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A novel strong fluorescent three-dimensional supramolecular coordination polymer based on bridging terephthalate ☆

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Abstract

A novel coordination polymer $[Cd(bpy)(tp)(H_2O)]_n$ (1) has been prepared through hydrothermal reaction and structurally characterized, and the compound gives strong fluorescent emission. The structure of the compound consists of CdN_2O_4 octahedron linked through bridging terephthalate (tp) into 1D structure, and then a 3D supramolecular structure is formed adopting herringbone packing in the solid state through π - π stacking and hydrogen bonding interactions. © 2003 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Strong fluorescence; Hydrogen bonds; π - π stacking; Herringbone network

The design and synthesis of coordination polymer have attracted much attention in recent years owing to their fascinating molecular structures [1] and potential application, such as magnetism [2], electrical conductivity [3], adsorption [4], separation [5], biology [6] and catalysis [7]. Mostly coordination polymer are constructed by using appropriate organic ligand, especially bridging ligands containing multi-dentate oxygen, nitrogen, or sulfur donors, to coordinate to transition metal centers [8]. The bridging ligand is one of the important factors that greatly influences the structure of coordination polymer [9].

Terephthalates (tp) have been used in many synthetic systems because they can form short bridges via one carboxylato end or long bridges via the benzene ring, leading a great variety of structures by formation of binuclear metal complexes [10], tetranuclear metal complexes [11], 1D [12], 2D [13] and 3D [2a,14] coordination polymers. In addition, Zn(II), Cd(II) and Ag(I), d^{10} metal complexes including tp give strange photoluminescent phenomena [12c,12d,14b,15]. Here, we report a new coordination polymer [Cd(bpy)(tp) (H₂O)]_n which possesses strong fluorescent property.

The compound **1** was prepared from a mixture of $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.133 g, 0.5 mmol), tp (0.084 g, 0.5 mmol), bpy (0.078 g, 0.5 mmol), NaOH (0.04g, 1 mmol) and H₂O (16 ml) in a 25-ml Teflon-lined stainless steel autoclave and heated for 7 days at 180 °C [16].

X-ray crystallography [17] reveals that compound **1** consists of 1D zigzag $[Cd(bpy)(tp)(H_2O)]_n$ chain. The molecular structure and atom-labeling scheme of the title compound **1** is given in Fig. 1. The cadmium atom has a distorted octahedral coordination environment with two carboxylato-oxygen atoms O(1) and O(2) from a tp, a nitrogen atom N(1) from bpy and another oxygen atom O(5) from a water molecule in equatorial positions and the nitrogen atom N(2) from the same bpy and one carboxylato-oxygen atom O(4B) from the other tp in axial ones. The bpy ligand acts as a typical chelating

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Fig. 1. The molecular structure and atom-labeling scheme of 1.

ligand terminally coordination to the Cd(II) metal center. The terephthalate acting as a good bridge ligand can have many diverse coordinated mode [2a,18] (Scheme 1). Here, tp adopts a rare tridentate coordinated mode b in Scheme 1 to link to two metal centers. The bridging tp ligand unlike the free molecule is no coplanar and highly twisty. The torsion angle of the two carboxylato and the phenyl is 5.63° and 12.58°, respectively. The distance of the two adjacent Cd(II) is 11.304 Å, resulting in [Cd(bpy)(tp)(H₂O)]_n zigzag chains. And the Cd··· Cd···Cd angle formed by the three adjacent Cd(II) atoms is 104.17°. Both carboxylate ends function in an asymmetric chelate mode, as evidenced by the Cd(1)– O(1) [2.3686(13) Å] and Cd(1)–O(2) [2.3841(13) Å] bond lengths.

Hydrogen bond interactions are usually important in the synthesis of supramolecular architecture [19]. There are persistent 1D O-H···O hydrogen bond interactions between adjacent [Cd(bpy)(tp)(H₂O)]_n chains. The distance of the carboxylate groups and coordinated H₂O is 2.697 Å and O-H···O angle is 177.51°, which indicates a strong O-H···O hydrogen bond and plays an important role in the stabilization of the layer structure and the control of the orientation of the tp ligands. At the same time aromatic π - π stacking interactions are also apparent in 1. Here are two kinds of the π - π stacking interactions and three aromatic distances in one rectangular unit. The two bpy ligands



Scheme 1. Typical coordination modes for the tp ligand.

are parallel and the centroid–centroid distance is 3.4961 Å. In addition there are π – π stacking interactions between the phenyl of the tp and the bpy, and two distances of the adjacent phenyl and pyridyl are 3.2539 and 4.0417 Å, respectively. Therefore, through hydrogen bonds and π – π stacking interactions, the undulating layers further extend to a supramolecular network (Fig. 2(a)) in which the π – π stacking rectangular units are arranged perpendicularly each other and distributed alternately forming a "herringbone-like" structure [20] (Fig. 2(b)).

The UV spectrum of **1** in the solid state exhibits two high-energy absorptions at 253 and 301 nm, which can be due to an interligand π - π * transition. In the solid state at ambient temperature, a fluorescent emission of **1** at 379 nm is so strong that the slit of the excited light



Fig. 2. (a) Perspective view of the 3D supramolecular network along the c-axis. (b) Representation of the supramolecular network along the c-axis showing the herringbone arrangement of tapes in adjacent stacks.



Fig. 3. Fluorescence emission spectrum of 1 in the solid state at room temperature.

 $(\lambda_{\text{exc}} = 320 \text{ nm})$ was 2.5 cm while the emission slit is 5 cm Fig. 3, which may be assigned to the symmetry decrease of tp (seriously twisted) in 1 [14b] or the chelating of the tp ligands to cadmium ions that effectively increases the rigidity of the ligand and reduces the loss of energy via radiationless decay of the interligand emission excited state [12c].

The TG curve shows there are three-step weight losses from room temperature to 650 °C, which correspond to the removal of coordinated H₂O, tp and bpy ligands, respectively. It should be noted that no obvious weight loss was observed in the temperature range 317-347 °C after the decomposition of the tp ligand. Therefore, the TGA curve of **1** indicates that the chelating coordination of Cd and bpy ligand is far more stable than that of the Cd and tp ligand.

In conclusion, we report a novel 1D coordination polymer $[Cd(bpy)(tp)(H_2O)]_n$ (1) which exhibit a 3D herringbone-like supramolecular structure. The title compound gives strong fluorescent emission.

Supplementary material

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, IR, UV, TG spectra of compound 1 were available from the authors on request.

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- [17] Crystal data for C₁₈H₁₄CdN₂O₅ (1): Monoclinic, space group $P2_1/n$, a = 10.017(2) Å, b = 16.324(3) Å, c = 11.457(2) Å, $\beta = 112.50(3)^{\circ}$, V = 1730.8(6) Å³, Z = 4, $D_{calc} = 1.730$ g/cm³, $\mu = 1.294$ mm⁻¹, F(000) = 896, T = 293(2) K. 17,091 reflections

measured $(2.29^{\circ} < \mu < 27.48^{\circ}, \lambda = 0.71073 \text{ Å})$, 3970 unique $(R_{\text{int}} = 0.0318)$. Structure solution and refinement based on 3970 independent reflections with $I > 2\sigma(I)$ and 291 parameters gave $R_1(wR_2) = 0.0209 \ (0.0448)$ and S = 0.932.

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