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A supramolecular microporous network of zinc(II) coordination polymer for highly selective fluorescent detection of Pb^{2+}

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A hydrogen bonded microporous network with Lewis basic N sites, viz., $\{[Zn(TZ\text{-}HIP)(HPYTZ)(H2O)2]\cdot 3H_2O\}_n$ [TZ-HIP = 5-(tetrazol-5-yl)isophthalic acid, HPYTZ = 3,5-di(4-pyridyl)-1H-1,2,4- triazolate ligand] has been obtained from the dual ligand system of polydentate N-heterocyclic carboxylate and dipyridyl-type ligands. Single crystal X-ray diffraction analysis shows that the adjacent Zn(II) centers are bridged by HTZ-H_2IP ligand to form 1D chain with HPYTZ molecules as free lateral arms. The paralleled chains are connected by H-bonding interactions to produce the 3D microporous network with 1D pores. It is interesting that the uncoordinated N atoms (Lewis base sites) pores cause Pb^{2+} ions to produce a remarkably enhancing effect on the luminescent intensity of the zinc complex with high sensitivity in the detection range of 10^{-3}-10^{-5}mol L^{-1} concentration limit. This coordination polymer may be used as a sensing material for developing a highly selective and sensitive Pb^{2+} sensor in the biological and environmental materials.

Keywords: Coordination polymers, Dual ligand systems, Microporous networks, Fluorescence, Sensing materials, Zinc, Lead

Lead pollution is a persisting problem to human health, as well as a long-lasting danger to the environment.[1,2] Even very low levels of lead exposure can cause neurological, reproductive, cardiovascular, and developmental disorders.[3-5] Thus, it is very important to develop a simple, inexpensive and rapid method for detection Pb^{2+} with high sensitivity and selectivity in real samples at a very low concentrations. Among various detection techniques, optical detection (via fluorescence changes or colorimetric changes) is the most convenient method due to its simplicity and low detection limit.[6-12] The most important advantage of a fluorescent probe would be the intracellular detection.

Recently, the emergence of multi-functional coordination polymers (CPs) materials is the most significant achievement in fluorescent sensing.[13-15] Differential recognition/binding with guest substrates confined by tunable pore size and functionalized pore surfaces, which can be transduced into externally optical signals, have enabled the CPs to become a new type of fluorescent sensing material for the sensing of ions and small molecules recently.[16-18] Some of those CPs show excellent luminescent sensing properties towards metal ions such as Al^{3+}, Cu^{2+}, Fe^{3+}, etc. This is because the Lewis basic coordination sites existing in the networks of CPs can interact with specific metal ions, resulting in changes in the luminescent intensity of the CPs-based material. Recently, some CPs bearing such sites have been reported, including Eu(III)-CPs with many Lewis basic pyridine nitrogen atoms for sensing of Cu^{2+} ions,[19,20] and Zn(II)-CPs with uncoordinated Lewis-base sites showing excellent luminescence sensing of inorganic ions.[21] However, little work has been devoted to the development of CPs as fluorescent probes that are sensitive to heavy metal like Pb^{2+} ions.

Herein, we present a synthetic strategy to create a multifunctional coordination polymers by employing polydentate N-heterocyclic carboxylate and triazolate-type ligands, such as 5-(tetrazol-5-yl)- isophthalic acid and 3,5-di(4-pyridyl)-1H-1,2,4- triazolate ligand, which has multiple coordinate sites involving polyzole nitrogen atoms, pyridyl nitrogen atoms and carboxylate oxygen atoms. They are both good bridging ligands for constructing multifunctional CPs.[22-29] By such design, a hydrogen-bonded microporous network with exposed Lewis basic nitrogen atoms ($\{[Zn(TZ\text{-}HIP)(HPYTZ)(H_2O)_2]\cdot 3H_2O\}_n$), has been prepared hydrothermally. Further, we have demonstrated that this CPs is capable of detecting Pb^{2+} in water samples. As a sensing material for Pb^{2+}, this CPs has several features including simple preparation procedure, fast detection time, excellent selectivity for Pb^{2+}, and high sensitivity with a detection range of 10^{-3}-10^{-5}mol L^{-1} concentration limit.

Experimental

All reagents used herein were of analytical grade and used as purchased without further purification. Elemental analyses (C, H, N) were performed on a Flash EA 2000 elemental analyzer. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer over a range of 4000–600 cm^{-1}. The thermogravimetric analyses (TGA**)** were performed on a SII EXStar6000 TG/DTA6300 analyzer in flowing N_2 with a heating rate of 10 °C/min. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer using monochromated Cu-Kα radiation (λ = 0.154 18 nm; generator current: 40 mA; generator voltage: 40 kV; scanning scope: 2θ° = 5–50). Luminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Herein, the compounds were synthesized by the hydrothermal method. A mixture of HTZ-H_2IP (0.1 mmol, 23.4 mg), HPYTZ (0.1 mmol, 22.3 mg), $Zn(OAC)_2{\cdot}2H_2O$ (0.1 mmol, 22.0 mg), N,N'-dimethylformamide (DMF, 1.0 mL), and H_2O (5.0 mL) was placed in a 23 mL Teflon liner stainless steel reactor. The vessel was heated to 120 °C for 4 days, and then cooled at 5 °C h^{-1} to room temperature. The obtained colorless crystals filtered off, washed with mother liquid, and dried under ambient conditions. Yield: 42%. Anal. (%): Calc. for $C_{21}H_{23}N_9O_9Zn$: C 41.29, H 3.79, N 20.64. Found: C 42.06, H 3.82, N 20.29. Selected IR (cm^{-1}): 3322 m, 1698 m, 1596 s, 1562 vs, 1554s, 1503 m, 1492 m, 1425 m, 1396 vs, 1303 w, 1294 m, 1215 m, 1146 m, 1013 m, 985 m, 894 m, 861 m, 848 s, 748 m, 722 s, 704 m, 683 m.

Suitable single crystals of complex were mounted on a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.071073 nm) using Φ/ω scan technique at room temperature. Semi-empirical absorption corrections were applied using SADABS. The structures were solved using direct method and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for those bound to water molecules, which were initially located in a difference Fourier map and included in the final refinement by applying geometrical restraints with the O-H distances being fixed at 0.85 Å and U_{iso}(H) equivalent to 1.5 times of U_{eq}(O). All calculations were performed using the SHELXTL-97 program package.[30] Some disordered solvent H_2O molecules in complex are squeezed by PLATON/SQUEEZE program.[31] The details of the structure solutions and final refinements for both complexes are summarized in Table 1. Selected bond distances and angles and hydrogen bonds are listed in Table S1 and Table S2 (Supplementary data).

Results and discussion

Hydrothermal method has been proven to be a powerful approach for the preparation of sparingly organic-inorganic hybrid materials.[32] However, the crystal growth is influenced by various hydrothermal parameters such as the pH value, temperature, molar ratio of the reactant and reactant solvent, etc.[33,34]. In this study, the reaction of melt salt with HTZ-H_2IP and HPYTZ in 1:1:1 molar ratio and reaction medium of DMF and H_2O mixture (V_{DMF}:V_{H2O} = 1:5) produced single crystals suitable for X-ray diffraction analysis. The broad bands in the ~3400–3200 cm^{-1} region in the IR spectra of the zinc coordination polymer belong to the O-H stretching modes within coordinated and guest water molecules.

Table 1 — Crystal and structure refinement data for $\{[Zn(TZ\text{-}HIP)(HPYTZ)(H2O)2]{\cdot}3H_2O\}_n$

Formula	$C_{21}H_{23}N_9O_9Zn$
Formula wt	610.85
Temp. (K)	296(2)
Crystal system	Triclinic
Space group	*P-1*
a (Å)	9.7381
b (Å)	10.8146
c (Å)	16.7466
a (°)	88.643
β (°)	73.4230
γ (°)	63.6540
Vol. ($Å^3$)	1503.85
Z	2
D_{calc} (g cm^{-3})	1.230
μ (mm^{-1})	0.862
F(000)	568
GOF	1.134
R_1	0.0384
$\omega R_2[I>2\sigma(I)]$	0.1225
R_1	0.0488
ωR_2 (all data)	0.1261
θ Range (°)	1.28~25.5
Refl coll/unique	10067 / 5594
R_{int}	0.0258
Completeness to θ (%)	99.7
Data/restraints/parameters	5594 / 0 / 334
$\Delta\rho_{max}$ and $\Delta\rho_{min}$(e nm^{-3})	298, -339
Max. and min. transmission	0.8330 and 0.7581

Single crystal X-ray analysis reveals $\{[Zn(TZ\text{-}HIP)(HPYTZ)(H_2O)_2]\cdot 3H_2O\}_n$ displays hydrogen bonded supramolecular microporous networks. The asymmetric unit contains one Zn(II) atom, one HPYTZ molecule, one double-deprotonated TZ-HIP dianion, two coordinated H_2O and three disordered H_2O molecule as affirmed by TG and elemental analyses. As shown in Fig. 1(a), each Zn(II) ion is five coordinated by three oxygen atoms from one carboxylate group of HTZ-H_2IP and two coordinated water (Zn-O: 1.9761(19) Å-2.143(3) Å), and two nitrogen atoms differentiated from tetrazol group of HTZ-H_2IP and HPYTZ ligands (Zn-N: 2.051(2) Å and 2.053(2) Å), displaying a highly distorted trigonal bipyramidal coordination environment. Therein, the TZ groups, HIP groups and HPYTZ molecules lie in the equatorial plane due to the hard to rotate rigid aromatic ring, and two coordination H_2O occupy the axial positions.

The ZnO_3N_2 polyhedron is bridged by HIP and TZ groups of two HTZ-H_2IP ligands along the *a* direction, forming a 1D chain with HPYTZ molecules as free lateral arms (Fig. 1b). The parallel chains are connected by H-bonds between H_2O molecule and HTZ-H_2IP ligand [O(5W)-H(2W)...N(3); *d*(O5 ···N3) = 2.794(3) Å; ∠(H-O···N3) = 164.8°, O(5W)-H(1W)...O(2); *d*(O5···O2) = 2.716(3) Å; ∠(H-O···O2) = 169.4°, O(6W)-H(3W)...N(1); *d*(O6···N1) = 3.479(4) Å; ∠(H-O···N1) = 161.4°, O(6W)-H(3W)...N(4); *d*(O6···N4) = 2.781(3) Å; ∠(H-O···N4) = 169.7°] forming a layered motif (Supplementary data, Fig. S1). Two adjacent layer blocks are stacked along the *c* direction by the -AAAA- mode and cohered together by H-bonds between pyridine N atoms of HPYTZ molecules and carboxylate O atoms of HIP groups [O(3)-H(22)...N(8) = 2.632(4) Å, ∠(H-O3···N8) = 174.9°] producing its 3D supramolecular networks (Fig. 1c and Fig. 1d) showing linear channels with free aperture of about 5.28 × 12.78 $Å^2$ (the short distance does not include the van der Waals radii) (Supplementary data, Fig. S2). The channels extend parallel to the 1D polymeric chains with

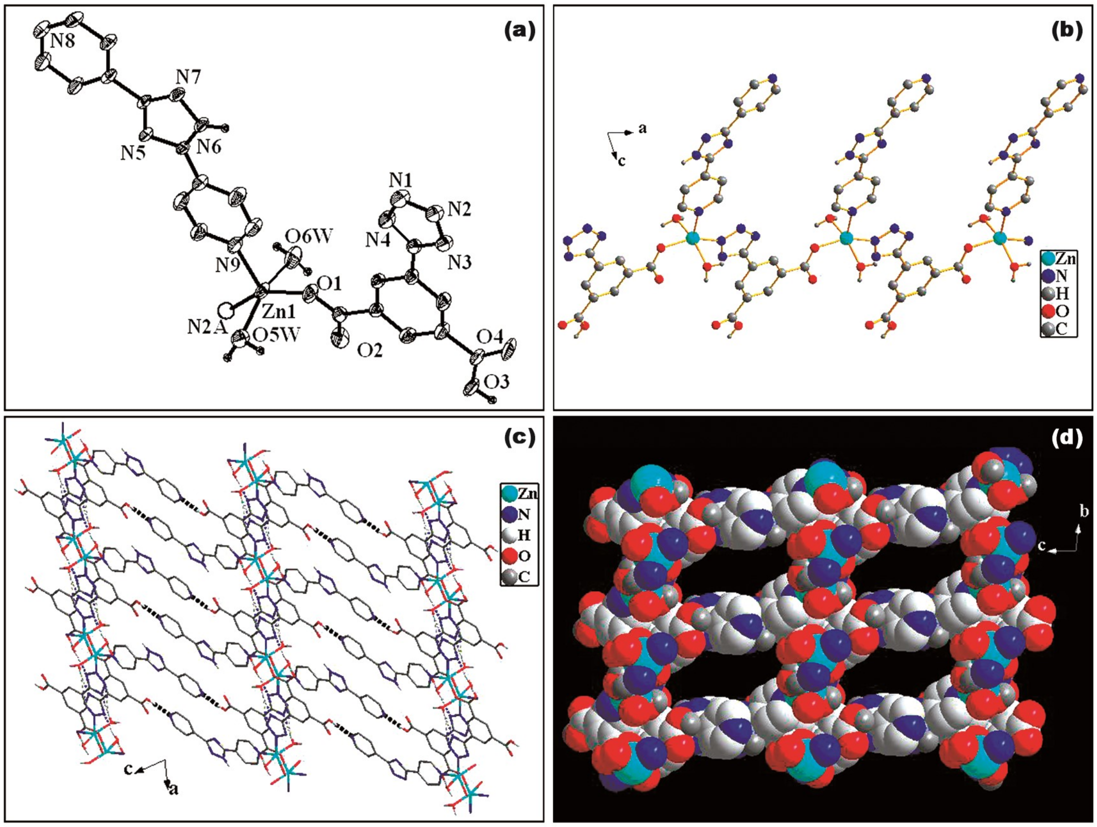

Fig. 1 — (a) View of coordination environment of Zn(II), (b) View of a 1D chain featuring TZ-HIP-bridged Zn(II), (c) Side view of 3D supramolecular network consisting of 1D polymeric chains cohered by H-bonds, and, (d) Stacking view of the supramolecular microporous network. [Symmetry codes: ^{A}1+ x, -1+y, z; Displacement ellipsoids are drawn at the 30% probability level and all hydrogen atoms of carbon atoms are omitted for clarity].

the solvent accessible void of ~31.4%. The details of H-bonds are summarized in supplementary data (Table S2).

Thermogravimetric analysis (TGA) experiments were conducted to determine the thermal stabilities of the complex. TGA reveals that the loss of guest water molecules starts at room temperature (Fig. 2a). The first weight loss of ~15.30% not only includes the loss of three lattice water molecules per formula unit (calcd: 8.85%), but also the loss of two ligated water molecules per formula unit (calcd: 5.89%). The residual solid starts to decompose at 227 °C with a series of consecutive weight losses until 750 °C. The final residual species holds a weight of 34.19% of the total sample, which may be a mixture and could not be specifically identified.

In order to further prove the purity of supramolecular structure, the washed and dried complex was examined by powder X-ray diffraction (PXRD), as shown in Fig. 2b. The result shows the complex still has good crystallinity, because all major peaks in experimental PXRD match quite well that of simulated, indicating that reasonable crystalline phase purity has been obtained. The difference in intensity may be due to the preferred orientation of the microcrystalline powder samples.

The solid-state photoluminescent properties of both the free ligands and zinc complex were investigated in the solid state at room temperature (Supplementary data, Fig. S3). The emission peak of HPYTZ ligand is observed at about 475 nm, whereas the emission peak of zinc complex occurs at 455 nm, both of which may

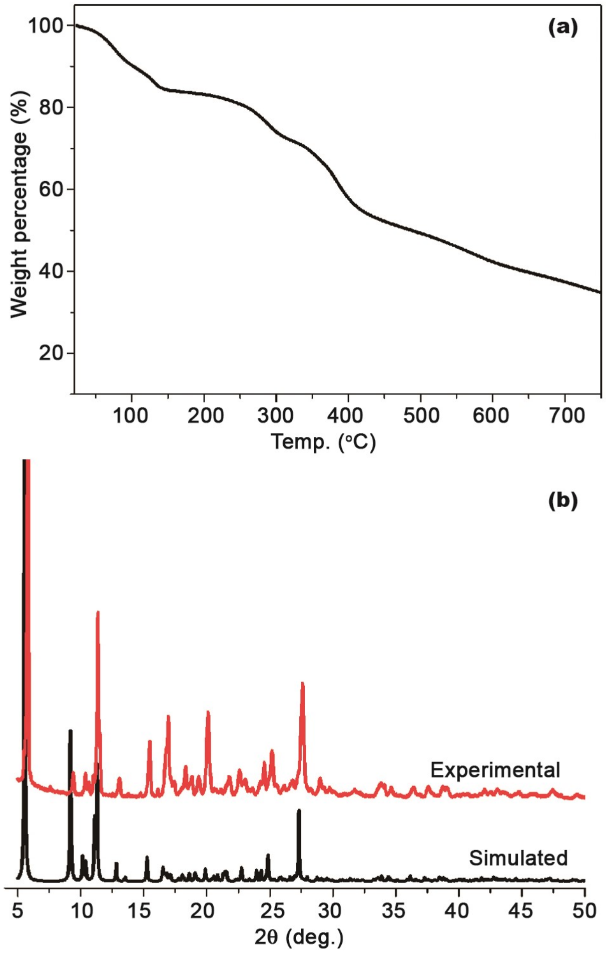

Fig. 2 — (a) TGA and (b) PXRD curves of Zn(II) coordination polymer.

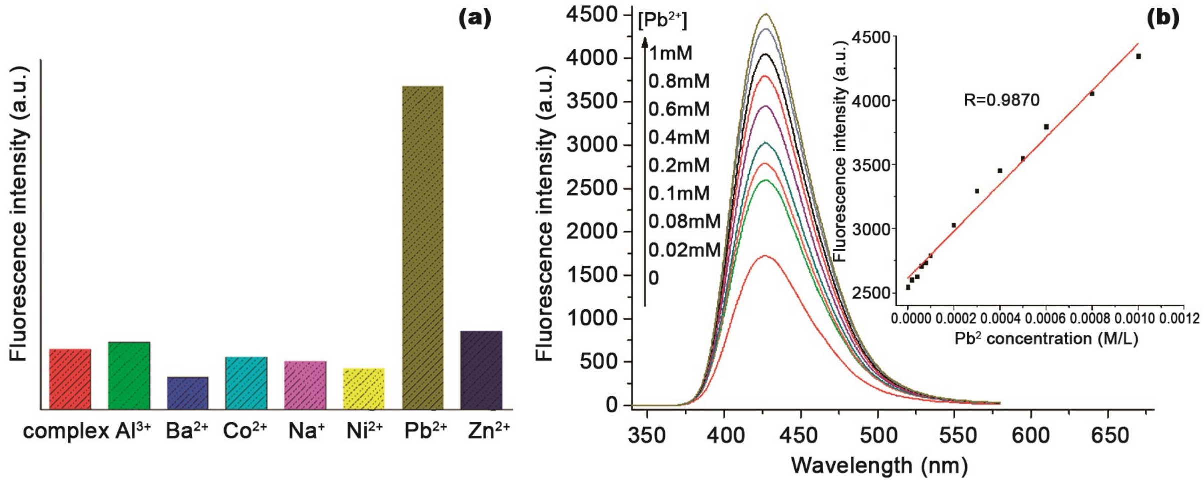

Fig. 3 — (a) Luminescence intensities of the Zn(II) complex treated with different metal ions (0-0.01 mol L^{-1}) in water at ambient temperature, and, (b) Fluorescence responses of the Zn(II) complex for the determination of Pb^{2+} in water. [Inset: linear relationship of fluorescence intensity as a function of Pb^{2+} concentrations].

be assigned to the intraligand charge transfer of HPYTZ ligand since similar emission is observed for the free HPYTZ ligand, and also the HTZ-H_2IP coligand shows almost no contribution to the emissions due to very weak fluorescent emission. Further, an intense emission band at 427 nm was observed in the aqueous solution of zinc complex. In order to examine the ability of selective sensing of metal ions, the complex was ground, and then dispersed by ultrasonic into an aqueous solution containing 0.01 mol/L of nitrate salts of Al^{3+}, Ba^{2+}, Co^{2+}, Na^{+}, Ni^{2+}, Pb^{2+} and Zn^{2+} for 2 h. As presented in Fig. 3(a), there exists a significant enhancing effect to the luminescent intensity of the Zn(II) complex on addition of Pb^{2+} ions. This effect may be used for fabrication of a high-performance luminescence sensor for detecting Pb^{2+} ions. The enhancing effect largely due to the interactions between Pb^{2+} ions and the uncoordinated N atom of the ligands, which may cause the electrons of ligands to transfer from the complex to Pb^{2+} ions, resulting in the observed luminescent enhancement.

Furthermore, the luminescent enhancing of the Zn(II) complex was examined as a function of $Pb(NO_3)_2$ concentration in the range of 0–0.0 mol L^{-1}. The solid samples were immersed in different concentrations of $Pb(NO_3)_2$ for 2 h, and then their luminescence intensity at 427 nm was recorded. When Pb^{2+} concentration increased from 0–0.01 mol L^{-1}, the fluorescence intensity of complex increased continuously (Fig. 3(b)). Pb^{2+}concentrations were proportional to the fluorescence intensity of complex in the range of 10^{-3}-10^{-5} mol L^{-1} (inset in Fig. 3(b)). This concentration limit can detect microscale Pb^{2+} in the solution.

In summary, a hydrogen bonded microporous network with exposed nitrogen atoms displays highly selective sensing of Pb ions through increasing fluorescence. As a sensing material for Pb^{2+}, this compound has distinct features including simple preparation procedure, fast detection time, excellent selectivity for Pb^{2+}, and high sensitivity with a detection range of 10^{-3}-10^{-5} mol L^{-1} concentration limit. Thus, the Zn(II) coordination polymer prepared herein has the potential application as a highly selective and sensitive Pb^{2+} sensor in the biological and environmental fields. Results show that the Lewis base sites in CPs-based materials are critical for the fluorescence response process.

Supplementary data

X-ray crystallographic file (CIF) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1560073. These are available free of charge via the Internet at http://www.ccdc.cam.ac.uk/conts/retrieving. html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, viz., Table S1 & S2 and Figs. S1-S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(08)826-831_SupplData.pdf.

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