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Isomer transformation and photoluminescence in novel coordination polymers constructed from 1,4-cyclohexanedicarboxylic acid and imidazole

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Abstract

Three novel coordination polymers $[M(\text{chdc})(\text{imi})]_n$ (chdc = 1,4-cyclohexanedicarboxylic dianion, imi = imidazole, M = Ni **1**, Co **2** and Zn **3**) have been synthesized by solvothermal technique and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The *trans*-chdc have been partially transformed into *cis*-chdc and the *cis*-chdc have been separated from the mixture of *cis*- and *trans*-chdc in the synthetic reactions of the three compounds. The three compounds exhibit similar one dimension chain-like architecture constructed by their M(II) dimers interconnected via double strands of *cis*-chdc-bridge. M(II) atom of the dimer exhibits a square-pyramidal geometry and interaction happens within two metal centers. Both compounds **1** and **2** do not exhibit emission spectra whereas compound **3** shows intense photoluminescence property at room temperature.

Keywords: 1,4-cyclohexanedicarboxylic acid; Solvothermal synthesis; Imidazole; Transformation; Photoluminescence

1. Introduction

The rational design and synthesis of novel coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and molecular sensing [1–11]. Consequently, a variety of coordination polymers with interesting compositions and topologies have been prepared through taking certain factors into account, such as the coordination nature of the metal ion and the shape, functionality, flexibility, and symmetry of organic ligand [12–20]. A guiding principle of our work is the attempt to control the conformations of flexible spacer ligands in the architecture of the products. 1, 4-cyclohexanedicarboxylic acid (chdcH_2) possesses a chair-type structure with *cis*- and *trans*-conformations, it can connect metal ions in different directions and attracts researchers' great interest. A serial of metal–chdc complexes with different coordination networks have been reported previously [21–27]. If some organic nitrogen donors such as 1,10-phenanthroline, 2,2′-bipyridine [28–30] are introduced into the framework of metal–chdc complexes, it is expected that novel coordination polymer with special properties can be constructed. Imidazole as an exo-bidentate rigid nitrogen donor is rarely investigated in the architecture of flexible chdc system. Previous chdc-involved complexes were usually synthesized by hydrothermal technique [21–30], but water as a good coordination ligand or hydrogen bonding synthon is easily incorporated into the final product. In the

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present work we utilized solvothermal technique, replacing water by ethanol and synthesized three novel coordination polymers [M(chdc)(imi)]$_n$ (M = Co **1**, Ni **2** and Zn **3**). The *trans*-chdc have been partially transformed into *cis*-chdc and the *cis*-chdc have been separated from the mixture of *cis*- and *trans*-chdc in the synthetic reactions of the three compounds. The three compounds exhibit similar one-dimensional chain-like structure constructed by their M(II) dimers interconnected via double strands of *cis*-chdc-bridge. Due to the different metal ions in the structure, only compound **3** shows intense photoluminescence property.

2. Experimental section

2.1. Synthesis and characterization

All chemicals purchased were of reagent grade and used without further purification. C, H, N elemental analyses were performed on Perkin-Elmer 240c elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 170SXFT/IR spectrometer. X-ray power diffraction (XRD) analyses were obtained on a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 0.154056$ nm). The 2θ range used was from 5° to 40° in steps of $4^\circ\,\mathrm{min}^{-1}$. Excitation and emission spectra were obtained on a Spex FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a Spex 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source. All measurements were performed at room temperature.

2.2. Synthesis of [M(chdc)$_2$(imi)$_2$]$_n$

A mixture of $NiCl_2 \cdot 6H_2O$ (0.5 mmol, 0.119 g), chdcH$_2$ (mixture of *cis* and *trans* 99%) (1 mmol, 0.172 g), imidazole (0.5 mmol, 0.034 g), NaOH (0.75 mmol, 0.30 g) and ethanol (10 mL) was sealed in Teflon-lined autoclaves and heated at 160 °C for 3 days, followed by slow cooling to room temperature. The resulting green block crystals of **1** were isolated by mechanical separation from a blue amorphous solid, then washed with ethanol (yield: ca. 30% based on chdcH$_2$). Elemental Analysis Calculated for $C_{11}H_{14}NiN_2O_4$: C, 44.44; H, 4.71; N, 9.43%. Found: C, 44.59; H, 4.80; N, 9.48%.

The syntheses of **2** and **3** were similar to that described above except using $CoCl_2 \cdot 6H_2O$ (0.5 mmol, 0.119 g) or $ZnCl_2$ (0.5 mmol, 0.068 g) instead of $NiCl_2 \cdot 6H_2O$, and blue crystals of **2** and pink crystals of **3** were yielded (yields: ca. 30% based on chdcH$_2$). Elemental Anal. Calculated for $C_{11}H_{14}CoN_2O_4$: C, 44.44; H, 4.71; N, 9.43%. Found: C, 44.51; H, 4.78; N, 9.58%. Calculated for $C_{11}H_{14}ZnN_2O_4$: C, 43.56; H, 4.62; N, 9.24%. Found: C, 43.51; H, 4.80; N, 9.40%.

2.3. X-ray crystallography

Single crystals of dimensions $0.25 \times 0.18 \times 0.13\,\mathrm{mm}^3$ for **1**, $0.38 \times 0.32 \times 0.21\,\mathrm{mm}^3$ for **2**, $0.42 \times 0.40 \times 0.38\,\mathrm{mm}^3$ for **3** were used for structure determination. XRD data of **1**, **2** and **3** were collected on a Bruker-AXS CCD area detector-equipped diffractometer with graphite-monochromatized Mo$K\alpha$ ($\lambda = 0.07103$ Å) radiation at room temperature. A total of 6345 (2171 unique, $R_{\mathrm{int}} = 0.0248$) reflections of **1** ($-16 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 20$, $2.35 < \theta < 25.03$), a total of 6116 (2163 unique, $R_{\mathrm{int}} = 0.0698$) reflections of **2** ($-16 \leqslant h \leqslant 16$, $-8 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 20$, $2.34 < \theta < 25.03$), a total of 6376 (2181 unique, $R_{\mathrm{int}} = 0.0286$) reflections of **3** ($-16 \leqslant h \leqslant 13$, $-12 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 17$, $2.33 < \theta < 25.02$) were measured. An empirical absorption correction from ψ scan was applied. All the structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added in their calculated positions. All calculations were performed using the SHELXTL-97 program [31,32]. The CCDC reference numbers are the following: 257 267 for **1**, 258 191 for **2**, 259 389 for **3**. Crystal data and structure refinements for compounds **1**, **2** and **3** are listed in Table 1. Selected bond lengths and angles for **1** are listed in Table 2. Bond lengths and angles for **2** and **3** are available in supplementary information.

3. Results and discussion

3.1. Synthesis

Hydrothermal or solvothermal synthesis has recently been proved a useful technique in preparation of organic–inorganic hybrid materials. In a relatively low temperature and autogenous pressure environment, problems of different solubility for ligands are minimized. In our cases, the species of solvent is of crucial important for the crystallization of the three compounds. If water was involved in the preparations, the crystals obtained were not in good quality. The mole ratio of chdcH$_2$ and imidazole can range from 1: 1 to 1:0.3, which indicates the amount of imidazole is not very crucial if that of chdcH$_2$ is fixed. The preparations of the three compounds were not susceptible to the reaction temperature. The temperature can range from 80 to 170 °C if only boiling state of solvent ethanol is kept constant.