A 7-fold interpenetrated 3D porous coordination polymer (PCP) with nitrobenzene sensing properties

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Abstract

A Zn(II)-based porous coordination polymer (PCP) $\{[\text{Zn}_2(\text{ppt})_2(\text{fdc})(\text{H}_2\text{O})_2] \cdot 2\text{DMF}\}_n$ (**1**) (H_2fdc = 9H-fluorene-2,7-dicarboxylic acid, Hppt = 3-(2-pyrazinyl)-5-(4-pyridyl)-1,2,4-triazole) has been synthesized under hydrothermal conditions. The resulting PCP shows a 7-fold interpenetrated 3D structure that can be simplified as a diamond-like structure with ZnI as node and fdc^- and $\text{Zn}(\text{ppt})_2$ as spacers. It exhibits strong luminescence at room temperature in solid-state. Luminescent property study shows that **1** can be used as a fluorescent sensor for nitrobenzene (NB).

Keywords: zinc coordination polymer; 7-fold interpenetrated; fluorescence; nitrobenzene sensing

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Nitrobenzene (NB) is widely used as an important raw material in plastic processing, chemical synthesis of pesticides and the production of aniline^[1,2]. Moreover, it is an important component of industrial explosives and it can be found in many mines all over the world.^[3-5] Due to its high toxicity and accumulation characteristics it could lead to serious environmental and security problems. So it is urgent to detect such toxicity substance. However, the traditional methods like gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC) are used for detecting these substances still have many drawbacks such as expensive instrumentation, low portability and selectivity.^[6] It is still a challenge to gain novel luminescent sensors.

Porous coordination polymers (PCPs) also known as metal-organic frameworks (MOFs) have received considerable attention because of their potential applications in the fields such as photoluminescence, gas storage/separation, magnetic properties, sensor and catalysis.^[7-12] Among these applications, the luminescent properties of MOFs have attracted attention for a long time. Recently, Ma *et al.* reported a novel Zn-MOF $[\text{Zn}_3(\text{TDPAT})(\text{H}_2\text{O})_3]$ [TDPAT = 2,4,6-tris(3,5-dicarboxyl phenylamino)-1,3,5-triazine] with high luminescent intensity. After dispersed in different solvents, the compound shows highly selective sensor for NB.^[13] Liu *et al.* reported a porous luminescent Zn-MOF $[\text{Zn}_2(\text{TCPPE})]$ $\{\text{H}_4\text{TCPPE} = \text{tetrakis}[4-(4\text{-carboxyphenyl})\text{phenyl}]\text{ethane}\}$ with highly fluorescence quenching effect towards NB.^[14] Thus the luminescent MOFs are ideal sensors for NB.

The suitable ligand is important to build a luminescent PCP. We noticed that fluorene has large π conjugation system and always shows strong fluorescent intensity. Moreover, it is easy to introduce functional group at the aromatic 2,7-positions.^[15] In this paper, we use the 9H-fluorene-2,7-dicarboxylic acid (H_2fdc)^[16] to construct a Zn-based luminescent PCP with the support of 3-(pyridine-4-yl)-5-(pyridin-2-yl)-1H-1,2,4-triazole (Hppt)^[17]. In the present work, compound $\{[\text{Zn}_2(\text{ppt})_2(\text{fdc})(\text{H}_2\text{O})_2] \cdot 2\text{DMF}\}_n$ (**1**) was obtained under hydrothermal conditions. It has a 7-fold interpenetrated 3D structure. This interpenetrating phenomenon can be observed frequently in the self-assembling system.^[18,19] The luminescent and sensing properties of compound **1** were studied at room temperature.

Compound **1** was prepared by mixing H₂fdc, Hppt, Zn(NO₃)₂·6H₂O in a H₂O/DMF solution in a 6 mL sealed glass-tube under hydrothermal conditions.^[20] It is found that temperature and molar ratio are important for the formation of the pure product. When the temperature was raised to 120 °C, an unknown light yellow precipitate was formed that was not characterized. Increasing in the content of H₂fdc [H₂fdc:Hppt:Zn(NO₃)₂·6H₂O = 2:1:4] or reduction of H₂fdc [H₂fdc:Hppt:Zn(NO₃)₂·6H₂O = 1:2:4] will lead to the formation of the uncharacterized white precipitate.

Figure 1 View of the coordination environments of Zn(II) ions in compound **1**.

Symmetry codes: A: 1-x, y, 3/2-z; B: 1-x, -1+y, 1/2-z.

Single crystal X-ray diffraction analysis reveals that compound **1** has a 7-fold 3D interpenetrated framework that crystallizes in the monoclinic space group C2/c.^[21] The asymmetric unit consists of two distinct zinc atoms with each has 0.5 occupation, one ppt⁻, half a fdc²⁻ ligand and one coordinated water (Figure 1). Both Zn1 and Zn2 are six-coordinated in an octahedral geometry. Zn1 is coordinated by four oxygen atoms (O2, O3, O2A, O3A.) from two equivalent fdc²⁻ ligands and two nitrogen atoms (N6 and N6A) from two ppt⁻ anions. Zn2 is coordinated by four nitrogen atoms (N2, N4, N2B, N4B) from two ppt⁻ anions and two oxygen atoms (O1 and O1B) from two coordinated water molecules. The Zn-O and Zn-N bond lengths are in the range of 2.105(7)-2.397(7) Å and 2.035(2)-2.192(3) Å, respectively, which are comparable to [Zn₄(Hbpvp)₂(BTC)₃(HCOO)(H₂O)₂·4H₂O [Zn-O: 2.005(3)-2.276(3); bpvp = 3,5-bis-(2-(pyridin-4-yl)vinyl)pyridine; H₃BTC = 1,3,5-benzenetricarboxylic acid]^[22] and {[Zn₂(TZI)(OH)(H₂O)₂](H₂O)}_n [Zn-N: 2.018(4)-2.138(4); H₃TZI = 5-(1H-tetrazol-5-yl)isophthalic acid].^[23] The Zn1 atoms were bridged by two carboxylate groups into a zigzag chain along the c-axis.

These chains are connected by $\text{Zn}(\text{ppt})_2$ into a 3D network with large pores. From a topological point of view, the 3D architecture can be treated as a 6^6 diamondoid network with Zn1 as node and fdc^- and $\text{Zn}(\text{ppt})_2$ as spacers.^[24] Although the single 3D net has a large pore size, its void space is interpenetrated by other six independent 3D frameworks, resulting in the 7-fold interpenetrated structure (Figure S1). The potential void in each unit cell is $1042.7 \text{ \AA}^3$ (24.1% of the unit cell volume).

Figure 2 View of the 3D framework for compound **1** along the c-axis.

The experimental powder X-ray diffraction (PXRD) patterns are in good agreement with the simulated ones, indicating the obtained crystal materials are identical (Figure S2). In different organic solvents compound **1** could maintain its crystalline, confirming the stability of compound **1**. Thermogravimetric analysis shows a weight loss (19.5%) in the temperature range 50-250 °C, in agreement with the calculated value of 18.0% for the removal of two guest DMF and two coordinated water molecules (Figure S3).

The luminescent properties for compound **1** as well as the free ligands were investigated in solid-state at room temperature. As shown in Figure 3a, the emission peaks of the free ligands Hppt and H_2fdc display fluorescent emission band at 543 nm and 425 nm, respectively. In comparison, compound **1** shows an emission peak at 466 nm with fluorescent intensity of 6912, which is stronger than that for H_2fdc (429) and Hppt (979). The fluorescent enhancement in compound **1** can partly attribute to the formation of the 3-D structure, which has enabled the rigidity. In addition, the $\pi \cdots \pi$ stacking interactions (the closest distance between the aryl planes is $3.527 \text{ \AA}$) in compound **1** also contribute to the enhancement of fluorescence.^[25] The high fluorescent intensity makes it possible to sense small

molecules.

Figure 3 (a) The emission spectra for compound **1** ($\lambda_{\text{ex}} = 354 \text{ nm}$), Hppt ($\lambda_{\text{ex}} = 318 \text{ nm}$) and H₂fdc ($\lambda_{\text{ex}} = 375 \text{ nm}$).

(b) Emission spectra of compound **1** dispersed in different solvents ($\lambda_{\text{ex}} = 419 \text{ nm}$).

The luminescent properties of compound **1** dispersed in different solvents such as ethanol, chlorobenzene, dichloromethane, acetonitrile, acetone, methanol, ethanol and nitrobenzene have been studied systematically. As shown in Figure 3b, the maximum emission peaks show an obvious red-shift in organic solvents except nitrobenzene. This red-shift is attribute to the solvatochromatic effect.^[26,27] Interestingly, the fluorescence of compound **1** disappeared in nitrobenzene solution. This is the typical fluorescent quenching phenomena, which may be due to the electron transfer from the benzene groups of H₂fdc and Hppt ligands to nitrobenzene.^[28-30] Thus, compound **1** could be used as a probe for sensing nitrobenzene.

In summary, we synthesized a 7-fold interpenetrated luminescent PCP with H₂fdc and Hppt as ligands. It displays high fluorescence intensity and shows highly sensing property on nitrobenzene. This work reveals that the using of potential fluorescent ligand such as H₂fdc could form typical PCP for sensing of toxic chemical molecules. Further work is in progress to study the sensing properties for toxic metal ions.

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Appendix A. Supplementary data

CCDC 1445023 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data containing Table S1, Figures S1, S2, S3 and S4 to this article can be found online at

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[20] A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (12 mg, 0.04 mmol), Hppt (4.48 mg, 0.02 mmol), H_2fdc (5.04 mg, 0.02 mmol), 0.5 mL of H_2O and 1.5 mL of DMF were sealed in a 6 mL glass-tube and heated at 90 °C for 2 days. Pale yellow crystals were obtained after the mixture was cooled to room temperature (Yield: 36%, based on Hppt). Anal. calcd for $\text{C}_{43}\text{H}_{40}\text{N}_{14}\text{O}_8\text{Zn}_2$: C, 51.05; H, 3.99; N, 19.38. Found: C, 50.84; H, 3.92; N, 19.11%. IR (KBr, cm^{-1}): 3411.7 $\text{cm}^{-1}(\text{s})$, 1655.6 $\text{cm}^{-1}(\text{s})$, 1618.6 $\text{cm}^{-1}(\text{s})$, 1437.1 $\text{cm}^{-1}(\text{m})$, 1385.9 $\text{cm}^{-1}(\text{m})$, 1325.5 $\text{cm}^{-1}(\text{m})$, 1187.5 $\text{cm}^{-1}(\text{w})$, 1061.0 $\text{cm}^{-1}(\text{w})$, 771.2 $\text{cm}^{-1}(\text{w})$, 716.4 $\text{cm}^{-1}(\text{w})$.

[21] Single crystal X-ray diffraction data for compound **1** was carried out on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure was solved with direct method and refined with the full-matrix least-square method on F^2 using SHELXL.^[31] All of the non-hydrogen atoms were refined anisotropically. All the H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic data for compound **1**: $\text{C}_{43}\text{H}_{40}\text{N}_{14}\text{O}_8\text{Zn}_2$, $M_r = 1011.67$, monoclinic, space group $C2/c$, $a = 33.619 \text{ \AA}$, $b = 7.0530 \text{ \AA}$, $c = 20.347 \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 116.04^\circ$, $\gamma = 90.00^\circ$, $V = 4334.8 \text{ \AA}^3$, $Z = 4$, $D_c = 1.550 \text{ g/cm}^3$, $F(000) = 2080.0$, $\text{GOF} = 1.093$, $\mu = 1.179 \text{ mm}^{-1}$, $R(\text{int}) = 0.0256$, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0323$ and $wR_2 = 0.0873$.

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