3d–4f Metal–Organic Framework with Dual Luminescent Centers That Efficiently Discriminates the Isomer and Homologues of Small Organic Molecules

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ABSTRACT: A 3d-4f luminescent metal-organic framework (MOF), $[Tb_2(Cu_8I_8)(C_{12}H_8NO_2)_6(H_2O)_4]$ ·SC₄H₈O₂ (4), and three analogues { $[La_2(Cu_8I_8)(C_{12}H_8NO_2)_6(C_4H_8O_2)_2(H_2O)_2]$ · $3C_4H_8O_2$ ·2H₂O (1), $[Ce_2(Cu_8I_8)(C_{12}H_8NO_2)_6(H_2O)_4]$ · $5C_4H_8O_2$ (2), and $[Eu_2(Cu_8I_8)(C_{12}H_8NO_2)_6(H_2O)_4]$ ·SC₄H₈O₂ (3)}, were self-assembled from copper(I) halide clusters and lanthanide metal ions with an organic linker [3-(pyridin-4-yl)benzoic acid] under solvothermal conditions. Compound 4 with high quantum yield ($\Phi = 68\%$) exhibits reversible luminescence behavior, accompanying the removal and recovery



of guest molecules (1,4-dioxane). Because of the unique porous structure and dual luminescent centers of compound 4, it can efficiently differentiate benzene series with different sizes and provide readouts in corresponding optical signals. Furthermore, it also can unambiguously discriminate the isomers, homologues, and other small molecules with similar structural motifs from one another. The luminescent color of the MOF sensor in different guest solvents has obvious changes that can be clearly distinguished by the naked eye. This multicolor luminescence originates from emissions of the dual luminescent centers, and the emissions have shifted, enhanced, weakened, or quenched to different degrees.

INTRODUCTION

Multinuclear copper(I) halide cluster complexes with d¹⁰ electron configurations exhibit intense photoluminescence properties with potential applications as organic light-emitting diodes.¹ They also respond to exterior stimuli such as thermal treatment (thermochromism) and mechanical grinding (piezo-chromism).² Analysis of the reports on copper(I) halide cluster complexes in the literature suggests that they are promising multistimuli-responsive luminescent materials.³

Lanthanide metal-organic frameworks (Ln-MOFs), selfassembled from lanthanide metal ions with and organic linker, are a very promising class of luminescent MOF materials.⁴ Because many Ln-MOFs exhibit sharp and characteristic emissions, luminescent Ln-MOFs are attractive candidates for chemical-sensing applications. Up to now, Ln-MOFs have been extensively studied in sensing ions, vapors, explosives, etc.⁵ However, most sensors with only one optical signal are usually based on fluorescence quenching, which lacks sufficient chemical selectivity and sensitivity. It has been our long-sought goal to explore a MOF sensor that can clearly differentiate diverse small organic molecules and provide a unique readout on the basis of Ln-MOFs. Introducing a second luminescent center [copper(I) halide clusters] would be a novel strategy to construct a MOF sensor with high recognition selectivity and sensing capability. The dual luminescent center may effectively

improve the detection selectivity and enhance the visible distinguishability when small organic molecules with similar chemical and physical properties are probed. Because emission lights of the dual luminescent centers enhance, weaken, or quench at different degrees, the MOF sensor would display various optical signals corresponding to different analytes. To the best of our knowledge, investigations of MOF sensors with dual luminescent centers are very limited up to now.⁶

In this work, we aim to design and synthesize a MOF with dual luminescent centers by using an organic ligand with two different functional groups [3-(pyridin-4-yl)benzoic acid (Hpba)] to connect the copper(I) halide cluster and lanthanide metal ion. Through a study of the hard and soft (Lewis) acid and base theory, the neutral nitrogen and carboxyl in Hpba are inclined to connect Cu⁺ and Ln³⁺, respectively. Four 3d–4f luminescent MOFs, $[La_2(Cu_8I_8)(pba)_6(C_4H_8O_2)_2(H_2O)_2]$. $3C_4H_8O_2 \cdot 2H_2O$ (1), $[Ce_2(Cu_8I_8)(pba)_6(H_2O)_4] \cdot 5C_4H_8O_2$ (2), $[Eu_2(Cu_8I_8)(pba)_6(H_2O)_4] \cdot 5C_4H_8O_2$ (3), and $[Tb_2(Cu_8I_8)(pba)_6(H_2O)_4] \cdot 5C_4H_8O_2$ (4), are synthesized under the same solvothermal conditions.

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EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents used in the syntheses were obtained from commercial sources without any purification. Elemental analyses were measured on a PerkinElmer 2400 elemental analyzer. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer with KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out by a Q500 V20.10 Build 36 thermogravimetric analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. The powder X-ray diffraction (PXRD) experiments were performed on a Rigaku D/max 2550 powder X-ray diffractometer with Cu K α radiation. The quantum yields were measured with an integrating sphere (C-701, Labsphere Inc.) and a 365 nm Ocean Optics LLS-LED as the excitation source, and the laser was introduced into the sphere through an optical fiber. The luminescence spectra were measured on a FluoroMax-4 fluorescence spectrometer at room temperature. In the chemical-sensing study, all of the luminescence spectra were recorded in the same test conditions. and the slit widths of excitation and emission spectra were 2.0 nm.

Synthesis of Compound 4. Tb(NO₃)₃ (0.045 g, 0.1 mmol), CuI (19 mg, 0.1 mmol), KI (0.032 g, 0.2 mmol), and 3-(pyridin-4-yl)benzoic acid (Hpba; 0.030 g, 0.15 mmol) were placed in 5 mL of a 2:3 (v/v) $H_2O/C_4H_8O_2$ (1,4-dioxane) solution, stirred for a few hours, and then transferred to and sealed in a Teflon-lined steel autoclave. The autoclave was kept in a 100 °C oven for 5 days. After cooling to room temperature, light-yellow block crystals were collected by filtration and washed with 1,4-dioxane (yield 54%). Compounds 1–3 were synthesized in the same conditions. Elem anal. Calcd for compound 4: C, 31.19; H, 2.73; N, 2.37; O, 11.74. Found: C, 31.66; H, 2.86; N, 2.23; O, 11.96. Selected IR peak (cm⁻¹): 2961, 2852, 1552, 1400, 1120, 769.

Preparation of Sample 4a. The synthetic samples (4) were activated under vacuum at 100 °C for 4 h, giving rise to 4a. The TGA curves and IR spectra of 4a show that the guests have been removed (Supporting Information, Figures S6 and S7).

Preparation of 4a guest. A total of 5.0 mg of a crystal powder of 4a was immersed in different pure guest solvents (5.0 mL). Then the samples were treated by ultrasonication and aged for 4 days before fluorescence testing.

X-ray Crystallography. Single-crystal diffraction data for compound 4 and the analogues were collected on a Rigaku RAXIS-RAPID diffractometer equipped with a narrow-focus, 5.4 kW sealed-tube X-ray source (graphite-monochromated Mo K α radiation with $\lambda = 0.71073$ Å). Data processing was accomplished with the *PROCESS-AUTO* processing program. Direct methods were used to solve the structure using the *SHELXL* crystallographic software package. All non-hydrogen atoms were refined anisotropically. The crystallographic information and structure refinement details are summarized in Table S1.

RESULTS AND DISCUSSION

Crystal Structure. X-ray crystal structure analysis reveals that the four compounds are analogues and they crystallize in the triclinic P1 space group. In these MOFs, as shown in Figure 1, the Cu₈I₈ cluster is formed by connecting two Cu₄I₄ clusters together through two Cu-I bonds, and the six copper centers of Cu₈I₈ bind six nitrogen atoms from six Hpba molecules. The coordination sphere of the Ln³⁺ ion is made up of eight oxygen atoms arising from six carboxylate groups of Hpba and two terminal water molecules, except that one terminal water molecule is replaced by 1,4-dioxane in compound 1. The eightcoordinated Ln³⁺ ions are further bridged by carboxylate groups to form an infinite one-dimensional (1D) chain running along the *a* axis. Each Cu₈I₈ cluster is connected with four lanthanide carboxylate chains through organic linkers to generate an interesting three-dimensional (3D) framework with two different sizes of 1D channels (about 7.7 \times 9.7 Å and 10.8 \times



Figure 1. (a) Structure of the Cu_8I_8 cluster. (b) Structure of the 1D lanthanide carboxylate chain. (c) 3D structure of the MOFs.

14.3 Å) propagated along the *a* axis. The channels are occupied by guest molecules (1,4-dioxane; Supporting Information, Figure S15).

Photoluminescence Properties. These analogues display unique photoluminescence properties. The luminescence spectra of the MOF analogues and Hpba have been measured in the solid state at room temperature. Among the analogues, the excitations are around 380 nm (Supporting Information, Figure S8), and compounds 1 and 2 display a broad emission band around 615 nm (Figure 2). Because the La^{3+} and Ce^{3+} ions are without characteristic emissions and the fluorescence



Figure 2. Luminescent emission spectra of the four compounds and desolvated sample 4a.

of Hpba exhibits one emission maximum at 425 nm, which is much weaker than the metal-based emission (Supporting Information, Figure S9), we conclude that the strong and broad emission band is assigned to the Cu₈I₈ cluster. Different from compounds 1 and 2, compounds 3 and 4 provide the characteristic emission band feature of the Ln³⁺ ion except emission from the copper(I) halide cluster (Figure 2). For compound 3, the characteristic Eu³⁺ emissions are covered by the peak of the copper(I) halide cluster. The weak emissions have been detected at 590, 616, and 698 nm, corresponding ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ to transitions of Eu^{3+, 7} For compound 4, the fluorescence peaks at 487, 545, and 620 nm could be attributed to ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$, and ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ transitions of the Tb³⁺ ion.⁸ Because compound 4 displays two distinct emission bands from different luminescent centers, we mainly focus on 4, and its luminescent propertyies will be studied and discussed in this work.

Sensing of Organic Solvent Molecules. Although there have been reports of MOF sensors probing different analytes, clearly distinguishing small organic molecules and their unique readouts based on a host MOF sensor is still a challenge, especially for the isomers. Here we select a desolvated sample (4a) of compound 4 as the sensor and benzene, toluene, pxylene, and mesitylene as the analytes for the chemical-sensing study. The solvent-free framework 4a is obtained by calcination of the synthetic samples under vacuum at 100 °C for 4 h, and the photoluminescence behavior has been measured (Figure 2). 4a displays a broad emission around 687 nm that originated from the copper(I) halide cluster. Compared to the emission of 4, the broad emission band has weakened and shifted (615 \rightarrow 687 nm), while the Tb³⁺ emission bands have almost disappeared. Moreover, the quantum yields of 68% and 13% for 4 and 4a, respectively, also confirm that the emission has greatly weakened. The chemical-sensing study is performed by soaking 4a crystal powder in selected guest solvents, followed by luminescence testing. While the powder of 4a is suspended in each guest liquid (4a)guest), the fluorescence spectra are recorded under excitation at 380 nm, and photographs are taken after excitation at 365 nm using a commercial ultraviolet (UV) lamp. The intensity changes and peak shifts are clearly illustrated in the emission spectra, and the differences can be distinguished in the images by the naked eye (Figure 3). The emissions from two luminescent centers have changed to different degrees, which results in alteration of the optical signal. In benzene, toluene, and p-xylene solvents, the Tb³⁺ emissions have obviously been enhanced, while the emissions that originated from the copper(I) halide cluster have blueshifted. However, in the mesitylene solvent, the crystal powder displays a red emission, which is assigned to the copper(I)halide cluster, and the Tb³⁺ emissions have almost disappeared. In the emission spectra, the enhancing or quenching of characteristic Tb³⁺ emissions can be clearly observed. However, the emission peak of the copper(I) halide cluster has been covered when the Tb³⁺ emissions sharply enhance in benzene, toluene and *p*-xylene solvents. In order to clearly record how the emission originating from the copper(I) halide cluster has changed in different guest solvents, we select compound 2 with a single emission band as the sensor. The chemical-sensing tests have been conducted in the same manner as that of 4a by soaking a desolvated sample (2a) of compound 2 in benzene, toluene, p-xylene, and mesitylene solvents (Figure 4). Compared to the emission of 2a, the emissions have a large blue shift (about 695 \rightarrow 600 nm) and enhanced in benzene,



Figure 3. Luminescence spectra and photographs of **4a** crystal powder after immersion in different guest solvents: (a) 1,4-dioxane; (b) benzene; (c) toluene; (d) *p*-xylene; (e) mesitylene.



Figure 4. Luminescent emission spectra of 2, 2a, and 2a guest (benzene, toluene, *p*-xylene, and mesitylene) after excitation at 380 nm.

toluene, and *p*-xylene solvents. Just like 4a mesitylene, 2a mesitylene displays a red emission that is similar to the emission of 2a. Especially, 2a guest (toluene and *p*-xylene) exhibits another higher-energy (HE) emission band around 490 nm. According to the research results of Ford and co-workers on copper(I) halide cluster complexes, the HE band should be attributed to a metal-to-ligand charge-transfer (MLCT) excited state.¹⁰

Sensing Mechanism. The selected guest solvents have similar chemical and physical properties, but they are of different sizes. Thus, we speculate that the host should selectively recognize guest molecules by size. Because the guest molecules of different sizes would display diverse arrangement modes in the channel, these would directly affect interaction of the guest and framework. In order to confirm the above speculation, we first analyze the PXRD patterns of samples **4** and **4a**. They are different, and the first diffraction peak of **4a** has shifted to low angle (Figure 5). After **4a** is immersed in 1,4-dioxane, the PXRD pattern



Figure 5. PXRD patterns of 4 and 4a.



Figure 6. PXRD patterns of 4a after soaking in different guest solvents.

recovers to the initial state (Figure 6). The same results are obtained in the PXRD test results of the other analogues (Supporting Information, Figures S1 and S2). These results illustrate that the framework has changed when 4 transforms into 4a. Because the available single-crystal data have not been obtained, it is difficult to directly point out what specific change has happened. Then, the PXRD patterns of all of the samples $(4a \supset guest)$ show that the framework has not collapsed and that most of the patterns are different from the pattern of 4a and become nearly the same as the pattern of 4. However, the pattern of 4a>mesitylene identifies with the pattern of 4a (Figure 6). Studying the size of the guests and channel reveals that all of the guest molecules can enter the large and small channels except mesitylene, which is too large to enter the small channel and only enters the large channel. These results confirm that whether the guests can enter the small channel largely affects the structure of the framework. Finally, we further confirm that mesitylene cannot enter the small channel through a solvent-exchanged experiment. The solventexchanged sample is prepared by immersing the as-synthesized sample 4 in mesitylene for 3 days to remove the 1,4-dioxane solvates; the extract is decanted every 4 h, and fresh mesitylene

is replaced. The PXRD results show that the pattern of the mesitylene-exchanged sample is nearly the same as the pattern of sample 4 (Supporting Information, Figure S4), which implies that the large and small channels are filled with guest molecules. Considering the size of mesitylene, we speculate that the large channel would be occupied by mesitylene and the 1,4-dioxane guests in the small channel would be kept inside. This speculation has been verified in the fluorescence test results. The emissions of the mesitylene-exchanged sample are completely different from that of 4 or 4aDmesitylene (Figure 7), indicating that the guests in the channels are not just 1,4-



Figure 7. Emission spectra of 4, 4a, 4a⊃mesitylene, and the solventexchanged sample.

dioxane or mesitylene. They should be 1,4-dioxane and mesitylene, which coexist in the channels. We have also confirmed speculation by the ¹H NMR spectra of the 4aDmesitylene and mesitylene-exchanged samples (Supporting Information, Figures S12–S14).

We have also analyzed the emissions originating from dual luminescent centers in compound 4. For the center of the copper(I) halide cluster, the emission is assigned to a tripletcluster-centered (³CC) excited state, a combination of halideto-metal charge-transfer (XMCT) and d-s transitions.^{10,11} Because a HE emission band has been detected in the sensing tests, the MLCT excited state is another important factor that directly affects the emission of the copper(I) halide cluster. For the Tb³⁺ center, because the fluorescence of Hpba is not observed in the sensing tests, the energy should be effectively transferred to the lanthanide ion from the organic ligand (ligand-to-metal energy transfer, LMET).¹² The fluorescence peaks at 487, 545, 584, and 620 nm could be attributed to ${}^{5}D_{4}$ \rightarrow ⁷F₆, ⁵D₄ \rightarrow ⁷F₅, ⁵D₄ \rightarrow 7F₄, and ⁵D₄ \rightarrow 7F₃ transitions of the Tb³⁺ ion,⁸ respectively. According to the reported literature, the structure change would affect the fluorescence of the copper(I) halide cluster complexes or Ln-MOFs.¹³ Thus, we speculate that the sensing mechanism should be attributed to the change of the structure. This change is likely to directly affect the ligand and copper(I) halide cluster to different degrees. On the one hand, the ligand may distort,¹⁴ which influences the LMET^{13c} and MLCT progress.¹⁰ On the other hand, the expansion, contraction, or distortion of the copper(I) halide cluster would affect the energy of the cluster-centered excited state.¹¹ When the guest molecules enter into the small and large channels, the framework is different from the solvent-free framework and the emission bands completely change. When the guest molecules only enter the large channels, the

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framework has no obvious difference from the solvent-free framework and the emissions are nearly the same as the emission of the desolvated sample. Only the intensities are different. In addition, the UV–vis absorption spectra of solvent molecules show that none of them has any observable absorption intensity around 380 nm (Supporting Information, Figure S11). Thus, there is no competition between the absorption of the solvents and the excitation of 4a⊃guest, which results in quenching.¹⁵

Differentiating the Isomers, Homologues, and Chlorides. The recognition selectivity and sensing capability of 4a is not only manifested by probing the benzene series. As shown in Figure 8, even the isomers (ether, butyl alcohol, 2-butyl alcohol,



Figure 8. Luminescence spectra and photographs of the **4a** crystal powder after immersion in isomers: (a) ether; (b) butyl alcohol; (c) 2-butyl alcohol; (d) *tert*-butanol.

and tert-butanol) are unambiguously differentiable. Attributed to the different sizes of the isomers, ether and butyl alcohol can enter the small and large channels while 2-butyl alcohol and tert-butanol can only enter the large channel. Thus, in ether and butyl alcohol solvents, 4a exhibits Tb³⁺ emissions at different intensities while the emission originating from the copper(I)halide cluster has been covered. When 4a is immersed in 2butyl alcohol and *tert*-butanol, the Tb³⁺ emissions have almost disappeared and different intensities of red emissions originating from the copper(I) halide cluster are shown. Whether or not the isomers enter the small channel has been confirmed by the PXRD patterns of 4a Just (ether, butyl alcohol, 2-butyl alcohol, and tert-butanol; Supporting Information, Figure S5). Furthermore, the homologues of butyl alcohol (methanol, ethanol, and *n*-propanol) and other small molecules with similar structural motifs, such as chloride $(CH_2Cl_2, CHCl_3)$ and CCl₄), can also be effectively recognized (Figures 9 and 10)

Fast Response to Organic Solvent Molecules. Apart from its excellent sensing capability, 4a also has fast response



Figure 9. Luminescence spectra of the 4a crystal powder after immersion in homologues (methanol, ethanol, and *n*-propanol). Inset: Luminescence photographs for (a) methanol, (b) ethanol, and (c) *n*-propanol.



Figure 10. Luminescence spectra of the **4a** crystal powder after immersion in chloride $(CH_2Cl_2, CHCl_3, and CCl_4)$. Inset: Luminescence photographs for (a) CH_2Cl_2 , (b) $CHCl_3$, and (c) CCl_4 .

after immersion in guest solvents. An experiment of fast response is shown in Figure 11; the emission lights completely



Figure 11. Luminescence photographs of 4a with fast response to guest molecules in about 1 s: (a) 4a; (b) one drop of methanol is added on 4a; (c) one drop of 1,4-dioxane is added on 4a.

change in about 1 s. When one drop of methanol is added on the desolvated sample of **4a** (about 1.0 mg), which is placed on a glass slide, the emission light immediately turns green. After the sample dries, one drop of 1,4-dioxane is added onto the sample, and the emission light changes again in about 1 s. The whole experiment of fast response has been recorded in a video (see the Supporting Information).

CONCLUSION

In summary, we have successfully prepared a 3d-4f luminescent MOF that exhibits high recognition selectivity and sensing capability. Different from the conventional sensor

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of Ln-MOF, this MOF contains dual luminescent centers and a unique porous structure. It effectively differentiates diverse small organic molecules (benzene series, isomers, homologues, and chlorides) and provides readouts in corresponding optical signals. After analysis and discussion, we think that the change of the structure directly results in luminescence enhancing, weakening, or quenching. Although the sensing mechanism needs further investigation, this work demonstrates that the design of a MOF sensor with dual luminescent centers is an effective strategy to improve sensing ability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02193.

Experimental details, crystal data, IR spectra, XRD patterns, TGA, luminescence spectra, and UV-vis absorption and ¹H NMR spectra (PDF)

X-ray crystallographic data in CIF format (CIF)

Whole experiment of fast response (ZIP)

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Notes

The authors declare no competing financial interest.

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