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A new mixed ligand based Cd(II) 2D coordination polymer with functional sites: Photoluminescence and photocatalytic properties

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ABSTRACT

The solvothermal reaction of $Cd(OAc)_2{\cdot}2H_2O$ with 5-(4-carboxyphenoxy)isophthalic acid (H_3L) as ligand and 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (bpz) as co-ligand afforded a new coordination polymer $[Cd(L)(Hbpz)]_n$ (**1**), which was characterized. Compound **1** shows 2D layer network which can work as highly sensitive sensor to detect Fe^{3+} by the decrease in its luminescence intensity because of the existence of active sites. The photocatalytic activity towards the degradation of methyl violet (MV) in polluted water was explored. In addition, the photocatalytic activity of **1** against the photodecomposition of organic dye has been addressed using density of states (DOS) calculations.

The coordination polymers (CPs) constitute a potential class of hybrid material that possess metal ions/metal clusters as well as the tunability associated with the organic linkers [1,2]. The emergence of good performances of CPs in various research areas arises because of the formation of different structures by CPs [3,4]. To construct the targeted CPs, the precise selection of organic ligands is one of the most important criterion. To construct the targeted CPs, the strategy of using the mixed ligand assembly had been widely adopted [4,5]. In our previous reports we have demonstrated that the structural diversity of coordination polymers can be tuned by changing the shapes of the auxiliary *N*-donor ligands [6]. In previous reports, the ligand 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (bpz) was selected to construct CPs because of its versatile coordination capability and considerable flexibility that was introduced because of the free rotation of the two pyrazole rings around the central C–C bond [7–10]. Thus, bpz ligand can offer variable bridging conformation and can modulate the dimensionalities and topologies of the resulting networks [7]. Moreover, the structural diversity in CPs obtained using 5-(4-carboxyphenoxy)isophthalic acid (H_3L) ligand can be ascribed to the C–O–C angles that can create different bridging groups due to the angular tricarboxylate ligand. At the same time, aromatic multicarboxylate ligands present versatile coordination modes and are very effective building blocks for construction of coordination polymers [7–10].

As an extension in this line of study [6,11], we plan to investigate the structure-directing roles of angular tricarboxylate ligand in the formation of divalent coordination polymers by combining neutral auxiliary pyrazole-based ligand. Herein, we report the synthesis and structure of a new two dimensional Cd(II) coordination polymer comprising of mixed ligand *viz.* 5-(4-carboxyphenoxy)isophthalic acid (H_3L) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (bpz) as well as its thermal, luminescent sensing and photocatalytic properties. The results of these investigations are presented herewith.

1. Materials and methods

1.1. General considerations

All the chemicals were purchased from the commercial sources and used without further purification. The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. The simulated powder patterns

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were calculated using Mercury 2.0. Fourier transform infrared (FT-IR) spectra as KBr pellet were recorded using a Nicolet Impact 750 FTIR in the range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from room temperature to 650 °C at a heating rate of 10 °C min^{-1}, using a SDT Q600 thermogravimetric analyzer.

1.2. X-ray crystallography

Single crystal X-ray diffraction data collection was carried out on Bruker SMART APEX diffractometer that was equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using the ω-scan technique. The intensities against the absorption effects were corrected by using SADABS. The structure was solved by direct method (SHLEXS-2014) and refined using the full-matrix least-squares procedure based on F^2 (Shelxl-2014) [12]. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The relevant geometrical parameters for **1** are presented in Table S1.

Crystal Data **1**: $C_{25}H_{21}CdN_4O_7$, M = 601.87, Monoclinic, *C*2/*c*, a = 22.017(3) Å, b = 18.801(3) Å, c = 16.258(3) Å, β = 127.691(3)°, V = 5325.7(15) $Å^3$, Z = 8, D_{calc} = 1.501 mg m^{-3}, F(0 0 0) = 2424, crystal size 0.210 × 0.200 × 0.190 mm, reflections collected 18,167, independent reflections 4692 [R(int) = 0.0318], final indices [I > 2σ(I)] R_1 = 0.0495, wR_2 = 0.1467, R indices (all data) R_1 = 0.0627, wR_2 = 0.1687, gof 1.033, largest difference peak and hole 2.361 and −0.820 e $Å^{-3}$. CCDC No. **1820009**.

1.3. Synthesis

$[Cd(L)(Hbpz)]_n$ (**1**): The ligands 5-(4-carboxyphenoxy)isophthalic acid (H_3L) (0.10 mmol, 0.031 g) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (bpz) (0.10 mmol, 0.020 g) as well as $Cd(OOCCH_3)_2{\cdot}2H_2O$ (0.10 mmol, 0.027 g) were dissolved in 10 mL of H_2O and the mixture was stirred for 30 min and then transferred and sealed in a 25 mL Teflon-lined reactor and heated to 160 °C for 72 h, and thereafter cooled to room temperature at a rate of 5 °C/h. Yellow block crystals of **1** were obtained in 62% yield based on cadmium. IR: 3397(v); 2924(m); 1615(m); 1557(vs); 1509(m); 1450(s); 1372(vs); 1246(vs); 1108(m); 970(m); 779(m); 724(m); 640(m).

1.4. Photoluminescence measurements

The photoluminescence properties of **1** were investigated as its aqueous suspension at room temperature using a RF-5301PC spectrofluorophotometer. The excitation and emission slit widths were set to 15.0 and 10.0 nm, respectively. The different aqueous emulsions were prepared by adding 5 mg of finely divided **1** into 3 mL of distilled water and then ultrasonicating the mixture for 30 min before testing.

1.5. Photocatalytic method

The photocatalytic reaction was performed as follows: The 50 mg of **1** was dispersed in 50 mL aqueous solution of MV (10 mg/L) under stirring in the dark for 30 min to ensure the establishment of an adsorption–desorption equilibrium. Then the mixed solution was exposed to UV irradiation from an Hg lamp (250 W) and kept under continuous stirring during irradiation for 100 min. The batches of 5 mL were taken out after every 10 min and collected by centrifugation for analysis by UV–Vis spectrometer. Also, the simple control experiment was also performed under the same condition without adding any catalyst.

1.6. Computational details

In order to get information regarding the probable photocatalytic mechanism of 1 density functional theory (DFT) calculations were performed. The geometry optimizations were performed using the B3LYP exchange-correlation functional [13]. For all the atoms except Cd 6-31G** basis set was used for geometry optimization, while for Cd CEP-121G basis set was used. All the calculations were performed using Gaussian 09 programme [14a]. GaussSum 3.1 was used to obtain density of state (DOS) plots [14b].

2. Results and discussion

2.1. Crystal structure

$[Cd(L)(Hbpz)]_n$: The single crystal X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic crystal system with *C*2/*c* space group. The asymmetric unit of **1** comprises of one Cd(II) ion, one L ligand, and one protonated bpz ligand. The coordination environment of the Cd(II) ion is presented in Fig. 1a. The Cd1 center is having octahedral geometry and is bonded by two pyrazole nitrogen atoms from two bpz ligands (Cd1–N2 = 2.207(4) and Cd1–N3 = 2.306(5) Å) and four oxygen atoms from two adjacent L anions (Cd1–O1 = 2.424(4), Cd1–O2 = 2.301(4), Cd1–O3 = 2.555(7), Cd1–O4 = 2.302(4) Å). Three carboxylic groups of the H_3L ligand are completely deprotonated and two of three carboxylate groups connect two Cd(II) centers to form a 1D [–L–Cd–L–] chain, while the third carboxylate group does not undergo coordination and may function as the potential active site (Fig. 1c). Interestingly, the uncoordinated carboxyl groups point towards the interior of channels (Fig. 1d). Each bpz ligand display *anti*-conformation and connects two Cd(II) ions, forming a 1D infinite chain (Fig. 1b). These 1D infinite [–bpz–Cd–bpz–] chains are bridged by the above 1D [–L–Cd–L–] chains to construct a 2D grid-like network (Fig. 1d). Recently we had reported a coordination polymer having formula $[Zn(L)(bpz)]_n$ (H_2L = 4,4′-{[1,2-phenylenebis-(methylene)]bis (oxy)} dibenzoic acid) [6d] where the L^{2-} and bpz ligands link the chains to give the 2D network. The adjacent 2D networks thread into the space of each other to generate a 3D supramolecular structure. The different type of networks in the CP are arising because of the various conformations of the two carboxylate linkers. Sun et al., also have reported a series of Cu(II)-based MOFs using diverse dicarboxylates as auxiliary ligands under solvothermal conditions. The results indicated that changing the dicarboxylates from flexible aliphatic, rigid aromatic, to semi-rigid may lead to the different structural motifs which obviously can be controlled [7,15].

2.2. IR spectra, X-ray powder diffraction studies and thermal stability

The IR spectrum of **1** displays main characteristic absorption bands in the range of 1372–1615 cm^{-1} which can mainly be attributed to the asymmetric and symmetric stretching vibrations associated with the carboxylate groups [16]. The characteristic absorption band of –COOH group was not observed at 1700 cm^{-1} which indicates complete deprotonation of carboxylate groups of H_3L ligand [17]. The bands at ~1509 cm^{-1} can be assigned to the ν(C═N) of the imidazole ring of bpz ligand (Fig. S1). To determine whether the crystal structures are truly the representative of the bulk materials used for property studies, X-ray powder diffraction (XRPD) experiments were carried out for **1** (Fig. S2). The diffraction peaks of the experimental and simulated patterns matches fairly will with the key positions which confirms the phase purity of the bulk sample. To evaluate the thermal stability of **1**, thermogravimetric analyses (TGA) were performed under nitrogen atmosphere (Fig. S3). For anhydrous **1**, the decomposition of the organic ligands occurs from a temperature of 320 °C. The large weight loss occurred in a temperature range from 342 to 875 °C, corresponding to the decomposition of the organic ligands (obsd 79.5%, calcd 81.3%). The remaining residue is attributed to the generation of CdO (obsd 22.6%, calcd 21.3%).