	78.89(3)	78.80(1)	78.79(1)
Volume (Å ³)	3682.6(13)	2551.91(9)	3003.3(10)	2961.54(16)	2961.54(16)
<i>Z</i>	2	4	2	2	2
<i>D</i> _{calcd} (mg m ⁻³)	1.608	2.268	2.073	2.129	2.140
μ (mm ⁻¹)	3.086	5.890	4.750	5.384	5.709
<i>F</i> (0 0 0)	1734	1656	1808	1824	1832
θ range (°)	3.01–27.48	2.80–25.00	3.07–27.48	3.08–27.55	2.96–25.00
Limiting indices	–13 ≤ <i>h</i> ≤ 13 –24 ≤ <i>k</i> ≤ 24 –25 ≤ <i>l</i> ≤ 25	–11 ≤ <i>h</i> ≤ 12 –15 ≤ <i>k</i> ≤ 16 –20 ≤ <i>l</i> ≤ 15	–13 ≤ <i>h</i> ≤ 14 –18 ≤ <i>k</i> ≤ 18 –26 ≤ <i>l</i> ≤ 26	–14 ≤ <i>h</i> ≤ 13 –18 ≤ <i>k</i> ≤ 18 –24 ≤ <i>l</i> ≤ 25	–12 ≤ <i>h</i> ≤ 12 –16 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 19
GOF on <i>F</i> ²	1.091	1.025	1.096	1.147	0.965
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0394/0.1039	0.0292/0.0761	0.0281/0.0860	0.0404/0.1143	0.0246/0.0536
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0503/0.1144	0.0340/0.0774	0.0329/0.0974	0.0489/0.1227	0.0330/0.0548
Largest residuals (e Å ⁻³)	2.057/–1.096	1.300/–1773	1.328/–1.498	1.571/–2.143	1.210/–1.147

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}$$

2-D structure, these results can be easily understood considering the following factors: First, different molar ratio of reactants affects the linking between carboxyl oxygen atoms and metal atoms. The metal/ligand ratio plays an important role in this system. By alteration of the metal/ligand ratio in the initial reaction system, we could transform the structure from 3-D network (coordination polymer **1**) to 2-D architecture (coordination polymer **2**). Coordination polymer **1** is well synthesized when the metal/ligand ratio is 1: 1. Coordination polymer **2** is obtained only when the molar ratio is 1:3. With the increase of metal/ligand ratio higher dimension crystal structure can be obtained. Second, the pH value is one of influencing factors for synthesis of coordination polymers **1** and **2**. Higher pH value in the reaction system can enhance the coordination competence of 1,3-H₂BDC ligand in the crystal structure. In the synthesis of coordination polymer **1**, as the existence of phen, pH value for coordination polymer **1** (at ca. 6.5) is higher than that for coordination polymer **2** (at ca. 4.0), which result in forming the 3-D structure of coordination polymer **1**. Therefore, higher pH value is another reason for the formation of 3-D structure rather than 2-D structure, which is consistent with the experimental results. Moreover, DMF and ethanol molecules enhance the coordination interaction between the metal dysprosium ions and ligand, and weaken the coordination competition of water, so high dimension coordination polymer **1** (3-D) was obtained.

3.2. IR analysis

Coordination polymers **1–5** were characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis. The elemental analysis results revealed that the components of the five coordination polymers were in accordance with the formula, respectively. The signals in coordination polymer **1** at 1641 and 1393 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups, respectively. The signals at 1543 cm⁻¹ correspond to the C=N stretching vibrations of phen, while signals at 845 and 731 cm⁻¹ correspond to the C–H bending vibrations of phen. The signals in

coordination polymer **2** at 1602 and 1372 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of carboxylate groups, respectively. The IR spectra of coordination polymers **3–5** are fully identical. Those indicate that the three coordination polymers may be isostructural, which was further confirmed by the X-ray diffraction analysis. For example, the asymmetric stretching vibrations of the carboxylate groups in coordination polymers **3–5** were observed at ca. 1612 cm⁻¹ as a broad band, and the band of symmetric stretching vibrations was observed at ca.1534 cm⁻¹. From **1** to **5**, the stretching vibrations of the carboxylate groups shift toward lower frequency and greatly reduced in intensity compared to that of free ligand, which indicated the coordination interaction between the oxygen atoms of carboxylate groups and the metal ions.

3.3. Description of crystal structures

3.3.1. $\{[Dy_3(1,3-BDC)_4(NO_3)(phen)_3 \cdot 2H_2O]_n\}$ (**1**)

The coordination polymer **1** has 99 non-hydrogen atoms in its asymmetric unit, which has three Dy³⁺ ion, four 1,3-BDC²⁻, three phen, one NO₃⁻, and two free water molecules with all in general positions, as shown in Fig. 1. The Dy1 is nine-coordinated by seven carboxyl oxygen atoms (O1, O2, O3, O4, O5, O6, and O6A) from two 1,3-BDC²⁻ ligands, and two nitrogen atoms (N3, and N4) from phen ligand, and display distorted tricapped trigonal prismatic arrangement around the central Dy³⁺, the coordinated environment of Dy1 is shown in Fig. 2. The Dy1–O bond lengths are 2.462 (2), 2.430 (2), 2.351 (3), 2.316 (3), 2.412 (2), 2.326 (2) and 2.733 (2) Å, respectively. The Dy1–N bond lengths are 2.541 (3) and 2.583 (3) Å, respectively. The Dy2 is eight-coordinated by four carboxyl oxygen atoms (O7, O8, O9, and O10) from two 1,3-BDC²⁻ ligands, and two oxygen atoms (O17, and O18) from one NO₃⁻, and two nitrogen atoms (N1, and N2) from phen ligand. Dy2 displayed square antiprism geometry arrangement around the central Dy³⁺. The coordinated environment around Dy2 is shown in Fig. 2. The Dy2–O bond distances are in the range of 2.263 (3)–2.496 (3) Å. The Dy2–N bond lengths are 2.562 (3) and 2.547 (3) Å, respectively. The Dy3 is eight-coordinated

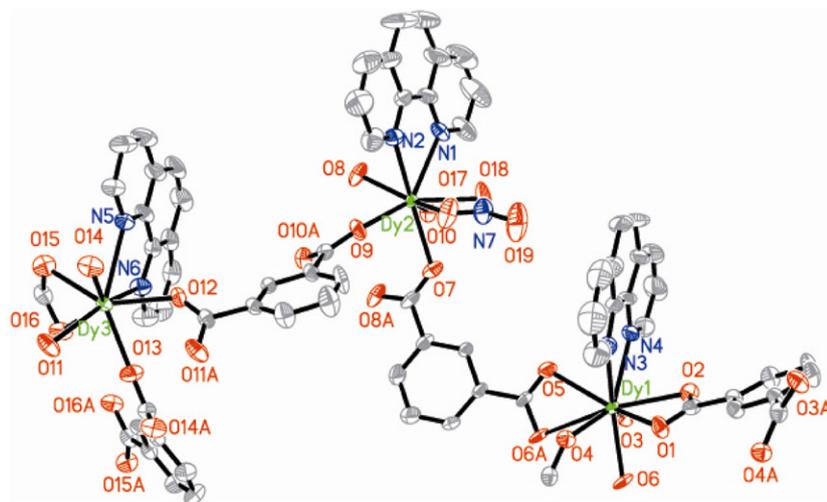


Fig. 1. The structural unit of coordination polymer **1** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). Symmetry codes: (a) $1-x, -y, 1-z$.

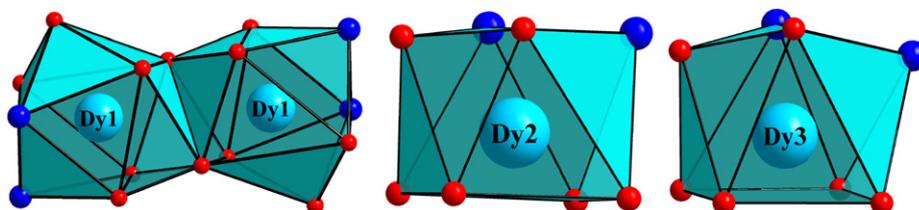


Fig. 2. The coordinated environment of Dy1, Dy2, and Dy3 in the coordination polymer **1**.

by six carboxyl oxygen atoms (O11, O12, O13, O14, O15, and O16) from two 1,3-BDC²⁻ ligands, and two nitrogen atoms (N5, and N6) from phen ligand. Dy3 displayed distorted bi-capped trigonal prismatic arrangement around the central Dy³⁺. The coordinated environment around Dy3 is also shown in Fig. 2. The Dy3–O bond distances are in the range of 2.295 (3)–2.439 (3) Å. The two Dy3–N bond lengths are 2.622 (3) and 2.520 (3) Å, respectively. The O–Dy–O bond angles are in the range of 49.94 (7)°–160.01 (8)°. The O–Dy–N bond angles are in the range of 68.77 (9)°–146.26 (11)°. The N–Dy–N bond angles are in the range of 63.41 (10)°–64.81 (12)°. The central Dy1 and other central Dy1 ions are connected through μ_2 -oxygen atom (O6) and μ_1 -oxygen atom (O3, O4 and O5) to form a face-shared dimer [see Fig. 3(a)]. The dimer units are connected through oxygen atom (O1, O2, O3 and O4) according to Scheme 1A giving rise to an infinite one-dimensional chains Dy1–O–Dy1 [see Fig. 3(b)]. The Dy–Dy distances have two distinct values, 4.014 and 8.476 Å, respectively. The central Dy2 ion is connected to each other through μ_1 -oxygen atom (O7, O8, O9 and O10) to form a dimer (Dy2)₂O₈ [see Fig. 3(c)]. The central Dy3 ion is connected to each other through μ_1 -oxygen atom (O11, O12, O13 and O14) to form a dimer [see Fig. 3(d)]. The dimer units are connected through oxygen atom (O13, O14, O15 and O16) according to Scheme 1A giving rise to an infinite one-dimensional chains Dy3–O–Dy3 [see Fig. 3(e)]. The two Dy–Dy distances are 4.273 and 7.992 Å, respectively. Dimer units (Dy2)₂O₈ connect to the metal center of the Dy3–O–Dy3 line in the coordination mode of 1,3-BDC²⁻ ligand as is shown in Scheme 1B, forming a 2-D layer structure [see Fig. 3(f)]. Dy1–O–Dy1 lines and these 2-D layer structures connect to the metal center Dy1 and Dy2 cations (Scheme 1C), forming a 3-D network along [001] direction [see Fig. 3(g)].

If ignore phen ligands and NO₃⁻, the dysprosium dimer (Dy₂) as a secondary building unit are connected adjacent four dysprosium dimers by 1,3-BDC²⁻, can be 4-connected plane quadrilateral node,

the 1,3-BDC²⁻ ligands act as linear bridges between the dysprosium dimer nodes. Such connectivity repeats infinitely, resulting in a novel 4-connected net with the Schläfli symbol of {6⁴.8²}₂{6⁶}, the topology is shown in Fig. 4(a). The layered structure is parallel to the *ab* plane and linked by the Dy₂ chains with trapeziform 6-member ring to generate the 3-D framework containing 8-member ring channels, as shown in Fig. 4(b). From the topological view, coordination polymer **1** is formed by 8-member ring channels along the [100] direction with the 8-member ring pore size being 19.79 × 27.07 Å.

3.3.2. {[Dy₂(1,3-BDC)₃(H₂O)₂]·H₂O}_n (**2**)

The coordination polymer **2** has 41 non-hydrogen atoms in the asymmetric unit, of which two Dy³⁺ are crystallographically independent. The asymmetric unit contains two Dy³⁺ ions, three 1,3-BDC²⁻, two terminal water molecules and one free water molecule with all in general positions (Fig. 5). Dy1 is eight-coordinated: eight carboxylate atoms (O_{COO}⁻) from three different 1,3-BDC²⁻ ligands, and displays a bi-capped trigonal prismatic structure. Dy2 is seven-coordinated: five carboxylate atoms (O_{COO}⁻) from three 1,3-BDC²⁻ ligands, and two terminal water molecules, with a tricapped trigonal prismatic structure. The structure is shown in Fig. 5. The Dy–O distances range from 2.237 (3) to 2.632 (3) Å. The O–Dy–O bond angles range from 51.37 (11)° to 156.23 (13)°. The coordination modes of 1,3-BDC²⁻ in coordination polymer **2** are shown in Scheme 1A–C. In coordination polymer **2**, the 1,3-BDC²⁻ ligand participate in metal center, 1,3-BDC²⁻ ligand exists distortion relative to the free ligand, coordinative carboxyl deviate from the benzene ring plane, the dihedral angles between the benzene rings and the coordinating carboxylic plane range from 5.4 (4)° to 38.7 (3)°.

Dy1 and Dy2 form a mono-(CN=7) and a bi-(CN=8) capped trigonal prismatic arrangement. In coordination polymer **2**,

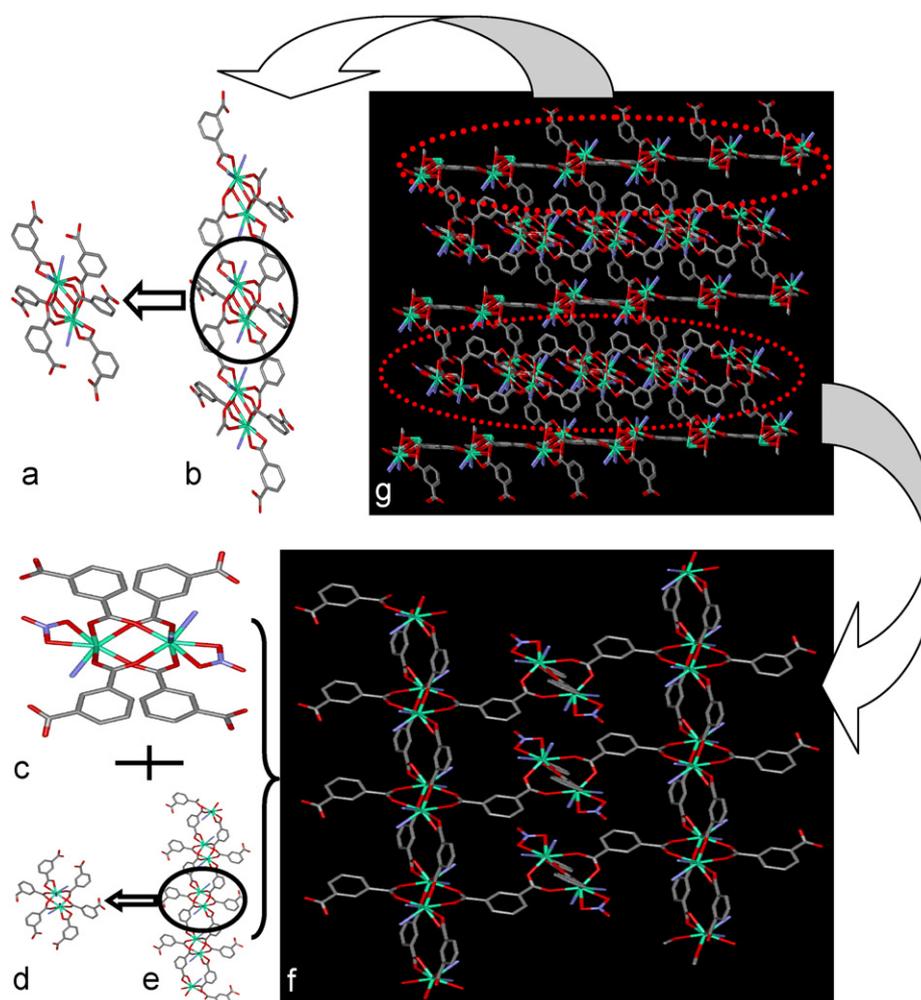
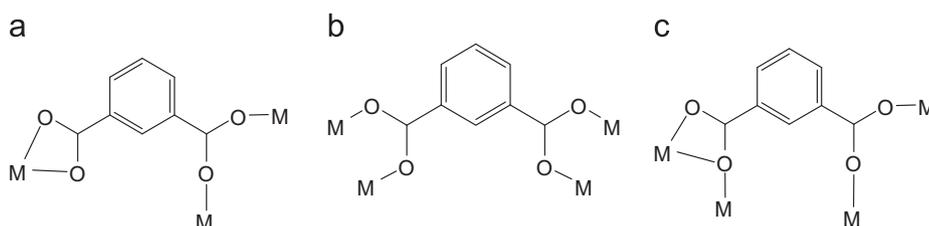


Fig. 3. (a) The face-shared dimer of Dy1. (b) The infinite 1-D chains Dy1–O–Dy1. (c) The dimer $(\text{Dy}2)_2\text{O}_8$ of Dy2. (d) The dimer of Dy3. (e) The infinite 1-D chains Dy3–O–Dy3. (f) The infinite 2-D layer structure. (g) The 3-D network structure along $[0\ 0\ 1]$ (water molecules, hydrogen and phen ligand atoms are omitted for clarity).



Scheme 1. The coordination modes of 1,3-BDC ligand in the coordination polymer.

Dy1 and Dy2 are interlaced and connected through bridging carboxyl oxygen atoms $\mu_1\text{-O}$ and $\mu_2\text{-O}$ from the $1,3\text{-BDC}^{2-}$ ligand to form an infinite helix structure along b -axis direction, as shown in Fig. 6. Two helix chains form 2-D layer structure (Fig. 6) through the $1,3\text{-BDC}^{2-}$ ligand. By the involvement of water molecules in the formation of hydrogen bonds, the stability of coordination polymers is enhanced. If ignore water molecules, center metal Dy1 and Dy2 can be 3-connected node (Dy_2), the $1,3\text{-BDC}^{2-}$ ligands act as linear bridges between the adjacent nodes. Such connectivity repeats infinitely, resulting in a 2-D hcb network, the 6-member ring pore size being 15.25×20.05 Å [Fig. 6(b)]. The isostructural coordination polymers $\{[\text{Ln}_2(1,3\text{-BDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ ($\text{Ln}=\text{Y}, \text{Gd}, \text{Ho}$) of coordination polymer 2 has been reported. [20a,22] Although we use different temperature and solvent, it was found that the structure of 2 is similar to the structure reported, based on single-crystal X-ray diffraction data,

which indicates that the reaction temperature and solvent have no or only a minor effect on the structure of coordination polymer 2.

Though the coordination modes of $1,3\text{-BDC}^{2-}$ ligand (Scheme 1A–C) in coordination polymers 1 and 2 are identical, the structures are very different. Coordination polymer 1 has 3-D network structure, while 2 has 2-D layer structure. In coordination polymer 1, four nitrogen atoms of two phen ligands occupy two coordination place of Dy1 and Dy3 cations, which make Dy1 and Dy3 grow into 1-D line structure along a direction, meanwhile, restrain the growth along b and c directions. Ligands phen and NO_3^- occupy four coordination places of square antiprism geometry of Dy2 cation, which seal up the growth of Dy2 in all directions. But $(\text{Dy}2)_2\text{O}_8$ dimer units can connect adjacent 1-D lines along b or c direction, forming 3-D coordination polymer 1. In coordination polymer 2, only two coordination water molecules occupy two coordination place of Dy2 cation, which restrain the growth of Dy2 cation along a and c direction, forming

1-D lines along b direction, moreover, Dy1 cation only expand along $[10-1]$ plane. The grow directions of Dy1 and Dy2 cations are identical, accordingly, coordination polymer **2** can only form 2-D layer structure rather than 3-D network.

3.3.3. $\{[Ln_4(1,3-BDC)_6(DMF)(H_2O)_4] \cdot DMF \cdot 2H_2O\}_n$ [$Ln = Tb$ (**3**), Ho (**4**), Er (**5**)]

Coordination polymers **3–5** are isomorphous, therefore, only the structure of coordination polymer **3** is described in detail. In coordination polymer **3**, the asymmetric unit cell contains four Tb^{3+} ion, six $1,3-BDC^{2-}$ ligands, one coordinated DMF molecule, four coordinated water molecules, one free DMF molecule, and two free

water molecules, with all in general positions. The four terbium ions have completely different chemical environment. Tb1 is seven-coordinated by four carboxylate oxygen atoms (O1, O9, O19 and O21) from four $1,3-BDC^{2-}$ ligands, and three oxygen atoms (O25, O26 and O27) from three terminal water molecules. Tb2 is seven-coordinated by seven carboxyl oxygen atoms (O3, O8, O11, O12, O13, O17 and O24) from six $1,3-BDC^{2-}$ ligands. Tb4 is seven-coordinated by five carboxyl oxygen atoms (O2, O7, O10, O20 and O23) from five $1,3-BDC^{2-}$ ligands, and one oxygen atom (O28) from one coordinated water molecule, and one oxygen atom (O29) from one coordinated DMF molecule. Tb3 ion is nine-coordinated by two carboxylate oxygen atoms (O5 and O6) from one $1,3-BDC^{2-}$ ligand, three carboxylate oxygen atoms (O14, O15 and O16) from one $1,3-BDC^{2-}$ ligand, and three oxygen atoms (O4, O18 and O22) from three $1,3-BDC^{2-}$ ligands. The structure is shown in Fig. 7. The Tb–O distances range from 2.240 (4) to 2.576 (4) Å. The O–Tb–O bond angles range from 51.64 (11)° to 173.77 (14)°. The coordination modes of $1,3-BDC^{2-}$ in coordination polymer **3** are shown in Scheme 1A and B.

In coordination polymer **3**, neighboring Tb^{3+} ions are connected through bridging carboxyl oxygen atoms from the $1,3-BDC^{2-}$ ligand, giving rise to an infinite symmetrical one-dimensional chain (Fig. 8a), and two infinite chains are linked through the $1,3-BDC^{2-}$ ligand to form 2-D layered structure by back-back configuration (Fig. 8b). If ignore DMF ligands and water molecules, center metal Tb1 and Tb4 can be 3-connected triangular node (Tb14), Tb2 and Tb3 can be 4-connected tetrahedron node (Tb23), the $1,3-BDC^{2-}$ ligands act as linear bridges between the adjacent nodes. Such connectivity repeats infinitely, resulting in a (3,4)-connected net with the point symbol of $\{4^2 \cdot 6^3 \cdot 8\}\{4^2 \cdot 6\}$. The topology is shown in Fig. 8c. A 3-D supramolecular structure is obtained by hydrogen bonding interactions, which were formed by the oxygen atoms of coordination water and DMF ligands and the hydrogen atoms of lattice water or DMF ligands. The free water molecules and the free DMF molecule are inserted into the layers (Fig. 9).

3.4. Nitrogen adsorption–desorption measurements and powder X-ray diffraction

The N_2 adsorption–desorption isotherms of coordination polymer **1** is shown in Fig. 10. It clearly indicates Type IV isotherms

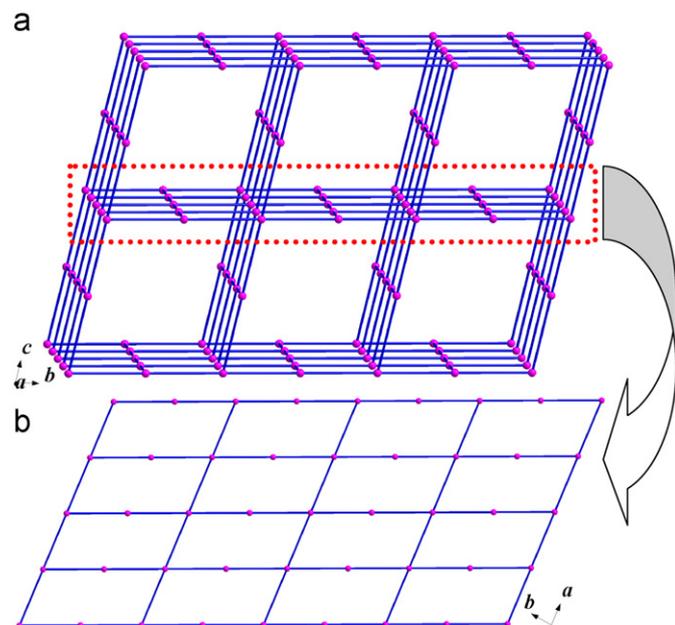


Fig. 4. (a) Topological view of the 3-D structure of **1** with 8-member ring channels along the $[1\ 0\ 0]$ direction. (b) The layered structure is parallel to the ab plane and linked by the Dy_2 chains with the 6-member ring. (Color code: Dy_2 , pink ball; $1,3-BDC^{2-}$, blue line.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

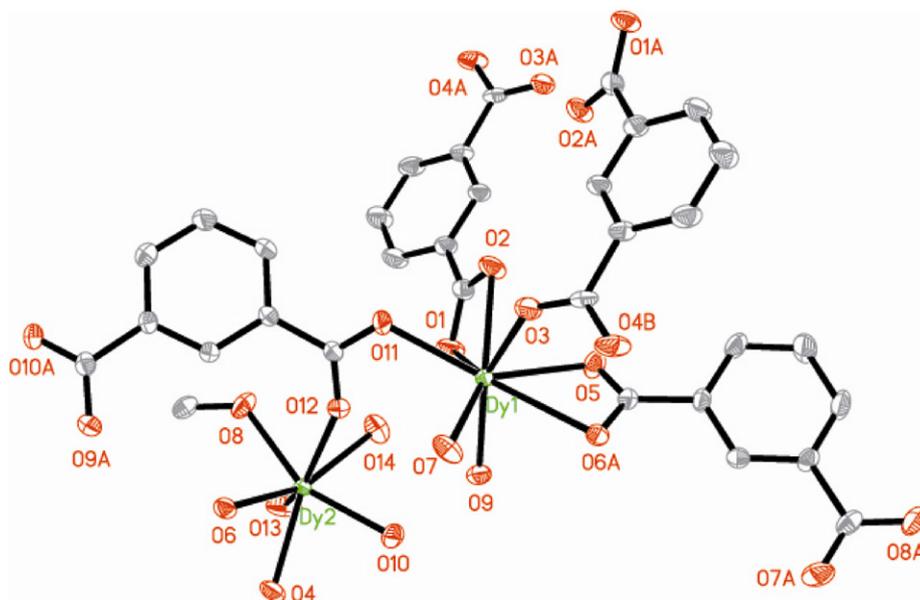


Fig. 5. The metal coordination environment in coordination polymer **2** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). Symmetry codes: (a) $-x, -0.5+y, 0.5-z$.

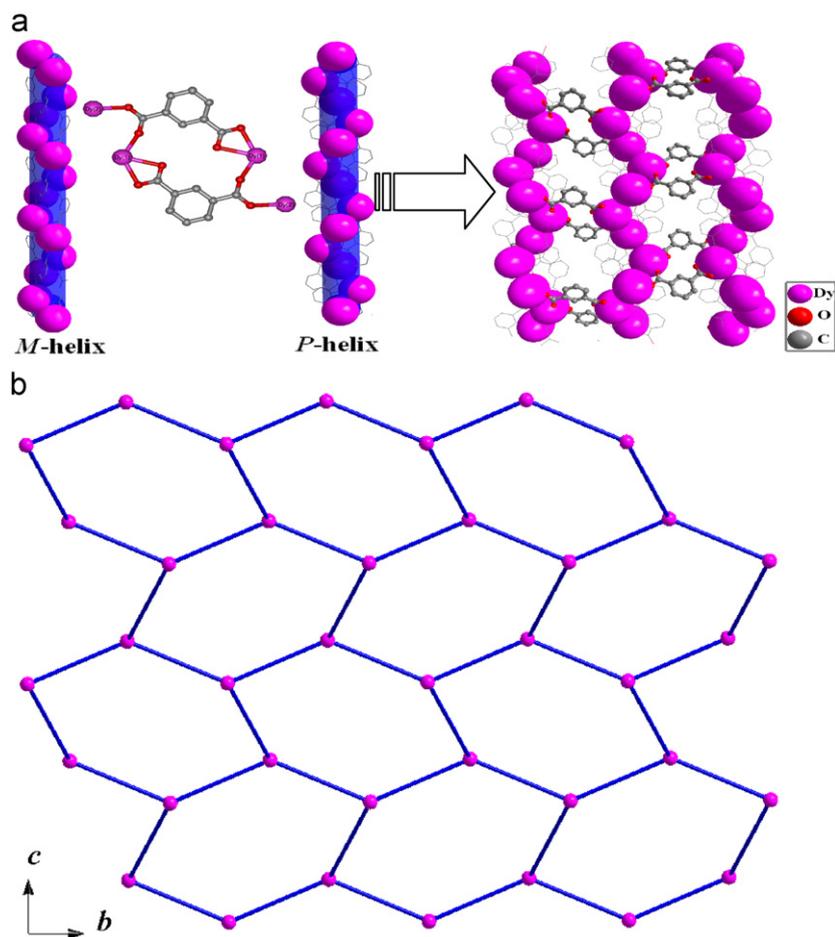


Fig. 6. (a) The illustration of left-handed helix (*M*-helix) and right-handed helix (*P*-helix) along the *b* axis direction, and 2-D layer structure (water molecules and hydrogen atoms are omitted for clarity) in coordination polymer **2**. (b) The layered structure is parallel to the *ac* plane with the 6-member ring. (Color code: Dy₂, pink ball; 1,3-BDC²⁻, blue line.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

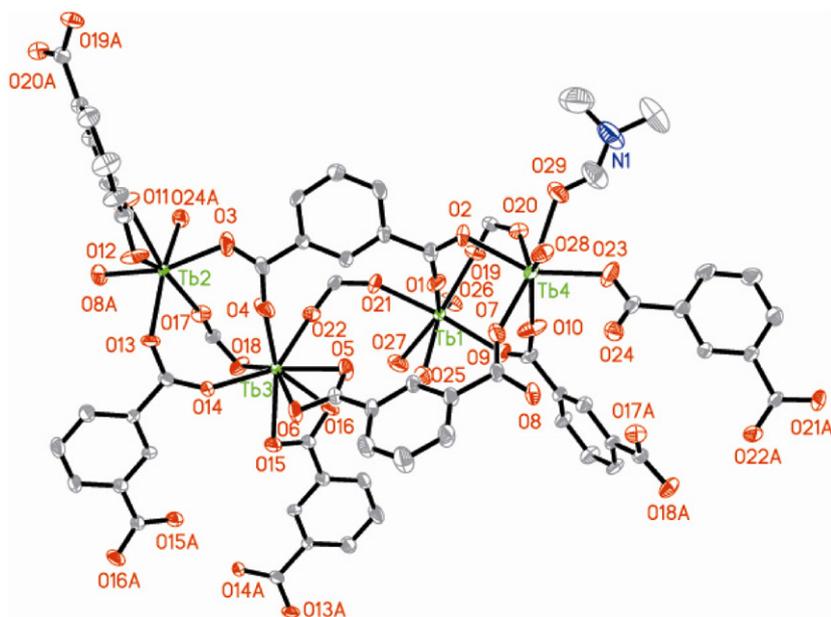


Fig. 7. The metal coordination environment in coordination polymer **3** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). Symmetry codes: (a) *x*, 1 + *y*, *z*.

with H4-type hysteresis loops at high relative pressure according to the IUPAC classification [23]. From the two branches of adsorption–desorption isotherms, the hysteresis loops remain

nearly horizontal at wide range of the relative pressure P/P_0 , which shows that coordination polymer **1** is associated with narrow slit-like pore. The surface area (8.95 m²/g) was calculated

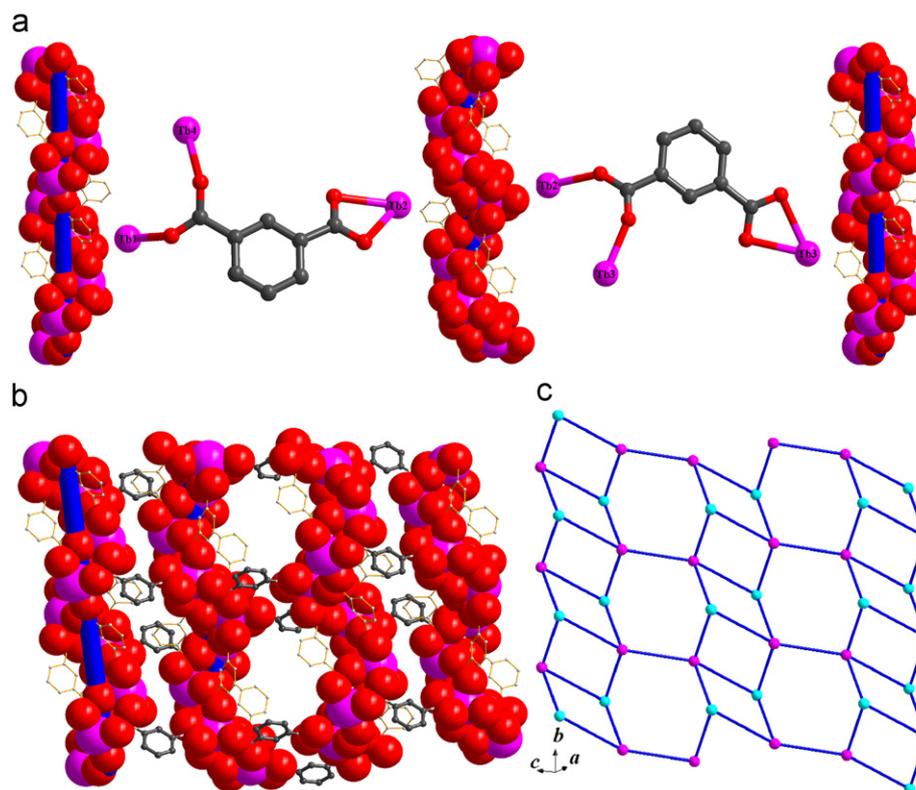


Fig. 8. (a) The illustration of a 1-D zigzag chain in coordination polymer **3**. (b) The illustration of 2-D layer structure in coordination polymer **3** (water molecules, DMF and hydrogen atoms are omitted for clarity). (c) The terbium and 1,3-BDC²⁻ layers with (3,4)-connected network of coordination polymer **3**. (The DMF ligands, water molecules and hydrogen atoms in the framework are omitted for clarity. Color code: Tb14, turquoise ball; Tb23, pink ball; 1,3-BDC²⁻, blue line.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

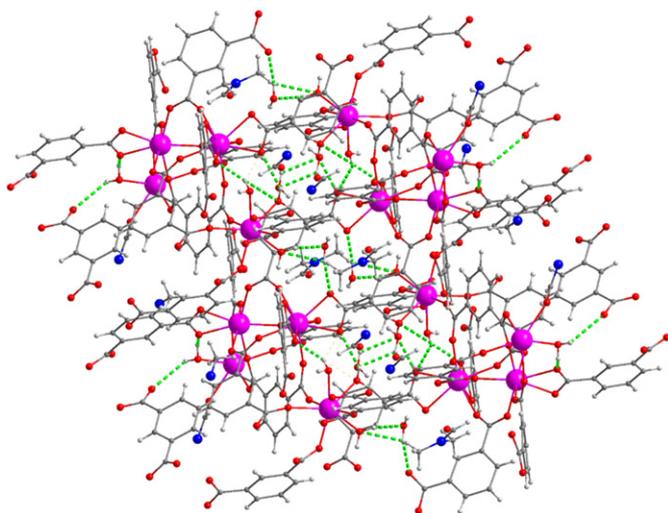


Fig. 9. A 3-D supramolecular structure of coordination polymer **3**.

using Brunauer–Emmett–Teller (BET) and micropore volume (0.031 cm³/g) as well as the pore size (152.42 Å) using Barrett–Joyner–Halenda (BJH) methods, respectively. The surface area observed for coordination polymer **1** is obviously smaller compared with its percent effective free volume of 23.3% (total potential solvent volume of 850.5 Å³ out of per unit cell volume of 3686.6 Å³) calculated with PLATON. The results show that approximately 19.77 mL of N₂ was adsorbed per 1.0 g of sample at 1 atm (Fig. 10), exhibiting certain adsorption for N₂. The adsorption isotherm clearly indicates surface adsorption, the N₂ molecules perhaps not diffusing into the micropores [24].

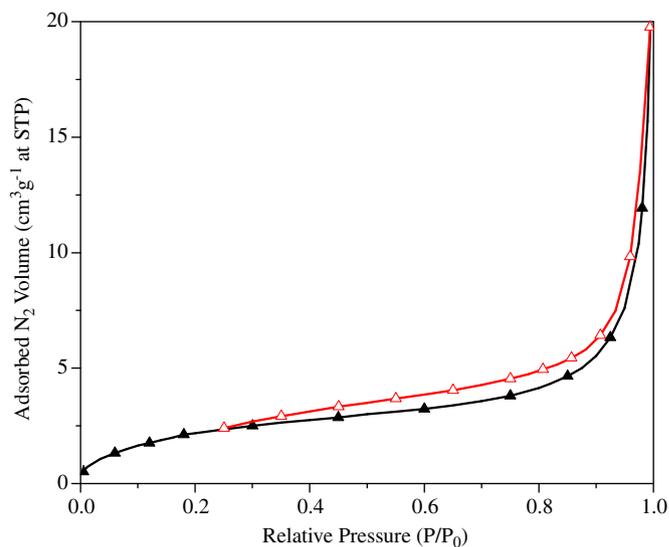


Fig. 10. N₂ adsorption–desorption isotherms of coordination polymer **1**.

In order to confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) experiments were carried out on coordination polymers **1–5** (see Supporting information Figs. S1–S5). The PXRD patterns indicated that the patterns are entirely consistent with the simulated PXRD pattern generated based on the structures determined by the single-crystal XRD of coordination polymers **1–5**. The similar PXRD pattern (Fig. 11) of coordination polymers **3–5** indicated that the coordination polymers **3–5** are isomorphous.

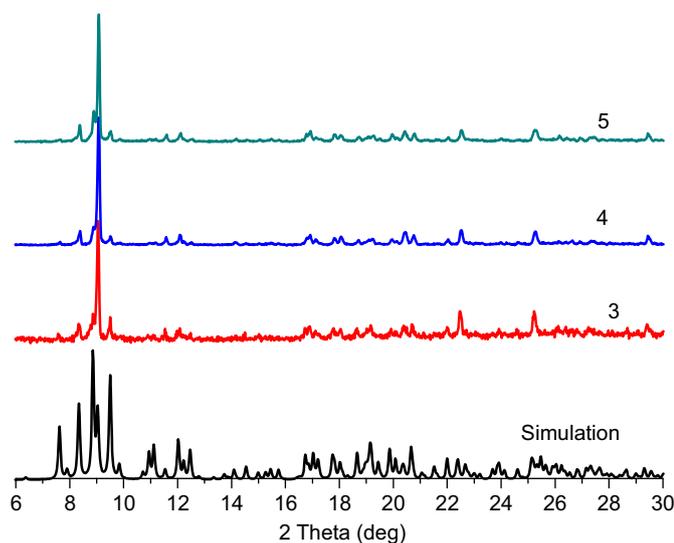


Fig. 11. PXRD patterns of coordination polymers 3–5, compared with a simulated pattern.

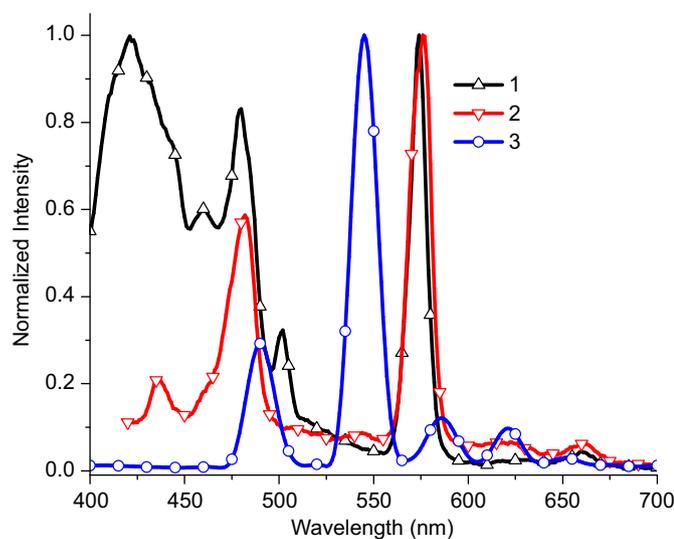


Fig. 12. Solid-state emission spectra for coordination polymers 1–3 at room temperature (excited at 345, 300, and 392 nm, respectively).

3.5. Photoluminescence properties

The luminescence spectra of coordination polymers 1–5 are measured, whereas, the characteristic emission bands for corresponding lanthanide in coordination polymers 4 and 5 were not observed. Under the excitation of 345 nm light, coordination polymer 1 shows three characteristic emission bands of the dysprosium (III) ion in the visible region: 480 nm (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$), 574 nm (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$), and 660 nm (${}^4F_{9/2} \rightarrow {}^6H_{11/2}$). Coordination polymer 1 displays a fluorescence emission band at $\lambda_{\max} = 421$ nm, which corresponds to $S_1 \rightarrow S_0$ transfer of coordinated 1,3-BDC²⁻ ligands, and is slightly disturbed by the dysprosium ion (Fig. 12).

Under the excitation of 300 nm light, the two emission groups for coordination polymer 2 in the ranges of 400–440 and 470–700 nm are shown in Fig. 12. The emissions at 482, 576 and 662 nm are attributed to the characteristic emission of ${}^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2, 13/2$ and $11/2$) transitions of the Dy³⁺ ion [25,26]. It is obvious that the intensity of the yellow emission, corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, is slightly stronger than that of the

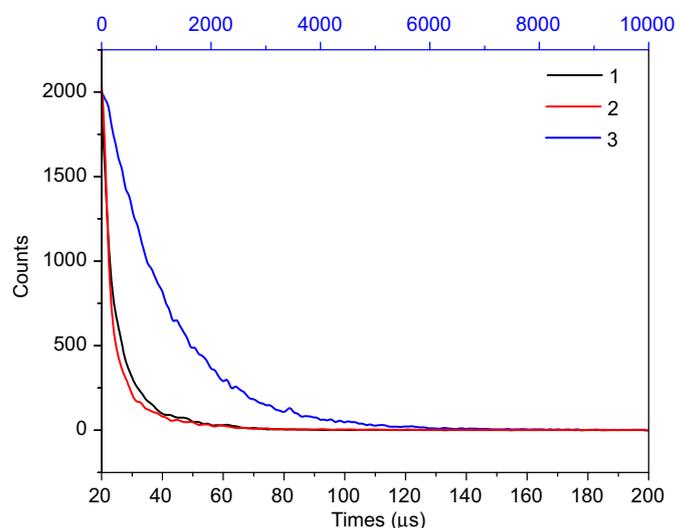


Fig. 13. The luminescence decay curves for coordination polymers 1–3.

blue emission. The broad blue band ranging from 400 to 440 nm could be assigned to the emission of ligand-to-metal charge transfer (LMCT) [26]. The intensity of the metal-centered transitions is strongly relative to that of the broad LMCT band, which implies that the direct metal excitation is comparable to the sensitized process, as the extinction coefficients of the metal emission are much lower than that of the ligands [27].

Under the excitation of 392 nm, coordination polymer 3 shows a strong visible emission in the green region. The emission spectrum of coordination polymer 3 is depicted in Fig. 12, which can be assigned to ${}^5D_4 \rightarrow {}^7F_J$ ($J = 3-6$) transitions of the Tb³⁺ ion (Fig. 12), specifically, at 490 (${}^5D_4 \rightarrow {}^7F_6$), 545 (${}^5D_4 \rightarrow {}^7F_5$), 586 (${}^5D_4 \rightarrow {}^7F_4$) and 621 nm (${}^5D_4 \rightarrow {}^7F_3$), respectively [28].

To understand the photoluminescent properties of coordination polymers 1–3, we also performed time-resolved measurements of coordination polymers 1–3 by using the time-correlated single photon counting (TCSPC) technique. As shown in Fig. 13, the decay curves for solid coordination polymers 1–3 exhibit double-exponential behavior, $I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ [29], where I and I_0 are the luminescent intensities at time $t = t$ and $t = 0$, respectively, whereas τ_1 and τ_2 are defined as the luminescent lifetimes. The fluorescence decay lifetimes of coordination polymers 1–3 are $\tau_1 = 3.53 \mu\text{s}$ (48.74%), $\tau_2 = 12.52 \mu\text{s}$ (51.26%) (for coordination polymer 1), $\tau_1 = 2.03 \mu\text{s}$ (39.87%), $\tau_2 = 12.29 \mu\text{s}$ (60.13%) (for coordination polymer 2), and $\tau_1 = 100.00 \mu\text{s}$ (0.06%), $\tau_2 = 1149.83 \mu\text{s}$ (99.94%) (for coordination polymer 3), respectively [30].

4. Conclusions

In conclusion, by modifying the pH value and metal/ligand ratio, we have successfully prepared five 1,3-H₂BDC-based Ln(III) coordination polymers. These coordination polymers present three different structural types: 3-D framework for coordination polymer 1, which is a 4-connected 3-D MOFs net with 1-D open channels, and this dehydrated porous material can absorb for N₂, with a determined BET surface area of 8.95 m²/g. A 2-D structure for coordination polymer 2, in which two helix chains are connected through the 1,3-BDC ligand, leading to the formation of 2-D layered structure. Coordination polymers 3–5 are isomorphous, displayed 2-D layer structure, 3-D supramolecular structure is obtained by hydrogen bonding interactions. The luminescence properties of coordination polymers 1–5 have been

measured and discussed. Coordination polymers **1** and **2** have displayed characteristic emissions of dysprosium ions in the solid state at room temperature, the fluorescence decay lifetimes of coordination polymers **1** and **2** are $\tau_1=3.53\ \mu\text{s}$ (48.74%), $\tau_2=12.52\ \mu\text{s}$ (51.26%), and $\tau_1=2.03\ \mu\text{s}$ (39.87%), $\tau_2=12.29\ \mu\text{s}$ (60.13%) (for coordination polymer **2**), respectively. Coordination polymer **3** exhibits a strong characteristic green emission of the Tb^{3+} ion at 545 nm and shows luminescence lifetimes at millisecond. The coordination polymer **3** displays ligand-sensitized intense green luminescence emission, with lifetimes at the millisecond order and may be potential photoactive materials. The characteristic emission bands for corresponding lanthanide in coordination polymers **4** and **5** were not observed.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc.2012.07.018>.

References

- [1] (a) J. Brunner, R. Kraemer, J. Am. Chem. Soc. 126 (2004) 13626; (b) J. Xu, J. Cheng, W. Su, M. Hong, Cryst. Growth Des. 11 (2011) 2294; (c) S.M. Fang, E.C. Sañudo, M. Hu, Q. Zhang, S.T. Ma, L.R. Jia, C. Wang, J.Y. Tang, M. Du, C.S. Liu, Cryst. Growth Des. 11 (2011) 811.
- [2] (a) H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389; (b) Z.M. Zhang, Y.G. Li, S. Yao, E.B. Wang, Y.H. Wang, R. Clérac, Angew. Chem. Int. Ed. 48 (2009) 1581; (c) A.K. Cheetham, G. Férey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268; (d) Y.H. Zhao, Z.M. Su, Y. Wang, Y.M. Fu, S.D. Liu, P. Li, Inorg. Chem. Commun. 10 (2007) 410.
- [3] (a) H. Deng, C.J. Doonan, H. Furukawa, R.B. Ferreira, J. Towne, C.B. Knobler, B. Wang, O.M. Yaghi, Science 327 (2010) 846; (b) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano, T. Nagano, J. Am. Chem. Soc. 126 (2004) 12470; (c) C. Benelli, D. Gatteschi, Chem. Rev. 102 (2002) 2369; (d) J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357; (e) K.Z. Shao, Y.H. Zhao, X.L. Wang, Y.Q. Lan, D.J. Wang, Z.M. Su, R.S. Wang, Inorg. Chem. 48 (2009) 10.
- [4] (a) Q.T. He, X.P. Li, Y. Liu, Z.Q. Yu, W. Wang, C.Y. Su, Angew. Chem. Int. Ed. 48 (2009) 6156; (b) C.A. Bauer, T.V. Timofeeva, T.B. Settersten, B.D. Patterson, V.H. Liu, B.A. Simmons, M.D. Allendorf, J. Am. Chem. Soc. 129 (2007) 7136; (c) G.M. Cockrell, G. Zhang, D.G. VanDerveer, R.P. Thummel, R.D. Hancock, J. Am. Chem. Soc. 130 (2008) 1420.
- [5] (a) R.Q. Fan, Y.L. Yang, Y.B. Yin, W. Hasi, Y. Mu, Inorg. Chem. 48 (2009) 6034; (b) A.X. Tian, J. Ying, J. Peng, J.Q. Sha, H.J. Pang, P.P. Zhang, Y. Chen, M. Zhu, Z.M. Su, Inorg. Chem. 48 (2009) 100; (c) R.Q. Fan, D.S. Zhu, Y. Mu, G.H. Li, Y.L. Yang, Q. Su, S.H. Feng, Eur. J. Inorg. Chem. (2004) 4891; (d) R.Q. Fan, D.S. Zhu, H. Ding, Y. Mu, Q. Su, H. Xia, Synth. Met. 149 (2005) 135; (e) Q. Chu, G.X. Liu, Y.Q. Huang, X.F. Wang, W.Y. Sun, Dalton Trans. (2007) 4302.
- [6] (a) R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa, Angew. Chem. Int. Ed. 41 (2002) 133; (b) H. Deng, Y.H. Li, Y.C. Qiu, Z.H. Liu, M. Zeller, Inorg. Chem. Commun. 11 (2008) 1151; (c) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, J. Am. Chem. Soc. 129 (2007) 2607; (d) E.M.W.M. van Dongen, L.M. Dekkers, K. Spijker, E.W. Meijer, L.W.J. Klomp, M. Merckx, J. Am. Chem. Soc. 128 (2006) 10754.
- [7] (a) L. Cañadillas-Delgado, O. Fabelo, J. Pasán, F.S. Delgado, M. Déniz, E. Sepúlveda, M.M. Laz, M. Julve, C. Ruiz-Pérez, Cryst. Growth Des. 8 (2008) 1313; (b) Y.H. Zhao, H.B. Xu, Y.M. Fu, K.Z. Shao, S.Y. Yang, Z.M. Su, X.R. Hao, D.X. Zhu, E.B. Wang, Cryst. Growth Des. 8 (2008) 3566; (c) X. Gu, D. Xue, Cryst. Growth Des. 7 (2007) 1726.
- [8] (a) S. Raphael, M.L.P. Reddy, A.H. Cowley, M. Findlater, Eur. J. Inorg. Chem. (2008) 4387; (b) D.T. de Lill, A. de Bettencourt-Dias, C.L. Cahill, Inorg. Chem. 46 (2007) 3960.
- [9] (a) X.F. Guo, M.L. Feng, Z.L. Xie, J.R. Li, X.Y. Huang, Dalton Trans. (2008) 3101; (b) D.J. Zhang, T.Y. Song, J. Shi, W.R. Yin, P. Zhang, L. Wang, Y. Wang, K.R. Ma, Y. Fan, J.N. Xu, Inorg. Chem. Commun. 10 (2007) 1067.
- [10] (a) X. Yan, Z. Cai, C. Yi, W. Liu, M. Tan, Y. Tang, Inorg. Chem. 50 (2011) 2346; (b) R. Cong, T. Yang, Z. Wang, J. Sun, F. Liao, Y. Wang, J. Lin, Inorg. Chem. 50 (2011) 1767.
- [11] (a) J.C.G. Bünzli, C. Piguet, Chem. Rev. 102 (2002) 1897; (b) H.S. Wang, B. Zhao, B. Zhai, W. Shi, P. Cheng, D.Z. Liao, S.P. Yan, Cryst. Growth Des. 7 (2007) 1851; (c) D. Weng, X. Zheng, L. Li, W. Yang, L. Jin, Dalton Trans. (2007) 4822.
- [12] (a) A.K. Cheetham, C.N.R. Rao, R.K. Feller, Chem. Commun. (2006) 4780; (b) C.N.R. Rao, S. Natarajan, R. Vaidyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466.
- [13] (a) Y.B. Wang, W.J. Zhuang, L.P. Jin, S.Z. Lu, J. Mol. Struct. 737 (2005) 165; (b) N. Wang, S. Yue, Y. Liu, H. Yang, H. Wu, Cryst. Growth Des. 9 (2009) 368.
- [14] (a) Y.G. Huang, B.L. Wu, D. Yuan, Y.Q. Xu, F.L. Jiang, M.C. Hong, Inorg. Chem. 46 (2007) 1171; (b) W.P. Wu, Y.Y. Wang, Y.P. Wu, J.Q. Liu, X.R. Zeng, Q.Z. Shi, S.M. Peng, CrystEngComm 9 (2007) 753.
- [15] T. Whitfield, L.M. Zheng, X. Wang, A.J. Jacobson, Solid State Sci. 3 (2001) 829.
- [16] (a) B. Zhao, L. Yi, Y. Dai, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem. 44 (2005) 911; (b) H.H. Song, Y.J. Li, Inorg. Chim. Acta 361 (2008) 1421; (c) M.S. Liu, Q.Y. Yu, Y.P. Cai, C.Y. Su, X.M. Lin, X.X. Zhou, J.W. Cai, Cryst. Growth Des. 8 (2008) 4083.
- [17] (a) X. Shi, G. Zhu, X. Wang, G. Li, Q. Fang, G. Wu, G. Tian, M. Xue, X. Zhao, R. Wang, S. Qiu, Cryst. Growth Des. 5 (2005) 207; (b) Z. Wang, Y.H. Xing, C.G. Wang, L.X. Sun, J. Zhang, M.F. Ge, S.Y. Niu, CrystEngComm 12 (2010) 762; (c) J. Fan, Z.H. Wang, M. Yang, X. Yin, W.G. Zhang, Z.F. Huang, R.H. Zeng, CrystEngComm 12 (2010) 216; (d) Y.W. Li, Y.H. Wang, Y.G. Li, E.B. Wang, J. Solid State Chem. 181 (2008) 1485.
- [18] (a) X. Shi, G. Zhu, X. Wang, G. Li, Q. Fang, X. Zhao, G. Wu, G. Tian, M. Xue, R. Wang, S. Qiu, Cryst. Growth Des. 5 (2005) 341; (b) S. Surblé, C. Serre, F. Millange, F. Pellé, G. Férey, Solid State Sci. 9 (2007) 131; (c) X. Gu, D. Xue, Cryst. Growth Des. 6 (2006) 2551.
- [19] G.B. Che, C.B. Liu, B. Liu, Q.W. Wang, Z.L. Xu, CrystEngComm 10 (2008) 184.
- [20] (a) P. Mahata, K.V. Ramya, S. Natarajan, Dalton Trans. 36 (2007) 4017; (b) P. Mahata, S. Natarajan, Inorg. Chem. 46 (2007) 1250; (c) A. Thirumurugan, S. Natarajan, Cryst. Growth Des. 6 (2006) 983; (d) A. Thirumurugan, S. Natarajan, Dalton Trans. 18 (2004) 2923; (e) A. Thirumurugan, S. Natarajan, Eur. J. Inorg. Chem. (2004) 762.
- [21] G.M. Scheldrick, SHELXTL NT Crystal Structure Analysis Package, version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999.
- [22] (a) R.S. Zhou, X.B. Cui, J.F. Song, X.Y. Xu, J.Q. Xu, T.G. Wang, J. Solid State Chem. 181 (2008) 2099; (b) F. Fu, S.P. Chen, Y.X. Ren, S.L. Gao, Acta Chim. Sin. 66 (2008) 1663.
- [23] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.
- [24] X. Li, B.L. Wu, C.Y. Niu, Y.Y. Niu, H.Y. Zhang, Cryst. Growth Des. 9 (2009) 3423.
- [25] (a) Y. Li, F.K. Zheng, X. Liu, W.Q. Zou, G.C. Guo, C.Z. Lu, J.S. Huang, Inorg. Chem. 45 (2006) 6308; (b) M.V. Lucky, S. Sivakumar, M.L.P. Reddy, A.K. Paul, S. Natarajan, Cryst. Growth Des. 11 (2011) 857; (c) N.N. Katia, A. Lecointre, M. Regueiro-Figueroa, C. Platas-Iglesias, L.J. Charbonnière, Inorg. Chem. 50 (2011) 1689.
- [26] (a) H.L. Gao, L. Yi, B. Zhao, X.Q. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Inorg. Chem. 45 (2006) 5980; (b) R. Feng, L. Chen, Q.H. Chen, X.C. Shan, Y.L. Gai, F.L. Jiang, M.C. Hong, Cryst. Growth Des. 11 (2011) 1705.
- [27] Y.Q. Sun, J. Zhang, G.Y. Yang, Chem. Commun. (2006) 1947.
- [28] J. Qin, D. Du, L. Chen, X. Sun, Y. Lan, Z. Su, J. Solid State Chem. 184 (2011) 373.
- [29] E.G. Moore, G. Szigethy, J. Xu, L.O. Pålsson, A. Beeby, K.N. Raymond, Angew. Chem. Int. Ed. 47 (2008) 9500.
- [30] (a) S. Quici, M. Cavazzini, G. Marzanni, G. Accorsi, N. Armaroli, B. Ventura, F. Barigelli, Inorg. Chem. 44 (2005) 529; (b) M.F. Wu, M.S. Wang, S.P. Guo, F.K. Zheng, H.F. Chen, X.M. Jiang, G.N. Liu, G.C. Guo, J.S. Huang, Cryst. Growth Des. 11 (2011) 372.