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A multi-chemosensor based on Zn-MOF: Ratio-dependent color transition detection of Hg (II) and highly sensitive sensor of Cr (VI)

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ABSTRACT

Accurate and visual methods aimed to pollution monitoring were insistent demands of scientists. For this purpose, a novel metal-organic framework (MOF), formulated as $[Zn(tpbpc)_2]$·solvent (Htpbpc = 4′-[4,2′;6′,4″]-terpyridin-4′-yl-biphenyl-4-carboxylic acid), has been isolated and structurally characterized; it exhibits unique (2,8)-connected 8T20 (MOF.ttd) topology with binuclear $[Zn_2(COO)_4N_4]_n$ secondary building units (SBUs) as 8-c nodes and $tpbpc^-$ ligands as 2-c nodes. Strikingly, this is the first multi-responsive MOFs fluorescent sensor for simultaneously detecting Hg^{2+}, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions with high sensitivity and low detection limits in aqueous solution. Meanwhile, the fluorescent sensor for Hg^{2+} exhibits a color transition in seconds which can be observed by the naked eyes. What is more, the chemosensor based on the Zn-MOF for detecting Cr(VI) ions possesses a very low detection down to 10^{-8} M, which is the lowest detection limit among all reported up to date. Importantly, the luminescence can be fast regenerated and its sensing ability can be recycled for more than six times. In addition, the simple MOF-based fluorescent test paper was successfully prepared, which provided a reliable and visual detection of Hg^{2+}, CrO_4^{2-} and $Cr_2O_7^{2-}$ in practical application.

1. Introduction

Recently, the extremely releasing toxic metal ions into the ecological environment from industrial or other pathways have brought about severe global environmental problems and biological health problems because of its toxicity, water stability, and non-degradability [1,2]. Specially, the accumulation of Hg^{2+} in human body, even at a very low concentration, can cause a variety of diseases, such as digestive, kidney, and neurological diseases [3,4]. Chromium, as a kind of common element, is widely used in industrial production, and exists stably in environment with two forms, Cr(VI) and Cr(III) ions. Among them, Cr(VI) is carcinogenic pollutant which can also give rise to environment pollution and human diseases: DNA mutagenesis, cancer, water contamination, and so on. Therefore, the Hg(II) and Cr(VI) have been classified as extremely toxic pollution by the United States Environmental Protection Agency (U.S. EPA) [5–7]. More important, it is imperative to detect Cr(VI) and Hg(II) ions in aqueous solution.

Metal–organic frameworks (MOFs), as a novel class of crystalline porous materials, are fabricated of inorganic metal ions/clusters linked by appropriate organic ligands. Thereinto, luminescent metal–organic frameworks (LMOFs) are bright, flourishing series of potential materials, which not only display prominent optical properties but also possess designable architectures, well-defined topologies, tunable chemical and physical properties [8–11]. Several reasons effect the luminescent properties of MOFs, such as the structural diversity, coordination environments of the metal centers, and the characteristics of the pore channels, which connect guest species through coordination bonds, hydrogen-bonding and π–π interactions, etc [12,13]. For these reasons, considerable efforts have been made to tune the channel microenvironment, and a delicately designed LMOFs can be used to sensitively and selectively recognize to differential ions and small molecules [14–16]. Up to now, some multifunctional luminescent MOFs have been constructed for harmful ions detection [17–19]. Nevertheless, as is well-known, there are no reports based on MOFs to distinguish Cr(VI) and Hg(II) ions through fluorescence change. In this contribution, a three pyridine rings carboxylate ligand was used to combine with Zn(II) to form a new 3D MOF, $[Zn(tpbpc)_2]$·solvent (Zn-MOF), which exhibits a characteristic luminescence output. Meanwhile, the uncoordinated nitrogen atoms in the pore channel as functional sites can offer an ideal environment to metal ions and thus resulting in a regenerable ratiometric manner in response to Hg^{2+} or high selectivity and

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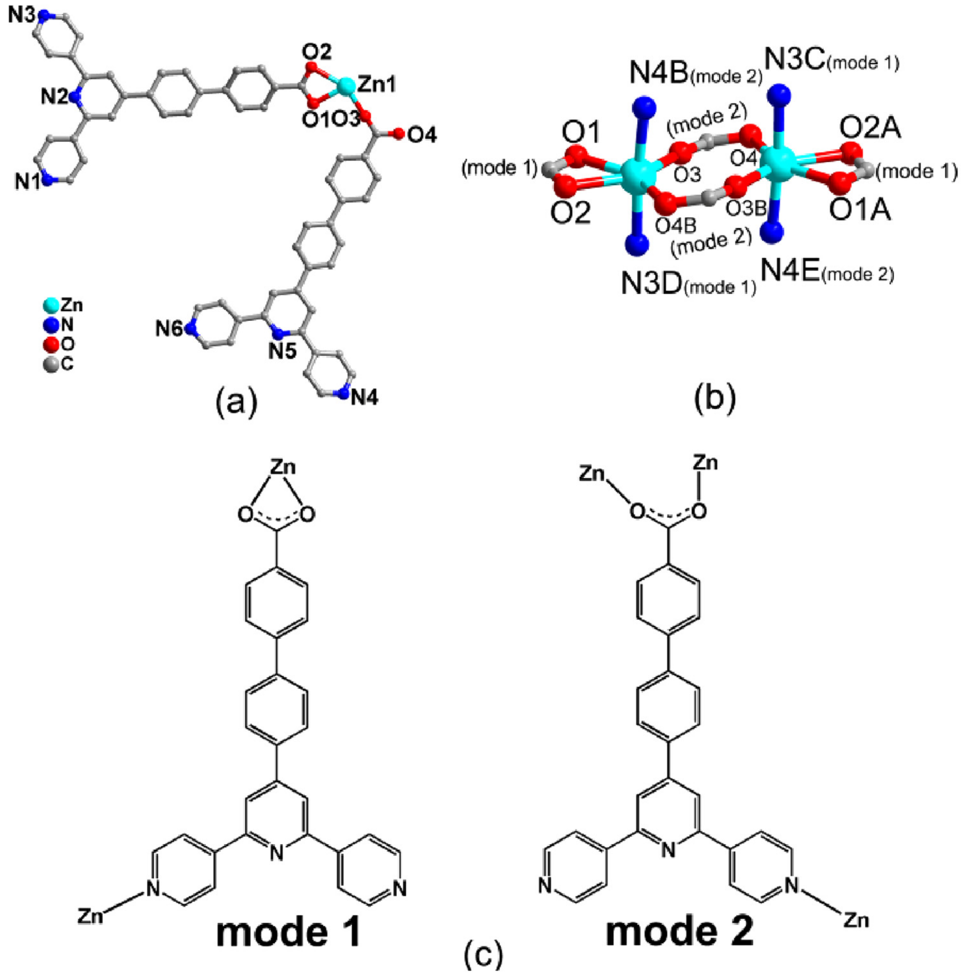

Fig. 1. (a) The asymmetrical unit of Zn-MOF with hydrogen atoms omitted for clarity. (b) Coordination environment of dinuclear SBUs $[Zn_2(COO)_4N_4]_n$ unit. A: $-x+1$, $-y+2$, $-z$; B: $x+1$, $-y+2.5$, $z+0.5$; C: $-x+1$, $y+1.5$, $-z+0.5$; D: x, $-y+0.5$, $z-0.5$; E: $-x$, $y-0.5$, $-z-0.5$. (c) Different coordination modes of $tpbpc^-$ ligands in Zn-MOF.

sensitivity to CrO_4^{2-} and $Cr_2O_7^{2-}$ in aqueous media with a broad linearity region.

2. Experimental

2.1. Materials and methods

All reagents and medicines were purchased from commercial sources and used as received. Infrared spectra were taken out on a PerkinElmer Spectrum Two FT-IR spectrometer from 4000 to 400 cm^{-1} with KBr pellet. Powder X-ray diffraction patterns (PXRD) were measured using crushed single crystals on an EMPYREAN PANALYTICAL apparatus with Cu–Kα radiation ($\lambda = 1.5406$ Å). Thermogravimetric analysis of Zn-MOF was measured from 30 to 1300 °C under nitrogen protection recording on a NETZSCH STA409 pc instrument. Fluorescence spectra were carried out on an Edinburgh FLS920 spectrophotometer using 150 W xenon lamp. The slit width of both excitation and the emission source were kept at 2.5 nm to maintain consistency.

2.2. Synthesis of $[Zn(tpbpc)_2]$·solvent (Zn-MOF)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.05 mmol, 0.0149 g), Htpbpc (0.03 mmol, 0.0129 g), DMF (4 mL), and H_2O (4 mL) were placed in a 23 mL Teflon-lined stainless steel autoclave, which was heated at 120 °C for 3 days and then cooled down to room temperature with a rate of 5 °C/h. After washing with deionized water and drying at ambient temperature, colorless block crystals were obtained, which were insoluble in common organic solvents. Yield: 0.01 g, 72.28% (based on Htpbpc ligand). Anal.Calcd for $C_{56}H_{36}N_6O_4Zn$ (%): C, 72.93; H, 3.93; N, 9.11. Found: C, 72.68; H, 3.85; N, 9.06. IR (KBr pellet, cm^{-1}): 1667.63 (s), 1598.08 (s), 1533.88 (s), 1405.81 (s), 1094.84 (m), 1063.7 (m), 1003.55 (m), 852.75 (m), 825.33 (vs), 783.87 (vs), 733.71 (m), 706.29 (m), 637.74 (s), 504.99 (m).

2.3. Crystallographic data collection and refinement

Crystallographic data for Zn-MOF were collected on an Agilent X calibur E X-ray single-crystal diffractometer equipped at 293(2) K with graphite monochromated Cu–Kα radiation ($\lambda = 1.54184$ Å). The empirical absorption corrections were taken out using the SADABS program [20]. The structure of Zn-MOF was solved by direct method and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F^2 values with the SHELX-2014 program [21]. All H atoms were added on appropriate positions in theory using the riding model. From the difference Fourier maps of the Zn-MOF, a number of diffuse scattered peaks with electron density were observed, which can be assigned to the disordered water molecules. PLATON/SQUEEZE [22] was further used to refine the structure because of the residual electron density peaks obtained were diffused. The crystallographic data and selected bond lengths and angles for the Zn-MOF are listed in Tables S1 and S2. CCDC reference no.:1535119 for the Zn-MOF.