



Synthesis and photoluminescent properties of four homochiral supramolecular compounds with butterfly-like chains



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ARTICLE INFO

Article history:

Received 29 March 2014

Accepted 9 June 2014

Available online 10 June 2014

Keywords:

Homochiral

Photoluminescence

Supramolecular compounds

Coordination polymers

ABSTRACT

Four photoluminescent homochiral supramolecular compounds based on enantiopure 2-(1-hydroxy-ethyl)-3H-benzimidazole-5-carboxylate ligand have been synthesized successfully, and all of them are built from fascinating butterfly-like chains via hydrogen bonding interactions.

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The self-assembly of molecular component motifs into supramolecular architectures with a higher dimensionality is ubiquitous in nature and constitutes one of the most powerful approaches for the generation of functional crystalline materials [1]. Hydrogen bonding interaction is one of the most important secondary interactions to fabricate supramolecular assemblies with highly complex and often symmetrical architectures. In addition, hydrogen bonding interaction is one of the main driving forces to govern the selectively molecular recognition behaviors [2]. An enhanced understanding about supramolecular interactions in the context of crystal packing may be of great help in the design and synthesis of novel functional crystalline materials with intriguing structures and desired physical and chemical properties.

Among numerous coordination polymers, those possess fascinating supramolecular architecture are of great interest, hydrogen bonding interaction playing important roles in these CPs or MOFs. Great progress in coordination polymers (CPs) or metal-organic frameworks (MOFs) has been achieved during the past several decades [3]. Of particular interest is the creation of chiral CPs that may be utilized in the processes such as enantioselective separation [4]. In general, there exist two main strategies to generate the chiral compounds: direct assembly from enantiopure building block (e.g. enantiopure ligand) or from the spatial organization of achiral precursors (crystallized in chiral space groups) [5].

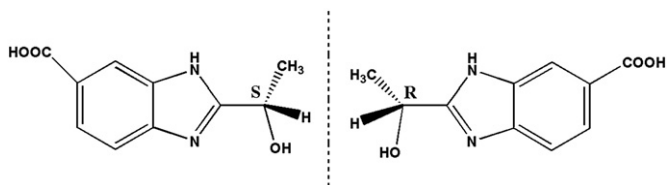
In this work, we employ a homochiral ligand, 2-(1-hydroxy-ethyl)-3H-benzimidazole-5-carboxylic acid (Hebimc), to assemble with

Cd^{2+} ion under different conditions. Two photoluminescent enantiomeric supramolecular compounds, $[\text{Cd}(\text{D-ebimc})_2] \cdot 4(\text{H}_2\text{O})$ (**1D**) and $[\text{Cd}(\text{L-ebimc})_2] \cdot 4(\text{H}_2\text{O})$ (**1L**) were synthesized hydrothermally. Notably, with the addition of ethyleneurea (e-urea) as co-solvent, other two enantiomeric supramolecular compounds $[\text{Cd}_2(\text{D-ebimc})_4] \cdot 2(\text{e-urea}) \cdot 4(\text{H}_2\text{O})$ (**2D**) and $[\text{Cd}_2(\text{L-ebimc})_4] \cdot 2(\text{e-urea}) \cdot 4(\text{H}_2\text{O})$ (**2L**) have been prepared successfully [6]. X-ray single-crystal diffraction study reveals that all supramolecular compounds formed by hydrogen bonding interactions are based on fascinating butterfly-like chains (See Scheme 1).

Colorless prism crystals of **1L** and **1D** are crystallized in the chiral monoclinic space group C_2 with Flack parameters of 0.031(12) and 0.04(4), respectively, demonstrating the homochiral nature of the single crystals [7]. Since **1L** and **1D** are enantiomers and present similar structures, only the structure of **1D** is discussed here in detail. As depicted in Fig. 1, the fundamental building unit of **1D** consists of one Cd(II) ion, two D-ebimc ligand and four lattice water molecules. In **1D**, the central Cd(II) ion is located in an octahedral coordination environment with two O atoms and two N atoms from two separated D-ebimc ligand, two carboxylic O atoms from another two separated D-ebimc ligand occupy the remaining two coordination sites of Cd(II) ion. The bond lengths of Cd–O and Cd–N are in the range of 2.252(7) to 2.598(9) Å and 2.270(8) to 2.273(7) Å, respectively. Each six coordinated Cd(II) ion connects two neighboring Cd(II) ions through four μ_2 -bridging D-ebimc ligands with a Cd–Cd distance of 7.9659(14) Å.

The adjacent Cd(II) ions are interconnected by the μ_2 -bridging D-ebimc ligands to generate the infinite chain along *c*-axis (Fig. 2a). It is noteworthy that the plane containing ebimc(1) and ebimc(2) is approximately perpendicular to the plane containing ebimc(3) and ebimc(4)

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Scheme 1. Schematic drawing of L-Hebimc (left) and its mirror image D-Hebimc.

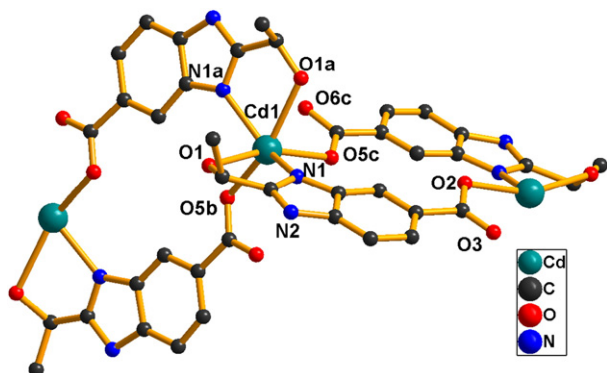


Fig. 1. The coordination environment in **1D** with hydrogen atoms and free water molecules omitted for clarity. Symmetry codes: a) $-x, y, -z + 1$; b) $x, y, z + 1$; and c) $-x, y, -z$.

(Fig. 2a). The dihedral angle between two planes is 84.5° . What's rare and fascinating is the infinite chain looks like a butterfly on the ab plane (Fig. 2b).

Another prominent structural feature of **1D** is the presence of abundant hydrogen bonding interactions (N–H···O, Table S1, see the supporting information) between these butterfly-like chains (Fig. 2c). Each butterfly-like chain connects four adjacent chains through N–H···O hydrogen bonds to give an interesting three-dimensional (3D) supramolecular framework. Furthermore, this 3D framework shows large irregular channels along the c axis (Fig. 2d). The diagonal distance in each channel is about 6.643 \AA .

Compare to **1D**, a significant difference of the synthetic condition of **2D** is the addition of ethyleneurea (e-urea) as a co-solvent. **2L** and **2D** are crystallized in the chiral monoclinic space group $P2_1$ with Flack parameters of $-0.02(2)$ and $-0.029(19)$, respectively, indicating enantiomeric purity of the single crystals. Similarly, **2L** and **2D** are supramolecular enantiomers and present similar structures. Hence, only the structure of **2D** is discussed here in detail.

Unlike **1D**, the fundamental building units of **2D** consist of two segments. In the structure of **2D**, it contains four Cd(II) ions, eight D-ebimc ligands, four free e-urea molecules and eight free water molecules (Fig. 3a). The linkage between Cd(II) ions and D-ebimc ligands is similar to that in **1D**. In each segment, the adjacent Cd(II) ions are interconnected by the μ_2 -bridging ebimc ligands to generate a chain. As a result, such two isolated segments extend to two parallel chains (Fig. 3b).

Similarly, in the structure of **2D**, there exists rich hydrogen bonding interactions (N–H···O, Table S2, see the supporting information) between these infinite butterfly-like chains, and **2D** also presents a 3D supramolecular framework with channels (Fig. 3c). It is noteworthy that

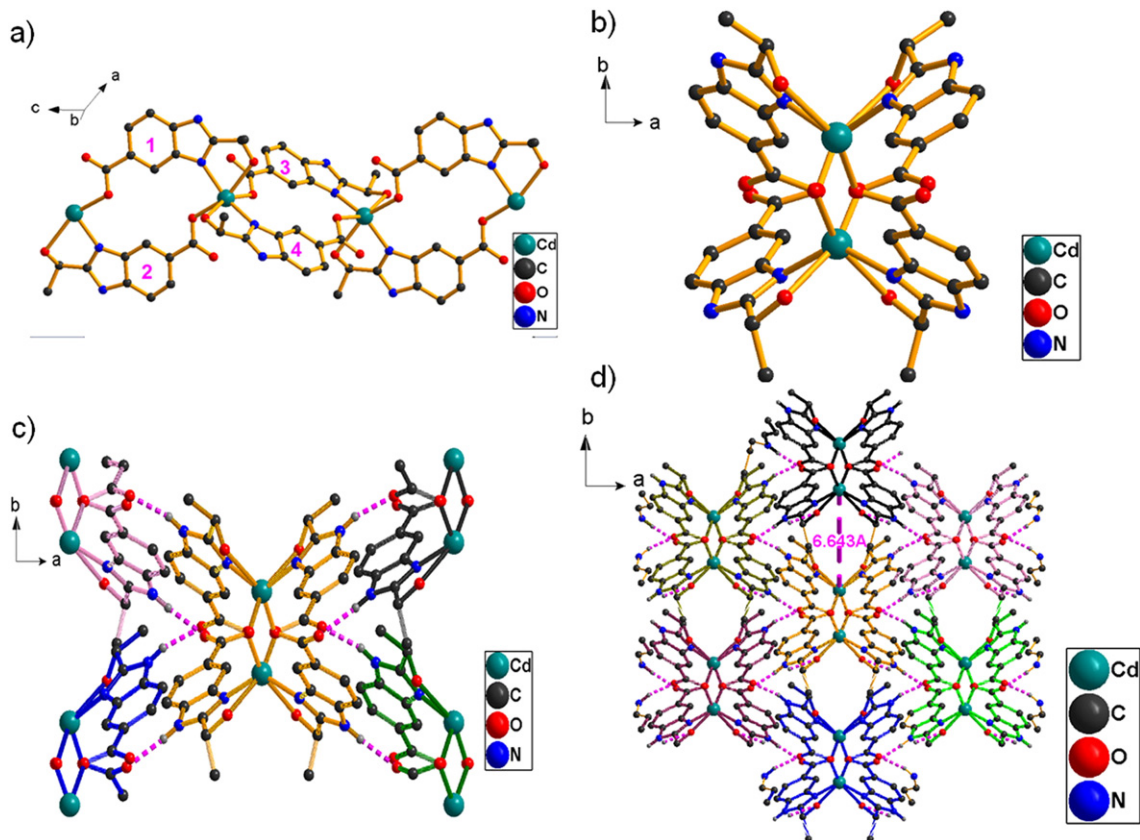


Fig. 2. a) The infinite chain along the c axis in **1D**; b) the “butterfly” structure on the ab plane in **1D**; c) the butterfly-like chain connects four adjacent chains through N–H···O hydrogen bonds (red dashed lines) in **1D**; d) the 3D supramolecular framework with irregular channels along the c axis in **1D**.

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