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Short communication

A pair of nonporous homochiral cobalt-based coordination polymers for enantioselective recognition and electrocatalysis

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ABSTRACT

A pair of nonporous enantiomers [Co(H_2O)(bpy)(L-Mand)]•H_2O•Cl (**L-1**) and [Co(H_2O)(bpy)(L-Mand)]•H_2O•Cl (**D-1**) (L-Mand = L-Mandelic acid, D-Mand = D-Mandelic acid, bpy = 4,4′-bipyridine) with 3D supermolecule framework possess excellent enantioselective recognition and electrocatalysis ability towards L- and/or D-tart.

Chirality has become increasingly significant in many fields such as pharmaceutics, chemical industry, agriculture and clinical analysis [1–4]. Many biomolecules are chiral, they can exist in one of two enantiomeric forms that only differ in that their structures are mirror images of each other. Because only one enantiomer tends to be physiologically active while the other is inactive or even toxic [5]. The production and availability of enantiomerically pure compounds are thus of great importance to the fine chemical and pharmaceutical industries. Methods available to provide enantiopure chemical products include resolution of racemates, isolation from natural sources, fermentation and asymmetric catalysis, with resolution and catalysis still being used most often [6,7].

Recently, there has been increasing interest in creating homochiral porous metal-organic frameworks (MOFs) due to their many advantages, including their highly crystalline nature, high catalyst loading, uniform catalytic centers, and wide structural and functional variations of the frameworks [8–15]. Chiral catalysis and enantioselective recognition act as the core issues of chemistry and play significant roles in current chemical industry, as well as pharmacy and biomimetic chemistry [16–18]. In general, a good solid catalyst with high catalytic activity should have large, accessible pores/channels allowing facile diffusion of substrates and products [19]. However, the chiral porous MOFs always suffer from the special legends design, active species loading, as well as the nonactive porous structures.

Besides the porous MOFs, another strategy for the chiral catalyst design is the fabrication of the chiral surface. These chiral surfaces offer the possibility of developing heterogeneous enantioselective catalysts and electrochemical sensors, which can more readily be separated from the products and reused [20–22]. Based on their chiral facts, nonporous chiral coordination polymers endued with easy fabrication and structure and property tunable ability should be regarded as promising potential chiral catalyst. However, only few reports focused on this topic [23,24], and the exploration for the fabrication of nonporous chiral coordination polymers as well as their applications on enantioselective recognition and catalysis are quite scarce in chemistry and material science.

Here we report two nonporous homochiral coordination polymers, namely [Co(H_2O)(bpy)(L-Mand)]·H_2O·Cl (**L-1**) and [Co(H_2O)(bpy)(D-Mand)]·H_2O·Cl (**D-1**) from cobalt salt with 4,4′-bpy, L- and/or D-Mandelic acid. Both **L-1** and **D-1** exhibit 3D nonporous chiral supermolecule framework. The further electrochemical experiments indicated that these cobalt-based nonporous homochiral coordination polymers (**L-1** and **D-1**) possess good enantioselective recognition and electrocatalysis ability towards L- and/or D-tart, respectively.

Single crystal X-ray diffraction analysis reveals that compounds **L-1** and **D-1** are enantiomers (Scheme 1), and so only the structure of **L-1** will be discussed in detail. Compound **L-1** crystallizes in the chiral monoclinic system with space group $P2_1$, and the flack parameter of 0.01(4) further indicates that the absolute configuration is correct. As illustrated in Fig. 1a, the asymmetric unit of **L-1** contains one crystallographically independent Co atom, one L-Mand ligand, one 4,4′-bpy ligand and one coordinated water molecule. The Co1 center displays a distorted octahedral [CoN_2O_4] geometry, being coordinated by three oxygen atoms from two L-Mand ligands, one coordinated water molecule and two nitrogen atoms from two 4,4′-bpy ligands. Bond distances of Co—N (Co—N, 2.134(6)–2.173(6) Å) and Co—O (Co—O, 2.033(6)–2.151(6) Å) around the Co1 center are in the normal range.

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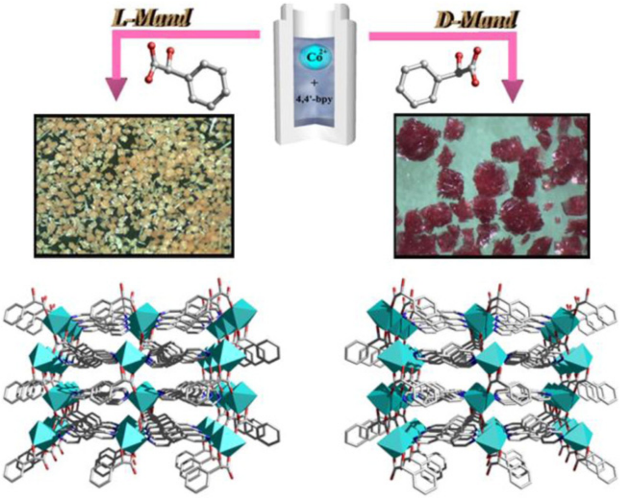

Scheme 1. Schematic representation of the synthesis of **L-1** and **D-1** assembled from cobalt salt with mixed ligands 4.4′-bpy and L- and/or D-Mand. The crystal images were observed by the Polarization Microscope.

In **L-1**, the 4,4′-bpy bridges Co atoms into a 1D nonlinear chain, and the whole L-Mand acts as tridentate ligand to extend adjacent chains into 2D wavelike layer (4^4-sql, Fig. 1b) via its one bidentate carboxylate groups and one monodentate hydroxy group (Scheme S1). The benzene ring groups of L-Mand act as arms, dangling on the up and down sides of the layer. Another note worthy aspect of **L-1** is the Co atoms are bridged by L-Mand ligand to form an infinite left-handed helical chains running along a crystallographic 2_1 axis in the *b* direction with a pitch of 9.244 Å (Fig. 2). The adjacent same-handed helical chains are further interconnected through the 4,4′-bpy ligand to generate a 2D chiral layer of rectangular cavities. (11.2 × 5.2 Å, Fig. 1b). Packing arrangement of **L-1** along the *c* axes is shown in Fig. 1c. Due to the free water molecules participate in extensive hydrogen-bonding interactions with coordinated water molecules, the adjacent layers are connected to each other in ABAB sequence, which ultimately forms a 3D supramolecular framework. The spacing and alignment of tridentate L-Mand ligand provide sufficient voids for the benzene ring arms in adjacent layers to interdigitate each other, forming a 3D nonporous chiral supermolecule framework(Figure S2).

In order to testify the nonporous nature of **L-1**, the N_2, CO_2 and H_2 sorption isotherms were performed at 77, 195 and 77 K on the activated samples, respectively. Experimental result reveals that the N_2, CO_2 and H_2 are hardly adsorbed owing to the blockage of the open windows (Fig. 3a), which further indicates that **L-1** is nonporous structure indeed.

To confirm the enantiomeric nature of **L-1** and **D-1**, the circular-dichroism (CD) spectra of **L-1** and **D-1** have been investigated. As shown in Fig. 3b, the CD spectra of **L-1** and **D-1** are mirror images of one another, which conclusively demonstrates that **L-1** and **D-1** are enantiomers. In the wavelength range of 200–400 nm, **L-1** shows positive Cotton effects at $\lambda = 219$ and negative Cotton effects at $\lambda = 259$ nm. The CD spectra of **L-1** and **D-1** in the solid state show that the chirality transfers from the chiral mandelic acid molecules to the whole framework.

Metal ions properly situated in a chiral environment can act as an asymmetric catalyst. Some metal ions with unsaturated coordination environments (typically coordinated with water or other solvent molecules that can be readily removed) can be utilized as a catalyst in chemical transformations, especially as a Lewis acid catalyst. Cobalt plays an important role in current petrochemical and plastic industries, as both a hetero and homogeneous catalyst [25–27]. In light of the catalytic ability of Co ion, **L-1** and **D-1** were anticipated to possess enantioselective catalytic abilities for the reaction of chiral molecules. With this important prerequisite in mind, the electrochemical method was introduced into our further experiments to test the enantioselective recognition and electrocatalysis ability of **L-1** and **D-1** towards L- and D-tart, respectively.

Typically, the **L-1** and **D-1** modified carbon paste electrode (**L-** and **D**-CPE) were fabricated as follows: 0.2 g graphite powder and 0.02 g **L-** and/or **D-1** were mixed and ground together by an agate

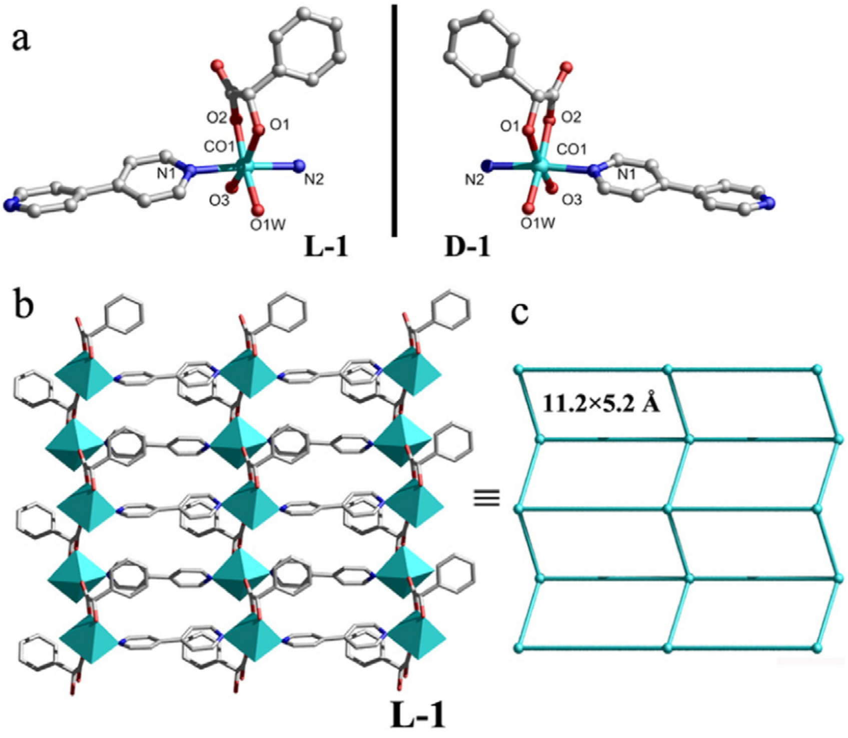

Fig. 1. (a) The asymmetric units of **L-1** and **D-1**. (b) The 2D chiral layer of rectangular cavities. Hydrogen atoms, lattice water molecules and free Cl^- are omitted for clarity.