Synthesis of homochiral helical metal–organic frameworks based on lactate derivatives

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1. Introduction

Homochiral metal–organic frameworks (HMOFs) have received attention due to their distinctive structures, diverse topologies, and potential applications in enantioselective processes \[1–8\]. In the structures of HMOFs, absolute helicity often goes with chirality, which will offer a possible way to understand the handedness of compounds by research on the relationship between chirality of molecular building blocks and helicity of polymeric structures \[9, 10\]. Actually, chirality and helicity are universally bound to each other in the living world such as proteins and nucleic acids \[11–14\]. Thus, the homochiral helical metal–organic frameworks (HHMOFs) which combine helicity and chirality into one crystal phase have

ABSTRACT

A pair of homochiral metal–organic frameworks (HMOFs) based on semi-rigid 5-(1-carboxyethoxy)isophthalic acid (H\textsubscript{3}CIA), [Zn\textsubscript{5}((R)-CIA)]\textsubscript{3}(OH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}\cdot\text{NH}_2(CH\textsubscript{3})\textsubscript{2}\cdot4.5H\textsubscript{2}O (1-D) and [Zn\textsubscript{5}((S)-CIA)]\textsubscript{3}(OH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}\cdot\text{NH}_2(CH\textsubscript{3})\textsubscript{2}\cdot4.5H\textsubscript{2}O (1-L), were synthesized and structurally characterized. They are enantiomers and exhibit 3-D framework structures. In each structure, the CIA ligands link the Zn centers into a homochiral open framework with tetranuclear and trinuclear Zn-clusters. An interesting double helix built from the connectivity between CIA ligands and Zn centers is presented. The chiral nature of 1-D and 1-L was further confirmed by CD spectra. Photoluminescence of 1-D was also investigated in the solid state at room temperature.

1. Introduction

Homochiral metal–organic frameworks (HMOFs) have received attention due to their distinctive structures, diverse topologies, and potential applications in enantioselective processes \[1–8\]. In the structures of HMOFs, absolute helicity often goes with chirality, which will offer a possible way to understand the handedness of compounds by research on the relationship between chirality of molecular building blocks and helicity of polymeric structures \[9, 10\]. Actually, chirality and helicity are universally bound to each other in the living world such as proteins and nucleic acids \[11–14\]. Thus, the homochiral helical metal–organic frameworks (HHMOFs) which combine helicity and chirality into one crystal phase have
been attracting attention in coordination chemistry and material chemistry [15–18]. Although great progress has been made in recent years, the rational synthesis of the HHMOFs is still a huge challenge. Research has shown that self-assembly of metal ions with enantiopure organic ligands should be the most effective synthesis to construct HHMOFs. Therefore, rational design and selection of enantiopure ligands is a key factor to get HHMOFs [19, 23].

In order to construct HHMOFs, we have synthesized a pair of chiral ligands ((S)-H$_3$CIA and (R)-H$_3$CIA) with up to three advantages from natural lactic acid and dimethyl 5-hydroxyisophthalate (Scheme 1) [24]. The first advantage comes from two rigid carboxylate groups that can efficiently construct interesting structures. The second is the enantiopure lactic acid unit which provides the chiral source for construction of HMOFs. The third is that, multiple coordination modes of three carboxyl moieties have superiority in the synthesis of fascinating coordination polymers. For the above advantages, the (S)-H$_3$CIA and (R)-H$_3$CIA should be the ideal enantiopure linkers and have provided a new approach to design and construct HHMOFs.

In this work, a pair of Zn-based HHMOFs, [Zn$_5$((R)-CIA)$_3$(OH)$_2$(H$_2$O)$_4$]·NH$_2$(CH$_3$)$_2$·4.5H$_2$O (1-D) and [Zn$_5$((S)-CIA)$_3$(OH)$_2$(H$_2$O)$_4$]·NH$_2$(CH$_3$)$_2$·4.5H$_2$O (1-L), have been synthesized in mixed H$_2$O and DMA solvents at 100 °C, respectively. The 1-D and 1-L exhibit 3D architecture with two kinds of Zn-clusters and two unique helical chains around the crystallographic 2, _1_ screw axis.

2. Experimental details

2.1. General information

All reagents and solvents used in the reactions were purchased commercially and used without purification. The enantiopure linkers (S)-H$_3$CIA and (R)-H$_3$CIA were synthesized from L-(−)-lactic acid methyl ester, D-(−)-lactic acid methyl ester and dimethyl 5-hydroxyisophthalate. Elemental analyses and photoluminescent properties were carried out by the analysis center of our institute. FT-IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer from 400–4000 cm$^{-1}$. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu K$_\alpha$ radiation (λ = 1.54056 Å). Thermal stability studies were performed on a NETSCHZ STA-449C thermo analyzer with a heating rate of 10 °C min$^{-1}$ under an N$_2$ atmosphere.

2.2. Measurements of solid CD spectra

The mixture of sample and 50 mg of dry KCl powder was well grounded and then pressed into a disk for CD measurement with a MOS-450 spectropolarimeter.

2.3. Synthesis of [Zn$_5$((R)-CIA)$_3$(OH)$_2$(H$_2$O)$_4$]·NH$_2$(CH$_3$)$_2$·4.5H$_2$O (1-D)

A mixture of (R)-H$_3$CIA (26 mg, 0.1 mmol), Zn(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol), and pyrazine (80 mg, 1 mmol) was dissolved in a solvent mixture of DMF and H$_2$O (3 mL/1 mL) in a screw-capped vial. The reaction mixture was heated at 100 °C for seven days and then cooled to room temperature. Colorless block crystals (33 mg, 75%, based on (R)-H$_3$CIA) were obtained after filtration. Elemental analysis calcd (%) for 1-D: C, 32.35; H, 2.64; N, 1.08. Found: C, 33.44; H, 2.72; N, 0.97. IR (solid KBr pellet, cm$^{-1}$): 3342.4s, 1627.2s, 1588.8s, 1464.2s, 1425.6s, 1387.2s, 1299.2 s, 1262.4 m, 1130.2 m, 1092.8 m, 1054.4 w, 1004.8 w, 872.1 w, 771.2 m, and 721.6 m.

2.4. Synthesis of [Zn$_5$((S)-CIA)$_3$(OH)$_2$(H$_2$O)$_4$]·NH$_2$(CH$_3$)$_2$·4.5H$_2$O (1-L)

The same procedure as 1-D, except (S)-H$_3$CIA was used. Colorless block crystals (36 mg, 80%, based on (S)-H$_3$CIA) were obtained after filtration. Elemental analysis calcd (%) for 1-D: C, 32.35; H, 2.64; N, 1.08.
Table 1. Summary of crystal data and refinement results.

| Compound reference | 1-D            | 1-L            |
|--------------------|----------------|----------------|
| Chemical formula   | C_{35}H_{37.5}NO_{31.5}Zn_{5} | C_{35}H_{37.5}NO_{31.5}Zn_{5} |
| Formula mass       | 1298.47        | 1303.01        |
| Crystal system     | Monoclinic     | Monoclinic     |
| a (Å)              | 31.8327(8)     | 31.8327(8)     |
| b (Å)              | 16.8072(4)     | 16.8078(4)     |
| c (Å)              | 8.8262(3)      | 8.8200(2)      |
| α (°)              | 90.00          | 90.00          |
| β (°)              | 93.933(2)      | 93.933(2)      |
| γ (°)              | 90.00          | 90.00          |
| Unit cell volume (Å³) | 4711.4(2)  | 4707.92(19)   |
| Temperature (K)    | 293(2)         | 291.47(10)     |
| Space group        | C2             | C2             |
| No. of formula units per unit cell, Z | 4        | 4              |
| Radiation type     | MoKα           | CuKα           |
| Absorption coefficient, μ mm⁻¹ | 2.612       | 3.770          |
| No. of reflections measured | 17,514     | 9403           |
| No. of independent reflections | 8568       | 6443           |
| R_{int} values (I > 2σ(I)) | 0.0273     | 0.0239         |
| Final R values (all data) | 0.0298     | 0.0297         |
| Final wR² values (all data) | 0.0731     | 0.0767         |
| Goodness of fit on F² | 1.006       | 1.006          |
| Flack parameter    | 0.004(8)       | −0.01(2)       |

Found: C, 32.14; H, 2.96; N, 0.92. IR (solid KBr pellet, cm⁻¹): 3355.2s, 1627.2s, 1562.4s, 1464.8s, 1419.2s, 1393.6s, 1299.2w, 1262.4w, 1129.6 m, 1086.4w, 1054.4 m, 771.2 m, and 728.0 m.

Figure 1. Schematic illustrations of the structure of 1-D: three different coordination modes of (R)-CIA³⁻ ligand (a), tetranuclear Zn-cluster substructure (b) and trinuclear Zn-cluster substructure (c).
2.5 X-ray determination

A summary of crystal data and refinement details is provided in Table 1.

3. Results and discussion

X-ray diffraction studies have revealed that 1-D and 1-L crystallize in monoclinic space group C2 with Flack parameters of 0.006(8) and −0.01(2), respectively, which indicate enantiomeric purity of the single crystals (Table S1). As 1-D and 1-L are enantiomers, we mainly focused on the structural details of 1-D. The asymmetric unit of 1-D is composed of five independent Zn(II) ions, three deprotonated...
Figure 4. The solid-state CD spectra of 1-D and 1-L.

Figure 5. The fluorescent emission spectra of 1-D and (R)-H₃CIA.

Scheme 1. The enantiopure linkers: (R)-H₃CIA and (S)-H₃CIA.
(R)-CIA\(^{3-}\) ligands, two \(\mu_2\)-OH groups, four coordinated water molecules, four and a half lattice water molecules, and a \(\text{[NH}_2\text{CH}_3\text{]}^+\). Three deprotonated (R)-CIA\(^{3-}\) ligands in 1-D show different coordination modes. The first (R)-CIA\(^{3-}\) ligand is a \(\kappa_2\)-linker to connect five Zn(II) ions, the second (R)-CIA\(^{3-}\) ligand is a \(\kappa_6\)-linker to connect six Zn(II) ions, and the third (S)-CIA\(^{3-}\) ligand is a \(\kappa_5\)-linker connecting four Zn(II) ions (Figure 1(a)). For the unique coordination modes of (R)-CIA ligands, a tetranuclear Zn (Zn(1), Zn(1a), Zn(3), Zn(3a)) unit Zn\(_4\)O\(_2\)(CO\(_2\))\(_6\) and a trinuclear Zn (Zn(2), Zn(4), Zn(5)) unit Zn\(_3\)O\(_3\)(CO\(_2\))\(_6\) are formed (Figure 1(b) and (c)).

In the tetrameric core, Zn(3) shows distorted octahedral ZnO\(_6\) coordination from two carboxylate O of two (S)-CIA\(^{3-}\) ligands, two O from two \(\mu_2\)-OH groups, and two O from two coordinated waters. The Zn(4) has a tetrahedral ZnO\(_4\) coordination from three carboxylates and one oxygen of \(\mu_3\)-OH (Figure 1(b)). In the trimeric unit, Zn(2) and Zn(5) also exhibit distorted octahedral geometries: Zn(2) is coordinated by five oxygens from four carboxylates and one of \(\mu_3\)-OH; Zn(5) is coordinated by three oxygens from three bridging carboxylates, two waters, and one of \(\mu_3\)-OH. Unlike Zn(2) and Zn(5), Zn(4) is coordinated to three carboxylate oxygens and a \(\mu_1\)-OH group, which shows a tetrahedral geometry (Figure 1(c)).

The second outstanding structural feature of 1-D (or 1-L) is the presence of a double helix (Figure 2(a) and (b)). As depicted in Figure 2(a), the Zn2 ion of the tri-nuclear Zn-cluster is coordinated by the isophthalate unit from (R)-CIA\(^{3-}\) ligand to form an infinite left-handed helical chain running along the b-axis. In the same way, an infinite left-handed helical chain is also constructed by the Zn2 ion and CIA fragment with lactic acid unit and a half isophthalate unit in 1-D (Figure 2(a)). The opposite phenomenon (double helix with right-handed helical chains) exists in 1-L (Figure 2(b)). A 2D homochiral helical layer is formed by the connection of tetrnuclear Zn-clusters and trinuclear Zn-clusters through CIA\(^{3-}\) ligands (Figure 2(c)). From the viewpoint of structural topology, the two kinds of Zn-clusters and the CIA\(^{3-}\) ligands can be regarded as 6- and 3-connected nodes, respectively. Thus, the 2D framework of ligands (Figure 2(c)).

At room temperature, the solid-state circular dichroism (CD) spectra of 1-D and 1-L were tested to further demonstrate their homochirality (Figure 4). The CD curve of 1-D shows an obvious positive cotton effect (CE) peak at 360 nm, revealing its homochiral nature. Furthermore, a mirror image is also observed for 1-D, confirming that 1-D and 1-L are enantiomers.

To characterize thermal behaviors of the complexes, thermal gravimetric analyses (TGA) of 1-D and 1-L were carried out from 30 °C to 800 °C under nitrogen (Figure S4). The TG curves of 1-D and 1-L show the first weight loss of 10.7% from 30 to 150 °C, corresponding to the loss of guest molecules. A gradual weight loss from 150 °C is attributed to release of coordinated water; the anhydrous component began to decompose at 350 °C.

Luminescent compounds have attracted attention for their applications in chemical sensors, photochemistry, and electroluminescent display [25]. The photoluminescence properties of 1-D were studied in the solid state at room temperature. Excitation of microcrystalline samples of 1-D at 327 nm produces intense luminescence with the peak maximum at 378 nm. To understand the nature of the emission band, the photoluminescence of (S)-H\(_3\)CIA is also shown in Figure 5, upon excitation at 336 nm, which has similar emissions at 404 nm. In comparison to (R)-H\(_3\)CIA, the emission maxima of 1-D have a blue shift, which may be attributed to a charge transfer transition between ligand and metal center, and a change in the highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of deprotonated (R)-CIA\(^{3-}\) to metal centers [26, 27].

### 4. Conclusion

By the employment of two predesigned lactate derivative ligands ((R)-CIA and (S)-CIA) to assemble with Zn\(^{2+}\) ions, a pair of HMOFs has been synthesized. Compound 1-D (or 1-L) exhibits a 3D supramolecular structure with double helix and two types of Zn-clusters. The chiral nature of 1-D and 1-L was confirmed.
by CD spectra. Moreover, the photoluminescence of 1-D was also tested and may be a candidate – as a photoactive material.

**Supplementary material**

CCDC 1420104 and 1420105 contain the supplementary crystallographic data for 1-D and 1-L. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). IR spectra, PXRD patterns, and TGA curves associated with this article can be found in the online version.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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