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Conformation-Controlled Luminescent Properties of Lanthanide Clusters Containing *p-tert*-Butylsulfonylcalix[4]arene

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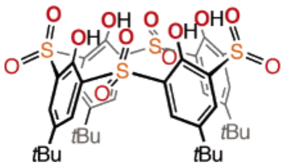
Dinuclear and cubane-shaped lanthanide cluster complexes containing Eu^{III} and Tb^{III} were synthesized by step-by-step construction using *p-tert*-butylsulfonylcalix[4]arene as a cluster-forming ligand. The sulfonylcalixarene adopts a pinched-cone conformation in the dinuclear complexes and a cone conformation in the cubane complexes. Because the calixarene has a large π-conjugate system expanding over the entire molecule, it behaves as a good antenna chromophore for UV and near-UV light, and a slight conformational change of the calixarene (from cone to pinched-cone and vice versa) has an effect on the energy levels of excited S$_1$ and T$_1$ states. As a result, selectivity is observed in the luminescent properties of dinuclear and cubane-shaped systems of Eu^{III} and Tb^{III}.

Nanosized metal complexes are highly advantageous for generating functionalized nanomaterials, owing to their ease of structure design, synthesis, and tuning of properties.[1] These advantages are attained by bottom-up construction:[2] the combining of a variety of metal ions and well-organized organic ligands results in the accomplishment of synergetic effects.[3,4] We are investigating novel functionality in nanosized complexes constructed with thiacalixarene derivatives[5,6] including *p-tert*-butylsulfonylcalix[4]arene ($H_4\mathbf{L}$; Chart 1);[6] several types of nanoarchitectures have been constructed using rational synthetic procedures.[5,6] It has been shown that ligands of this series exhibit a high potential as templates for metal−cluster formation. Moreover, they may act as a superior antenna chromophore for UV and near-UV excitation compared to the original methylene-bridged calixarenes[4] because the thiacalixarene derivatives possess large π-conjugate systems that expand over the entire molecule. Here we report two types of nanoclusters of Eu^{III} and Tb^{III} supported by $\mathbf{L}^{4-}$, which exhibit peculiar luminescent properties controlled by slight conformational changes in the ligand.

Chart 1. *p-tert*-Butylsulfonylcalix[4]arene, $H_4\mathbf{L}$



Dinuclear $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Ln}_2(\mathbf{L})_2(\mathrm{H_2O})_4]$ $[(n\mathrm{Bu}_4\mathrm{N})_2\cdot\mathbf{1}$[7] with Ln = Eu; $(n\mathrm{Bu}_4\mathrm{N})_2\cdot\mathbf{2}$ with Ln = Tb] were obtained using a

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(7) Crystal data for $(n\mathrm{Bu}_4\mathrm{N})_2\cdot\mathbf{1}\cdot4\mathrm{MeNO}_2$: monoclinic, $P2_1/n$, $a = 17.1149(6)$ Å, $b = 14.5303(6)$ Å, $c = 26.5117(11)$ Å, $\beta = 95.7910(10)°$, $U = 6559.4(4)$ Å^3, $Z = 2$, $T = 100(2)$ K, wR2 = 0.102 (11 565 unique reflections), R1 = 0.057 [6148 reflections with $I > 2\sigma(I)$] using

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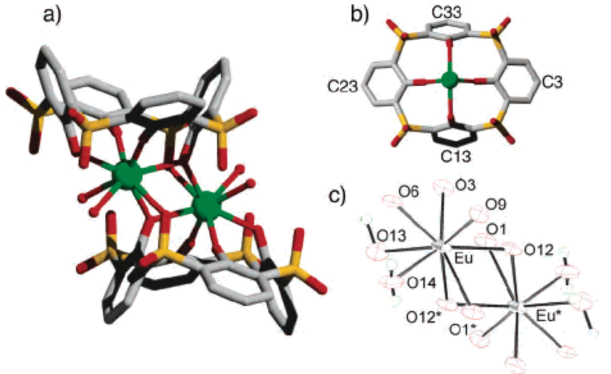

Figure 1. Crystal structure of $\mathbf{1}^{2-}$. (a) Side view of the molecule. (b) Mononuclear core involving one calixarene ligand and one Eu^{III} ion. Hydrogen atoms and *t*Bu groups are omitted. Each atom is depicted as follows: Eu, green; S, orange; O, red; C, gray. (c) ORTEP drawing of the Eu_2 core with thermal ellipsoids at 50% probability. Symmetry transformation: $*, -x, -y, -z + 2$.

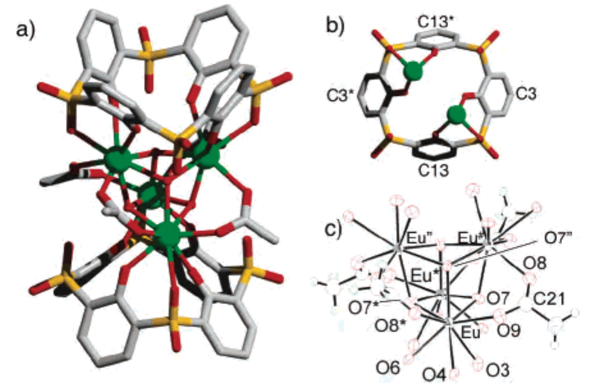

Figure 2. Crystal structure of $\mathbf{3}^{4-}$. (a) Side view of the molecule. (b) Dinuclear core involving one ligand and two Eu^{III} ions. (c) ORTEP drawing of the Eu_4 core. Symmetry transformations: $*, -x + {}^1/_2, -y + {}^1/_2, z$; $''$, $x, -y + {}^1/_2, -z + {}^1/_2$; $^{\#}, -x + {}^1/_2, y, -z + {}^1/_2$.

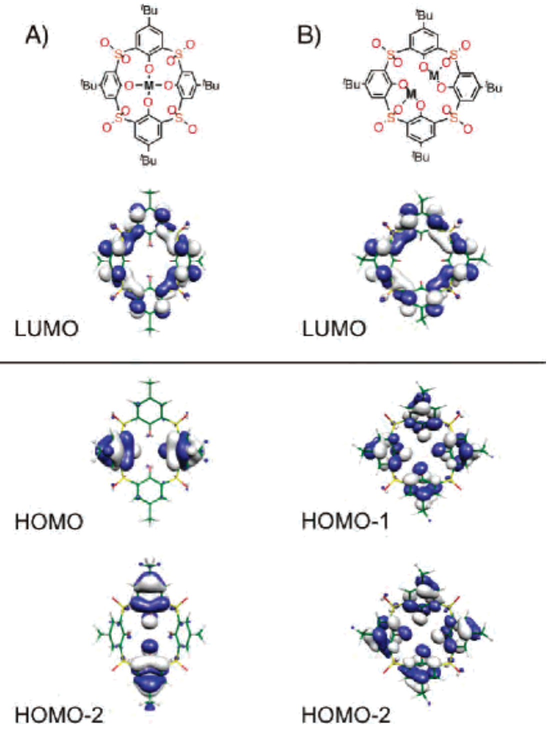

Figure 3. Frontier MOs of idealized models for half of the dinuclear system with a pinched-cone conformation (A) and the cubane system with a cone conformation (B). The S_1 state is practically a HOMO → LUMO excitation in the former and a HOMO-1 → LUMO excitation in the latter. In the T_1 state, the main coefficients occur for the same orbital couples as those in S_1. A similar situation applies for the S_2 and T_2 pairs of states, which are due to HOMO-2 → LUMO excitations in both cases.

procedure similar to the published procedure for synthesizing Gd^{III} dinuclear complexes.[6b] These complexes are isostructural (Figure 1) and may be regarded as a dimer of mononuclear units $\{Ln(\mathbf{L})\}^-$, in which pinched-conic $\mathbf{L}^{4-}$ behaves as a tetradentate ligand via four phenoxo oxygen atoms (Figure 1b), and assembly of two units results in the formation of a dinuclear cluster core sharing two phenoxo oxygen atoms from two units. Reaction of $(n\text{Bu}_4\text{N})_2[\text{Ln}_2(\mathbf{L})_2(\text{H}_2\text{O})_4]$, $\text{Ln(AcO)}_3\cdot n\text{H}_2\text{O}$, and $n\text{Bu}_4\text{NOH}$ in a 1:2:4 molar ratio afforded isostructural cubane-type complexes of $(n\text{Bu}_4\text{N})_4[\text{Ln}_4(\mathbf{L})_2(\text{OH})_4(\text{AcO})_4]$ [$(n\text{Bu}_4\text{N})_4\cdot\mathbf{3}$[7] and $(n\text{Bu}_4\text{N})_4\cdot\mathbf{4}$, with Ln = Eu and Tb, respectively] as pale-yellow colored crystals with a relatively high yield (Figure 2). This type of step-by-step cluster formation is beneficial in the design of heteronuclear clusters. The highly symmetrical complexes $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$ are again regarded as assemblages of two smaller units, $\{Ln_2(\mathbf{L})\}^{2+}$, in which a conic $\mathbf{L}^{4-}$ acts as a bis-tridentate ligand (via two phenoxo oxygens and one sulfonyl oxygen) for each lanthanide ion, and the two units are assembled to form a cubane cluster further supported by four μ_3-hydroxo ligands (O7) and four bridging acetate ligands (O8 and O9).

$\mathbf{L}^{4-}$ involves a large, flexible π-conjugate system expanding over the entire ligand, and its optical properties are very sensitive to small changes in conformation. In dinuclear complexes, $\mathbf{L}^{4-}$ adopts a pinched-cone conformation with a distance ratio $d_{C13-C33}/d_{C3-C23}$ of 0.71, while in cubane systems, it takes a cone conformation with a ratio $d_{C13-C13*}/d_{C3-C3*}$ of 0.83. On the basis of time-dependent density functional theory calculations for idealized models (Figure 3),[8] it is thought that the effective higher symmetry of the ligand in the cubane system (B) is reflected in the overall delocalization of occupied molecular orbitals (MOs) and, consequently, in a lower transition energy to the delocalized lowest unoccupied MO (LUMO). In the dinuclear system, the occupied MOs are less delocalized (A), so that the cost of transition toward the delocalized LUMO is higher for both singlet and triplet promotions. This was confirmed by spectroscopic studies in the solid state; the calixarene unit functions as a good antenna chromophore for UV and near-UV light, with absorption at 340 nm for $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ and 356 nm for $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$, with the latter pair exhibiting a bathochromic shift compared to the former and showing a tailing absorption reaching to the visible region, up to 430 nm (Figure S4 in the Supporting Information). The energy levels of the ligand-based excited states were also estimated from exited, fluorescence, and phosphorescence spectra,

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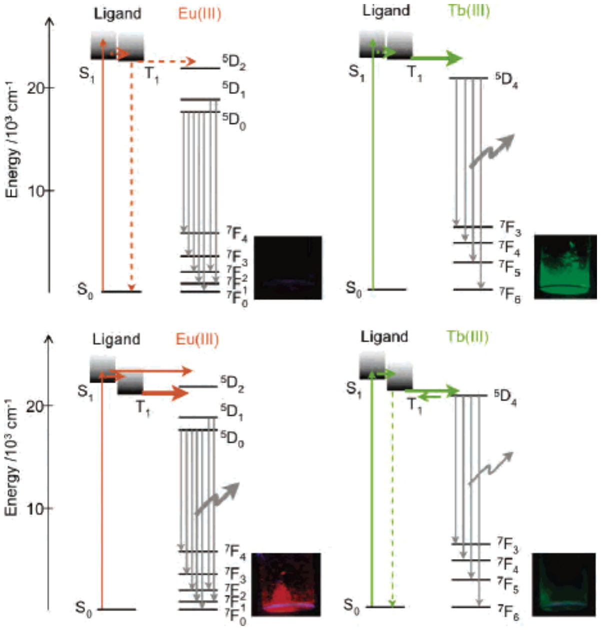
532 parameters. Crystal data for $(n\text{Bu}_4\text{N})_4\cdot\mathbf{3}\cdot6\text{DMF}$: tetragonal, $P4_2/n$, $a = 17.6531(13)$ Å, $c = 31.496(3)$ Å, $U = 9815.1(15)$ Å^3, $Z = 2$, $T = 100$ K, w$R2 = 0.102$ (8512 unique reflections), $R1 = 0.057$ [2660 reflections with $I > 2\sigma(I)$] using 790 parameters.

(8) The calculations were performed with *Gaussian03*.

Scheme 1. Energy Diagram for Complexes $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ (Top) and $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$ (Bottom), Respectively, Estimated from the Spectroscopic Data



which are shown in Figures S3 and S5 in the Supporting Information for Gd^{III} dinuclear[6b] and cubane complexes. The dinuclear system exhibits fluorescence at 453 nm (22 100 cm^{-1}) and phosphorescence at 468 nm (21 400 cm^{-1}) with a shoulder at 457 nm (21 900 cm^{-1}); in contrast, the cubane system shows fluorescence and phosphorescence in lower-energy regions, at 462 nm (21 600 cm^{-1}) and 482 nm (20 700 cm^{-1}), respectively.

This slight difference in ligand-based S_1 and T_1 levels causes significant differences in the luminescent properties of complexes $\mathbf{1}^{2-}-\mathbf{4}^{4-}$. The Tb dimer $\mathbf{2}^{2-}$ shows strong luminescence in the solid state ($\lambda_{ex} = 365$ nm), while the related Eu dimer $\mathbf{1}^{2-}$ does not show any luminescence at room temperature (Scheme 1). Meanwhile, the cubane complexes exhibit an opposing trend; the Eu cubane $\mathbf{3}^{4-}$ is strongly luminescent, while the Tb cubane $\mathbf{4}^{4-}$ shows very weak luminescence under the same experimental conditions.[9] Because the ligand absorptions appear near the visible region, the ligand T_1 state and the excited Ln^{III}* state are located close together, and therefore the exact point at which the energies of these states match is the determinant of luminescence.[10] The T_1 levels in $\mathbf{2}^{2-}$ and $\mathbf{3}^{4-}$ are located above the Ln^{III}* levels, which prevents back-transfer processes from Ln^{III} to the ligand; efficient energy-transfer processes take place from the ligand T_1 level to the $^5D_4$ level of Tb^{III} in $\mathbf{2}^{2-}$ and the $^5D_1$ level of Eu^{III} in $\mathbf{3}^{4-}$. In the case of $\mathbf{1}^{2-}$ and $\mathbf{4}^{4-}$, a smaller energy difference between T_1 and $^5D_2$ ($\mathbf{1}^{2-}$) or $^5D_4$ ($\mathbf{4}^{4-}$) accelerates the $^5D_j \rightarrow T_1$ back-transfer process,[9] which results in very weak luminescence, or none, at room temperature.

In conclusion, we have investigated the luminescent behavior of di- and tetranuclear lanthanide clusters containing *p-tert*-butylsulfonylcalix[4]arene, which functions as a good antenna chromophore for UV and near-UV light. Because the ligand contains a large π-conjugate system expanding over the entire molecule, the functionality of the antenna is very sensitive to molecular symmetry; hence, it may be controlled via conformational changes, without any chemical modifications.

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Supporting Information Available: Experimental procedure for the preparation of the complex and details of X-ray crystallographic analyses (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) At 77 K, precise luminescence was observed for both $\mathbf{1}^{2-}$ and $\mathbf{4}^{4-}$. For the case of $\mathbf{4}^{4-}$ at room temperature, ligand-based luminescence was observed together with the Tb^{III}-based luminescence. The band shape and position are similar to those of the corresponding Gd cubane complex (Figure S6 in the Supporting Information), and this suggests the presence of a $^5D_j \rightarrow T_1$ (or S_1) back-transfer process. The intensity of this luminescence decreased as the temperature was lowered. Ligand-based luminescence of $\mathbf{1}^{2-}$ was not observed at ambient temperature, with a similar manner for the corresponding Gd dinuclear complex (see Figure S5 and its legend in the Supporting Information).

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