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Luminescent microporous metal–organic framework with functional Lewis basic sites on the pore surface: Quantifiable evaluation of luminescent sensing mechanisms towards Fe^{3+}

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ABSTRACT

A systematic study has been conducted on a novel luminescent metal-organic framework, $\{[Zn(bpyp)(L\text{-}OH)]\cdot DMF\cdot 2H_2O\}_n$ (**1**), to explore its sensing mechanisms to Fe^{3+}. Structure analyses show that compound **1** exist pyridine N atoms and -OH groups on the pore surface for specific sensing of metal ions via Lewis acid-base interactions. On this consideration, the quenching mechanisms are studied and the processes are controlled by multiple mechanisms in which dynamic and static mechanisms are calculated, achieving the quantification evaluation of the quenching process. This work not only achieves the quantitative evaluation of the luminescence quenching but also provides certain insights into the quenching process, and the possible mechanisms explored in this work may inspire future research and design of target luminescent metal-organic frameworks (LMOFs) with specific functions.

1. Introduction

Metal-organic frameworks (MOFs), a kind of porous materials formed by assembly of metal ions with functional organic ligands, have attracted intense research attention due to their versatile structural features and great potentials in a wide range of applications [1–6]. The luminescent MOFs are of great interest as sensing materials, owing to their unique fluorimetric detection methods which possess outstanding sensitivity, rapid detection speed and convenience operation [7–9]. Embedding active functional groups such as $–NH_2$, –OH, –COOH and pyridyl groups into the organic ligands to construct MOFs can largely improve their ability to recognize and sense neutral and ionic species [10–14]. To date, MOFs have been developed as materials for the sensors in various application fields. For example, Maji's group has reported a ligand-based luminescent MOF for the selective sensing and removal of metal ions, by exploiting the functional –OH groups on their pore surface [15]. A flexible metal–organic framework turn-off luminescent sensor for the detection of Fe^{3+} and picric acid has been reported by Zhou and co-workers [16]. Jiang's group reported an amine-functionalized metal–organic framework as a sensing platform for DNA detection [17]. Besides, luminescent MOFs can also function as thermometer by the change of color and intensity [18]. However, though the luminescent MOFs working as functional sensors have covered a wide scope, systemic studies and quantitative evaluations on the sensing mechanisms have been rarely explored.

Fe^{3+} ions play a crucial role in many biochemical processes, such as the storage and transport of oxygen to tissues and enzymatic reactions of the mitochondrial respiratory chain [19–21]. Either its excess or deficiency is so detrimental that may cause damage to nucleic acids and proteins such as anemia, diabetes, heart failure, liver damage and Parkinson's disease and so on [22–24]. Thus, the monitoring of Fe^{3+} ions in a highly effective and fast method to detect trace amount Fe^{3+} over other metal ions is of much concern.

We herein report a novel microporous compound, $\{[Zn(bpyp)(L\text{-}OH)]\cdot DMF\cdot 2H_2O\}_n$ (1) [bpyp=2,5-bis(pyrid-4-yl) pyridine, L-OH=5-hydroxyisophthalic acid, DMF=dimethylformamide], containing uncoordinated –OH and pyridyl groups in interlayer channels. Specifically, we show that the compound 1 can work as highly sensitive sensor to Fe^{3+} by luminescent quenching. Besides, the corresponding dynamic and static quenching constants are calculated, achieving the quantification evaluation of the quenching process.

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2. Experimental section

2.1. Materials and general methods

All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400–4000 cm^{-1} region. Photoluminescence analyses were performed on an Edinburgh FLS55 luminescence spectrometer. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-line Century Series epr spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. An Axis ultra spectrometer was selected to measure X-ray photoelectron spectroscopy (XPS).

2.2. Synthesis of $\{[Zn(bpyp)(L\text{-}OH)]\cdot DMF\cdot 2H_2O\}_n$ (1)

A mixture of bpyp (23.3 mg, 0.10 mmol), L-OH (18.8 mg, 0.10 mmol) and $Zn(CH_3COOH)_2\cdot 2H_2O$ (22.2 mg, 0.10 mmol) was dissolved in DMF (2 mL) in a screw-capped vial. After one drop of HNO_3 (62%, aq.) and two drops of H_2O were added to the mixture, the vial was capped and placed in an oven at 105 ºC for 96 h. The resulting single crystals were washed with DMF and dried in air to give **1**. Yield: 35%. Elemental analysis calcd (%) for $C_{26}H_{26}ZnN_4O_8$: C, 53.12; H, 4.46; N, 9.53. Found: C, 54.14; H, 4.87; N, 10.02%. IR (KBr, cm^{-1}; see Fig. S1): 3738(m), 3439(s), 3030(w), 2776(m), 2457(w), 1549(m), 1377(s), 1016(m), 888(m), 815(m), 713(m), 561 (m).

2.3. X-ray data collection and structure determination

The diffraction data were collected at 295(2) for **1**, with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo Kα radiation (λ=0.71073 Å). Absorption corrections were carried out utilizing SADABS routine [25]. The structure was solved by direct methods and refined using the SHELXTL 97 software [26]. Atoms were located from iterative examination of difference Fmaps following least squares refinements of the earlier models. All the atoms except hydrogen atoms, which were fixed at calculated positions and refined by using a riding mode, were refined anisotropically until full convergence was achieved. It was necessary to constrain or restrain a number of bond lengths and angles in the structure in order get a stable refinement and chemically reasonable model. For **1**, the microporous framework was occupied by extremely electron density, which could be assigned to be free solvent molecules. Because these guest solvents in the crystal is highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules [27], and sets of solvent-free diffraction intensities were produced. The free solvent molecules for the **1** were determined by combining single crystal structures, element a microanalysis and TGA date. The crystallographic data and selected bond lengths and angles for **1** are listed in Table S1 and Table S2. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center.

3. Results and discussion

3.1. The structural features

Single crystal X-ray diffraction analysis reveals that polymer **1** possesses a network structure and crystallizes in monoclinic space group *P*21/c. The structure of **1** contains only a distorted tetrahedral Zn(II) atom, which is coordinated to two bpyp and two L-OH ligands with the average Zn–O and Zn–N bond distances of 1.917 and 2.066 Å, respectively. The view of the coordination geometry is shown in Fig. 1**a**. In **1**, the bpyp ligands alternately bridge Zn(II) atoms to form infinite $[Zn(bpyp)]_n$ chains. The adjacent chains are further connected by L-OH to construct wavelike 2D (4, 4) grids layer. It is particularly worth mentioning that the polymeric sheets are further interlinked by hydrogen-bonding interactions (Fig. S2) (O–H···O=2.659 Å) to form an overall three-dimensional channels structure, large cavities are decorated by uncoordinated pyridyl and –OH, as illustrated in Fig. 1**b**. The PLATON calculations suggest that the solvent-accessible volume and porosity are 748.5 $Å^3$ and 28.7% void space after excluding DMF and H_2O.

3.2. Thermal analysis

In order to identify the thermal stability of complex **1**, the thermogravimetric analyses (TGA) has been studied (Fig. S3). The

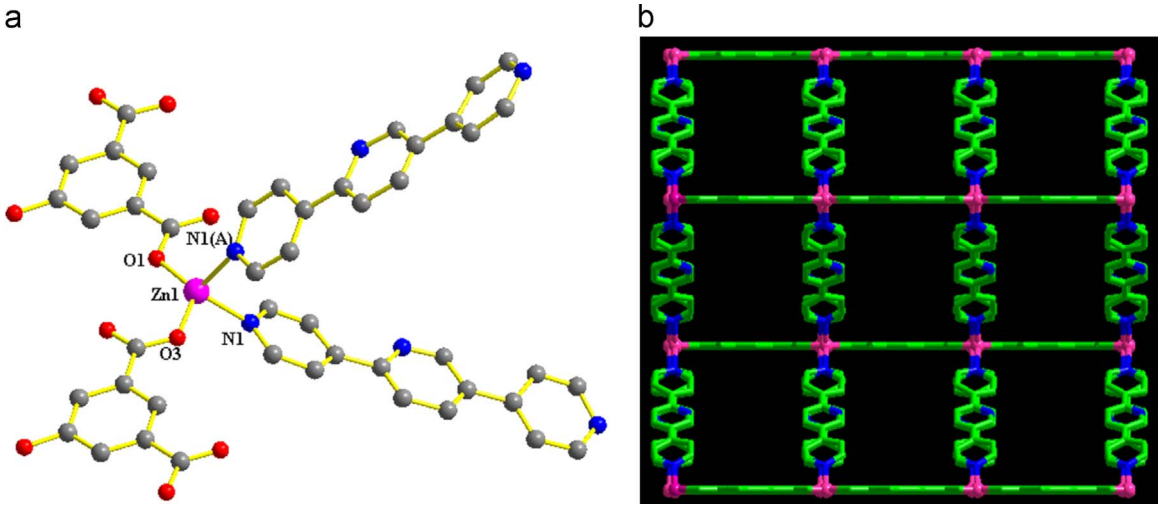

Fig. 1. (a) The coordination environment of Zn in **1** (Symmetry codes: A x, y, 0.5−z); (b) 3D channels structure with uncoordinated pyridyl and –OH.