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Four thiophene-pyridyl-amide-based Zn^{II}/Cd^{II} coordination polymers: Assembly, structures, photocatalytic properties and fluorescent recognition for Fe^{3+}

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ABSTRACT

By tuning metal ions and combining with different dicarboxylates, four new semi-rigid thiophene-bis-pyridyl-bis-amide-based coordination polymers, namely, [Zn(3-bptpa)(1,3-BDC)]·DMA·$2H_2O$ (**1**), [Zn(3-bptpa)(5-MIP)] (**2**), [Cd(3-bptpa)(1,3-BDC)]·$2H_2O$ (**3**) and [Cd(3-bptpa)(5-MIP)]·$4H_2O$ (**4**) (3-bptpa=*N,N′*-bis(pyridine-3-yl)thiophene-2,5-dicarboxamide, 1,3-H_2BDC=1,3-benzenedicarboxylic acid, 5-H_2MIP=5-methylisophthalic acid, DMA=*N,N*-dimethylacetamide), were solvothermally/hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction analyses, IR spectra, UV–vis diffuse-reflectance spectra (DRS), powder X-ray diffraction (PXRD) and thermal gravimetric analyses (TG). The structural analysis reveals that Zn-complexes **1** and **2** are similar 2D networks. While Cd-complexes **3** and **4** exhibit similar 2-fold interpenetrating 3D α-Po frameworks with the $(4^{12}\cdot6^3)$ topology. The photocatalytic properties for the degradation of methylene blue (MB) under ultraviolet light irradiation of the title complexes have been investigated in detail. Furthermore, the luminescent sensing behaviors for metal cations of **1–4** have been studied, the results indicate that **3** is an excellent fluorescent probe, with high sensitivity, selectivity, and simple regeneration, for environmentally relevant Fe^{3+} ions.

1. Introduction

Coordination polymers (CPs) have been continuously gaining great attention due to their intriguing architectures and topologies [1–4]. The main feature of CPs is that the linkers as well as nodes can be carefully selected and designed depending on the targeted properties [5–7]. Therefore, the CPs have become multidisciplinary field of research given their wide range of properties pertaining to gas storage and separation [8], heterogeneous catalysis [9], chemical sensing [10], and guest species exchange or recognition [11]. Generally, the networks and properties of CPs can be influenced by various key factors, such as the metal ions, ligands, molar ratio of solvents, temperature and so on [12,13]. Among these, the design and use of organic ligands are highly important for the assembly of CPs materials with desired motifs and functions [14,15].

Bis-pyridyl-bis-amide as a kind of excellent bridging ligands, have appealed great interest in the past few years due to their various coordination groups (pyridyl and carbonyl) and two types of hydrogen bonding sites from the amide group (the –NH moieties acting as electron acceptors and the –C=O groups acting as electron donors) as well, which are important for molecular recognition and constructing supramolecular arrays [16]. In addition, the dicarboxylates as a kind of important multidentate O-donor ligands, show diverse coordination modes and play a significant part in the growth of the literature of CPs [17]. The use of these linkers together gives a better opportunity to fine tune the structure and nature of target CPs [18,19]. Chen et al. have reported some charming CPs based on a series of flexible bis-pyridyl-bis-amide ligands [20–22]. Our group also prepared a series of transition metal CPs derived from rigid/flexible bis-pyridyl-bis-amide ligands [23–25]. However, to the best of our knowledge, construction of CPs with semi-rigid thiophene-bis-pyridyl-bis-amide and dicarboxylate mixed ligands is still a challenging work [26].

Environmental pollution is increasing due to the fast growth of chemical industries and the release of various types of industrial contaminant into water [27]. The industrial contaminants include chlorinated organic complexes, volatile organic complexes, and fertilizers, dyes *etc*. Among these toxic threats, dyes are more concerned to us because of their high chemical and biological stability, which makes them difficult to be removed from water. Among the various methods for the treatment of contaminants, especially the organic dyes, photocatalytic degradation has been proved to be an economical and efficient way to degrade organic recalcitrant contaminants [28]. As a class of

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promising materials in the family of photocatalysts, CPs, which exhibit a valence band position and band gap (Eg) similar to those of TiO_2, possess apparent features in the field of photocatalytic decomposition of organic dyes [29]. Additionally, the upsurge in research on CPs as photocatalysts in photocatalytic decomposition of organic dyes could furnish a clean strategy to deal with refractory pollutants and would also enrich the catalysis field.

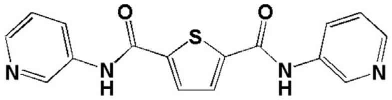
As is known, ferrum, in the form of Fe^{3+}, is an indispensable biological element to the formation of hemoglobin and muscle and is also widely used in industry production. Accordingly, the massive utilizations of the Fe^{3+} ions have brought severe environmental pollutants and may cause health problems [30,31]. Both excess and deficiency of Fe^{3+} ions can disturb cellular homeostasis and metabolism. Therefore, it is extremely important and urgent to seek a new material with high selectivity and sensitivity for probing Fe^{3+}. In this regard, luminescent CPs are among the most extensively investigated detection probes for their short response time, high sensibility, simplicity and so on [32–35]. Some luminescent CPs are used as sensor for Fe^{3+} ions based on electron transfer, or interactions between Fe^{3+} ions and Lewis base groups (pyridyl nitrogen, $-NH_2$ or –OH) of the organic ligands [31,34–36]. Therefore, the selection of organic ligands is important to control the structures and functions of CPs. Moreover, it is equally important that the metal ions have a d^{10} configuration to yield luminescent CPs.

Thus, in this work, a thiophene-bis-pyridyl-bis-amide *N,N′*-bis(pyridine-3-yl)thiophene-2,5-dicarboxamide (3-bptpa) ligand (Scheme 1) is employed to combine with dicarboxylates to construct Zn/Cd–CPs. As a result, we obtained four novel Zn/Cd–CPs, namely, [Zn(3-bptpa)(1,3-BDC)]·DMA·$2H_2O$ (**1**), [Zn(3-bptpa)(5-MIP)] (**2**), [Cd(3-bptpa)(1,3-BDC)]·$2H_2O$ (**3**) and [Cd(3-bptpa)(5-MIP)]·$4H_2O$ (**4**) (1,3-H_2BDC=1,3-benzenedicarboxylic acid, 5-H_2MIP=5-methylisophthalic acid, DMA=*N,N*-dimethylacetamide) based on the 3-bptpa ligand. These materials are synthesized under solvothermal/hydrothermal conditions and structurally characterized. Furthermore, the photoluminescent sensing and photocatalytic properties of the title complexes have been investigated. The experimental data verify that complex **3** exhibit good Fe^{3+} recognition in suspension, further confirming the rationality of selection of 3-bptpa as organic molecules.

2. Experimental

2.1. Materials and general methods

Synthesis of the ligand 3-bptpa was previously reported by literatures [37]. All other reagents and solvents for syntheses were purchased from Aladdin Industrial Corporation (Shanghai) and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C element analyzer. Infrared spectra were recorded on a 640 FT-IR Spectrometer with KBr pellets in the 500–4000 cm^{-1} region. Powder X-ray diffraction (PXRD) data were taken on a D/teX Ultra diffractometer equipped with Cu Kα (λ=1.5406 Å) radiation. Thermal analysis were performed with a Pyris Diamond TG/DTA thermal analyzer. The solid-state fluorescence spectra were monitored with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The micro-sized crystal particles were obtained by the MSK-SFM-12M micro vibration ball mill. The solid-state diffuse-reflectance UV/vis spectra for powder samples were obtained by using a Perkin-Elmer Lambda 750 UV/vis spectrometer. UV–vis absorption spectra were conducted by use of a SP-1901 UV–vis spectrophotometer.



Scheme 1. The semi-rigid bis-pyridyl-bis-amide (3-bptpa) ligand used in this work.

2.2. Preparation of complexes **1**–**4**

2.2.1. [Zn(3-bptpa)(1,3-BDC)]·DMA·$2H_2O$ (1)

1. A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.059 g, 0.2 mmol), 3-bptpa (0.032 g, 0.10 mmol), 1,3-H_2BDC (0.016 g, 0.10 mmol) was dissolved in DMA–H_2O mixed solvent (6 mL; v/v, 2/1, DMA=*N,N*-dimethylacetamide) and was vigorously stirred for 30 min at ambient temperature, then infunded to a 25 mL Telfon reactor and heated to 85 °C for 4 days. Then the autoclave was gradually cooled to room temperature. Colorless block-shaped crystals of **1** were obtained. Yield 24% based on Zn. Anal. Calcd. for $C_{28}H_{29}N_5O_9SZn$ (676.99): C 49.67, H 4.32, N 10.34. Found: C 49.56, H 4.39, N 10.25%. IR (KBr, cm^{-1}): 3391 m, 1674 s, 1607 s, 1498 s, 1423 s, 1355 s, 1296 s, 1136w, 819 s.

2.2.2. [Zn(3-bptpa)(5-MIP)] (2)

Complex **2** was got in the same manner as **1** except that H_2MIP (0.018 g, 0.10 mmol) was used to instead of 1,3-H_2BDC and DMF–H_2O (DMF=*N,N*-dimethylformamide) mixed solvent (5 mL; v/v, 1/4) was utilized in place of DMA–H_2O, and the reaction temperature was changed to 120 °C. Colorless block-shaped crystals of **2** were produced. Yield 23% based on Zn. Anal. Calcd. for $C_{25}H_{18}N_4O_6SZn$ (567.86): C 52.88, H 3.19, N 9.86. Found: C 52.96, H 3.11, N 9.76%. IR (KBr, cm^{-1}): 1640 s, 1587 s, 1492 s, 1427 s, 1337 m, 1304 m, 1134w, 822 s.

2.2.3. [Cd(3-bptpa)(1,3-BDC)]·$2H_2O$ (3)

$CdCl_2\cdot 2.5H_2O$ (0.046 g, 0.2 mmol), 3-bptpa (0.032 g, 0.10 mmol), 1,3-H_2BDC (0.016 g, 0.1 mmol), H_2O (8 mL) and NaOH (0.012 g, 0.3 mmol) was placed in a 25 mL Teflon reactor. The mixture was stirred for 30 min at ambient temperature and heated at 120 °C for 4 days, and then the autoclave was gradually cooled to room temperature. Colorless block shaped crystals of **3** were afforded. Yield 14% based on Cd. Anal. Calcd. for $C_{24}H_{20}N_4O_8SCd$ (636.90): C 45.26, H 3.16, N 8.79. Found: C 45.39, H 3.22, N 8.71%. IR (KBr, cm^{-1}): 3424 m, 1648 s, 1603 s, 1484 s, 1419 m, 1332 s, 1297 s, 1133w, 815 s.

2.2.4. Synthesis of [Cd(3-bptpa)(5-MIP)]·$4H_2O$ (4)

Colorless crystals of complex **4** was obtained by a similar procedure to that used for **3**, except that H_2MIP (0.018 g, 0.10 mmol) was used to replace 1,3-H_2BDC. Yield 15% based on Cd. Anal. Calcd. for $C_{25}H_{26}N_4O_{10}SCd$ (686.96): C 43.71, H 3.81, N 8.15. Found: C 43.76, H 3.76, N 8.08%. IR (KBr, cm^{-1}): 3417 m, 1665 s, 1612 s, 1488 s, 1423 s, 1331 s, 1295 s, 1110w, 805 s.

2.3. X-ray crystallography

X-ray diffraction analysis data for complexes **1**–**4** were collected with a Bruker-APEX-II CCD X-ray diffractometer (Bruker Corporation, Germany) with Mo-Kα (λ=0.71073 Å) at 296(2) K. All of the structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXL program [38,39]. Anisotropic refinement was applied to all the non-hydrogen atoms. The H atoms of the organic ligands were placed theoretically and treated isotropically. During the refinement, the command 'ISOR' was used to restrain the non-H atoms C25–C28, O5, O8, N5, O1W, O2W in complex **1**, O2W in **3**, O4W in **4**. Furthermore, the H atoms of the lattice water molecules O2W in **3** and O4W in **4** were not located in the different Fourier maps but were included in the structure factor calculations. A summary of their crystallographic data and structure refinement is provided in Table 1. Selected bond distances and angles of the title complexes are listed in Table S1 (ESI).