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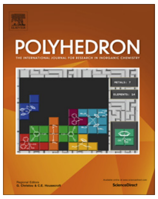

2D → 3D interlocking Zn(II) arrays directed by uncoordinated groups: Fluorescent behaviors, recycling and enhancements of photocatalytic properties

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ABSTRACT

To investigate the effect of the uncoordinated groups of “V”-type dipyridylamide on the interlocking arrays of Zn(II) coordination polymers, $[Zn(L^1)(1,4\text{-bdc})]\cdot H_2O$ (**1**) and $[Zn(L^2)(1,4\text{-bdc})]\cdot H_2O$ (**2**) [L^1 = *N*,*N*′-bis(pyridin-3-yl)-5-hydroxybenzene-1,3-dicarboxamide, L^2 = *N*,*N*′-bis(pyridine-3-yl)-5-methylbenzene-1,3-dicarboxamide, 1,4-H_2bdc = 1,4-benzenedicarboxylic acid] have been hydrothermally synthesized and structurally characterized by IR, TG and X-ray single-crystal diffraction. Complex **1** is a 2D 6^3 network based on [Zn(1,4-bdc)] zigzag chains and $[Zn(L^1)]_2$ loops, which is further extended into 2D → 3D parallel polycatenation array. Complex **2** features a 2D (4,4) network derived from [Zn(1,4-bdc)] zigzag chains and $[Zn(L^1)]$ helixes, which is further extended into 2D → 3D inclined interpenetration array. The effect of the uncoordinated groups of “V”-type dipyridylamide on the structures of the title complexes was discussed. The fluorescent behaviors of **1**–**2** in aqueous solutions with Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} were investigated. The photocatalytic properties of complexes **1**–**2**, Ag loaded CPs composite materials (Ag@**1**–**2**) and Fe^{3+}-functionalized composite materials (Fe^{3+}@**1**–**2**) for the degradation of methylene blue (MB) under ultraviolet light irradiation have been investigated.

1. Introduction

Coordination polymers (CPs) built from metal ions and adjustable organic ligands, are regarded as the new functional materials for catalysis, fluorescent sensor, magnetism and so on [1–5]. The rational design and synthesis of desired structural and functional CPs are very important, since the function of CPs are directly related to their structures [6,7]. Generally speaking the organic ligands play a key role on CPs and the structural changes of the ligand, such as geometry and the relative orientation of the donor; even the substituents on organic ligands can result in the variation of the final CPs [8,9]. Therefore, using similar ligands with different uncoordinated groups to construct CPs is considered to be an effective way to investigate the influence of organic ligands on the structure.

Dipyridylamides and aromatic dicarboxylates have displayed excellent coordination ability and flexibility in the construction of functional CPs [10,11]. For instance, Chen’s group has reported an interpenetrating network based on Cu ions and *N*,*N*′-di(4-pyridyl) adipoamide [12]. Luo and co-workers have synthesized a self-catenated network from N1,N4-bis(pyridin-3-ylmethyl)naphthalene-1,4-dicarboxamide ligand [13]. However, there is still a lack of systematic understanding on the effects of different uncoordinated groups of “V”-type dipyridylamides on the structures of CPs and a further study is meaningful for constructing new functional CPs.

On the other hand, as a new kind of promising photocatalyst, CPs show various merits in the field of photocatalytic degradation of dyes under ultraviolet light irradiation [14,15]. However, owing to the low quantum yields, CPs based photocatalyst with an excellent photocatalytic activity are seldom reported [16,17]. In this respect, Ag is an ideal option for improving the photocatalytic activity on the degradation of dyes, because Ag can act as a trap to capture photogenerated electron-hole pairs and leads to their separation [18,19]. To the best of our knowledge, the research on metal loaded dipyridylamide-based-CPs has never been reported.

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In addition, d^{10} metal CPs have been synthesized to detect toxic metal ions [20–22]. However, the recycling CPs containing toxic metal ions become another toxic substance and it is difficult to deal with. Based on the above considerations, to investigate the effects of uncoordinated groups of dipyridylamides on the structures of target CPs, two "V" type dicarboxamide ligands [*N*,*N′*-bis(pyridin-3-yl)-5-hydroxybenzene-1,3-dicarboxamide (L^1), *N*,*N′*-bis(pyridine-3-yl)-5-methylbenzene-1,3-dicarboxamide (L^2)] with different uncoordinated groups and one linear dicarboxylic acid (1,4-H_2bdc = 1,4-benzenedicarboxylic acid) were selected for constructing Zn coordination polymers. As a result, two coordination polymers [Zn(L^1)(1,4-bdc)]·H_2O (**1**) and [Zn(L^2)(1,4-bdc)]·H_2O (**2**) were synthesized under hydrothermal conditions. The effect of the uncoordinated groups of "V"-type dipyridylamide on the structures of the title complexes was discussed. Both **1** and **2** show the fluorescent sensing behaviors for Fe^{3+}. To improve the photocatalytic activities of the two new CPs, we loaded Ag onto the surfaces and synthesized two Ag loaded CPs composite materials (Ag@**1** and Ag@**2**). The photocatalytic activities of the recyclable Fe^{3+}-functionalized composite materials (Fe^{3+}@**1** and Fe^{3+}@**2**) and Ag loaded CPs composite materials (Ag@**1** and Ag@**2**) for the degradation of methylene blue (MB) under ultraviolet light were studied.

2. Experimental

2.1. Materials and measurements

N,*N′*-Bis(pyridin-3-yl)-5-hydroxybenzene-1,3-dicarboxamide (L^1) and *N*,*N′*-bis(pyridine-3-yl)-5-methylbenzene-1,3-dicarboxamide (L^2) were prepared according to the method reported in Ref. [23]. IR spectra (KBr pellets), thermogravimetric analyses (TGAs) and powder X-ray diffraction were performed with a Varian-640 spectrometer, Pyris Diamond TG instrument and Ultima IV diffractometer (40 kV and 40 mA, Cu Kα), respectively. The luminescence spectra were obtained with a Hitachi F-4500 fluorescence/phosphorescence spectrometer and the UV–Vis absorption spectra were carried out by SP-1901 UV–Vis spectrophotometer.

2.2. Preparation of complexes **1–2**

2.2.1. Synthesis of [Zn(L^1)(1,4-bdc)]·H_2O (**1**)

A mixture of $ZnSO_4·7H_2O$ (0.1 mmol), L^1 (0.1 mmol), 1,4-H_2bdc (0.1 mmol), NaOH (0.2 mmol), H_2O (8 mL) was sealed in a 25 mL Teflon-lined autoclave under autogenous pressure at 120 °C for 4 days. After cooling to the room temperature, colorless block crystals of **1** suitable for X-ray diffraction were obtained in 16% yield based on Zn. *Anal.* Calc. for $C_{26}H_{20}ZnN_4O_8$: C, 53.67; H, 3.47; N, 9.63; Found (%): C, 53.62; H, 3.42; N, 9.67%. IR (KBr, cm^{-1}): 3440m, 3307w, 3086w, 1688m, 1590m, 1555s, 1484m, 1404m, 1381m, 1343m, 1227m, 1140w, 1060w, 838w, 803w, 750m, 697m, 644.

2.2.2. Synthesis of [Zn(L^2)(1,4-bdc)]·H_2O (**2**)

The preparation of **2** was similar to that of **1**, except that L^2 was used instead of L^1. Colorless block crystals of **2** were obtained in 10% yield based on Zn. *Anal.* Calc. for $C_{27}H_{22}ZnN_4O_7$: C, 55.93; H, 3.82; N, 9.66; Found (%): C, 55.96; H, 3.80; N, 9.69%. IR (KBr, cm^{-1}): 3323m, 3123w, 3045w, 2994w, 2949w, 1683s, 1664m, 1587s, 1541s, 1484m, 1418s, 1380m, 1335m, 1290m, 1238s, 1186m, 1135m, 1102w, 1064w, 1012m, 883w, 825m, 799m, 748s, 696s, 644m, 592w.

2.3. X-Ray crystallography

The data of crystal structures of **1–2** were obtained with a Bruker SMART APEX II diffractometer and the related crystal structures were solved by direct methods using the SHELXS program of the SHELXTL crystallographic software package and refined on F^2 by the full-matrix least-squares methods [24]. The hydrogen atoms of organic ligands were generated geometrically onto the specific atoms and were refined isotropically. H(1B) and H(1C) of the water molecule (O1W) in **1** are disordered each with chemical occupancy of 0.5. Because of the highly disordered water molecule in complex **2**, the SQUEEZE route was employed to calculate the diffraction contribution from the water molecule. One lattice water molecule in **2** was not located in the different Fourier maps but was added to the formula, which was derived from crystallographic data combined with elemental and thermogravimetric analysis data. The crystal

Table 1
Crystal and refinement data for complexes **1** and **2**.

Complexes	1	2
Empirical formula	$C_{26}H_{20}ZnN_4O_8$	$C_{27}H_{22}ZnN_4O_7$
Fw	581.83	579.88
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cell dimensions		
a (Å)	21.3208(11)	18.2667(15)
b (Å)	16.1196(9)	30.420(2)
c (Å)	16.8844(9)	14.2830(12)
α (°)	90	90
β (°)	119.6380(10	127.0820(10)
γ (°)	90	90
V ($Å^3$)	5043.7(5)	6331.7(9)
Z	8	8
D_{calc} (g/cm^3)	1.532	1.179
μ (mm^{-1})	1.033	0.816
F(000)	2384	2304
R_{int}	0.0219	0.0618
R_1[a] [$I > 2\sigma(I)$]	0.0433	0.0452
wR_2[b] (all data)	0.1394	0.1181
Goodness-of-fit (GOF) on F^2	1.061	1.013
$\Delta\rho_{max}$ (e $Å^{-3}$)	1.432	0.271
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.699	−0.262

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

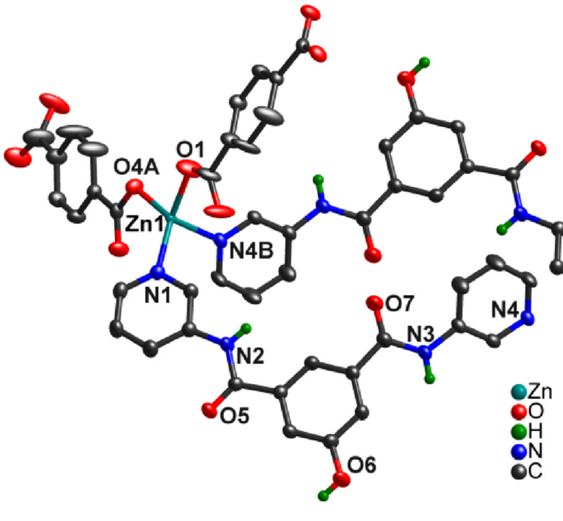

Fig. 1. The coordination environment of Zn^{II} ion in **1**.