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A 3D Ag(I) metal-organic framework for sensing luminescence and photocatalytic activities

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ABSTRACT

A fluorescent metal-organic framework (MOF), $[Ag(btx)_{0.5}(DCTP)_{0.5}]_n$ (**1**) (H_2DCTP = 2,5-dichloroterephthalic acid and btx = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene) has been hydrothermally synthesized and characterized by IR spectroscopy, elemental analysis, powder X-ray diffractions and thermogravimetry. The framework of **1** can be classified as a binodal (4,4)-connected PtS topological network. The fluorescence explorations demonstrated that **1** shows selective and sensitive detection towards $Cr_2O_7^{2-}$ with high quenching efficiency of $1.92 \times 10^4\ M^{-1}$. The rapid and efficient response of **1** to $Cr_2O_7^{2-}$ ion suggests that this material could be used as a luminescent sensor for $Cr_2O_7^{2-}$ ion. Meanwhile the photocatalytic properties of **1** for the degradation of RhB have also been investigated under UV radiation. The possible photocatalytic mechanisms were also speculated. Hence, **1** can become multi-functional material in sensitive detection and effective removal of some environment pollutants in industrial waste water solutions.

1. Introduction

Design and assembly of multifunctional metal-organic frameworks (MOFs) have been extensively investigated not only due to their fascinating architecture but also for the combination of the individual properties associated with inorganic and organic components [1–4]. Among all MOFs, fluorescent MOFs become potential candidates for sensing materials because of their high fluorescence intensity, tunable porosities and bulk-conjugated backbones being able to transmit host-guest interactions to detectable changes [5,6]. Nowadays, water pollution has become a global environmental issue, a lot of fluorescent MOFs have been prepared to detect toxic organic small molecules and ion pollutants from industrial wastewater [7–10]. The prime ion pollutants commonly contain $Cr_2O_7^{2-}$, owing to severe damage to human health and environment and can be adsorbed on solid substances and accumulated into sediments in water bodies. Hence, it is essential to explore new fluorescent materials for detection and capture of above ion. Besides, wastewaters also caused serious environmental pollution due to their toxicity and degradation-resistant [11–13]. An effective and environmentally-friendly method need to be adopted for degrading organic pollutants before draining the wastewater into the environment. Recently, photocatalysis technology has become promising method in the destruction of organic contaminants for their environmental protection, good reproducibility and easy handling [14–16]. Nevertheless, the application of metal-organic framework materials simultaneously treated as fluorescence probe and photocatalysts are still limit.

In this paper, we utilized flexible 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (btx) ligand and halogenated linear 2,5-dichloroterephthalic acid (H_2DCTP) to act as building blocks. Flexible N-donor bridging ligands not only possesses the merits of nitrogen heterocyclic ring, but also can freely twist to interact with metal centers, the btx ligand is good candidate for the formation of novel architectures for their good coordination abilities to metal centers and multiple coordination modes [17–20]. Finally, a 3D Ag(I) metal-organic framework, $[Ag(btx)_{0.5}(DCTP)_{0.5}]_n$ (**1**) were successfully synthesized by hydrothermal methods and characterized by IR spectroscopy, elemental analysis, powder X-ray diffractions and thermogravimetry. In addition, fluorescence sensing and photocatalytic activities of **1** have been investigated in detail.

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2. Experimental

2.1. Materials and methods

The reagents and solvents which we used were commercially available and did not need further purification. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku D/Max-2500 diffractometer. IR spectra were recorded on an Avatar 360 (Nicolet) spectrophotometer using KBr pellets in the region of 4000−400 cm^{-1}. The elemental analyses of C, H and N were carried out by a PerkinElmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed by heating the crystalline sample from room temperature to 800 °C on a NETZSCH TG 209 thermal analyzer with a heating rate of 10 $°C \cdot min^{-1}$ under N_2 atmosphere. The fluorescence spectra of solid samples were obtained by using FS5 fluorescence spectrophotometer equipped with a continuous xenon lamp. Solid-state UV/Vis diffuse reflectance spectra were measured using a UV−Vis Puxi T9 UV−visible spectrophotometer, and $BaSO_4$ was used as a reflectance standard.

2.2. Synthesis of $[Ag(btx)_{0.5}(DCTP)_{0.5}]_n$ (**1**)

A mixture of AgOAc (0.2 mmol, 33.4 mg), btx (0.1 mmol, 24.0 mg), H_2DCTP (0.1 mmol, 23.5 mg), and H_2O (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 140 °C for 3 days under autogenous pressure. Afterwards, the autoclave was cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block-like crystals were obtained. Yield: 32.6% based on Ag. Calcd for $C_{10}H_7AgN_3O_2Cl$ (344.51): C, 34.86; H, 2.05; N, 12.20%. Found: C, 34.75; H, 2.16; N, 12.25%. IR (KBr, cm^{-1}): 3114 w, 3087 w, 1580 s, 1519 m, 1406 s, 1318 m, 1146 m, 1074 m, 890 w, 823 w, 722 m, 672 m.

2.3. X-ray crystallography

Crystallographic data for **1** was performed on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) with ω scan mode at 296(2) K. The structure of **1** was solved by direct methods and refined with full-matrix least-squares technique based on F^2 using the SHELXL-2014 program [21]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed in geometrically calculated positions and refined with isotropic thermal parameters riding on the corresponding parent atoms. Crystallographic data and structure determination summaries for **1** are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1
The Crystal data and structure refinement for **1**.

	1
Formula	$C_{10}H_7N_3AgO_2Cl$
Formula weight	344.51
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	6.4600(3)
b (Å)	8.0210(4)
c (Å)	11.2580(5)
α (°)	100.551(6)
β (°)	106.423(5)
γ (°)	97.844(6)
V ($Å^3$)	539.0(4)
Z	2
D_c, mg/m^3	2.123
μ, mm^{-1}	2.108
$F(000)$	336
R_{int}	0.0193
GOF	1.118
R_1/wR_2 ($I > 2\sigma(I)$)	0.0421/0.1114
$\Delta\rho$ min/max, $eÅ^{-3}$	−0.821, 0.877

2.4. Photocatalytic experiments

We employ UV light irradiation to photodegrade the RhB (10 mg/L). The photodegradation process as follows: 0.01 mmol powders of **1** prepared by ultrasonic irradiation as heterogeneous catalyst was mixed together with 50 mL of RhB, magnetically stirred in the dark for 1 h to ensure the equilibrium. Then the solution was exposed to UV light from a 300 W high-pressure mercury lamp, kept stirring during irradiations. 3.0 mL of the suspension was taken out every several minutes, separated through centrifugation, and analyzed by an UV/visible spectrophotometer. In addition, the control experiments on the degradation of RhB in the absence of any photocatalysts under the same condition. The possible photocatalytic reaction mechanism has been tested through introducing 0.2 mL *t*-butyl alcohol (TBA), 15 mg benzoquinone (BQ), and 15 mg ammonium oxalate (AO) under same conditions, respectively.

2.5. Fluorescence measurements

In order to investigate the potential of **1** for sensing anions, 4 mg powders of **1** was immersed into 4 mL of water solutions containing 0.001 M K_yN ($N^{y-} = Cr_2O_7^{2-}$, NO_3^-, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, IO_3^-, CrO_4^{2-} or MnO_4^-), which was treated by ultrasonication for 1.0 h. Aging for over 24 h, shaking, filtering, and drying in air, fluorescence sample materials were obtained, the corresponding fluorescence emission spectra were recorded at room temperature.

3. Results and discussion

3.1. Crystal structure of $[Ag(btx)_{0.5}(DCTP)_{0.5}]_n$ (**1**)

1 crystallizes in triclinic space group $P\bar{1}$ and shows a three-dimensional structure. In the asymmetrical unit, there exists one independent Ag(I) center, one-half of btx ligand and half $DCTP^{2-}$ anion. As depicted in Fig. 1a, each Ag center coordinates to two bridging btx ligands (Ag1−N1 = 2.273(4) Å and Ag1−N3A = 2.318(4) Å, symmetry code: A = $x - 1, y, z$) and two bis-bidentate $DCTP^{2-}$ carboxylate oxygen atoms (Ag1−O2 = 2.353(4) Å and Ag1−O1B = 2.385(4) Å, symmetry code: B = $-x + 1, -y + 2, -z + 1$), giving a distorted tetrahedron geometry with a τ_4 value of 0.58 [22].

In **1**, the btx ligand shows *trans*-conformation with two triazole rings being in parallel fashion, and the $N_{donor} \cdots N\text{-}C_{sp3} \cdots C_{sp3}$ torsion angle for the btx ligand is 180.00°. The btx ligands adopt μ_4-bridging modes to bridge neighboring four Ag(I) centers to assemble into infinite 1D $[Ag_2(btx)]_n$ ladder chains (Fig. 1b). When searching the Cambridge Structural Database (version 5.37, Feb update 2017) for coordination modes of btx ligands, only two structures were found, featuring this μ_4-bridging coordination mode [23,24]. Moreover, each deprotonated $DCTP^{2-}$ ligand with (κ^1)-(κ^1)-(κ^1)-(κ^1)-μ_4 mode links the neighboring Ag atoms resulting in generation of a binuclear $[Ag_2(COO)_2]$ cluster, spanning the non-bonding distance of Ag···Ag is 3.481(2) Å, these binuclear units is then further linked through $DCTP^{2-}$ ligands alternately to form a 1D $[Ag_2(DCTP)]_n$ array (Fig. 1c). The $[Ag_2(DCTP)]_n$ chain motifs and ladder $[Ag_2(btx)]_n$ chain motifs intersect to form a 3D framework by sharing same Ag(I) ions (Fig. 1d), which is stabilized by hydrogen bonding between btx ligands and $DCTP^{2-}$ carbonyl groups (H6···O2 = 2.317(5) Å, C17−H17···O3 = 149°). In order to ascertain the underlying topology of **1,** a calculation is performed with TOPOS 4.0 professional software [25]. We have used the standard simplification mode with the Ag(I) center connects two btx ligands and