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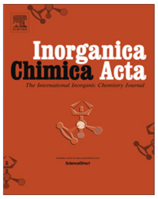

Research paper

Photoluminescence, magnetic and photocatalytic properties of three overlapping layered homochiral coordination polymers based on semi-rigid alanine ligands

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ABSTRACT

Three homochiral coordination polymers based on semi-rigid alanine ligands and varied auxiliary N-donor ligands, $[Cd(TMAla)(bpipa\text{-}4)]\cdot 2H_2O$ (**1**), $[Co_2(TMAla)_2(bipy)_2]\cdot 2.5H_2O$ (**2**), $[Co(TBAla)(bpee)(H_2O)_2]\cdot 3H_2O$ (**3**), (H_2TMAla = terephthaloyl-mono(L-alanine), H_2TBAla = terephthaloyl-bis(L-alanine), bpipa-4 = N,N′-bis(pyridin-4-yl)isophthalamide, bipy = 4,4′-bipyridine and bpee = 1,2-bis(4-pyridyl)ethylene), have been synthesized and structurally characterized. In these structures, the different metal ions are connected into two types of chains by the semi-rigid alanine ligands and various N-donor ligands in different direction, respectively, to generate diverse 2D layered coordination networks, which are further stacked into 3D supramolecular frameworks in an ABAB overlapping mode through interlayered hydrogen bonds. Complex **1** exhibits the 2D squamous sheet constructed by zigzag chains. Complex **2** shows a thick 2D layer motif formed through the looped and ladder-shaped chains. Complex **3** features a (4,4) grid 2D coordination network built via the zigzag and linear chains. Complex **1** displays a strong fluorescent emission at 402 nm in solid state at room temperature. Magnetic susceptibility measurement indicates weak antiferromagnetic interactions between the Co(II) ions in complex **2**. Meanwhile, complex **2** shows good photocatalytic activity for the degradation of methylene blue (MB) and methyl orange (MO) dyes under UV light.

1. Introduction

Metal-organic coordination polymers (CPs) have attracted much attention owing to their intriguing variety of structures and extensive applications in heterogeneous catalysis, gas adsorption and separation, photoluminescence sensors, magnetism, and so on [1–4]. It is well known that the rational design and selection of organic ligands according to their length, rigidity, coordination modes and functional groups plays an important role in the preparation of the targeted CPs. Therefore, the usage of chiral building blocks is the most effective approach for the fabrication of homochiral CPs [5,6]. The judicious selection of chiral linkers can give rise to the desired structural and multifunctional homochiral CPs. Several natural chiral amino acids, such as L-lactic acid [7,8], L-tartaric acid [9], L-aspartic acid [10], L-glutamic acid [11], and D-camphoric acid [12,13], have been widely utilized as organic linkers to construct homochiral CPs, which are inexpensive, non-toxic and readily available. However, natural amino acids are not ideal chiral ligands in the synthesis of higher-dimensional homochiral CPs, owing to their very flexible conformations. In order to improve on this limitation, rigid coordination functional groups are introduced to the N-substituted site of amino acid have been considered as an attractive synthetic strategy to create homochiral CPs [6b,14–17]. According to this strategy, two kinds of chiral ligands H_2TMAla and H_2TBAla have been synthesized by modifying the $-NH_2$ group of L-alanine with terephthalic acid in mono-substituted and bi-substituted, respectively, which are pictured in Scheme 1. Containing L-alanine and phenyl units, the H_2TMAla and H_2TBAla are semi-rigid chiral ligands and possess the bifunctional groups of the –NH and the –C=O moieties, which have unique potential to provide two types of hydrogen-bonding sites, the –NH groups acting as electron acceptors and the –C=O groups acting as electron donors. These distinctive chiral ligands can furnish a new approach to design and construct homochiral CPs with fascinating architectures and outstanding properties.

Recently, much effort is devoted to the removal of organic dyes from the liquid phase to decrease their adverse effects on the biosphere [18]. One promising application for CPs in this field is to

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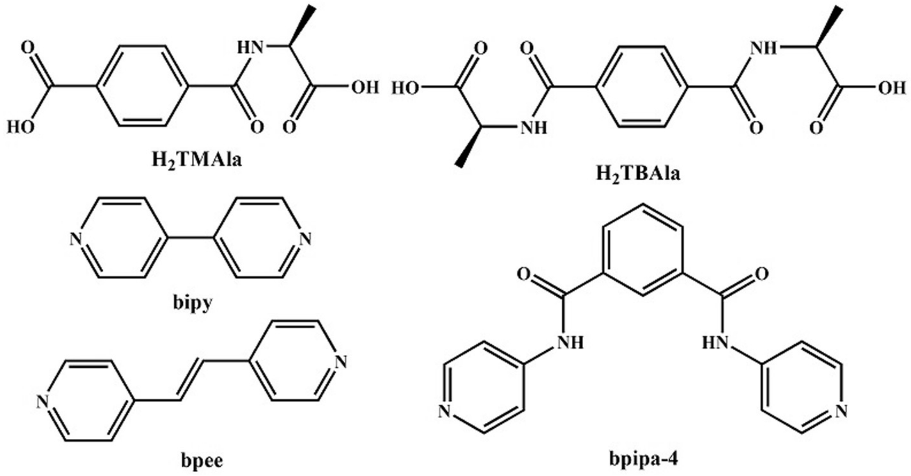

Scheme 1. Structures of H_2TMAla, H_2TBAla and three N-donor auxiliary ligands.

decomposing organic dyes by photocatalysts from aqueous solutions [19]. Some transition metal complexes have been proved to be efficient photocatalysts on the degradation of organic dyes [20]. However, reported chiral CPs photocatalysts are still very limited [21].

In order to obtain characteristic homochiral CPs of amino acids, we selected three N-donor auxiliary ligands with different shapes, lengths and rigidness/flexibility, i.e. V-shaped bpipa-4, linear bipy and bpee, to assist H_2TMAla and H_2TBAla to build homochiral CPs. Herein, three homochiral coordination polymers, [Cd (TMAla)(bpipa-4)]·$2H_2O$ (**1**), [Co_2(TMAla)$_2$(bipy)$_2$]·$2.5H_2O$ (**2**), [Co(TBAla)(bpee)(H_2O)$_2$]·$3H_2O$ (**3**), have been hydrothermally synthesized. The homochiral structures of these complexes are determined by single-crystal X-ray diffraction. The photoluminescence properties of complex **1** as well as the magnetic properties of complex **2** are investigated. The photocatalytic properties of complexes **1**–**3** show different degradative effects for MB and MO dyes.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents of analytical grade were commercial origin without further purification. The H_2TMAla, H_2TBAla and bpipa-4 ligands were prepared according to the literature procedures [15,22]. Elemental analyses for C, H, and N were performed on an Elementar Vario ELIIICHN elemental Analyzer. The IR spectra were recorded on a Bruker NicoletiS50 spectrometer in the 400–4000 cm^{-1} range. Powder X-ray diffraction (PXRD) data were recorded using a Bruker D8 ADVANCE. Solid-state photoluminescence spectra were measured on an F-4500 fluorescence spectrometer. Temperature-dependent and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-XL5 magnetometer. Diamagnetic corrections were made with Pascal's constants.

2.2. X-ray crystallography

Single-crystal X-ray diffraction analyses of **1**–**3** were carried out on a Bruker APEX II-CCD diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source at 298 K. All structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using SHELXTL-2013 program. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located in calculated positions and refined using the riding model. The hydrogen atoms of coordinated water molecules were placed from difference Fourier maps. However, the refinements with geometric restraints for the hydrogen atoms on the disordered lattice waters in complexes **1**–**3** were not convergent, so we choose not to include the disordered hydrogen atoms in the final refinements. The crystallographic data are listed in Table 1. The selected bond lengths and angles for **1**–**3** are listed in Tables S1–3. The hydrogen bonds for **1**–**3** are shown in Table S4.

2.3. Synthesis

2.3.1. Synthesis of [Cd(TMAla)(bpipa-4)]·$2H_2O$ (**1**)

A mixture of H_2TMAla (7.1 mg, 0.03 mmol), $Cd(NO_3)_2·6H_2O$ (9.3 mg, 0.03 mmol), bpipa-4 (9.6 mg, 0.03 mmol), NaOH (0.3 mL, 0.1 mol·L^{-1}), H_2O (2 mL) and methanol (3 mL) was stirred in a 23 mL Teflon-lined stainless steel container for 40 min, and then heated at 70 °C for 48 h. After cooling to ambient temperature, colorless block crystals of **1** were collected (yield, 38% based on H_2TMAla). Anal. Calc. for $C_{29}H_{23}CdN_5O_9$: C, 49.91; H, 3.32; N,

Table 1
Crystal data and structure refinements for complexes **1**–**3**.

Complex	**1**	**2**	**3**
Formula	$C_{29}H_{23}CdN_5O_9$	$C_{42}H_{34}Co_2N_6O_{12.5}$	$C_{26}H_{26}CoN_4O_{11}$
Formula weight	697.92	940.65	629.46
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	P_1	C_2
a (Å)	9.5001(5)	9.0976(8)	14.3556(17)
b (Å)	15.5981(7)	10.3656(9)	13.7309(17)
c (Å)	11.0488(5)	13.3008(12)	7.6820(9)
α (°)	90	91.255(3)	90
β (°)	103.8440(10)	90.074(3)	101.340(5)
γ (°)	90	108.746(3)	90
V (Å^3)	1589.69(13)	1187.42(18)	1484.7(3)
Z	2	1	2
D_{calc} (Mg·m^{-3})	1.458	1.315	1.408
μ (mm^{-1})	0.745	0.762	0.641
F(000)	704	482	650
θ range for data (°)	1.90 to 28.36	1.53 to 28.22	2.07 to 28.50
Reflection collected/unique	21887/6752	16331/8377	9885/3201
Data/restraints/parameters	6752/1/397	8377/9/586	3201/23/229
R_{int}	0.0387	0.0385	0.0883
GOF on F^2	1.041	1.006	1.080
$R_1{}^a/wR_2$ [$I > 2\sigma(I)$]	0.0397/0.1041	0.0450/0.1111	0.0873/0.2274
$R_1{}^b/wR_2$ (all data)	0.0465/0.1086	0.0650/0.1257	0.0923/0.2321
Flack	0.029(13)	0.06(2)	0.09(4)
Largest residues (e A^{-3})	0.713, −0.381	0.436, −0.279	1.153, −0.896