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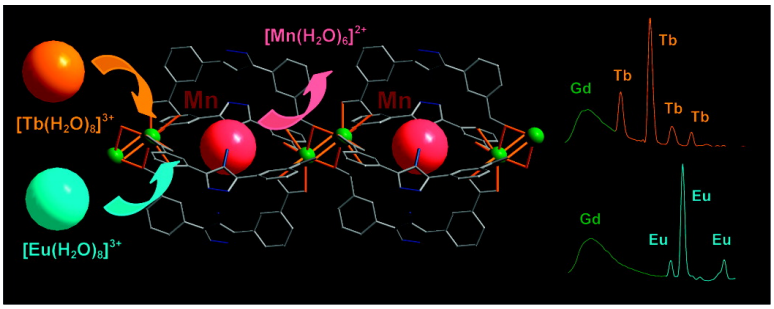

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Tunable Luminescent Lanthanide Coordination Polymers Based on Reversible Solid-State Ion-Exchange Monitored by Ion-Dependent Photoinduced Emission Spectra

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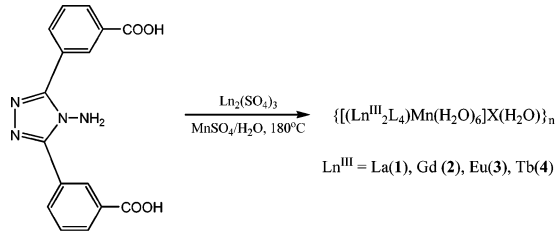
The study of coordination-driven self-assembled polymeric metal−organic frameworks (MOFs) is a very active interdisciplinary research area.[1] Such supramolecular assemblies have intriguing structures as well as potential applications as smart optoelectronic, magnetic, catalytic, and porous materials. To our knowledge, only a handful of lanthanide-based porous MOFs which are able to uptake and release guest species in a reversible manner have been reported.[2] In addition, IR, NMR, XRD, and single-crystal analysis are the main monitoring techniques to characterize reversible solid-state guest-exchange processes.[3] Up to now, however, the luminescence properties have rarely been used to monitor guest-exchange processes.[4b] The guest-dependent photoinduced emission spectra not only offer a facile monitoring technique to characterize solid-state guest-exchange processes but also provide a practical approach to access of tunable fluorescent materials.

Motivated by our interest in selective and reversible guest-exchange chemistry based on porous MOFs, we have initiated a synthetic program for the preparation of open MOFs, in which the bent five-membered heteroatom-ring-bridged ligands are chosen as the building blocks.[4] We present here the first family of lanthanide-based MOFs consisting of the nanosized Ln_2L_4 cagelike units which encapsulate the $[Mn(H_2O)_6]^{2+}$ cations. These porous coordination polymers can remain intact upon reversible ion-exchange with different Ln(III) cations, which was characterized by the ion-dependent photoinduced emission spectra and XRD patterns.

As shown in Scheme 1, reactions of the bent 1,2,4-trizole bridging ligand L with $Ln_2(SO_4)_3 \cdot 8H_2O$ in the presence of $MnSO_4 \cdot H_2O$ under hydrothermal conditions (H_2O, 180 °C), afforded the compounds $\{[(Ln^{III}_2L_4)Mn(H_2O)_6] \cdot x(H_2O)\}_n$ (Ln(III) = La (**1**), Gd (**2**), Eu (**3**), and Tb (**4**)) as colorless crystals in good yield (Supporting Information). Single-crystal analysis (Supporting Information) revealed that **1**−**4** feature a similar 1D chain motif. For example, the structure of **2** contains two crystallographically independent Gd(III) atoms, which are both found in eight-coordinated dodecahedral coordination spheres that are composed of eight carboxylate oxygen donors from six L ligands (Figure 1). The four of eight carboxylate groups from four L ligands behave as the μ_2-bridge to bind two Gd(1) ions together, resulting in a Gd_2O_{16} cluster with a close Gd(1)···Gd(1) contact of ∼4.0 Å. Such coordination mode plays a central role in the formation of **2** with a neutral 1D polymeric framework (Figure 1). The Gd−O bond distances range from 2.337(4) to 2.677(4) Å.

The most important structural feature of **1**−**4** is that these neutral 1D polymeric chains consist of the Ln_2L_4 tetragonal prisms[4b] enclosing the $[Mn(H_2O)_6]^{2+}$ cations (Figure 1). As shown in Figure 1, four bent L ligands bridge two Ln(2) ions to form the tetragonal prismatic cage. The dodecahedral coordination mode of Gd(III) center prevents a symmetric alignment of the L spacers,

Scheme 1. The Synthesis of Ln(III)-Coordination Polymers **1**−**4**



L

leading to the tetragonal prism being twisted. This structural arrangement leaves openings of 6.8−7.1 Å in the side of the cage. One distorted octahedral $[Mn(H_2O)_6]^{2+}$ cation is trapped inside and is hydrogen-bonded to the framework carboxylate moieties (Figure 1). Within the cage, the Gd···Gd distance is ∼11 Å and the distance between the two opposite trizole rings is ∼10 Å.

In the solid state, the Gd_2L_4 cage-containing chains extend along the crystallographic *c*-axis. As indicated in Figure 2, the tetragonal cagelike units permit the chains to arrange tidily in the crystallographic *ab* plane, generating the squarelike channels along the chain direction. Uncoordinated water molecules are located inside. When viewed down the crystallographic [110] direction, rectangular channels (crystallographic dimensions, 7.8 × 7.0 Å) are evident in **2** (Figure 2). So far, a number of 1D metal-organic polymers have been reported, 1D coordination polymers composed of the nanosized Ln_2L_4 tetragonal prisms, however, are unprecedented.

Coordination-driven lanthanide complexes have attracted considerable attention as promising sensory materials because of their intense luminescence.[5] The luminescence spectra of **1**−**4** were

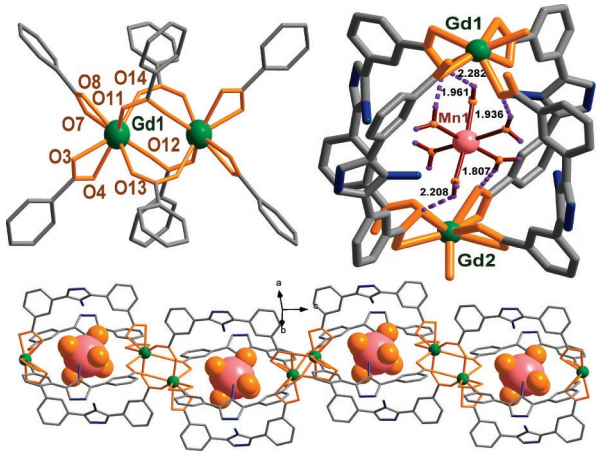


Figure 1. (Top-left) The coordination sphere of Gd(III); (top-right) the cage unit encapsulating $[Mn(H_2O)_6]^{2+}$ guest; (bottom) the 1D chain in **2**.

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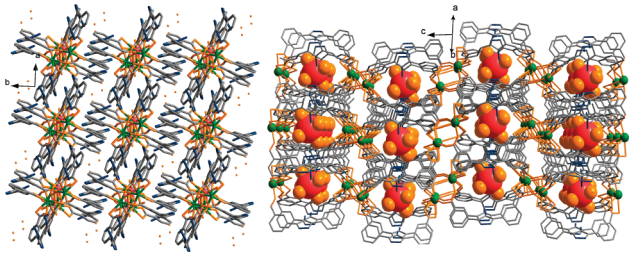

Figure 2. The solid state arrangement in **2**, viewed parallel (left) and perpendicular (right) to the chains.

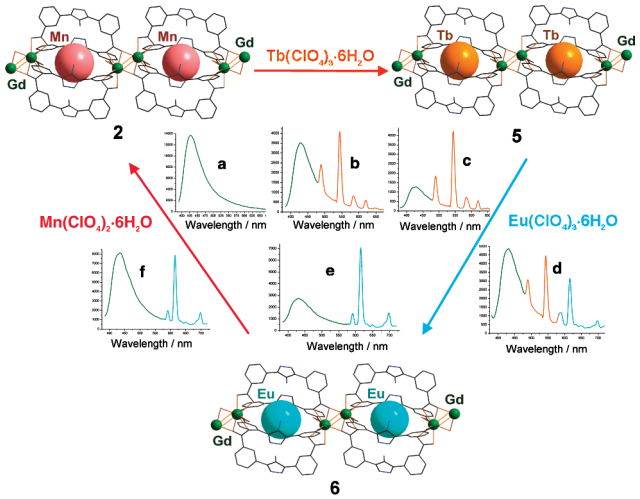

Figure 3. Guest-exchanging process of cation species based on **2**: (a−c) the solid-state emission spectra (λ_{ex} = 368 nm) of **2** stirred in a $Tb(ClO_4)_3$ aqueous solution at 0, 2, and 7 days, respectively; (c−e) the solid-state emission spectra (λ_{ex} = 368 nm) of **5** stirred in a $Eu(ClO_4)_3$ aqueous solution at 0, 2, and 7 days, respectively; (e−a) show the solid-state emission spectra (λ_{ex} = 368 nm) of **6** stirred in a $Mn(ClO_4)_2$ aqueous solution at 0, 2, and 7 days, respectively. The emission bands of **2**, **5**, and **6** are shown in green, orange, and cyan, respectively.

measured in the solid state. The fluorescence of **1** (λ_{ex} = 397 nm) and **2** (λ_{ex} = 368 nm) exhibit one emission maximum at 459 and 428 nm, respectively. Compared to the ligand emission (510 nm), the blue-shift luminescence of **1** and **2** is believed to be based upon ligand-to-metal-charge-transfer (LMCT).[6] Different from **1** and **2**, compounds **3** and **4** provide typical emission band features. For **3**, the emission bands arise from the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4) transitions of Eu(III). The corresponding emission bands are 578, 589, 611, 698 nm, respectively. Among these transitions, $^5D_0 \rightarrow {}^7F_2$ is the strongest. For **5**, four lines of Tb(III) emission can be detected in the visible spectrum, corresponding to transitions from the $^5D_4$ state: $^5D_4 \rightarrow {}^7F_6$ (489 nm), $^5D_4 \rightarrow {}^7F_5$ (542 nm), $^5D_4 \rightarrow {}^7F_4$ (585 nm), and $^5D_4 \rightarrow {}^7F_3$ (620 nm). The most prominent line was observed at 542 nm (Supporting Information).

The porous frameworks of **1**−**4** are able to undergo a reversible and controllable cation-exchange. The encapsulated $[Mn(H_2O)_6]^{2+}$ species are readily replaced reversibly by the $[Ln(H_2O)_8]^{3+}$ cations with preservation of the original crystal structure, which leads to luminescence tunability. For example, the crystals of **2** were stirred in an aqueous solution of $Tb(ClO_4)_3{\cdot}6H_2O$ (large excess) at room temperature for 7 days, generating a new host−guest complex $\{[(Gd_2L_4)Tb(H_2O)_8ClO_4]{\cdot}0.5(H_2O)\}_n$ (**5**). As shown in Figure 3, both emission bands of **2** and **5** are found in the emission spectrum after 2 days, which indicates that the encapsulated $[Mn(HO_2)_6]^{2+}$ in **2** were partially replaced by the $[Tb(H_2O)_8]^{3+}$ cations. As time goes on, the typical emission intensities of **5** increased, while the intensity of the fluorescence of **2** decreased. After 7 days, no more changes for the fluorescent intensities have been observed, indicating that the exchange reaction of Mn^{II} by Tb^{III} was finished. The XRD pattern of **5** indicates that the solid structure of **2** is maintained upon ion-exchange (Supporting Information). Besides the $Ln(ClO_4)_3$, the $LnCl_3$ or $Ln(NO_3)_3$ can also be used to perform the ion-exchange reactions, but takes a longer time (Supporting Information). Furthermore, the Tb(III) cation in **5** can be replaced by its analogue. For example, the crystals of **5** were stirred in an aqueous solution of $Eu(ClO_4)_3{\cdot}6H_2O$ (large excess) at room temperature for 7 days to generate the new complex $\{[(Gd_2L_4)Eu(H_2O)_8ClO_4]{\cdot}0.5(H_2O)\}_n$ (**6**), in which the $[Eu(H_2O)_8]^{3+}$ species are located. The emission spectra (Figure 3) and XRD pattern (Supporting Information) demonstrate this ion-exchange process well. More interesting is that **2** can be regenerated when **6** was treated by a large excess of $Mn(ClO_4)_2{\cdot}6H_2O$ in water for 7 days, which is well confirmed by the XRD pattern and emission spectrum (Supporting Information). Compounds **1**−**4** are completely insoluble in water owing to their polymeric natures (Supporting Information), so the possibility of a dissolution−recrystallization mechanism for explaining this reversible guest-exchange is impossible.

In conclusion, a series of 1D lanthanide-based coordination polymers consisting of Ln_2L_4 cage units with tunable luminescent properties based on reversible ion-dependent exchange was reported. Most importantly, it provides a promising and convenient approach to access the multifunctional luminescent materials that can provide tunable emissions by controlling the type of guest species. We believe that such a property should lead to new, tunable fluorescent materials and sensors.

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Supporting Information Available: Crystallographic data and CIF files of **1**−**4**, synthesis, emission spectra, TGA traces of **1**−**4**, and XRD patterns of **5**, **6**, and **2′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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