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Cadmium-Based Metal−Organic Framework as a Highly Selective and Sensitive Ratiometric Luminescent Sensor for Mercury(II)

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Supporting Information

ABSTRACT: A novel cadmium-based metal−organic framework (MOF) material with dual-emission signals has been constructed that can act as the first example of MOF-implicated ratiometric sensor for mercury(II) in pure water with a fast response, high selectivity, and sensitivity. The sensing mechanism is also discussed.

Mercury(II) (Hg^{2+}) is one of the most toxic and dangerous heavy-metal ions because of its threat to human health and environment.[1] Its accumulation in the human body causes a wide variety of diseases like digestive, kidney, and especially neurological diseases, even in a low concentration.[2] This has prompted the development of methods to selectively detect and quantify Hg^{2+} in aqueous solution. Luminescence-based methods have been widely used because of their high sensitivity, easy operation, and visualization. A few luminescent sensors for the detection of Hg^{2+} have been reported;[3] however, their widespread use is limited because of its inability to be used in pure water, cross-sensitivity toward other metal ions like Cu^{2+} and Pb^{2+}, time consumption, and/or sophisticated synthesis of probe materials. So, it remains a challenge to develop an effective fluorescent Hg^{2+} sensor.

Luminescent metal−organic frameworks (MOFs)[4,5] are bright, promising host matrixes for molecular-ion recognition owing to their designable architectures and tunable chemical and physical properties.[6] In most of the luminescent MOFs, the sensing functionality is fulfilled based on the change of the luminescence intensity in a single window, which is generally influenced by environmental interferences like fluctuations in the source intensity, photobleaching of the sensor, analyte concentration, etc., leading to errors in quantification. A simple yet sophisticated ratiometric sensing approach is one of the breakthroughs because it provides an inherent correction mechanism for environmental interferences.[7] Recently, some lanthanide-based MOFs have been constructed for ratiometric luminescent sensing;[8] nevertheless, to our knowledge, MOF-based ratiometic luminescent sensors for Hg^{2+} have been never explored. If it is possible to incorporate metal−ligand charge-transfer-related luminescence within MOFs where and when desired, it will add another dimension to luminescent functionalities to expand dual-emission signals for ratiometric application.[9] Because charge-transfer luminescence is commonly observed in d^{10} metal-based complexes, herein, we reported a dual-emission 3D MOF, $\{[Cd_{1.5}(C_{18}H_{10}O_{10})]\cdot(H_3O)(H_2O)_3\}_n$ (Cd−EDDA). It exhibited a significant advantage in that the luminescence output can result in a ratiometric manner in response to Hg^{2+} in aqueous media. In addition, the sensing mechanism is also further investigted.

A hydrothermal reaction of $Cd(ClO_4)_2\cdot 6H_2O$ and 5,5′-[ethane-1,2-diylbis(oxy)]diisophthalic acid (H_4EDDA) in water gave the colorless block crystal Cd−EDDA in high yield (80%). A single-crystal X-ray diffraction (XRD) study revealed that Cd−EDDA crystallizes in triclinic space group $P\bar{1}$. The fundamental building unit of compound Cd−EDDA consists of two independent cadmium atoms (Figure 1a). Cd(1) is coordinated by six oxygen atoms in octahedronal coordination geometry: two oxygen atoms from two bridging bidentate carboxylate groups of two $EDDA^{4-}$ ligands and four oxygen atoms from the four chelating-bridging tridentate carboxylate groups of the four $EDDA^{4-}$ ligands. The Cd(2) adopts pentagonal bipyramid coordination geometry with one oxygen atom from one bridging bidentate carboxylate group of a $EDDA^{4-}$ ligand, two oxygen atoms from one chelating bidentate carboxylate group of one $EDDA^{4-}$ ligand and four oxygen atoms from two chelating-bridging tridentate carboxylate groups of two

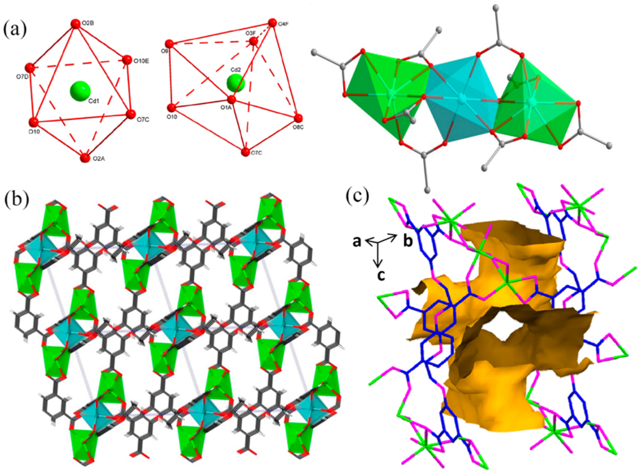

Figure 1. (a) Coordination environment of Cd^{2+} ions in Cd−EDDA. (b) View of the crystal packing of Cd−EDDA along the *a* direction. (c) Channel structure of Cd−EDDA.

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$EDDA^{4-}$ ligands. Cd(1) and Cd(2) are interconnected by carboxyl groups to form a $Cd_{1.5}$ unit, which further links its symmetric part through the ligands to construct a $Cd_3(CO_2)_8$ inorganic building unit with a nonbonding Cd···Cd distance of 3.4658(6) Å. These $Cd_3(CO_2)_8$ motifs, as secondary building units, are interconnected through carboxylate groups of $EDDA^{4-}$ to generate a 3D noninterpenetrating extended network with pores of approximate sizes of 7.5 × 5.1 $Å^2$ along *a* axis, 10.6 × 6.3 $Å^2$ along *b* axis and 5.9 × 6.5 $Å^2$ along *c* axis (Figure 1b,c). The solvent-accessible volume calculated by the *PLATON* program is 587.1 $Å^3$, which is 43.2% of the unit cell volume, and the thermogravimetric analysis curve of Cd−EDDA showed a weight loss of 8.65% between 26 and 150 °C, which corresponds to the loss of an uncoordinated H_2O molecule (calculated 8.46%), and the structure was maintained until 360 °C (Figure S4 in the Supporting Information, SI). Interestingly, the index of powder XRD patterns of the Cd−EDDA bulk sample immersed in water for 7 days evidenced the maintenance of the framework, indicating the feasibility of Cd−EDDA as a fluorescent probe in aqueous solution (Figure S5 in the SI).

Solid-state UV−vis absorption spectra of Cd−EDDA exhibited an intense absorption band centered at 310 nm, which can be assigned to the $\pi-\pi^*$ transition of 5,5′-[ethane-1,2-diylbis-(oxy)]diisophthalic acid. The fluorescence properties of the compound Cd−EDDA and deprotonated EDDA ligand were investigated in aqueous solution at room temperature (Figure S6 in the SI), It was found that free $EDDA^{4-}$ ligands display an intense emission band at 410 nm upon excitation at 310 nm, which may be caused by the $\pi^*-\pi$ transition.[10] Interestingly, complex Cd−EDDA exhibits the maximum emission at 350 nm besides a very weak fluorescence emission peak at 410 nm when excited at 310 nm. Compared to the free $EDDA^{4-}$ ligand, complex Cd−EDDA indeed results in much higher emission energy and a large blue shift of 60 nm for maximum emission; this indicates that the emission of Cd−EDDA at 350 nm may have originated from a charge transition between the ligand and metal ions, which is in agreement with the observation by Guo et al.[11]

The luminescence property of Cd−EDDA was investigated when the Hg^{2+} content was gradually added to the Cd−EDDA (0.55 mM) water standard emulsion. Upon an increase in the concentration of Hg^{2+}, the intensity of the emission at 350 nm dramatically decreases, while simultaneously the ligand-based emission at 410 nm becomes conspicuous (Figure 2a). On the basis of these results, it is obvious that the Cd−EDDA system can rationally detect Hg^{2+} in aqueous solution through a ratiometric fluorescence approach. The relative ratio of the fluorescence intensities at 410 and 350 nm [the original fluorescent intensity ratio (I_{410}/I_{350} = 0.40) is defined as 1.0] exhibits an 8.2-fold increase when the amount of added Hg^{2+} reaches 0.21 mM. Also, the chemodosimeter shows an excellent linear relationship between the emission ratios and the concentrations of Hg^{2+} from 4 to 25 μM, suggesting that the chemodosimeter Cd−EDDA is also potentially useful for the quantitative determination of Hg^{2+} (Figure 2b). Thus, the detection limit of Cd−EDDA toward Hg^{2+} is established at or below 2 nM according to the 3δ IUPAC criteria[3a,12] (Figure S9 in the SI), basically satisfying the maximum permitted level of 10 nM Hg^{2+} in drinking water regulated by the U.S. Environmental Protection Agency.[13] Of particular note was that fluorescence spectra were recorded after 15 s at room temperature in each case, displaying a fast response. The fluorescence intensity ratio versus [Hg^{2+}] plot can be curve-fitted into the Stern−Volmer equation:[14] $I_0/I = 1 + K_{sv}[M]$, where I_0 and I are the relative fluorescence intensity ratio before and after metal-ion incorporation, respectively, [M] is the metal-ion molar concentration, and K_{sv} is the Stern−Volmer constant (Figure S10 in the SI). Thus, the K_{sv} value is calculated to be 4.3 × 10^3 M^{-1}, which is comparable to those obtained by other fluorescent sensors for Hg^{2+} based on MOFs.[15] By comparison, a free deprotonated H_4EDDA ligand solution treated with excess Hg^{2+} ions almost showed no changes in the fluorescence intensity, indicating that there was no interaction between the ligands and Hg^{2+} (Figure S14 in the SI). Importantly, our system shows steady fluorescence in the pH range from 6.5 to 9.5, facilitating the detection of Hg^{2+} in aqueous media at physiological pH (Figure S11 in the SI).

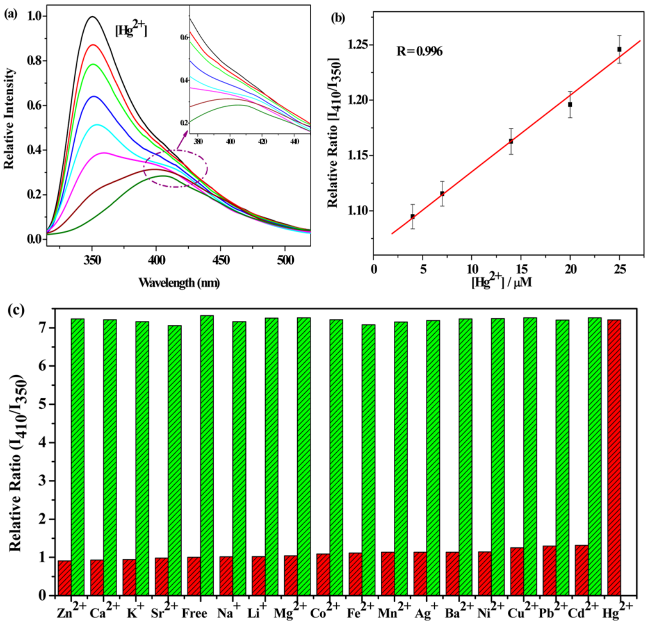

Figure 2. (a) Fluorescence spectra of Cd−EDDA (0.55 mM) as a function of the Hg^{2+} concentration (from top: 0.0, 0.007, 0.02, 0.04, 0.07, 0.10, 0.15, and 0.21 mM) in pure water with λ_{ex} = 310 nm. (b) Relative ratio of the fluorescence intensity change of Cd−EDDA (0.55 mM) with different Hg^{2+} contents. Each data point is an average of triplicates, and each error bar represents the data range. (c) Fluorescence responses of Cd−EDDA (0.55 mM) to various ions. The red bars represent the relative ratio of the emission intensities of Cd−EDDA in the presence of 0.21 mM metal ions. The blue bars represent a change of the relative ratio of the emission intensities that occurs upon the subsequent addition of 0.21 mM Hg^{2+} to the above solution.

To determine whether Cd−EDDA acts as a highly selective chemosensor for Hg^{2+}, some other metal ions were added consecutively into a suspension of Cd−EDDA under the same conditions (Figure 2c). No significant spectral changes of Cd−EDDA were observed in the presence of alkali, alkaline-earth or the transition-metal ions, (including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, and Cu^{2+}), even the other heavy-metal ions Cd^{2+} and Pb^{2+}, just caused a slight fluorescence change (the maximum emission ratio of I_{410}/I_{350} was 1.3). The competition experiments revealed that the Hg^{2+}-induced fluorescence response was unaffected in the background of 1 equiv of other metal ions, demonstrating that Cd−EDDA was a high selective sensor for Hg^{2+} detection. The high selectivity for Hg^{2+} is probably attributed to several integrated factors, such as the suitable open window size of the frameworks, the suitable radius, and the soft Lewis acidic and oxygen-abominating character of the Hg^{2+} ion.[16]

We tentatively explored the mechanism of the luminescence response to Hg^{2+}. A total of 5 mg of compound Cd−EDDA was dispersed in 10 mL of a Hg^{2+} solution with a concentration of 0.3 mM. After immersion for 5 min and 5 h, respectively, the concentrations of Cd^{2+} and Hg^{2+} in the filtrate solution were introduced for ICP determination. The Cd^{2+} concentration in the filtrate solution dramatically increased from 2.67 μM (5 min) to 11.9 μM (5 h); however, the added Hg^{2+} concentration remained nearly unchanged as the immersing time increased (Table S2 in the SI). There is no doubt that the Cd^{2+} cations are leached from Cd−EDDA. Further, powder XRD of the residues of mixed suspensions of Cd−EDDA and Hg^{2+} was employed to monitor the structure changes during Hg^{2+} solution treatment. A total of 24 h later, a few new peaks (marked with blue asterisks) come out in the XRD pattern besides the pattern of Cd−EDDA, which indicates that a new kind of structure may be formed after a long immersion time (Figure 3a). Fourier transform infrared spectra show that the vibration bands at 1725, 1205, and 1007 cm^{-1} for free H_4EDDA ligands were determined, accompanied by the disappearance of the MOF-related peaks at 1550 and 1061 cm^{-1}; thus, the new structure may be assigned as the free H_4EDDA ligands (Figure 3b). For verifying the above speculation, electrospray ionization mass spectrometry spectra exhibited an intense peak at m/z 389.3, which could doubtlessly be assigned to the species of H_3EDDA^- (Figure S12 in the SI). All of those results demonstrate that the sensing of Hg^{2+} by Cd−EDDA was attributed to the collapse of the crystal structure of Cd−EDDA and regeneration of the ligand induced by Hg^{2+}, thus resulting in the disappearance of the metal−ligand charge-transition emission at 350 nm and the emergence of the ligand-based emission at 410 nm. Even the addition of an ethylenediaminetetraacetic acid disodium salt (EDTA) or Na_2S aqueous solution cannot lead to recovery of its initial fluorescence of Cd−EDDA, which further suggested decomposition of the MOF results in its considerable photoluminescence changes (Figure S13 in the SI). To the best of our knowledge, this is the first report of MOF-implicated ratiometric sensing of Hg^{2+} in pure water.

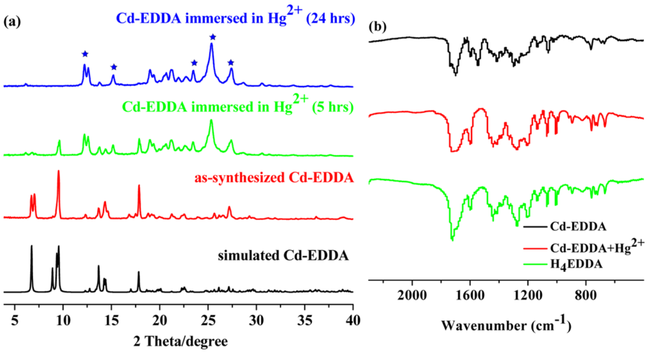

Figure 3. (a) Powder XRD patterns of Cd−EDDA simulated from single-crystal XRD results and as-synthesized Cd−EDDA and Cd−EDDA treated with Hg^{2+} for different times. The blue asterisks show the new generating peaks. (b) IR spectra of as-prepared Cd−EDDA and Cd−EDDA after immersion in a Hg^{2+} solution and H_4EDDA ligand.

In conclusion, we have successfully produced a new luminescent MOF Cd−EDDA. It exhibits a ratiometric fluorescence response to Hg^{2+} for the first time with a fast response (∼15 s). The especially high sensitivity of ca. 2 nM is below the permissible limits in drinking water set by the U.S. Environmental Protection Agency. Detailed experiments demonstrated that sensing of Hg^{2+} by Cd−EDDA was attributed to the collapse of the crystal structure of Cd−EDDA induced by Hg^{2+}. Its simple structure, sensitive and accurate signals, and rapid response will expand its application prospects.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01758.

Crystal data (CIF file) (CIF)
Experimental details and related spectra (PDF)

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Notes

The authors declare no competing financial interest.

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