

The variety of conformational isomerism of a flexible organic linker induced by the position and amounts of aromatic carboxylic groups



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ABSTRACT

Five new coordination polymers, namely $[Zn_4(L)_2(5-HIA)_2]_n \cdot nH_2O$ (**1**), $[Cd_2L(IPA)_2]_n \cdot 2nH_2O$ (**2**), $[Zn_6L_3(TPA)]_n \cdot 4nH_2O$ (**3**), $[Zn_8L_4(TMA)_8]_n \cdot nH_2O$ (**4**) and $[Co_2L(TMA)_2]_n \cdot 3nH_2O$ (**5**), have been hydrothermally prepared based on a tetrahedral linker, tetrakis(3-pyridylloxymethylene) methane (L), and different carboxylates (5-HIA = 5-hydroxyisophthalic acid, IA = isophthalic acid, TPA = terephthalic acid and TMA = trimesic acid). Complex **1** and **5** exhibit that L is sandwiched between two 2-D sheets, while **2** features a 3D structure with a $(ZnL)_n$ helix. Complex **3** exhibits a threefold interpenetration network. In **4**, a 2D sheet is generated by intermolecular hydrogen bonds and is further linked into a 3D network. The thermal stability and photoluminescent properties of these polymers were investigated.

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1. Introduction

Conformational isomerism has been receiving considerable interest since it is closely related with the physical, chemical and biological behaviors of some functional materials [1]. Therefore, conformational isomers can add much richness to organic and inorganic chemistry. The existence of conformational isomerism is attributed to the rotation of sp^2 – sp^3 single bonds as well as sp^3 – sp^3 single bonds in complexes [2]. When their rapid rotation is restricted, a certain conformation isomer is retained. Different conformers often exhibit quite distinct properties. In addition, some external conditions are also crucial in determining a certain conformation, such as hydrogen bonds, light stimulation, temperature, solvent effect, etc [3]. In particular, many reports are focused on some interesting behaviors of some guest molecules in confined systems [4]. However, no studies have been performed on what can cause conformational isomerism of a flexible linker in coordination polymers (CPs).

As a matter of fact, the rational selection of organic bridging linkers is of great importance in constructing MOFs. Tetrakis(4-pyridylloxymethylene) methane (tpom) is a suitable candidate for constructing MOFs due to its variety of coordination modes and tetrahedral configuration [5]. However, given that we intend

to gain an intensive understanding of the conformational isomerism of a flexible linker in different coordination environments, the semi-rigid ligand tetrakis(3-pyridylloxymethylene) methane (L) was selected to construct MOFs due to its specific tetrahedral configuration and flexible conformation [6]. Herein, tetrakis(3-pyridylloxymethylene) methane (L) and a series of different carboxylates were used to react with Zn, Cd or Co ions to obtain five complexes, i.e., $[Zn_4(L)_2(5-HIA)_2]_n \cdot nH_2O$ (**1**), $[Cd_2L(IPA)_2]_n \cdot 2nH_2O$ (**2**), $[Zn_6L_3(TPA)]_n \cdot 4nH_2O$ (**3**), $[Zn_8L_4(TMA)_8]_n \cdot nH_2O$ (**4**) and $[Co_2L(TMA)_2]_n \cdot 3nH_2O$ (**5**) (Scheme 1). In addition, the effect of position and amounts of aromatic carboxylic groups on the conformational diversity of L has been discussed. Also, the thermal stability, X-ray powder diffraction and solid state photoluminescence at room temperature for **1–5** have been investigated.

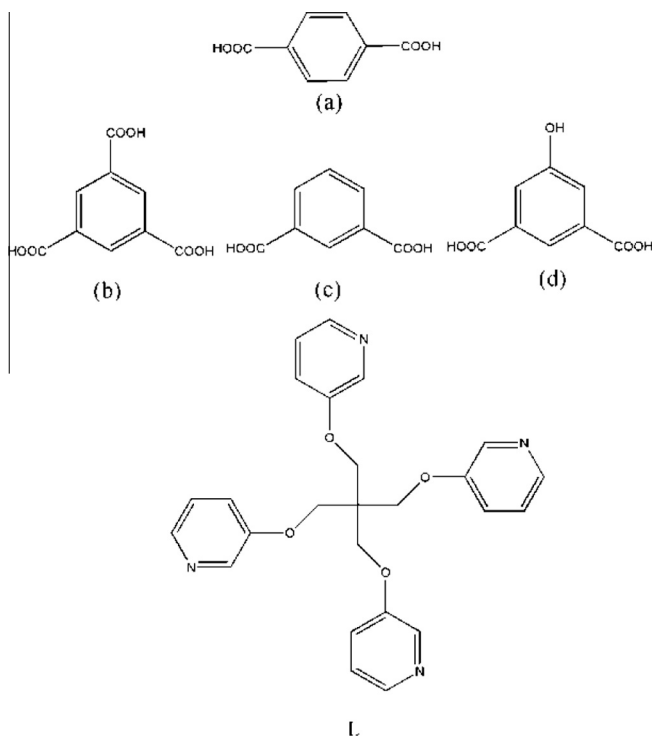
2. Experimental

2.1. Materials and characterization

The ligand L was prepared according to the literature [7]. All other reagents and solvents were commercially purchased without further purification. The C, H and N microanalyses were carried out with a Perkin–Elmer PE 2400 II CHN elemental analyzer. Infrared spectra were obtained on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000 – 400 cm^{-1} region. Thermal analysis (TG) was carried out in a nitrogen stream using a Seiko Extar 6000 TG/DTA equipment with a heating rate of 10 $^{\circ}C/min$. Powder

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Scheme 1. The structure of the organic ligands used in this study.

X-ray diffraction (PXRD) measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu $K\alpha$ radiation. Photoluminescence analyses were performed on a Hitachi 850 fluorescence spectrophotometer.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[Zn_4(L)_2(5-HIA)_2]_n \cdot nH_2O$ (**1**)

A mixture of L (0.0446 g, 0.1 mmol), 5-hydroxyisophthalic acid (0.0182 g, 0.1 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.0345 g, 0.20 mmol) in CH_3CN and H_2O (v:v = 3:3) was sealed in a 30 ml Teflon lined stainless steel vessel and heated to 90 °C for 3d. After the mixture was cooled to room temperature, brown rod-like crystals of **1** suitable for X-ray diffraction analyses were obtained in a yield of 39.8%. Elemental *Anal.* Calc. for $C_{82}H_{66}N_8O_{29}Zn_4$: C, 52.0; H, 3.9; N, 13.5. Found: C, 51.8; H, 3.8; N, 13.4%. IR data (KBr, cm^{-1}): 1568(s), 1398(s), 1469(s), 1230(s), 3666(w), 1429(s), 1280(s), 2360(m), 3149(m), 1143(w), 1072(s), 1028(s), 1014(s), 979(s), 993(m), 908(w), 788(w), 700(w).

2.2.2. Synthesis of $[Cd_2L(IPA)_2]_n \cdot 2nH_2O$ (**2**)

A mixture of L (0.0448 g, 0.1 mmol), isophthalic acid (0.0166 g, 0.1 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.0617 g, 0.20 mmol) in DMF and H_2O (v:v = 3:3) was sealed in a 30 ml Teflon lined stainless steel vessel and heated to 90 °C for 3d. After the mixture was cooled to room temperature, yellow transparent crystals of **2** suitable for X-ray diffraction analyses were obtained in a yield of 38.6%. Elemental *Anal.* Calc. for $C_{41}H_{40}N_4O_{16}Cd_2$: C, 46.0; H, 3.8; N, 5.2. Found: C, 46.1; H, 3.9; N, 5.1%. IR data (KBr, cm^{-1}): 3275(w), 3080(w), 2945(w), 2879(w), 2374(m), 2139(w), 1597(s), 1575(s), 1560(s), 1435(s), 1373(s), 1278(s), 1242(s), 1193(m), 1109(m), 1053(m), 1004(m), 806(m), 698(s), 572(m), 520(w).

2.2.3. Synthesis of $[Zn_6L_3(TPA)]_n \cdot 4nH_2O$ (**3**)

A mixture of L (0.0446 g, 0.1 mmol), H_2BDC (0.0166 g, 0.1 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.0586 g, 0.20 mmol) in DMF and

H_2O (v:v = 4: 2) was sealed in a 30 ml Teflon lined stainless steel vessel and heated to 90 °C for 3d. The product was washed with DMF and ethanol, and then dried in air. **3** was isolated as a single-phase product in a yield of 38.0%. Elemental *Anal.* Calc. for $C_{123}H_{104}N_{12}O_{40}Zn_6$: C, 53.1; H, 3.7; N, 6.1. Found: C, 53.3; H, 3.6; N, 6.2%. IR data (KBr, cm^{-1}): 3546(m), 3117(m), 1578(s), 1490(s), 1438(s), 1397(s), 1284(s), 1241(s), 758(w).

2.2.4. Synthesis of $[Zn_8L_4(TMA)_8]_n \cdot nH_2O$ (**4**)

A mixture of L (0.0446 g, 0.1 mmol), trimesic acid (0.0211 g, 0.1 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.0344 g, 0.20 mmol) in CH_3CN and H_2O (v:v = 1:5) was sealed in a 30 ml Teflon lined stainless steel vessel and heated to 90 °C for 3d. After the mixture was cooled to room temperature, orange flake crystals of **4** suitable for X-ray diffraction analyses were obtained in a yield of 31.5%. Elemental *Anal.* Calc. for $C_{174}H_{132}N_8O_{67}Zn_8$: C, 53.2; H, 3.4; N, 2.9. Found: C, 53.1; H, 3.5; N, 3.0%. IR data (KBr, cm^{-1}): 2947(s), 2187(s), 1718(s), 1514(s), 1276(w), 968(s), 730(s), 698(m).

2.2.5. Synthesis of $[Co_2L(TMA)_2]_n \cdot n(CH_3CN) \cdot 3nH_2O$ (**5**)

A mixture of L (0.0446 g, 0.1 mmol), trimesic acid (0.0211 g, 0.1 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.0583 g, 0.20 mmol) in CH_3CN and H_2O (v:v = 3:3) was sealed in a 30 ml Teflon lined stainless steel vessel and heated to 90 °C for 3d. After the mixture was cooled to room temperature, pink block crystals of **5** suitable for X-ray diffraction analyses were obtained in a yield of 36.9%. Elemental *Anal.* Calc. for $C_{45}H_{39}N_5O_{19}Co_2$: C, 50.4; H, 3.7; N, 6.5. Found: C, 50.6; H, 3.8; N, 6.8%. IR data (KBr, cm^{-1}): 1346(s), 1274(s), 1627(s), 1247(s), 1271(s), 1533(s), 1697(m), 1575(m), 1697(m), 1190(w), 852(w), 621(w).

2.3. Crystal structure determination

The single-crystal X-ray data collection for **1–5** was performed on a Bruker SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structures were solved by direct methods and refined by full matrix least-squares methods on F^2 using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms [8]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms of L were included in the structure factor calculations at idealized positions by using a riding model and refined isotropically. The metal atoms in each complex were located from the E-maps and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the linkers were generated theoretically onto the specific atoms and refined isotropically. The relevant crystallographic data are presented and selected bond lengths and angles are given in Tables S1–2 (in the ESI).

3. Results and discussion

3.1. Synthesis

With this tetrahedral linker in hand, we have successfully synthesized a series of coordination polymers together with different aromatic carboxylates under solvothermal conditions over three days. The addition of aromatic carboxylates plays an important role in the adjustment of the coordination environment and charge balance. In addition, the preparations of **1–5** were conducted with temperatures ranging from 90 to 120 °C, and the change of solvent polarity also greatly affects their degree of crystallinity in the course of the self-assembly reaction. An exploration of the synthesis of **1–5** with different ratios of solvent mixtures reveals that each

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