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Coordination-Driven Nanosized Lanthanide “Molecular Lantern” with Tunable Luminescent Properties

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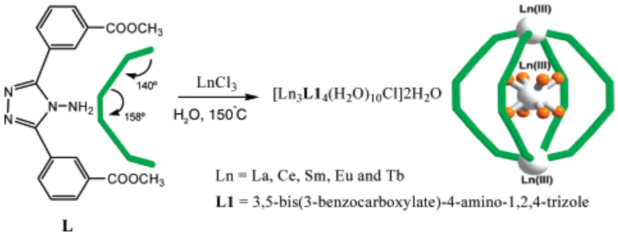
Coordination-driven self-assembly of discrete nanosized molecular cages has become one of the most active areas of supramolecular chemistry.[1] Over the past decade, extensive studies have been made on discrete molecular assemblies M_xL_y with various values of x and y.[2] Among these metal−ligand clusters, the assembly of M_2L_4 tetragonal cage remains quite rare, although a few such d-block metal supramolecular complexes have appeared in the literature recently.[3] Canonical symmetric Ln_2L_4 lanthanide cages have, to the best of our knowledge, never been described. This is clearly due to inherent difficulties in harmonizing the subtle relationship between the versatile coordination modes of the lanthanide metals (coordination numbers usually ≥8) and the ligand conformations in the synthetic cage systems. Lanthanide discrete cage-like assemblies, however, are of considerable interest in broad scientific areas, especially as the luminescent materials.

We have recently reported a series of coordination polymers and supramolecular complexes based on bent five-membered heteroatom-ring-bridged ligands.[4] By taking into account the bent geometry of such spacers, we wondered if the five-membered heteroatom ring-bridged 3,3′-biphenylcarboxylate type ligands could be used as an “organic clip”[5] to bind lanthanide ions into discrete molecular cages, especially the Ln_2L_4 tetragonal cages.

Depending on this ligand-directed approach,[3] a series of lanthanide nanosized tetragonal cages $Ln_2\mathbf{L1}_4$ (Ln(III) = La (**1**), Ce (**2**), Sm (**3**), Eu (**4**), and Tb (**5**)) which encapsulate $[Ln(H_2O)_8]^{3+}$ cations based on the bent 3,5-bis(3-benzocarboxylate)-4-amino-1,2,4-trizole ligand (**L1**) and $LnCl_3$ salts were synthesized (Supporting Information). As shown in Scheme 1, the lanthanide molecular cages $[Ln_3\mathbf{L1}_4(H_2O)_{10}Cl]\cdot 2H_2O$ were obtained as colorless cubic crystals with in situ generated carboxylate ligand via hydrolysis of **L** and $LnCl_3$ under hydrothermal conditions (H_2O/pyridine, 150 °C, 76 h) in high yield.[6] The X-ray crystal structure analysis (Supporting Information) revealed that **1**−**5** are isostructural. They crystallize in the high-symmetry tetragonal space group, *I*4/*m*. For example **3**, each Sm(2) node lies in a distorted single-capped square antiprism coordination sphere (Figure 1), which is defined by eight carboxylic oxygen and one aquo oxygen donors and with Sm−O distances range from 2.457 to 2.576 Å.[7] For **1**−**5**, the ligand donor to Ln(III) bond lengths simply reflect the ionic radius variation.[7]

Scheme 1. The Synthesis of $Ln_2\mathbf{L1}_4$ Tetragonal Cages



The most important structural feature of **1**−**5** is their cationic cage-like structure. As shown in Figure 1, four equivalent **L1** ligands act as the desired organic clip to bridge two Ln(2) ions to form a tetragonal prismatic cage. It is interesting that the two phenyl rings on the same **L1** ligand are basically coplanar, while the central triazole ring rotates by about 40° with respect to the phenyl plane and orients to the tangential direction of the cage. Such organized manner leaves an opening of ∼6.8 Å in the side of the cage. One cubic $[Ln(1)(H_2O)_8]^{3+}$ cation (∼2.8 × 2.8 × 2.8 Å^3) is trapped inside (Figure 1). Top view of **3** shows that the four ligands crosswise arrange around the Ln(2)···Ln(1)···Ln(2) axis and the two $Ln_2\mathbf{L1}_2$ planes are perpendicular to each other, which results in the tetragonal cage canonical. There is a crystallographically imposed C_4 axis passing through these three Ln(III) ions and σ_h mirror across the center of the molecule, leading to S_4 symmetry of the cage. The Ln···Ln distance is ca. 11 Å, and the distance between the two opposite trizole rings is ca. 14 Å. Up to date, only a few examples of M_2L_4 (M = Pd, Cu, Ni and Co) cages containing the metal connecting nodes with a square planar, 4 + 1 capped tetragonal planar or octahedral coordination geometry were reported recently.[3] To our knowledge, compounds **1**−**5** is the first family of lanthanide M_2L_4 nanocages.[8]

Compounds **1**−**5** exhibit the same arrangement in the crystal lattice. For example **3**, the canonical shape of the tetragonal prisms permits them to be in close proximity, which results in a 2D network driven by intermolecular $\pi-\pi$ interactions. Each prism interacts with four neighboring units through three sets of $\pi-\pi$ interactions to generate the elliptoid channels (effective cross section of ca. 6.8 × 7.9 Å^2), in which the $[Sm(H_2O)_8]^{3+}$ cations and Cl^- anions are located alternatively (Figure 2).

It is well-known that the lanthanide complexes that are attractive for their luminescent properties contributed to the “antenna effect”.[9]

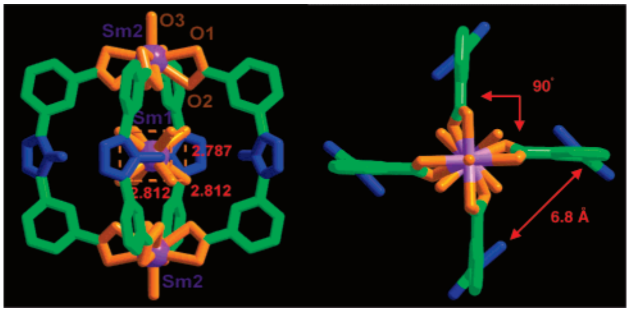


Figure 1. Compounds **1**−**5** are isostructural. Compound **3** only is shown in the figure: side (left) and top (right) views of **3** and the size of $[Sm(H_2O)_8]^{3+}$ guest.

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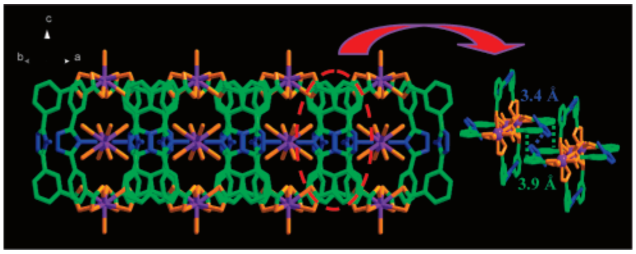

Figure 2. Side view of the 2D layer of **3** driven by the $\pi-\pi$ interactions.

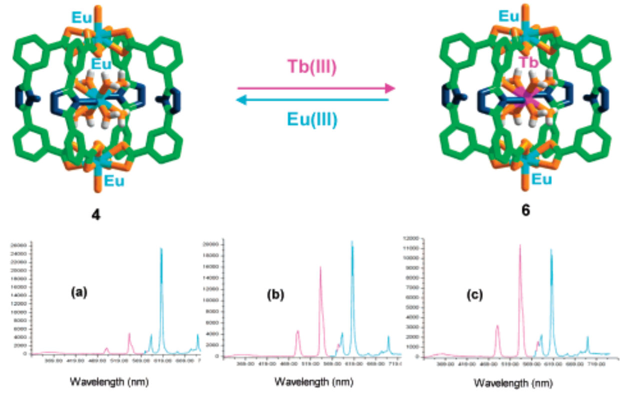

Figure 3. Guest-exchanging process of $[Ln(H_2O)_8]^{3+}$ based on **4**: Panels a, b, and c show the photoinduced solid-state emission spectra (λ_{ex} = 303 nm) of **4** stirred in a $TbCl_3$ aqueous solution at 12, 36, and 72 h, respectively. The emission bands of **4** and **6** are shown in cyan and purple, respectively.

The luminescent properties of the free ligand and its Ln(III) complexes **1**−**5** were investigated in the solid state. The emission color of the free ligand presents one emission maximum at 510 nm. The fluorescence of **1** exhibits one emission maximum at 437 nm, while **3** presents two emission maxima at 419 and 440 nm. The blue-shift luminescence of **1** and **3** originate from the emission of ligand-to-metal-charge-transfer (LMCT).[9a,10] Different from **1** and **3**, compounds **4** and **5** produce very typical emission band features. For **4**, the emission bands arise from the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions of Eu(III). The corresponding emission bands are 578, 592, 614, 618, and 698 nm, respectively. Among these transitions, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ are 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: $^5D_4 \rightarrow {}^7F_6$ (492 nm), $^5D_4 \rightarrow {}^7F_5$ (543 nm), $^5D_4 \rightarrow {}^7F_4$ (587 nm), and $^5D_4 \rightarrow {}^7F_3$ (620 nm). The most prominent line was observed at 543 nm (Figure S7). No significant emission was observed for **2** under the same experimental conditions.

Remarkably, the $[Ln(H_2O)_8]^{3+}$ guests within these Ln_2L_4 cages are mobile, and are readily replaced reversibly by their analogues with preservation of the original cage structure. For example, the crystals of **4** were stirred in an aqueous solution of $TbCl_3$ (large excess) at room temperature for 72 h, generating a new host−guest system $[Eu_2Tb\mathbf{L1}_4(H_2O)_{10}Cl]\cdot 2H_2O$ (**6**). The narrow emission bandwidth and diagnostic emission color of lanthanide cations allow for the easy simultaneous detection of different kinds of cations by emission spectra. As shown in Figure 3, both emission bands of **4** and **6** are found in the emission spectra after 12 h, which indicates that the encapsulated $[Eu(HO_2)_8]^{3+}$ in **4** were partially replaced by the $[Tb(H_2O)_8]^{3+}$ cations. As time goes on, the typical emission intensities of **6** increased, while the intensity of the fluorescence of **4** decreased. After 72 h, no more changes for the fluorescent intensities were observed, indicating that the exchange reaction of Eu^{III} by Tb^{III} finished. The XRD pattern of **6** is identical to that of original sample **4**, which indicates that the cage structure is maintained after the guest exchange (Figure S8). In addition, **4** could be regenerated when **6** was treated by a large excess of $EuCl_3$ in water after about 4 days (Figures S9−S11). It is interesting that these cages can remain intact upon ion-exchange with smaller cations. For example, the Tb^{3+} in **6** can be replaced by Mn^{2+} (Supporting Information). Because these $Ln_2^{III}L_4$ cages are insoluble in water, the possibility of a dissolution−recrystallization mechanism for explaining this reversible guest-exchange is unlikely. We believe that such a property of the $Ln_2^{III}L_4$ cages herein should lead to new, tunable fluorescent materials and sensors.

In summary, a new family of nanosized lantern-like cages Ln_2L_4 has been designed and synthesized based on a ligand-dominated approach. These nanoscopic cages can be the host for $[Ln(H_2O)_8]^{3+}$ cations.[11] More importantly, it provides a promising and convenient approach to access to the multifunctional luminescent materials that can provide tunable emissions by controlling the type of guest moieties.

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

References

(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (d) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975.

(2) (a) Swieger, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (b) Morgan, M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647. (c) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (d) Jacopozzi, P.; Dalcanale, E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 613. (e) Dinolfo, P. H.; Coropceanu, V.; Brèdas, J.-L.; Hupp, J. T. *J. Am. Chem. Soc.* **2006**, *128*, 12592.

(3) (a) Barbour, L. J.; Orr, W. G.; Atwood, J. L. *Nature* **1998**, *393*, 671. (b) McMorran, D. A.; Steel, P. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3295. (c) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1539. (d) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Smith, M. D.; Kaim, W.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2003**, *125*, 8595. (e) Amouri, H.; Mimassi, L.; Rager, M. N.; Mann, B. E.; Guyard-Duhayon, C.; Raehm, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4543.

(4) (a) Dong, Y.-B.; Zhang, Q.; Liu, L.-L.; Ma, J.-P.; Tang, B.; Huang, R.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 1514. (b) Dong, Y.-B.; Xu, H.-X.; Ma, J.-P.; Huang, R.-Q. *Inorg. Chem.* **2006**, *45*, 3325 and references therein. (c) Dong, Y.-B.; Sun, T.; Ma, J.-P.; Zhao, X.-X.; Huang, R.-Q. *Inorg. Chem.* **2006**, *45*, 10613 and references therein.

(5) Kryschenko, Y. K.; Seidel, S. R.; Muddiman, D. C.; Nepomuceno, A. I.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 9647.

(6) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511.

(7) Parker, D.; Puschmann, H.; Batsanov, A. S.; Senanayake, K. *Inorg. Chem.* **2003**, *42*, 8646 and references therein.

(8) Some novel rare earth cages were reported recently, see: Xu, J.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 2745 and references therein.

(9) (a) Bünzli, J. G. *Acc. Chem. Res.* **2006**, *39*, 53. (b) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201. (c) Liu, W.; Jiao, T.; Li, Y.; Liu, Q.; Tan, M.; Wang, H.; Wang, L. *J. Am. Chem. Soc.* **2004**, *126*, 2280 and references therein.

(10) Guo, X.; Zhu, G.; Fang, Q.; Xue, M.; Tian, G.; Sun, J.; Li, X.; Qiu, S. *Inorg. Chem.* **2005**, *44*, 3850.

(11) Wang, Z.-X.; Shen, X.-F.; Wang, J.; Zhang, P.; Li, Y.-Z.; Nfor, E. N.; Song, Y.; Ohkoshi, S.; Hashimoto, K.; You, X.-Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 1.

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