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Luminescent Microporous Metal–Organic Framework with Functional Lewis Basic Sites on the Pore Surface: Specific Sensing and Removal of Metal Ions

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Ⓢ *Supporting Information*

ABSTRACT: A three-dimensional luminescent metal–organic framework, $\{Mg(DHT)(DMF)_2\}_n$ (**1**), based on an excited-state intramolecular proton-transfer (ESIPT) responsive linker, 2,5-dihydroxyterephthalic acid (H_2DHT), has been synthesized, and its desolvated microporous framework with pendent −OH groups on the pore surface was exploited for the binding and specific sensing of metal ions via Lewis acid–base interactions. The luminescence intensity significantly quenches with Cu^{II} among various s- and d-block metal ions, and highly selective sensing of Cu^{II} ions has been realized in both solid and solution states (up to nanomolar concentration). The immobilized Cu^{II} metal ions can be selectively removed by chelating agents like ethylenediaminetetraacetic acid without any structural disintegration of the framework, as revealed by the luminescence and gas-adsorption studies.

Metal–organic frameworks (MOFs) are a novel class of crystalline porous materials with tunable pore size and a chemical environment for their inner pore surface, which has been extensively exploited for many functional properties like gas storage, catalysis, separation, emission, and drug delivery.[1] The recent immense interest in luminescent MOFs stems from their potential applications in light-emitting diodes, as molecular sensors, as probes in biomedical assays, and in cell biology.[2] On the other hand, the detection of a trace amount of metal ion is of paramount importance with regard to environmental and biomedical applications.[3] In this respect, luminescent porous network-based sensors would be very attractive because they can also capture metal ions, anions, or organic molecules and, hence, can be used for their removal unlike their molecular chemosensor counterparts. Moreover, we envisage that enhanced sensitivity can be expected through signal amplification in MOF based sensors. Although various luminescent MOFs based on chromophoric linkers and metal centers (lanthanide ions) have already been reported,[2] the design of corresponding analogues for the selective capture and sensing of metal ions remains challenging because this requires specific Lewis basic sites that can postsynthetically interact with the metal ions. In particular, real-time and easy detection of trace amounts of Cu^{II} is very important for the treatment of copper metabolism disorders such as Wilsons' disease and neurodegenerative disorders like Alzheimer's disease.[4] Therefore, the use of highly sensitive optical fluorescent technology to probe the presence of Cu^{II} at a nanomolar concentration level is very promising in real diagnostic query.[5]

The luminescent (metal- or ligand-centered) porous frameworks with free Lewis acidic/basic sites can act as anion/cation receptors and, hence, are attractive candidates as novel sensor materials.[6] The immobilization of free sites within the porous frameworks is difficult because they tend to coordinate with other metal ions to form higher dimensional structures. MOFs functionalized with free pyridyl,[6b] carboxylate,[6e] and amide groups aligned in the pore structure have been elegantly employed for the sensing of metal ions and catalytic activities. Recently, we have reported a luminescent porous MOF, $\{Mg(DHT)(DMF)_2\}_n$ (**1**; DMF = *N*,*N*-dimethylformamide), composed of an excited-state intramolecular proton-transfer (ESIPT) responsive linker, 2,5-dihydroxyterephthalic acid (H_2DHT), where the emission color can be tuned in solution as well as in the solid state based on the polarity of the solvent or guest molecules.[2c] The most characteristic feature of **1** is the presence of free Lewis basic −OH groups within the pores, which can, in turn, be used for the binding of different metal ions and thus for sensing functions (Figures 1 and S1 in the Supporting Information, SI).

Herein, we report for the first time a ligand-based luminescent MOF (**1**) for the selective sensing and removal of metal ions, by exploiting the functional OH groups on their pore surface. The desolvated framework $\{Mg(DHT)\}_n$ (**1a**) exhibits highly selective sensing of Cu^{II} ions in a dimethyl sulfoxide (DMSO) solution as well as in the solid state among a number of transition-metal and s-block metal ions. Moreover, the captured Cu^{II} ions can be removed from pores using chelating agents like EDTA without any structural change, demonstrating the reusability of the MOFs. Compound **1** features a three-dimensional (3D) framework with one-dimensional (1D) channels along the crystallographic *c* axis, which are occupied by coordinated DMF molecules. Upon removal of the coordinated DMF molecules, the 3D framework **1a** shows 1D square-shaped channels along the crystallographic *c* axis without any additional opening along the *a* and *b* axes.[2c] The desolvated framework **1a** contains 55.7% void space, and the dimensions of the channels are about 5.3 × 5.3 Å^2, which are occupied by the pendent −OH groups of DHT linkers

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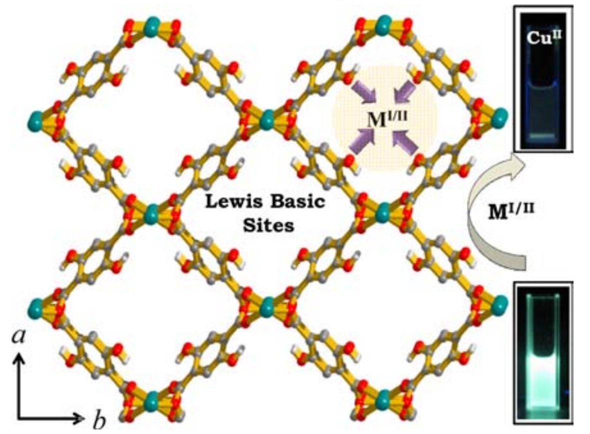

Figure 1. View of the 3D framework of **1a** along the crystallographic *c* axis showing Lewis basic pendant −OH groups and photographs under UV light corresponding to free **1a** and after its Cu^{II} immobilization in DMSO.

(Figures 1 and S1 in the SI). The framework **1a** is stable up to ∼400 °C, and permanent porosity of the framework has been confirmed by the type I CO_2 adsorption profile typical for microporous materials.[2c] Compound **1a** is partially soluble in organic solvents like DMSO, and the recovered solid from a DMSO solution or a DMSO-grinded sample of **1a** shows the composition $\{[Mg(DHT)]\cdot 2DMSO\}_n$ (**1b**). The powder X-ray diffraction (PXRD) patterns and the CO_2 adsorption studies of the DMSO-grinded samples retain the 3D porous structure, which rules out the possibility of disintegration of the compound into free ligand or metal salts in the presence of DMSO (Figures 4a and S2 in the SI).[2c]

Both a DMSO-grinded solid sample and a DMSO suspension of **1a** show large Stokes shifted green emission (λ_{max} = 508 nm) when excited at 370 nm because of the ESIPT state of the DHT linker.[2c] Therefore, we have studied the sensing properties of different metal ions with **1a** in DMSO. Compound **1a** was immersed in DMSO solutions containing different metal ions (10^{-3} M; M = Li^{I}, Na^{I}, Ca^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}), and the resulting solution in each case was continuously stirred to prepare metal-ion-incorporated product {M@Mg-MOF} (Scheme S1 in the SI). The solid products were filtered, washed with DMSO, and characterized by IR, PXRD, and energy-dispersive X-ray absorption studies. The PXRD patterns of the {M@MOF} sample after the incorporation of different metal ions shows sharp lines with slight shifting of the Bragg's peaks in comparison to **1b**, suggesting that the framework structure remains intact even after metal immobilization in a DMSO solution (Figure S3 in the SI). Fluorescence spectroscopic studies of the samples {M@Mg-MOF} obtained with different metal ions showed green emission when excited at 370 nm. Interestingly, the luminescence intensity of {M@Mg-MOF} is dependent on the nature of metal ions, providing room for selective sensing. For example, alkali, alkaline-earth, and transition metal ions with filled d shells (Zn^{II} and Cd^{II}) have no effect on the luminescent intensity after incorporation into the pores (Figures 2 and S4 in the SI). Interestingly, quenching in emission is observed with transition-metal ions like Ni^{II}, Co^{II}, and Cu^{II}; in particular, the quenching effect with Cu^{II} ions is the most significant. The luminescent intensity of the Cu^{II}-incorporated {Cu@Mg-MOF} form obtained from a 10^{-3} M $Cu(NO_3)_2$ solution is negligible compared to **1a**, suggesting a high sensitivity toward Cu^{II} for **1a** (Figure 3). The luminescent quenching effect of MOF **1a** by Cu^{II} has been further examined by time-resolved fluorescence studies. The fluorescence lifetime of 10.3 ns for **1a** is significantly reduced to 3.6 ns in the presence of 10^{-3} M $Cu(NO_3)_2$ (inset ii, Figure 3). The significant luminescent quenching with high sensitivity by **1a** further allowed visual detection of the existence of Cu^{II} when viewed under UV light (inset i, Figure 3). Furthermore, the absolute quantum yield has been decreased to 0.059% in {Cu@Mg-MOF} from 1.55% for the native framework, **1b**. The pore surfaces of the dehydrated MOF **1a** is occupied by the pendent −OH groups, and the nearest-neighbor distances between the −OH groups in the pores are 5.44, 7.11, and 7.17 Å (Figure S1 in the SI). Therefore, the immobilized metal ions on the pore surface can bind effectively with the free −OH groups. IR and X-ray photoelectron spectroscopy (XPS) spectra of the {Cu@Mg-MOF} sample clearly indicate that the Cu^{II} ion has been immobilized into the MOF structure (Figures S5 and S6 in the SI). The broad peak corresponding to the core-level XPS transition of Cu $2p_{3/2}$ appears at 931.9 eV, which is an agreement with the value of $Cu(OH)_2$, suggesting the binding of Cu^{II} ions through pendent −OH groups of **1a**. The energy-

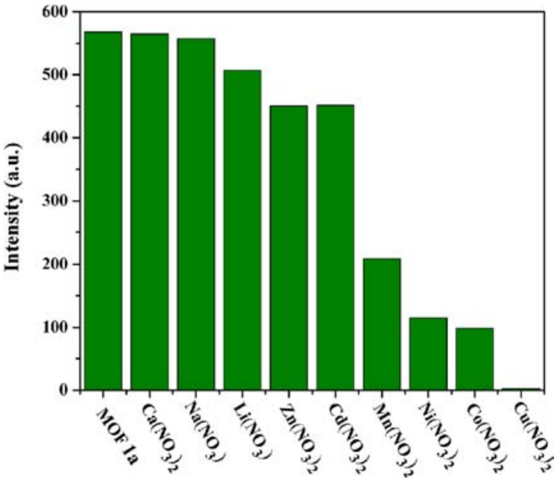

Figure 2. Comparison of the luminescence intensities of solid **1a** after immobilization with different metal ions (10^{-3} M) in DMSO.

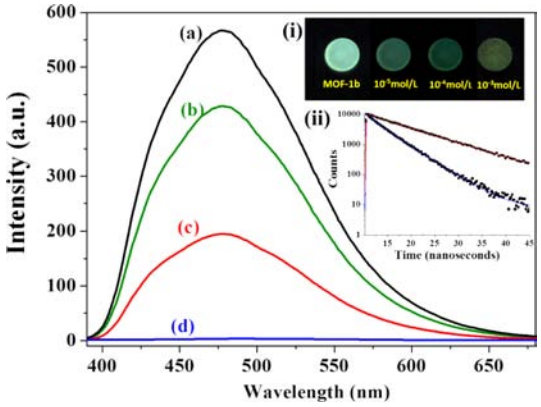

Figure 3. Luminescence spectra of solid {Cu@Mg-MOF} obtained after the incorporation of different concentrations of Cu^{II} in **1a** in DMSO: (a) **1a**; (b) 10^{-5} M; (c) 10^{-4} M; (d) 10^{-3} M. Insets: (i) Photographs of the corresponding samples under UV light; (ii) lifetime data for **1a** and {Cu@Mg-MOF} (10^{-3} M).

dispersive X-ray spectra and elemental analysis further indicated that 0.5 atom of Cu^{II} has been incorporated per formula unit of **1b** (Figure S7 in the SI). Furthermore, a CO_2 adsorption study with the {Cu@Mg-MOF} compound shows negligible uptake with a type II profile, which unequivocally suggests the presence of Cu^{II} on the pore surfaces (Figure 4b).

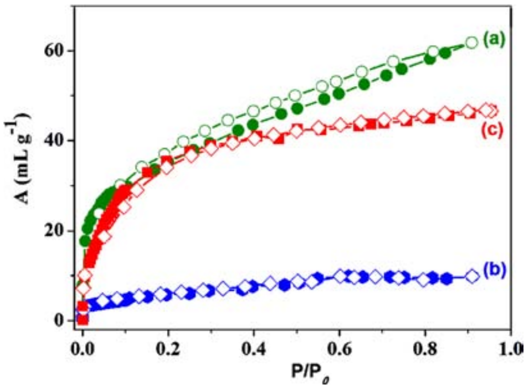

Figure 4. CO_2 adsorption (closed) and desorption (open symbol) isotherms at 195 K for (a) desolvated **1b**, (b) {Cu@Mg-MOF} and (c) a compound obtained from {Cu@Mg-MOF} after treatment with EDTA.

The quenching of the ligand-based emission in **1a** upon complexation with the paramagnetic transition-metal ions (Co^{II}, Ni^{II}, and Cu^{II}) could be due to the energy/charge-transfer processes through the partially filled d orbitals based on ligand-field transitions (d−d) or due to reabsorption of the emission energy for the d−d transition. Moreover, quenching is not observed with the Cd^{II}, Zn^{II}, alkali, and alkaline-earth metal ions with no unpaired electrons (filled d^{10} or p^6 configurations). The quenching effect can also be quantitatively determined by the Stern−Volmer equation. The Stern−Volmer quenching coefficient K_{sv} for Cu^{II} is calculated to be 170.2 M^{-1}, suggesting the highly selective and sensitive sensing of Cu^{II} in this framework. To show the feasibility of the sensing effect even in solution, we have done titration of MOF **1a** in a DMSO solution with increasing concentrations of $Cu(NO_3)_2$, and probing of the corresponding emission spectra (Figure S8 in the SI) suggests that quenching is pronounced even with a nanomolar concentration of $Cu(NO_3)_2$. Interestingly, a similar quenching effect is not observed with a free DHT ligand solution in DMSO with Cu^{II} (Figure S9 in the SI). Hence, it is evident that the confined small pores in MOF **1a** enhance the binding of Cu^{II} with the free −OH groups on pore surfaces. It is worth mentioning that the quenched fluorescence emission of {Cu@Mg-MOF} can be restored by removal of the metal ion using EDTA through complexation. More importantly, the recovered MOF after removal of Cu^{II} showed porous nature, which is evident from a CO_2 uptake profile similar to that of MOF **1a** (Figure 4c).[2c] Furthermore, the similarity in the PXRD pattern of the Cu^{II}-removed solid with that of **1a** indicates the reversal of encapsulation of metal ions into the MOF structure and the reusability of MOF for sensory applications (Figure S10 in the SI).

In conclusion, a ligand-based luminescent microporous MOF exhibiting remarkable selective quenching of the Cu^{II} ion in solution as well as in the solid state has been reported based on confined coordination space within the MOF structure having Lewis basic sites (pendent −OH groups). The foregoing results demonstrate that the novelty of the MOF system for specific sensing of metal ions relies on its porous structure to direct specific recognition, selectivity, and quantitative separation. Moreover, the reversal in the system allows one to reuse such MOF materials for further sensing functions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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