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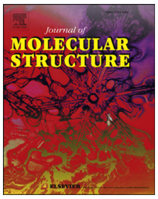

Two novel d^{10} metal coordination polymers based on an asymmetric polycarboxylate ligand: Synthesis, crystal structure, photoluminescence and photocatalysis

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Two novel coordination polymers (CPs), $[Cd_2(cbta)(phen)_2(H_2O)]_n$ (**1**), $\{[Zn_2(cbta)(phen)_2]\ [Zn_2(cbta)(phen)_2(H_2O)]\cdot 4H_2O\}_n$ (**2**) ($H_4cbta = $ 1-(2-carboxylphenoxy)-2,3,5-benzene tricarboxylic acid; phen = 1,10-phenanthroline), were synthesized and characterized by elemental analyses, FT-IR spectra, single-crystal X-ray diffraction analyses. CP **1** shows a 2D network structure based on tetranuclear Cd^{II} clusters and $(cbta)^{4-}$ ligands, which are arranged in a [ABAB$\cdots$] alternation to form a 3D supramolecular structures through $\pi\cdots\pi$ stacking interactions. Noticeably, CP **2** contains two kinds of independent units $[Zn_2(cbta)(phen)_2]$ (**A**) and $[Zn_2(cbta)(phen)_2(H_2O)]\cdot 4H_2O$ (**B**) to form a 1D+1D structure. A shows 1D double chain based on Zn1, Zn2, which are recognized each other to generate a 2D supramolecular network (A) by hydrogen bonding interactions. While B are ring chains comprised of Zn3, Zn4, which are linked into 2D supramolecular network (B) through $\pi\cdots\pi$ stacking interactions. The peculiar structural feature is that the neighboring 2D networks are arranged in a [ABAB$\cdots$] alternation to form a 3D supramolecular structure through hydrogen bonding interactions and C–H$\cdots\pi$ and C–H$\cdots$O week interactions. Especially the $(ctba)^{4-}$ ligands in **1**–**2** adopt three different conformations and coordination modes. The thermal stabilities, XRD, UV, photoluminescence properties of CPs **1**–**2** were also studied. Remarkably, CPs **1**–**2** exhibit photocatalytic activities for degradation of dye (MB) under UV light irradiation and show good stabilities toward UV-light photocatalysis.

1. Introduction

The crystal engineering of metal-organic frameworks (MOFs) are of intense attention because of their novel structures and promising properties in luminescence [1–3], magnetism [4,5], catalysis [6,7], gas absorption and separation [8–10], and so on. As is well known, applications of MOFs highly depend on their structures, so design and construction of the MOFs with desired structures and functions are extremely essential. There are many factors that influence the diversity of structures, such as geometric requirement of central metals, the nature of ligands, metal-to-ligand ratio, experimental conditions, etc [11–13]. Among these factors, organic ligands play a significant role in the construction of MOFs [14,15]. So many polycarboxylate ligands are often employed as bridging ligands to construct MOFs, due to their extension ability both in covalent bonding and in supramolecular interactions (H-bonding and aromatic stacking) [16–21]. However, in contrast to symmetrical carboxylates, the use of unsymmetrical carboxylate ligands has been reported infrequently [22–26].

1-(2-carboxylphenoxy)-2,3,5-benzene tricarboxylic acid (H_4cbta) is such an unsymmetrical polycarboxylate ligand, having four carboxyl groups attached to the two benzene rings. One benzene ring has one carboxyl group, and the other benzene ring has three carboxyl groups. So H_4cbta ligand has nine potential donor atoms, which can induce versatile coordination modes and fascinating structures. Furthermore, they have four carboxyl groups that may be completely or partially deprotonated, and can provide hydrogen bond donors and acceptors. Meanwhile, it possesses both rigidity and flexibility, since phenyl rings can freely rotate around the C–O–C bonds according to the small change in the coordination environment in order to minimize steric hindrance. Therefore, the H_4cbta ligand may be an excellent candidate for the

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construction of multidimensional CPs, especially 3D open or porous frameworks. However, CPs based on H_4cbta ligand have never been documented and much work is still necessary to understand the coordination chemistry of H_4cbta ligand.

With the aim of understanding the coordination chemistry of H_4cbta and studying the influence on the framework structures of their polymers, we have recently engaged in the research of this kind of CPs. Luckily, we have now obtained two CPs of 1-(2-carboxylphenoxy)-2,3,5-benzene tricarboxylic acid, $[Cd_2(cbta)(phen)_2(H_2O)]_n$ (**1**), $\{[Zn_2(cbta)(phen)_2][Zn_2(cbta)(phen)_2(H_2O)]\cdot 4H_2O\}_n$ (**2**). In this paper, we describe the synthesis, structure, photoluminescence and photocatalytic behaviors of two novel CPs.

2. Experimental section

2.1. Materials and methods

All chemicals and reagents were used as received from commercial sources without further purification. All reactions were carried out under hydrothermal conditions. Elemental analyses (C, H, N) were determined with an Elementar Vario EL III elemental analyzer; IR spectra were recorded as KBr pellets on a Bruker EQUINOX55 spectrophotometer in the 4000-400 cm^{-1} region. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere with a heating rate of 10 $^{\circ}C\cdot min^{-1}$ with a NETZSCHSTA 449C thermogravimetric analyzer. The powder X-ray diffraction pattern (PXRD) was recorded with a Rigaku D/Max 3III diffractometer.

Photocatalytic experiments in aqueous solutions were carried out in typical processes. A suspension containing CPs **1**–**2** (15 mg) and 25 mL of methylene blue (MB) (10 mg L^{-1}) solution was stirred in the dark for about 30 min to ensure the establishment of adsorption equilibrium before irradiation. They were then conducted on an XPA-7 type photochemical reactor equipped with a 100 W mercury lamp and the reaction temperature was maintained at about 25 °C by circulating cooling water. Every 15 min, a certain volume of samples were collected and separated by centrifugation to remove residual catalyst particles. Then the solution was analyzed by using Shimadzu UV–vis spectrometer. The concentration of MB was estimated by the absorbance at 664 nm, characteristic of MB.

2.2. Synthesis

2.2.1. Synthesis of $[Cd_2(cbta)(phen)_2(H_2O)]_n$ (1)

A mixture of $Cd(CH_3COO)_2\cdot 2H_2O$ (53.4 mg, 0.2 mmol), 1-(2-carboxyl- phenoxy)-2,3,5-benzene tricarboxylic acid (34.6 mg, 0.1 mmol), phen (18.0 mg, 0.1 mmol) and water (10 mL) was stirred and adjusted to pH 6.5 with 0.5 M NaOH solution, then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 160 °C for 96 h. Then cooling to 100 °C at a rate of 5 °C/h and kept to 100 °C for 24 h. After cooling to room temperature at a rate of 5 °C/h, colorless crystals were obtained, 55% yield based on Cd. Anal. Calcd for $C_{40}H_{24}Cd_2N_4O_{10}$ (945.43): C, 50.81, H, 2.56, N, 5.93%; Found: C, 50.86, H, 2.53, N, 5.91%. IR (KBr cm^{-1}): 3495 s, 1564 s, 1370 s, 1255 s, 1163 m, 1087 w, 979 m, 848 m, 751 s, 685 w, 646 w.

2.2.2. Synthesis of $\{[Zn_2(cbta)(phen)_2][Zn_2(cbta)(phen)_2(H_2O)]\cdot 4H_2O\}_n$ (2)

A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (47.5 mg, 0.2 mmol), 1-(2-carboxyl- phenoxy)-2,3,5-benzene tricarboxylic acid (34.6 mg, 0.1 mmol), phen (18.0 mg, 0.1 mmol) and water (10 mL) was stirred and adjusted to pH 6.5 with 0.5 M NaOH solution, then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 140 °C for 72 h. After cooling to room temperature at a rate of 5 °C/h, colorless crystals were obtained, 49% yield based on Zn. Anal. Calcd for $C_{80}H_{51}N_8O_{23}Zn_4$ (1753.77): C, 54.78, H, 2.93, N, 6.39%; Found: C, 54.81, H, 2.91, N, 6.35%. IR (KBr cm^{-1}): 3396 s, 1559 s, 1362 s, 1237 s, 1202 w, 1103 s, 987 m, 835 m, 780 m, 708s, 647 w.

2.2.3. Single crystal X-ray crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [27]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1**–**2** are summarized in Table 1, selected bond distances and bond angles are listed in Table S1.

3. Results and discussion

3.1. Crystal structure of $[Cd_2(cbta)(phen)_2(H_2O)]_n$ (1)

CP **1** crystallizes in monoclinic, space group $P2_1/c$ and the asymmetric unit of **1** contains two Cd^{II} atoms, one completely deprotonated $(cbta)^{4-}$ ion, two phen ligands and one coordinated water molecule. As illustrated in Fig. 1a, each Cd1 atom is coordinated by two nitrogen atoms [Cd1–N1 = 2.404(3), Cd1–N2 = 2.430(3) Å] from one chelating phen ligand, six oxygen atoms from three carboxylate groups of three $(cbta)^{4-}$ ligands. Interestingly, Cd1 center is an unusual eight-coordinate structure, which can be described as a distorted monocapped pentagonal bipyramid (Fig. 1b). Five atoms N2, O1, O2, O8B, and O4A comprise the equatorial plane, while another two atoms N1, O3A occupy the axial positions, O9B as cap atom. Cd atom with eight-coordinate is far less common in the complexes [28–31], and the structure of **1** is different from the reported eight-coordinate complexes [32], which can be described as a distorted pseudo-tetragonal antiprism. The Cd1–O distances fall in the range of 2.239(7)~2.628(2) Å similar to those found in other Cd carboxylate coordination polymers [33]. Whereas the Cd2 center ligated by two nitrogen atoms [Cd2–N3A = 2.337(3), Cd2–N4A = 2.356(3) Å] from one chelating

Table 1
Crystal data and structural refinement parameters for Compounds **1**–**2**.

Compound	1	2
Empirical formula	$C_{40}H_{24}Cd_2N_4O_{10}$	$C_{80}H_{51}N_8O_{23}Zn_4$
Formula weight	945.43	1753.77
Crystal system	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P-1*
a/Å	10.9384(9)	12.9810(7)
b/Å	24.130(2)	15.0097(8)
c/Å	15.3068(9)	19.9320(11)
α/°	90.00	96.1580(10)
β/°	124.331(4)	97.4560(10)
γ/°	90.00	99.5900(10)
$V/Å^3$	3336.3(4))	3763.8(4)
Z	4	2
ρ_{calc} (g cm^{-3})	2.534	1.547
F (000)	1872	1782
μ (mm^{-1})	1.098	1.344
Reflections collected	17399	19912
S on F^2	1.106	1.033
R_1 , wR_2[a] [$I > 2\sigma(I)$]	0.0287, 0.0725	0.0600, 0.1818
R_1 , wR_2[a] (all data)	0.0391, 0.0826	0.0923, 0.1987

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.