Systematic design and research on a series of cadmium coordination polymers assembled due to tetracarboxylate ligands

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ABSTRACT

A series of metal-organic frameworks (MOFs) have been prepared by tetracarboxylate ligands and Cd(II) ions under the hydrothermal or solvothermal conditions with the formulas of $\{[Cd_2(L_1)(H_2O)_4] \cdot H_2O\}_n$ (1), $\{[(CH_3)_2NH_2]_2[Cd(L_1)]\}_n$ (2), $[Cd(L_2)_{0.5}(H_2O)]_n$ (3), $\{[(CH_3)_2NH_2]_2 [Cd(L_2)] \cdot 2DMF\}_n$ (4), $[Cd(L_3)_{0.5}(H_2O)]_n$ (5), $\{[Cd(L_3)_{0.5}(H_2O)] \cdot CH_3OH\}_n$ (6), $\{[(CH_3)_2NH_2]_2[Cd_3(L_4)_2]\}_n$ (7) ($H_4L_1=$[1,1′:4′,1″-terphenyl]-2,2″,5,5″-tetracarboxylic acid; $H_4L_2=$[1,1′:4′,1″-terphenyl]-2′,4,4″,5′-tetracarboxylic acid; $H_4L_3=$[1,1′:3′,1″-terphenyl]-2′,3,3″,5′-tetracarboxylic acid; $H_4L_4=$[1,1′:4′,1″-terphenyl]-3,3″,5,5″-tetra-carboxylic acid), which are characterized by single-crystal X-ray diffraction, elemental analyses, IR, TGA and PXRD. Complex **1** exhibits a three-dimensional (3D) supramolecular framework based on two-dimensional (2D) coordination networks. Complexes **2** and **4** possess 3D framework based on the 1D right-handed helix channels. Complexes **3** and **7** are a 3D architecture containing two different channels. Isostructural complexes **5** and **6** display 3D framework. The different synthetic methods and coordination modes of the tetracarboxylates ligands have effect on formation of various MOFs. Moreover, the luminescent properties and N_2 adsorption behaviors have been reported.

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1. Introduction

In recent years, metal-organic frameworks (MOFs) as a new class of porous materials have become a very attractive area of research in coordination chemistry aiming to not only construct fascinating esthetic architectures with various novel topologies but also explore the potential applications in a wide variety of scientific fields [1–3]. The rational syntheses of MOFs play an important role in constructing multifunctional porous materials [4–5]. In the process of syntheses, the organic ligand as the most important factor has effect on the formation of the MOFs with multifarious architectures and the specific properties [6–7]. Especially, the organic polycarboxylate ligands are regarded as good candidates for building the porous MOFs with multinuclear nodes, helical structures and some novel topologies [8–9]. The rigid tetracarboxylate ligands based on terphenyl moiety are engaged in forming the some frameworks in view of their following characteristics: first, completely or partially deprotonated carboxyl groups possess the rich coordinated nodes and the strong coordinated abilities, leading to the formation of multidimensional architectures [10]; second, the terphenyl moiety with a bent degree of robustness provide the rigidity for the whole ligand, which

are favorable to avoid forming the interpenetration structures [11]; third, the abundant oxygen atoms from four carboxyl groups can be viewed as the potential hydrogen-bonding acceptors as well as donors, resulting in the high-dimensional supramolecular frameworks [12]. Moreover, the diversities of the coordination fashions may produce entirely different frameworks even though they have the same metal ions and tetracarboxylate ligands in the presence of disparate organic solvents.

To our knowledge, few reports studied the coordination polymers based on the tetracarboxylate ligands with terphenyl moiety so far. Zhang's group [10,11,13c,13d] used the quaterphenyl-2,5,2′,5′-tetracarboxylic acid (H_4L_1) and the N-containing ligands to obtain a series of transition metal coordination polymers including the unprecedented three-dimensional (3D) (4,4)-connected $(4 \cdot 6^4 \cdot 8^2)_2(4^2 \cdot 8^4)$ framework and the novel two-dimensional (2D) self-catenating network possessing three interpenetrating 4^4-sql subnets. Wang et al. [12] reported solvent-induced MOFs based on [1,1′:4′,1″-terphenyl]-2′,4,4″,5′-tetracarboxylic acid (H_4L_2) or [1,1′:3′,1″-terphenyl]-2′,3,3″,5′-tetracarboxylic acid (H_4L_3) featuring the good chemical stabilities and antiferromagnetic or high selectivity and sensitivity for Cu(II) ions and nitrobenzene. The ligand quaterphenyl-3,5,3′,5′-tetracarboxylic acid (H_4L_4) is introduced into the copper system to construct coordination-framework materials for the first time, which possesses remarkable H_2 adsorptive capacity [13b]. Hong and his coworkers [14] explored Eu(III) coordination polymers

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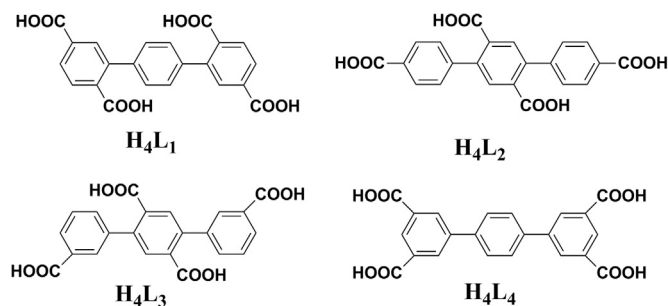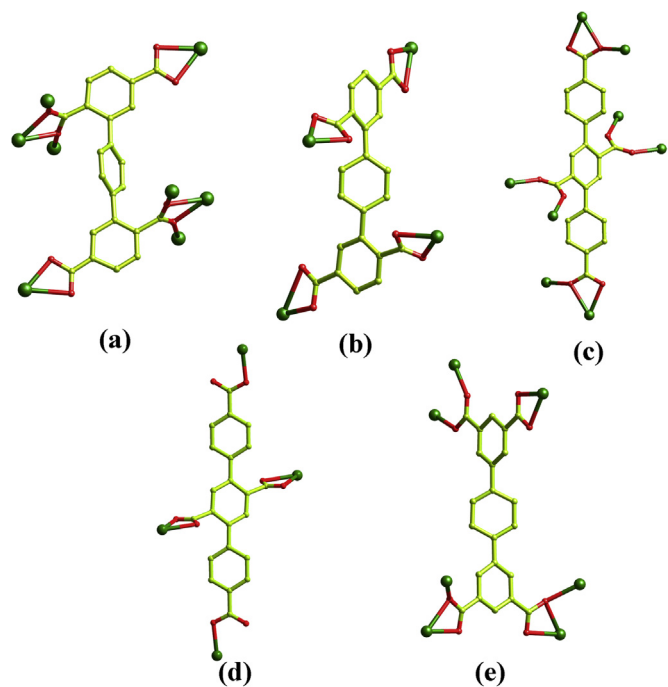
Scheme 1. The carboxylate ligands employed in this work.

containing H_4L_4 tetracarboxylate ligands, and the complexes exhibit enhanced luminescence properties. Based on the above interesting structures and excellent properties, it is worth researching the formation of coordination frameworks with terphenyl tetracarboxylate ligands further (Scheme 1).

On the basis of the aforementioned considerations, the hydrothermal or solvothermal assembly of four kinds of tetracarboxylate ligands and the metal Cd(II) ions results in the formation of seven high-dimensional MOFs, namely, $\{[Cd_2(L_1)(H_2O)_4] \cdot H_2O\}_n$ (**1**), $\{[(CH_3)_2NH_2]_2[Cd(L_1)]\}_n$ (**2**), $[Cd(L_2)_{0.5}(H_2O)]_n$ (**3**), $\{[(CH_3)_2NH_2]_2[Cd(L_2)] \cdot 2DMF\}_n$ (**4**), $[Cd(L_3)_{0.5}(H_2O)]_n$ (**5**), $\{[Cd(L_3)_{0.5}(H_2O)] \cdot CH_3OH\}_n$ (**6**), $\{[(CH_3)_2NH_2]_2[Cd_3(L_4)_2]\}_n$ (**7**), which are generated by one-dimensional (1D) infinite chains with different features. The synthetic methods and coordination modes of the tetracarboxylates ligands play important roles in the final MOFs. Moreover, the fluorescence properties of complexes **1**, **2**, **4**, **7** and N_2 adsorption properties of complexes **2**, **4–7** are investigated (Scheme 2).

2. Experimental

2.1. Materials and general methods

All reagents were obtained commercially and used without further purification. Elemental analyses (C, H, N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer. FT-IR spectra (KBr pellets) were performed with a Nicolet 170SX spectrophotometer. Thermogravimetric (TG) analyses were recorded on a Exstar SII TG/DTA 7200 integration thermal analyzer. The powder X-ray diffraction (PXRD) were carried out a Siemens D5005 diffractometer (Cu Kα radiation, $\lambda = 1.5410$ Å). Fluorescence spectra were performed on a Hitachi F-4600 fluorescence/phosphorescence spectrophotometer at room temperature. Nitrogen adsorption experiments were conducted at 77 K using a TriStarII3020 (Micromeritics Instrument Corporation) apparatus. Before adsorption measurements, the samples were degassed in vacuum at 393 K for 12 h.

2.2. Synthesis of $\{[Cd_2(L_1)(H_2O)_4] \cdot H_2O\}_n$ (**1**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (92.5 mg, 0.30 mmol), H_4L_1 (20.3 mg, 0.05 mmol), NaOH (6.0 mg, 0.15 mmol) and H_2O (10 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at 150 °C for 3 days. After cooling to room temperature at a speed of 10 °C/h, the colorless crystals of **1** were obtained and washed with distilled water. 12% yield based on Cd. Elemental analysis for $C_{22}H_{20}Cd_2O_{13}$, calcd (%): C, 36.84; H, 2.81. Found (%): C, 36.80; H, 2.77. IR data (KBr, cm^{-1}): 3568 (s), 3234 (s), 1525 (s), 1392 (s), 1265 (m), 1158 (w), 1105 (w), 1047 (w), 967 (w), 859 (m), 770 (m), 668 (w), 577 (w), 504 (w).

2.3. Synthesis of $\{[(CH_3)_2NH_2]_2[Cd(L_1)]\}_n$ (**2**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol), H_4L_1 (16.2 mg, 0.04 mmol), DMF (5 mL), CH_3OH (1 mL) and 1 mol/L HCl aqueous solution (0.15 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at 100 °C for 3 days. After cooling to room temperature at a speed of 10 °C/h, the colorless crystals of **2** were obtained and washed with DMF. 43% yield based on Cd. Elemental analysis for $C_{26}H_{26}CdN_2O_8$, calcd (%): C, 51.45; H, 4.32; N, 4.62. Found (%): C, 51.49; H, 4.26; N, 4.58. IR data (KBr, cm^{-1}): 3411 (w), 3035 (m), 2785 (m), 2462 (m), 1665 (s), 1571 (s), 1478 (m), 1411 (s), 1360 (s), 1255 (m), 1102 (m), 1024 (m), 919 (w), 847 (m), 779 (m), 662 (w), 573 (w), 536 (w), 509 (w).

2.4. Synthesis of $[Cd(L_2)_{0.5}(H_2O)]_n$ (**3**)

A mixture of $CdCl_2 \cdot 2.5H_2O$ (45.6 mg, 0.20 mmol), H_4L_2 (40.6 mg, 0.10 mmol), NaOH (6.0 mg, 0.15 mmol) and H_2O (10 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at 150 °C for 3 days. After cooling to room temperature at a speed of 10 °C/h, the colorless crystals of **3** were obtained and washed with distilled water. 7% yield based on Cd. Elemental analysis for $C_{11}H_7CdO_5$, calcd (%): C, 39.84; H, 2.13. Found (%): C, 39.76; H, 2.19. IR data (KBr, cm^{-1}): 3425 (s), 3017 (w), 1545 (s), 1425 (s), 1351 (s), 1247 (m), 1136 (w), 1077 (m), 911 (w), 895 (m), 836 (m), 771 (m), 679 (m), 584 (w), 521 (w).

2.5. Synthesis of $\{[(CH_3)_2NH_2]_2[Cd(L_2)] \cdot 2DMF\}_n$ (**4**)

The synthetic procedure was similar to that of **2**, except H_4L_2 (16.2 mg, 0.04 mmol) replaced H_4L_1. The colorless crystals of **4** were obtained and washed with DMF. 43% yield based on Cd. Elemental analysis for $C_{32}H_{40}CdN_4O_{10}$, calcd (%): C, 51.04; H, 5.35; N, 7.44. Found (%): C, 51.09; H, 5.37; N, 7.48. IR data (KBr, cm^{-1}): 3374 (w), 3058 (m), 2786 (m), 2471 (w), 1604 (m), 1581 (s), 1525 (s), 1469 (m), 1401 (s), 1344 (s), 1256 (m), 1182 (m), 1142 (w), 1015 (m), 874 (m), 785 (m), 676 (w), 572 (w), 543 (w).

Scheme 2. Coordination modes of carboxylate ligands in the title complexes.