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Three-Dimensional Lanthanide Anionic Metal−Organic Frameworks with Tunable Luminescent Properties Induced by Cation Exchange

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Three 3D lanthanide anionic metal−organic frameworks $\{K_5[Ln_5(IDC)_4(ox)_4]\}_n\cdot(20H_2O)_n$ with 1D channels were synthesized under hydrothermal conditions [Ln = Gd (**1**), Tb (**2**), and Dy (**3**)]. The K^+ ions within the 1D channel are easily exchanged with various cations. The emission intensities of Tb^{III} in **2** increased significantly upon the addition of Ca^{2+} ions, while the introduction of other metal ions caused the intensities to be either unchanged or weakened.

In the past decade, modification of the chemical properties of metal−organic frameworks (MOFs) is an ongoing challenge in the area of material chemistry.[1,2] Sometimes the exchange of metal ions or organic cations within anionic MOFs can adjust the chemical properties of a MOF,[3−5] and this could be achieved simply by immersing the sample into a solution containing certain metal salt or organic cations to generate a modified anionic MOF. For example, Long et al. found that the exchange of guest Mn^{2+} ions in a porous anionic MOF with selected cations leads to variation of the H_2 adsorption enthalpy.[4a] H_2 adsorption can also be enhanced by exchange of the guest cation with Li^+ ions in a 3D porous MOF.[4b] Recently, many porous lanthanide neutral MOFs have been constructed because of their superior functional properties and potential applications.[6−14] In particular, the attractive light-emitting properties of 4f elements make lanthanide MOFs particularly suitable for the development of optical devices and tunable luminescent sensors for chemical species.[6a,7] However, the tunable luminescent properties by guest cation exchange within anionic lanthanide-based MOFs are still rare.[5]

In comparison with a lanthanide-based neutral MOF, a lanthanide-based anionic MOF is beneficial for the modification of chemical properties through cation exchange because it does not introduce the counterions into the pores of MOF. We and others have illustrated that imidazole-4,5-dicarboxylate (IDC^{3-}), a rigid planar ligand containing multiple coordination sites, is beneficial for the construction of anionic MOFs, in which the pores are occupied by various guest cations.[15] The

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progress within the anionic and lanthanide-based neutral MOFs prompts us to rationally design and synthesize lanthanide-based anionic MOFs using IDC^{3-} as the building block for specific cation exchange and thus to modify the chemical properties of these lanthanide-based anionic MOFs. Herein, we present three unique 3D lanthanide-based anionic MOFs of $\{K_5[Ln_5(IDC)_4(ox)_4]\}_n \cdot (20H_2O)_n$, which are constructed by Ln^{III}, IDC^{3-}, and oxalate [Ln = Gd (**1**), Tb (**2**), and Dy (**3**)]. Luminescent studies reveal that the luminescent properties of **1**−**3** can be modified through the exchange of guest K^+ ions with various cations.

The colorless crystals of **1**−**3** were obtained in good yield by the hydrothermal reactions of $Ln(NO_3)_3 \cdot 6H_2O$, H_3IDC, H_2ox, and KOH (see the Supporting Information). The unit cell parameter measurements from selected crystals reveal that **1**−**3** are isomorphous, which is further confirmed by the powder X-ray diffraction (PXRD) and IR measurements (Figure S1 in the Supporting Information). Because of the poor crystal quality of **1** and **3**, only the structure of **2** was solved. The basic structural unit of **2** is a slightly distorted Tb_6L_4 octahedron (Figure S2 in the Supporting Information), which is constructed of four μ_3-IDC^{3-} bridging six Ln^{III}; the equatorial and axial Tb$\cdots$Tb distances are 9.249 and 10.022 Å, respectively. The Tb_6L_4 octahedra are linked via sharing of the vertexes into a 1D chain (Figure 1a), and the 1D chains are further connected by oxalates to generate a 3D framework with 1D channels along the *c* axis (Figure 1b). The size of the channel is ca. 6.9 × 7.8 Å, in which the K^+ ions locate on the surfaces of the channels and weakly interact with IDC^{3-}, oxalate, and water molecules (Figure 1b). The water molecules reside in the channels and are coordinated with K^+.

The thermogravimetric analysis (TGA) curves of **1**−**3** (Figure S3 in the Supporting Information) showed that the guest water molecules were lost below 150 °C, and the complexes are stable up to 350 °C, and then began to decompose upon further heating. The luminescent properties of **1**−**3** were determined at the excitation wavelength of 307 nm under ambient temperature, in which **2** and **3** display typical emission bands of Tb^{III} and Dy^{III}, respectively, while **1** exhibits a very weak luminescent emission maximum at 418 nm (Figure S4 in the Supporting Information). The luminescence of **1** originates from the emission of ligand-to-metal charge transfer.[5] For **2**, the four sharp lines at 489, 545, 589, and 619 nm can be assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$ transitions of Tb^{III}, respectively, and the two emission bands at 479 and 573 nm for **3** correspond to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{III}. The excitation and emission spectra of **1**−**3** in the solid state are almost identical with those of an emulsion of **1**−**3** in *N*,*N*-dimethylformamide (DMF), indicating that the framework of **1**−**3** remains in the DMF emulsion (Figure S4 in the Supporting Information).

To examine the possibility of modification of the luminescent properties through cation exchange, the solid sample of **2** was immersed in DMF containing various metal cations to generate an emulsion of **2**. The most striking feature is that the emission intensity of **2** is significantly increased upon the addition of 1−3 equiv of Ca^{2+} cations (Figure 2). The luminescent intensity at 545 nm in the presence of 3 equiv of Ca^{2+} ions is about twice as strong as that without Ca^{2+} ions. Furthermore, the fluorescence lifetime at 545 nm ($^5D_4 \rightarrow {}^7F_5$) of **2** is significantly increased from 158.90 to 287.48 μs upon the addition of 3 equiv of Ca^{2+} ions (Figure S5 in the Supporting Information) in DMF. However, the luminescent intensities do not change or only slightly increase in the presence of 3 equiv of Na^+, NH_4^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} cations (Figure 3). When 1−3 equiv of transition-metal ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} were added to the emulsion of **2** in DMF, the luminescent intensity was not enhanced but rather weakened dramatically or even quenched (Figures 3 and S6 in the Supporting Information). The results presented here were distinct from those of the reported Eu^{III} and Tb^{III} complexes,[12] in which the presence of Ca^{2+} ions did not effect the luminescent intensities. To our knowledge, **2** is the first lanthanide-based MOF as a promising Ca^{2+} ion-selective luminescent probe.

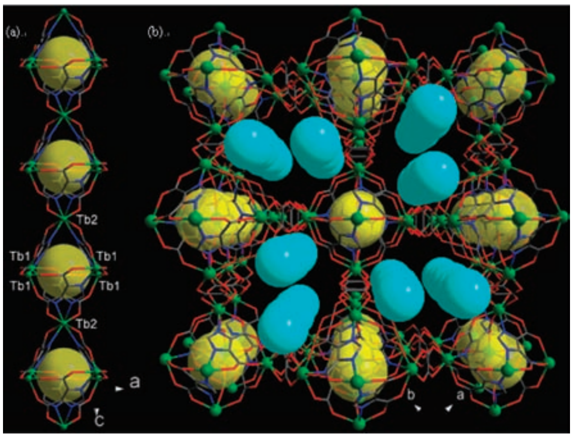

Figure 1. (a) 1D chain constructed via sharing of the vertexes of Tb_6L_4 octahedra in **2**. (b) View of a 3D MOF of **2** along the *c* axis, in which K^+ ions are located within the 1D channels (yellow spheres, octahedron-accessible cages; turquoise spheres, K^+ ions; the water molecules are omitted for clarity).

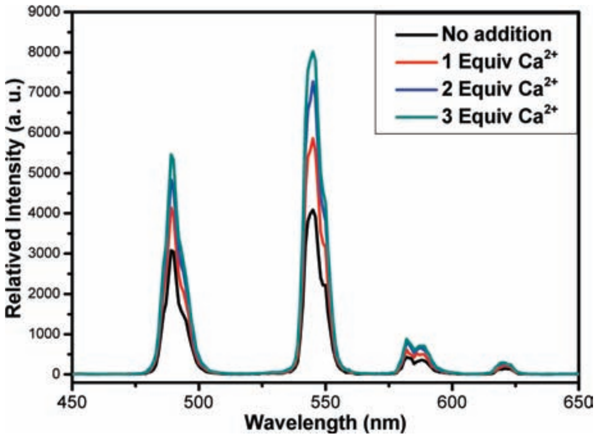

Figure 2. Emission spectra of an emulsion of **2** in DMF (10^{-3} M) in the presence of ∼0−3 equiv of Ca^{2+} ions (from $CaCl_2$, excited at 307 nm).

To elucidate the mechanism for such a luminescence enhancement or diminishment with the addition of various cations as well as to identify if the framework of **2** remains or collapses in the DMF emulsion, solid samples were obtained by centrifugal separation of the emulsion of **2** in DMF containing different metal salts, washing with water, and drying in air. The PXRD patterns of the solid samples are almost identical with that of as-synthesized **2** (Figure S7 in the Supporting Information), indicating that the framework

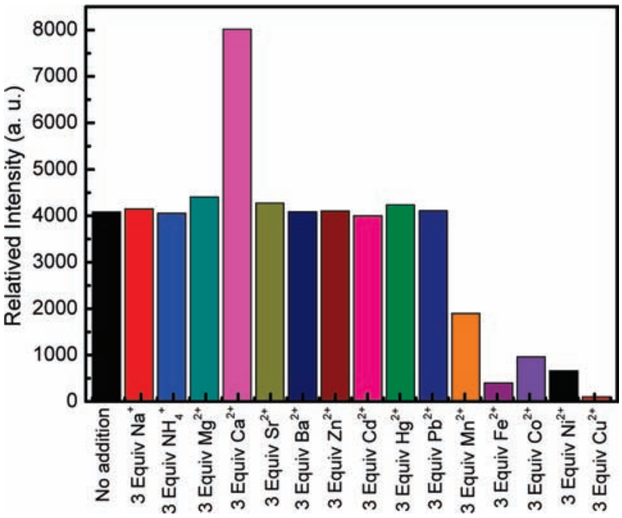

Figure 3. Luminescent intensities of a $^5D_4 \rightarrow {}^7F_5$ transition for an emulsion of **2** in DMF (10^{-3} M) at 545 nm upon the addition of various cations (excited at 307 nm).

of **2** remains after immersion in a DMF solution containing various metal cations. The results of energy-dispersive X-ray spectroscopy (EDS) analyses (Figure S8 in the Supporting Information) clearly demonstrate that the metal ions, such as Ca^{2+} ions, have been incorporated into the framework of **2** through ion exchange with K^+ ions. In comparison with other cations, the amount of exchanged Ca^{2+} within the channels of **2** is much more because of the stronger interactions between Ca^{2+} and ox^{2-} (K_{sp} values: MgC_2O_4, 4.8×10^{-6}; CaC_2O_4, 4.0×10^{-9}; SrC_2O_4, 1.6×10^{-7}; BaC_2O_4, 1.6×10^{-6}), and this was further confirmed by the results of inductively coupled plasma measurements. The amounts of exchanged Ca^{2+} in **2** are 5.75%, 7.94%, and 10.31% after treatment with 1, 2, and 3 equiv of Ca^{2+}, respectively. Under the same conditions, the amounts of exchanged Mg^{2+} in **2** are only 0.48%, 0.51%, and 0.86% after treatment with 1, 2, and 3 equiv of Mg^{2+}, respectively.

The luminescence of lanthanide complexes is produced through three steps.[6a] First, light is absorbed by the organic ligands attached to Ln^{III}, energy is then transferred onto one or several excited states of the Ln^{III}, and, finally, the Ln^{III} emits light. The luminescent intensity of Ln^{III} relies on the efficiency of the energy transfer from the ligand to Ln^{III}, and the vibration-induced deactivation of the ligand will reduce the efficiency of the energy transfer from the ligand to Ln^{III}. It has been found that the best way to minimize vibration-induced deactivation processes is to design a rigid metal ion environment, free of high-energy vibrations.[6a] In **2**, the large amounts of Ca^{2+} bonded to ox^{2-} and the strong interactions between Ca^{2+} and ox^{2-} make ox^{2-} become more rigid; this will reduce vibration-induced deactivation of ox^{2-} and increase the efficiency of the energy transfer from the ligand to Tb^{III}. In addition, the interactions between Ca^{2+} and ox^{2-} may also optimize the process of ligand (S_1) → ligand (T_1) → Ln* energy flow by adjusting the energy gap between the lowest ligand triplet state (T_1) and the Tb^{III} emitting level, resulting in a more efficient intramolecular energy transition from ox^{2-} to Tb^{III}. Therefore, the luminescent intensity of Tb^{III} in **2** is dramatically enhanced with the addition of Ca^{2+} ions. A similar mechanism for the enhancement of the emission intensity has also been found in other reported compounds.[6a,11a,11b,12a] When the K^+ ions in **2** were exchanged with various transition-metal ions, such as Cu^{2+} ions, etc., the luminescent intensities of Tb^{III} were weakened dramatically or even quenched because the interactions between transition-metal ions and ox^{2-} quench the S_1 state of ox^{2-} by d−d electron transfer of transition-metal ions, annihilating subsequent energy transfer onto the lanthanide ions.[6a,11c,11d,16]

The luminescent properties of **1** and **3** can also be tunable through the exchange of K^+ with Tb^{3+} ions (Figure S9 in the Supporting Information); the emission intensities of **1** and **3** are dramatically increased after the exchange of K^+ with Tb^{3+}. Furthermore, the fluorescence lifetime of the Tb^{3+}-exchanged solid sample (Tb-**1**) is 806.54 μs, which is even larger than the fluorescence lifetime of the solid sample of **2** (383.72 μs). The EDS and PXRD patterns of Tb-**1** indicate that the framework of **1** is maintained upon ion exchange (Figure S10 in the Supporting Information). The low background luminescence and tunable luminescent property of **1** imply that **1** can be used for the detection of Tb^{3+}.

In conclusion, three novel 3D lanthanide-based anionic MOFs with tunable luminescent properties induced by cation exchange were reported. The MOFs show the following unusual features: First, the structures of MOFs contain rare Ln_6L_4 octahedra. Second, **2** shows a remarkable increase in the luminescence emission of Tb^{III} upon the addition of Ca^{2+} ions, while the exchange of K^+ ions with other cations does not modulate or even quench the luminescence emission of Tb^{III} in **2**. Third, **1** shows low background luminescence and tunable luminescent properties. These results are significant for the development of tunable lanthanide luminescent materials.

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Supporting Information Available: Crystallographic data in CIF format, synthesis, structural figures, luminescent spectra, PXRD patterns, IR, TGA curves, and EDS patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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