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Highly Luminescent Superparamagnetic Diterbium(III) Complex Based on the Bifunctionality of *p-tert*-Butylsulfonylcalix[4]arene

Takashi Kajiwara,*[a] Miki Hasegawa,*[b] Ayumi Ishii,[b] Kensuke Katagiri,[a] Munkhtsetseg Baatar,[a] Shinya Takaishi,[a] Nobuhiko Iki,[c] and Masahiro Yamashita[a]

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A diterbium(III) complex was synthesized by using *p-tert*-butylsulfonylcalix[4]arene, which adopts a 1,2-alternate conformation, acts as a sensitive optical-antenna chromophore for UV and near-UV light and causes easy-axis magnetic anisotropy in the Tb^{III} ions. The complex showed efficient ff emission with a corrected quantum yield of ca. 85 % even at room temperature. In addition, it showed superparamagnetic behaviour due to slow magnetic relaxation at low temperatures.

Introduction

Lanthanide complexes have attracted considerable attention due to their electronic properties, including magnetism[1,2] and luminescence.[3,4] The current focus is on the construction of multifunctional lanthanide complexes based on these properties. Thus, we are developing a new and rational synthetic method for the preparation of multinuclear lanthanide complexes by using *p-tert*-butylsulfonylcalix[4]arene (H_4L, Scheme 1).[5] H_4L possesses a large π-conjugated system, which extends over the entire molecule, and its structural flexibility makes it possible to tune the energy levels of the frontier orbitals and thus the antenna chromophore properties for the ff emission.[5d] Because the T_1 level of the calixarene is adjacent to the $^5D_4$ level of the Tb^{III} ions, we can enhance or turn off the luminescence from the Tb^{III} centre by changing the conformation of the calixarene ligand. When the T_1 level is raised slightly higher than the $^5D_4$ level, which occurs when the calixarene adopts a less-symmetrical conformation, efficient ligand-to-metal energy transfer (LMET) becomes possible and very high luminescence from Tb^{III} could be realized. In the meantime, utilization of heavy lanthanide ions such as Tb^{III} and Dy^{III} are becoming more popular in the design of single-molecule magnets (SMMs), because of their large angular momenta ($J = 6$ with $g_J = 3/2$ for Tb^{III}) and strong magnetic anisotropy in the ground multiplet state. It is known that the symmetry of the crystal field around the Ln^{III} ion strongly affects its magnetic anisotropy.[2a,6] The relationship between the symmetry and the magnetic anisotropy could be used to control the SMM character by incorporating magnetic anisotropy. To realize strong easy-axis anisotropy, which is advantageous for the construction of SMMs, the negative charges of the donating atom set should be concentrated in a narrow area to stabilize the ground sublevel $|J, J_z> = |6, \pm6>$ from the $^7F_6$ state of Tb^{III}. Polyphenol ligands are effective for this purpose, as the calculated negative charge on the phenoxido oxygen atom is approximately two times larger than those of other anionic ligands, such as the nitrate ion, which were estimated from DFT calculations.[7] When the calixarene adopts a 1,2-alternate conformation (Scheme 1, right),[8] conditions for both strong luminescence and easy-axis anisotropy should be met. Here we report the bifunctionality of sulfonylcalix[4]arene in a diterbium(III) complex, which showed very strong luminescence and superparamagnetic behaviour.

[a] Department of Chemistry, Graduate School of Science, Tohoku University and CREST (JST),
Aramaki Aoba-ku, Sendai 980-8578, Japan
Fax: +81-22-795-6547
E-mail: kajiwara@agnus.chem.tohoku.ac.jp
[b] Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama-Gakuin University,
5-10-1 Fuchinobe, Sagamihara 229-8558, Japan
[c] Department of Environmental Studies, Graduate School of Environmental Studies, Tohoku University,
Aramaki Aoba-ku, Sendai 980-8579, Japan

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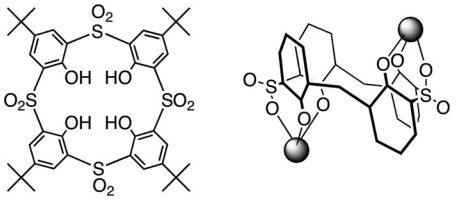

Scheme 1. Structure of H_4L (left) and schematic draw of bis(tridentate) coordination fashion in 1,2-alternate conformation (right).

Results and Discussion

The diterbium(III) complex was prepared by the reaction of terbium acetate, terbium nitrate and H_4L in a 4:2:3 ratio, which was followed by recrystallization from a dmf solution to give pale-yellow crystals of $[Tb_2(L)(NO_3)_2(dmf)_6]\cdot 2dmf$ (**1**·2dmf, Figure 1). The L^{4-} ligand adopts a 1,2-alternate conformation and acts as a bis(tridentate) facial ligand through two phenoxido oxygen atoms (O1 and O4) and one sulfonyl oxygen atom (O2). Similar tridentate *fac* coordination was also reported for $(n\text{-}Bu_4N)_4[Ln_4(L)_2(AcO)_4(\mu_3\text{-}OH)_4]$;[5d] however, L^{4-} adopted a more symmetrical cone conformation, and the Ln^{III} ions were further bridged by coligands (μ_3-OH and acetate ions) to form cuboidal clusters. Nitrate ions, as well as bulky dmf molecules, behave as terminating ligands to avoid cluster formation and expansion in **1**.[9] The absence of a bridging ligand causes the calixarene to adopt the 1,2-alternate conformation to minimize the repulsion between the metal centres. Each Tb is coordinated by three oxygen atoms from the calixarene, three oxygen atoms from dmf molecules (O10, O11 and O12) and two oxygen atoms from a nitrate ion in a κ^2O coordination fashion (O7 and O8). The coordination geometry can be regarded as a slightly distorted square antiprism, which is formed with two squares including O2/O4/O10/O12 and O1/O7/O8/O11. Single crystals of $[Gd_2(L)(NO_3)_2(dmf)_6]\cdot 2dmf$ (**2**·2dmf) were also obtained by using a similar procedure, and it was isostructural with **1**·2dmf.

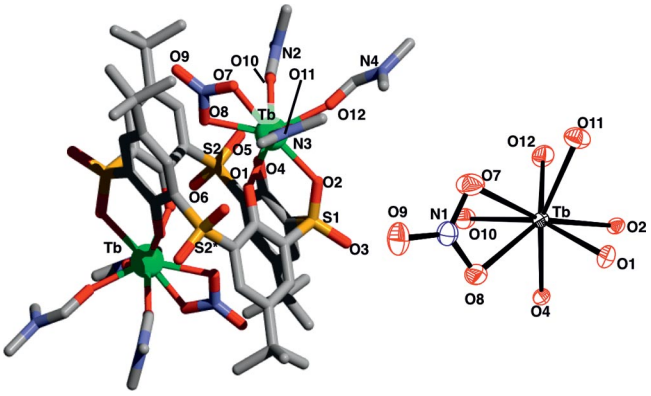

Figure 1. (left) Crystal structure and (right) ORTEP diagram of the core of complex **1**. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Tb–O4 2.2821(17), Tb–O1 2.2831(16), Tb–O12 2.3547(18), Tb–O10 2.3986(18), Tb–O2 2.4012(16), Tb–O11 2.4218(18), Tb–O7 2.4608(19), Tb–O8 2.4679(18); selected bond angles [°]: Tb···Tb(intramolecular) 6.5179(5), Tb···Tb(intermolecular) 8.3839(9). Symmetry operation: * 1 –*x*, 1 –*y*, –*z*.

The L^{4-} ligand in **2**, which exhibited absorptions at 360 nm (27800 cm^{-1}) and 337 nm (29700 cm^{-1}) in the solid state (Figure 2), functions as a sensitive optical-antenna chromophore for UV and near-UV light. The excited electronic states of the ligand were estimated from the positions of the fluorescence and phosphorescence maxima. For this complex, the fluorescence and phosphorescence peaks were observed at 439 nm (22800 cm^{-1}) and at 465 nm (21500 cm^{-1}), respectively, at 77 K. On the basis of these emissions, the triplet (T_1) level is much closer to the previous dinuclear $[Gd_2(L)_2(H_2O)_4]^{2-}$ (21400 cm^{-1}) than to the cuboidal $[Gd_4(L)_2(AcO)_4(OH)_4]^{4-}$ (20700 cm^{-1}),[5d] and it is slightly higher than the $^5D_4$ level of the Tb^{III} ions, which is advantageous for efficient LMET and strong ff luminescence (Figure 3). Compound **1**·2dmf in the solid state showed an efficient ff emission even at room temperature upon excitation at 365 nm with a negligible luminescence from the ligand centre at 439 nm, and a corrected quantum yield[10] was estimated for four ff bands (intensity was integrated in the range of 450–750 nm) estimated to be 85%. This extremely strong luminescence may be due to the accurate tuning of the excited level of L^{4-} by controlling the conformation, the long lifetime of the T_1 level of L^{4-} estimated as 2.9 ms for **2**·2dmf (Figure S1, which is slightly longer than those of L^{4-} in cone conformation, 2.5 ms) and also the presence of two luminescent centres coordinated by one calixarene, which enhances the probability of ff emission.

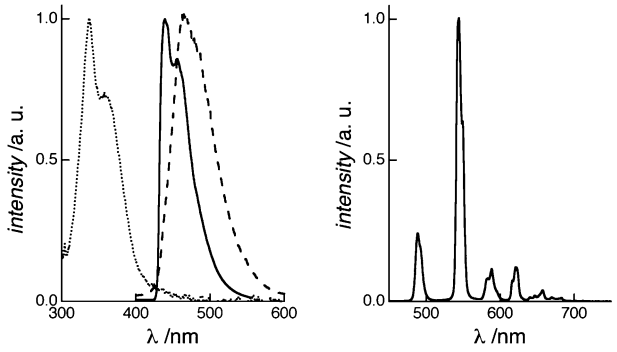

Figure 2. Ligand-centred absorption spectrum at room temperature (···) and luminescence (——) and phosphorescence spectra (– – –) at 77 K measured for a crystalline sample of **2**·2dmf (λ_{ex} = 360 nm) (left); luminescence spectrum of a crystalline sample of **1**·2dmf at room temperature (λ_{ex} = 365 nm) (right).

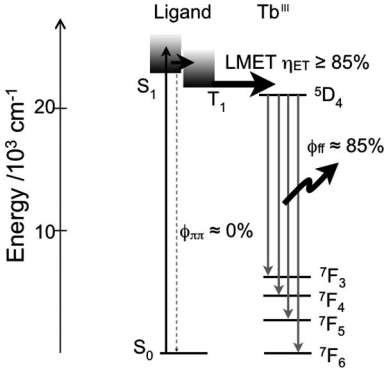

Figure 3. Energy diagram for complex **1**·2dmf estimated from the spectroscopic data.

The dc and ac magnetic susceptibility data were measured for microcrystalline samples of **1**·2dmf (Figure 4). The $\chi_M T$ values for a randomly oriented sample only showed slight temperature dependences. The $\chi_M T$ values

decrease upon lowering the temperature, which exhibited a presence of a magnetic anisotropy of the Tb^{III} ions. Oriented samples, which were aligned in a 5 T field at 2 K, showed completely deferent $\chi_M T$–T curves, especially in the low-temperature region. Because the intra- and intermolecular Tb···Tb distances are long enough to eliminate any magnetic interactions, the temperature dependence here should be due to the single-ion magnetic anisotropy of the Tb^{III} ions. The shape of the $\chi_M T$–T curve is typical for the presence of an easy-axis-type magnetic anisotropy. The data were analyzed by using a simple Hamiltonian by considering a second-order anisotropic parameter [Equation (1)],[11] and D/k_B was estimated to be negative and equal to –7.2 K, which is essential for single-molecule magnets. The ac susceptibility data for the aligned sample clearly showed frequency-dependent χ' and χ'' signals, indicating that slow magnetic relaxation occurred below 4 K. This superparamagnetic behaviour of **1**·2dmf is due to the double-well potential formed by the easy-axis anisotropy of the Tb^{III} ions; however, a maximum for χ'' was not observed down to 1.8 K, which indicates that fast spin-flipping pathways, such as a tunnelling process, still dominate in this temperature range.

$$\hat{H} = D(\hat{J}_z^2 - \hat{J}^2/3) - \beta g_J H \hat{J}_z \quad (1)$$

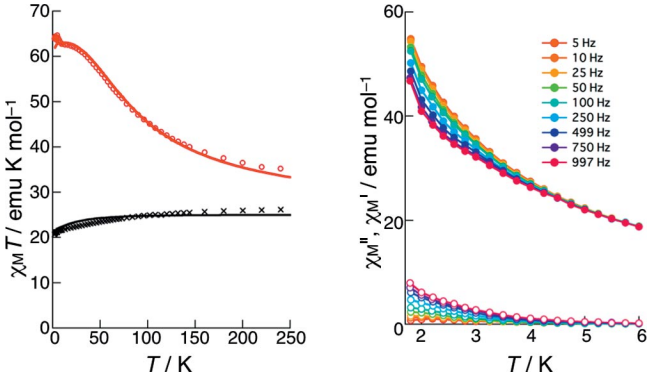

Figure 4. $\chi_M T$–T plots for aligned (○) and randomly oriented (×) polycrystalline samples of **1**·2dmf, both measured in a 1000 Oe dc field. For the former, the microcrystalline sample was aligned under 5 T dc field at 2 K, whereas for the latter, randomly oriented microcrystallines were fixed in eicosane. Solid curves are temperature dependence of calculated $\chi_M(//)T$ (for the aligned sample) and $\chi_M(//)T/3 + 2\chi_M(\perp)T/3$ (for the randomly oriented sample) values by using the parameters described in the main text (left). Temperature dependences of χ_M' (●) and χ_M'' (○) of **1**·2dmf measured in a 1000-Oe external dc field (right).

Conclusions

We showed that sulfonylcalix[4]arene exhibits bifunctionality by using conformational design, and the resulting Tb^{III} dinuclear complex showed highly efficient luminescence as well as a relatively strong uniaxial magnetic anisotropy. Compound **1**·2dmf could be a potential precursor for the construction of multifunctional nanomagnets, such as optically switchable SMMs and single-chain magnets.

Experimental Section

1·2dmf: A mixture of terbium(III) acetate (38 mg, 0.08 mmol), terbium(III) nitrate (18 mg, 0.04 mmol) and H_4L (51 mg, 0.06 mmol) in a 4:2:3 molar ratio in ethanol (10 mL) and dmf (2 mL) was heated at reflux for 1 h, and the colourless reaction solution was concentrated under reduced pressure to afford a white residue. The residue was recrystallized from warm dmf solution to give pale-yellow crystals of $[Tb_2(L)(NO_3)_2(dmf)_6]$·2dmf. Yield: 28 mg (50%). $C_{64}H_{100}N_{10}O_{26}S_4Tb_2$ (1871.62): calcd. C 40.61, H 5.13, N 6.47; found C 40.37, H 5.02, N 6.49.

2·2dmf: This compound was synthesized by the procedure outlined for **1**·2dmf by using terbium(III) acetate and terbium(III) nitrate.

Variable-temperature magnetic susceptibility measurements were performed with a SQUID magnetometer MPMS 5S (Quantum Design) at 0.1 T. Diamagnetic correction was determined from Pascal's constants.

X-ray data for all complexes were collected at low temperature with a Bruker AXS SMART-1000/CCD area detector by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Complete hemispheres of data were collected by using ω scans. Integrated intensities were obtained with SAINT+, and SADABS was used for absorption correction.[12] The structures were solved by direct methods by using SHELXS-97 and refined by least-squares on F^2, SHELXL-97.[11] Non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were treated by using a riding model. CCDC-688245 (for **1**) and -688246 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 1·2dmf: $C_{64}H_{100}N_{10}O_{26}S_4Tb_2$, M_r = 1871.62, triclinic, $P\bar{1}$, a = 12.4798(13) Å, b = 13.3594(14) Å, c = 14.3265(15) Å, α = 87.011(2)°, β = 64.387(2)°, γ = 68.740(2)°, V = 1991.6(4) Å^3, Z = 1, T = 100 K, $F(000)$ = 956, μ(Mo-K_α) = 1.946 mm^{-1}. Using 492 parameters, wR_2 = 0.0590 (11465 unique reflections), R_1 = 0.0336 [9223 reflections with $I > 2\sigma(I)$].

Crystal Data for 2·2dmf: $C_{64}H_{100}N_{10}O_{26}S_4Gd_2$, M_r = 1868.28, triclinic, $P\bar{1}$, a = 12.4712(13) Å, b = 13.3478(14) Å, c = 14.3144(15) Å, α = 86.969(2)°, β = 64.333(2)°, γ = 68.719(2)°, V = 1985.8(4) Å^3, Z = 1, T = 200 K, $F(000)$ = 954, μ(Mo-K_α) = 1.841 mm^{-1}. Using 492 parameters, wR_2 = 0.0626 (11416 unique reflections), R_1 = 0.0249 [11070 reflections with $I > 2\sigma(I)$].

Supporting Information (see footnote on the first page of this article): Additional X-ray structure refinement details and luminescent properties for **1**·2dmf and **2**·2dmf.

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