Energy transfer luminescence of Tb^{3+} ion complexed with calix[4]arenetetrasulfonate and the thia and sulfonyl analogue. The effect of bridging groups †

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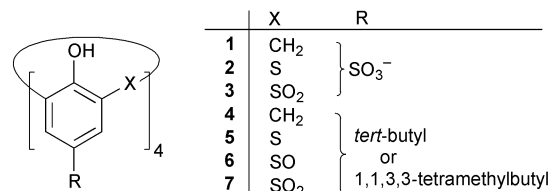
New analogues of calix[4]arenetetrasulfonate (**1**) were prepared, in which the methylene bridges are replaced by S (**2**) and SO$_2$ (**3**). The complexation ability of these calixarene ligands **1**–**3** toward Tb^{3+} ion and luminescence properties of the resulting complexes were examined. All the ligands formed complexes with lanthanide ions (Pr^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}), among which the Tb^{3+} complex exhibited strong energy transfer luminescence. The pH dependence of the luminescence intensity suggested that the analogues **2** and **3** possess higher complexation ability towards Tb^{3+} than the parent **1**, which should be ascribed to the higher acidity of the phenolic OH groups as well as the coordinating ability of the bridging groups S and SO$_2$. The composition of the complexes of **2** and **3** was determined to be Tb^{3+}·**2** and Tb^{3+}·**3** by a molar ratio method. The photophysical properties such as emission lifetimes (τ) and quantum yields (Φ) of the complexes were estimated. Both Tb^{3+}·**2** and Tb^{3+}·**3** gave comparable τ values (0.7 ms), which are larger than that of Tb^{3+}·(**1**)$_2$ (0.6 ms). Comparison of their lifetimes in D$_2$O solution suggested that Tb^{3+}·**2** and Tb^{3+}·**3** have four to five coordinated water molecules responsible for quenching. On the other hand, complex Tb^{3+}·**2** gave the largest Φ value (0.15), whereas Tb^{3+}·(**1**)$_2$ and Tb^{3+}·**3** gave very close Φ values (0.12 and 0.13, respectively). The results of this study showed that thiacalix[4]arenetetrasulfonate **2** and the sulfonyl analogue **3** are promising candidates for the scaffold to construct luminescence devices from the viewpoint of the higher complexation ability and luminescent performance.

Introduction

Recently, lanthanide complexes have drawn much attention as luminescent devices for biological assays, lasers, and optical amplification because of their attractive features such as long lifetime, large Stokes shift, and narrow emission band.[1–3] Choice of the ligand has been of key importance to obtain strong luminescence and long lifetime. Having a macrocyclic structure containing several phenol rings which not only are an inherent chromophore but are also ready for various transformations, calix[n]arenes have been conveniently utilized as ligands to form luminescent complexes with Tb^{3+} and Eu^{3+} ions. For instance, Shinkai et al. reported that calix[n]arenesulfonates (n = 4 (**1**), 6, and 8) could form highly luminescent complexes with Tb^{3+} ion.[4] Bünzli et al. studied photophysical processes of the luminescence of the complexes with p-tert-butylcalix[n]arenes (n = 5, 8).[5] Furthermore, modifications at the phenolic OH function with ligating groups such as amides,[6] bipyridines,[7] and crown ethers[8] have improved the luminescent ability of calix[4]arene complexes by increasing the encapsulating power of the ligand for metal ions to expel coordinated water responsible for quenching. Photosensitivity could also be enhanced by introducing efficient chromophores such as biphenyl,[9] chrysene,[10] and fluorescein.[11]

	X	R
1	CH$_2$	SO$_3^-$
2	S	
3	SO$_2$	
4	CH$_2$	tert-butyl
5	S	or
6	SO	1,1,3,3-tetramethylbutyl
7	SO$_2$	

Since we reported a convenient one-step synthesis of thia-calix[4]arenes (**5**),[12,13] we have disclosed their complexation ability toward specific metal ions owing to the coordination of bridging sulfur, which is not attainable with the conventional methylene-bridged calix[4]arenes (**4**).[14] The sulfide moiety of **5** could also be oxidized to afford either a sulfinyl (**6**) or sulfonyl analogue (**7**) by controlling the amount of the oxidizing agent.[15,16] Interestingly, these sulfur-containing calix[4]arenes (**5**–**7**) showed a preference for particular metal ions, depending upon the oxidation state of the sulfur.[16] The selectivity was explained on the basis of the hardness or softness of the bridging group (X), since it plays a crucial role in the formation of a complex with the aid of the cooperative binding of two adjacent phenoxide oxygens as exemplified by X-ray crystallography.[17–19]

Although calix[4]arenes **4** and **5** are essentially insoluble in water, replacement by the sulfo function of the p-alkyl substituents converts them into highly water-soluble sulfonates **1**[20] and **2**.[21] Furthermore, we recently succeeded in obtaining dioxo-thiacalix[4]arenetetrasulfonate (**3**). With water-soluble calixarene ligands **1**, **2**, and **3** in hand, we were prompted to find out

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† Electronic supplementary information (ESI) available: emission spectra of Sm^{3+} and Dy^{3+} ions complexed with **2**; emission spectra of Sm^{3+}, Eu^{3+} and Dy^{3+} complexed with **3**; continuous variation curves for the Tb^{3+} complexes with **2** and **3**. See http://www.rsc.org/suppdata/p2/b0/b009151k/
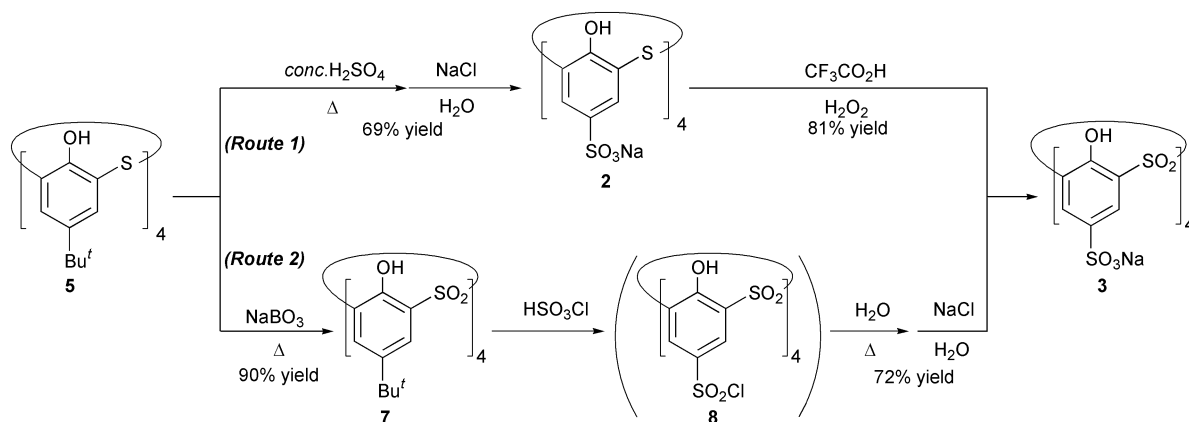
Scheme 1 Syntheses of calix[4]arenetetrasulfonate analogues **2** and **3**. For preparation of **7**, see ref. 15.

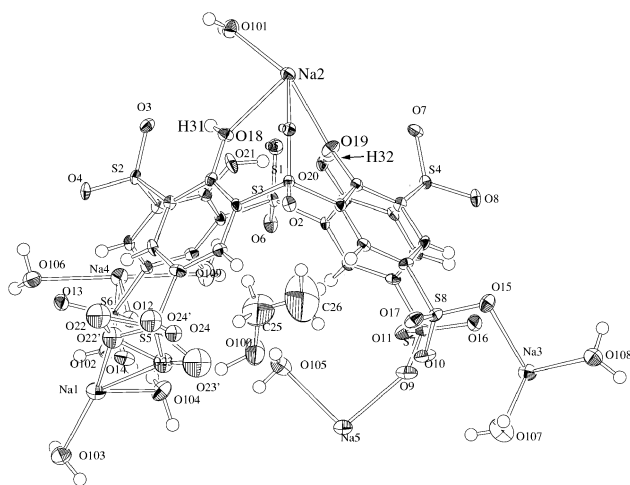**Fig. 1** ORTEP drawing for a single crystal of pentasodium salt of **3** including ethanol and water molecules ([C$_{24}$H$_{11}$O$_{24}$S$_8$Na$_5$·EtOH]· 9H$_2$O). Phenoxide oxygens O(18) and O(19) coordinating to Na(2)$^+$ have hydrogen atoms H(31) and H(32) with occupancy 0.5 each. Oxygens O(22), O(23), and O(24) on a SO$_3^-$ group show disorder.

how the bridging group X affects the energy transfer luminescence of a series of analogous metal complexes, and herein we report the results of a study on their complexation and photophysical properties with Tb^{3+} ion.

Results and discussion

Preparation of thia- and dioxothiacalix[4]arenetetrasulfonate

Atwood *et al.* reported the direct sulfonation procedure for preparation of tetrasulfonate **1** from **4** (R = Bu^t),[22] which was modified to prepare the thia-analogue **2** from **5** (R = Bu^t) in quite high yield (Scheme 1).[21] The sulfonyl analogue **3** was obtainable by either of two routes starting from **5** as shown in Scheme 1; first sulfation of **5** to **2** followed by oxidation to **3** (Route 1) or oxidation of **5** to *p-tert*-butyldioxothiacalix[4]-arene **7** followed by chlorosulfonation to **8** which was in turn directly subjected to hydrolysis to **3** (Route 2). Although the latter gave a slightly better yield of **3** than the former, this route required somewhat laborious microfiltration of the hydrolysis product of **8** to remove some impurities.

The ^{1}H NMR spectrum of sulfone **3** in D$_2$O solution is as simple as that of sulfide **2** in giving only one singlet for aromatic protons, since the only difference is the oxidation state of the bridging sulfur. To our pleasure, we were successful in obtaining the X-ray structure of **3** (Fig. 1), which clearly confirms that bridging sulfides were fully oxidized to sulfones. It should be noted that compound **3** was isolated as the pentasodium salt rather than the tetrasodium salt. As is shown, four Na$^+$ ions are associated with –SO$_3^-$ groups at the upper rim, whereas one

Na$^+$ ion is coordinated by oxygens of a bridging sulfone as well as two adjacent phenolic O$^-$ at the lower rim. Notably, the distance between Na$^+$ and O=S is 2.281(4) Å, which is shorter than the ones between Na$^+$ and O$^-$ (2.475(4), 2.399(4) Å), suggesting stronger coordination ability of SO$_2$ than O$^-$. Also, one ethanol molecule is included in the cavity of **3**, forming weak hydrogen bonds with closely located water molecules. Other structural features of the present crystal such as molecular packing, interactions between calixarene molecules, and so on are beyond the scope of this article.[23]

Attempts to prepare oxothiacalix[4]arenetetrasulfonate with X = SO *via* either oxidation of **2** with controlled amounts of the oxidizing agent or direct sulfonation of *p-tert*-butyl-oxothiacalix[4]arene **6** resulted in the formation of complex mixtures.

Complexation ability of calix[4]arenetetrasulfonates towards Tb^{3+} ion

The complexation behavior of calixarene ligands (L) **1**–**3** with selected ions (Pr^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+}) among 14 kinds of lanthanide ions was studied. The change of absorption spectra of both **2** and **3** upon addition of a lanthanide ion in aqueous solution suggested the formation of complexes with all the lanthanide ions examined. Irradiated with UV light, some complex solutions exhibited luminescence, depending on the metal ion species. For instance, the solution of **2** with Tb^{3+} ion exhibited very strong luminescence consisting of four emission bands (Fig. 2), which correspond to the transitions from ^{5}D$_4$ to ^{7}F$_6$ (488), ^{7}F$_5$ (543), ^{7}F$_4$ (583), and ^{7}F$_3$ (618 nm) of Tb^{3+}. By contrast, complexes of **2** with Sm^{3+} and Dy^{3+} luminesced weakly,[24] whereas the ones with Pr^{3+} and Eu^{3+} ions did not luminesce at all. Sulfonyl ligand **3** showed quite similar luminescence behavior to **2**, but the Tb^{3+} complex of the former exhibited stronger luminescence than that of the latter (Fig. 2). Other complexes of **3** gave weak (Sm^{3+}, Eu^{3+}, and Dy^{3+})[24] or no luminescence (Pr^{3+}). The conventional calix[4]arene **1** also formed a luminescent complex with Tb^{3+} ion,[4] the luminescence intensity of which was rather lower than the ones with **2** and **3** (Fig. 2). Considering these characteristic behaviors of Tb^{3+} ion, we focused our attention on the study of calixarene complexes with Tb^{3+} in detail.

The effect of pH on the luminescence intensity of solutions containing Tb^{3+} and a calix[4]arenetetrasulfonate (**1**–**3**) was studied to determine optimum pH for complex formation. As shown in Fig. 3, the intensity reached a maximum at pH 5.5 for **3** and at pH 8.5 for **2**, whereas the intensity of **1** apparently reached a plateau at pH 12 and then tended to increase again above pH 12.2, suggesting that the increase of the pH promoted deprotonation of the phenolic OH of the calixarene ligand to form phenolate O$^-$. The pH profile seems to suggest the acidity order to be **1** < **2** < **3**, as is consistent with the pK_a values evaluated by spectrophotometric titration.[25] For the complex of
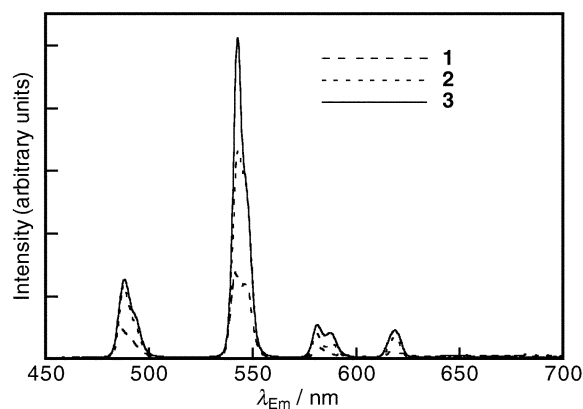
Fig. 2 Corrected emission spectra of Tb^{3+} ion complexed with **1–3**. [**1**, **2**, or **3**]$_{Total}$ = 4.0 × 10^{-6} M, [Tb^{3+}]$_{Total}$ = 2.0 × 10^{-7} M, [buffer] = 1 mM. λ_{Ex} = 290 (Tb^{3+}–**1**), 314 (Tb^{3+}–**2**), and 330 nm (Tb^{3+}–**3**). The pHs are 12.0 (Tb^{3+}–**1**), 9.7 (Tb^{3+}–**2**), and 6.5 (Tb^{3+}–**3**). Excitation and emission slit widths were 2.5 nm each.
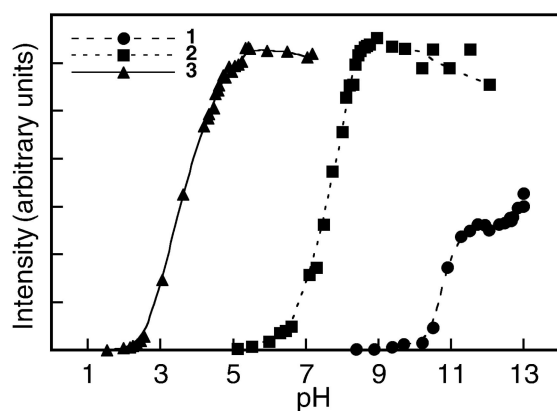

Fig. 3 The effect of the pH on the luminescence intensity of solutions containing Tb^{3+} ion and calix[4]arene (**1**, **2**, or **3**). [**1**, **2**, or **3**]$_{Total}$ = 4.0 × 10^{-6} M, [Tb^{3+}]$_{Total}$ = 2.0 × 10^{-7} M, [buffer] = 1 mM. λ_{Ex} = 263 (Tb^{3+}–**1**), 261 (Tb^{3+}–**2**), and 330 nm (Tb^{3+}–**3**). λ_{Em} = 543 nm. Excitation and emission slit widths were 5 and 10 nm, respectively.

1 with Tb^{3+}, Shinkai *et al.* proposed that two molecules of **1** sandwiched a Tb^{3+} ion by coordination of phenolic O⁻ at pH 12.5 (Fig. 4a).[4] Similarly, it is reasonable to assume coordination of the phenolate O⁻ of **2** and **3** to Tb^{3+} ion at pH 8.5 and 5.5, respectively, to form complexes exhibiting high energy-transfer luminescence as discussed below (Fig. 4b,c).

The stoichiometry of the Tb^{3+} complexes of **2** and **3** was determined to be 1 : 1 (= L : Tb^{3+}) by a molar ratio method (Fig. 5).[26] For the parent calix[4]arene **1**, on the other hand, Shinkai *et al.* reported that the stoichiometry should be 2 : 1 (= **1** : Tb^{3+}).[4] The difference in the stoichiometries of these complexes may be ascribed to the difference in coordination mode of the calix[4]arene ligands. For methylene bridged calix[4]arene **1**, only phenolates could be responsible for coordination as Shinkai proposed (Fig. 4a).[4] On the other hand, thiacalixarene **2** is assumed to be tridentate by ligation of one bridging group X (= S) and the two adjacent phenolates (O⁻) (Fig. 4b) by analogy to the *p-tert*-butyl counterpart **5**, which is tridentate as proposed by solvent extraction study[16] and, recently, evidenced by X-ray analysis of an Nd^{3+} complex.[27] Although the valences of the center metals are different, dioxothiacalix[4]arenes **3** and **7** have been revealed to coordinate *via* O⁻, X, O⁻ donors as evidenced by crystallographic analyses of Na^+–**3** complex (Fig. 1) and M^{2+}–**7** complex (M = Co and Ni), where X is the sulfonyl oxygen.[18] Therefore, it is reasonable to assume that dioxothiacalix[4]arene **3** may be also tridentate by O⁻, O, O⁻ ligation (Fig. 4c).[28]

In conclusion, the complexation ability of the calixarene ligands toward Tb^{3+} ion is in the order **1** < **2** < **3** owing to the
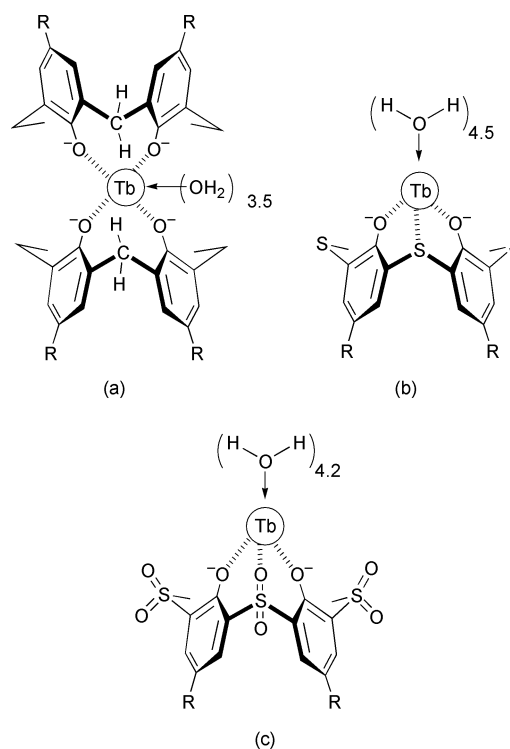

Fig. 4 Schematic representation of possible coordination modes of calix[4]arenes to Tb^{3+} ion. For clarity, only part of the calix[4]arene molecule is drawn. (a) Tb^{3+}·(**1**)$_2$, (b) Tb^{3+}·**2**, (c) Tb^{3+}·**3**. R = $-SO_3^-$.
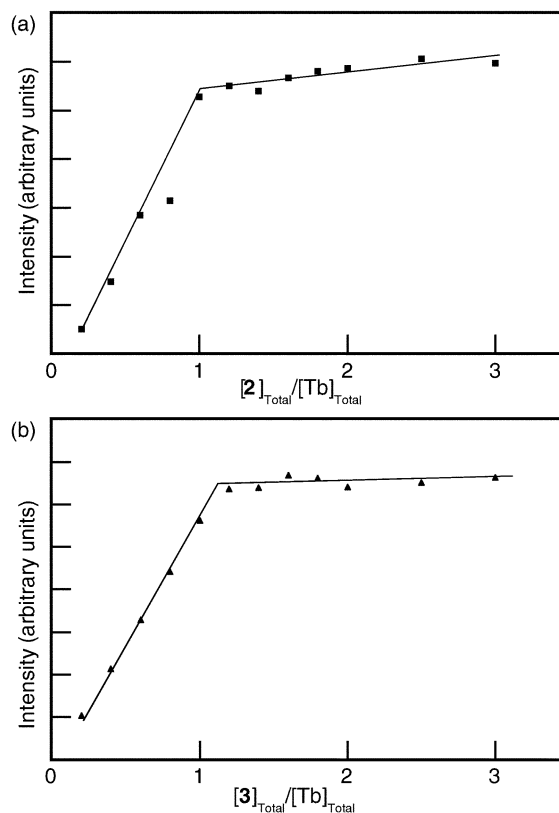

Fig. 5 Molar ratio curves for the Tb^{3+} complexes with calix[4]arene-tetrasulfonate analogues **2** and **3**. (a) L = **2**, [Tb^{3+}]$_{Total}$ = 4.0 × 10^{-7} M at pH 9.0, λ_{Ex} = 261 nm. (b) L = **3**, [Tb^{3+}]$_{Total}$ = 2.0 × 10^{-7} M at pH 6.5, λ_{Ex} = 330 nm.

acidity of the phenolic proton as well as the coordination ability of the bridging groups X. From a practical point of view, the ligands **2** and **3** have an advantage over **1**, because the former can quantitatively form Tb^{3+} complexes around the weakly
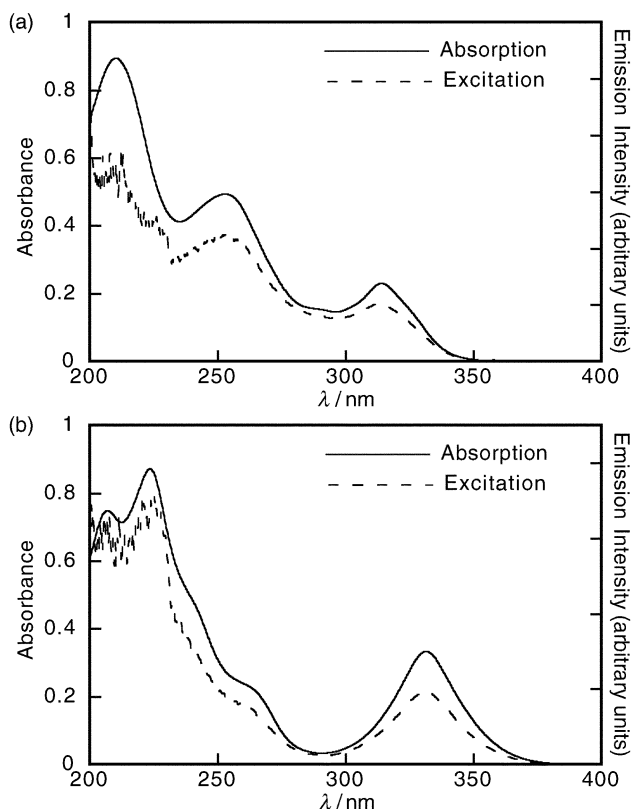
Fig. 6 Absorption and corrected excitation spectra of Tb^{3+} complexes with calixarene ligands **2** (a) and **3** (b). Absorption spectra: $[\mathbf{2} \text{ or } \mathbf{3}]_{Total} = [Tb^{3+}]_{Total} = 1.0 \times 10^{-5}$ M, [buffer] = 1 mM. The pHs of the solutions are the same as in Fig. 2. Excitation spectra: $[\mathbf{2} \text{ or } \mathbf{3}]_{Total} = 4.0 \times 10^{-9}$ M, $[Tb^{3+}]_{Total} = 2.0 \times 10^{-9}$ M. The pHs are 10.4 ($Tb^{3+} \cdot \mathbf{2}$) and 6.1 ($Tb^{3+} \cdot \mathbf{3}$), which were adjusted by NaOH. Excitation and emission slit widths were 10 and 20 nm, respectively.

acidic to weakly basic pH region. Hereinafter, the complexes are denoted by $Tb^{3+} \cdot (\mathbf{1})_2$, $Tb^{3+} \cdot \mathbf{2}$, and $Tb^{3+} \cdot \mathbf{3}$, respectively, to represent the stoichiometry.

Photophysical properties of the Tb^{3+} complexes

The source of the excitation energy for the Tb^{3+} ion is a question to be resolved. As shown in Fig. 6, the spectral profiles of absorption and excitation spectra of the complexes resemble each other for both $Tb^{3+} \cdot \mathbf{2}$ and $Tb^{3+} \cdot \mathbf{3}$ complexes. This suggests that the excited energy of the chromophoric benzene rings in the $^3\pi\pi^*$ state was transferred to the excited state ($^5D_3$ or $^5D_4$) in bound Tb^{3+}, as reported for the complex $Tb^{3+} \cdot (\mathbf{1})_2$.[4] In this context, the absence and faintness of the luminescence from Eu^{3+} complexes with **2** and **3**, respectively, are attributable to the photoinduced electron transfer from the benzene moiety to Eu^{3+} ion due to the ease of the reduction.[3]

We then determined their photophysical properties such as emission lifetime (τ) and luminescence quantum yield (Φ) (Table 1).[29] The τ values were estimated from the luminescence decay curves (Fig. 7). Complexes $Tb^{3+} \cdot \mathbf{2}$ and $Tb^{3+} \cdot \mathbf{3}$ gave almost the same τ value in H_2O (Table 1), indicating that **2** and **3** provided very similar coordination environments to let Tb^{3+} deactivate in a similar fashion. On the other hand, $Tb^{3+} \cdot (\mathbf{1})_2$ gave a smaller τ. It is noteworthy that these τ values are much smaller than those (typically $\tau = 1$–3 ms) of the Tb^{3+} complexes with calix[4]arenes having ligating groups to shield Tb^{3+} from water molecules.[6–8] This may suggest that the Tb^{3+} complexes of **1**–**3** were deactivated by coordinated water *via* energy transfer to the O–H stretching vibration.

Consequently, we determined the number of water molecules coordinated to Tb^{3+} ion (q) by measuring the τ in D_2O (Fig. 7) and using Horrocks eqn. (1), where A_{Tb} is a constant (= 4.19) for τ in milliseconds.[30]
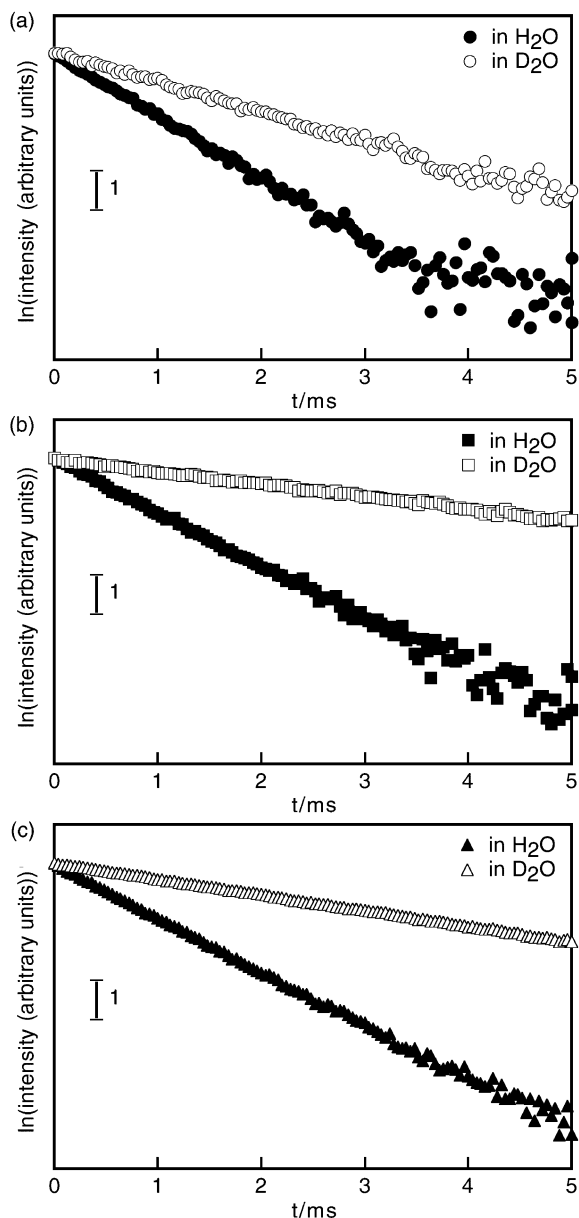

Fig. 7 Emission decay curves of Tb^{3+} complexes in H_2O and D_2O (24 °C). (a) $Tb^{3+} \cdot (\mathbf{1})_2$, (b) $Tb^{3+} \cdot \mathbf{2}$, (c) $Tb^{3+} \cdot \mathbf{3}$. $[\mathbf{1}, \mathbf{2}, \text{or } \mathbf{3}]_{Total} = 4.0 \times 10^{-6}$ mol dm^{-3}, $[Tb^{3+}]_{Total} = 2.0 \times 10^{-7}$ mol dm^{-3}, pH and pD = 12.0, 9.6, and 7.0 for **1**, **2**, and **3**, respectively. λ_{Ex}/nm = 263 for $Tb^{3+} \cdot (\mathbf{1})_2$, 261 for $Tb^{3+} \cdot \mathbf{2}$, 330 for $Tb^{3+} \cdot \mathbf{3}$.

Table 1 Photophysical properties of Tb^{3+} complexes with **1**, **2**, and **3**[a]

	τ_{H_2O}/ms	τ_{D_2O}/ms	q	Φ
$Tb^{3+} \cdot (\mathbf{1})_2$	0.613 ± 0.018	1.26 ± 0.04	3.5	$0.12_1 \pm 0.00_1$
$Tb^{3+} \cdot \mathbf{2}$	0.708 ± 0.020	3.13 ± 0.03	4.5	$0.15_4 \pm 0.00_2$
$Tb^{3+} \cdot \mathbf{3}$	0.704 ± 0.012	2.46 ± 0.02	4.2	$0.12_6 \pm 0.00_1$
Quinine[b]	—	—	—	0.546^c

[a] All measurements were done at 24 °C under nitrogen atmosphere.
[b] Measured in 0.5 M H_2SO_4 solution. [c] See ref. 33.

$$q = A_{Tb}(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}) \qquad (1)$$

The τ values estimated from Fig. 5 greatly increased in D_2O (Table 1), especially in the case of $Tb^{3+} \cdot \mathbf{3}$, clearly substantiating the mechanism of deactivation by coordinated water molecules. In fact, q was estimated to be 4–5 for $Tb^{3+} \cdot \mathbf{2}$ and $Tb^{3+} \cdot \mathbf{3}$ (Table 1).[31] This is quite consistent with the common coordination number of 8–9 for lanthanide ions,[1] because **2** and **3** are tridentate with occupation of three coordinating sites of

Tb^{3+} by two phenolate oxygen atoms and one bridging group X, as discussed earlier (Fig. 4). On the other hand, $Tb^{3+}\cdot(\mathbf{1})_2$ possesses 3–4 water molecules, which is best understood by assuming **1** to be bidentate with two phenolate oxygen atoms. It is noteworthy that, in D_2O, the τ value of $Tb^{3+}\cdot(\mathbf{1})_2$ was 2 or 3 times smaller than those of the others, suggesting that relaxation through the C–H vibration mode of the X = CH_2 was responsible for the deactivation.

The Φ values were estimated by comparison[32] with that of quinine sulfate as a standard.[33] The largest Φ (0.15) was given by $Tb^{3+}\cdot\mathbf{2}$, while the Φ values for $Tb^{3+}\cdot(\mathbf{1})_2$ and $Tb^{3+}\cdot\mathbf{3}$ were 0.12 and 0.13, respectively.[34] Thus, the replacement of CH_2 by S increased Φ values, whereas replacement by SO_2 did only slightly. This may be ascribed to the higher efficiency of the formation of the triplet excited state and/or energy transfer processes in $Tb^{3+}\cdot\mathbf{2}$ than in $Tb^{3+}\cdot\mathbf{3}$, since Φ is a product of the quantum yield of the triplet excited state of the chromophore (Φ_T), the efficiency of the energy transfer process (η_{ET}), the radiative rate constant (k_0), and the emission lifetime (τ) as in eqn. (2).[3]

$$\Phi = \Phi_T \eta_{ET} k_0 \tau \qquad (2)$$

Here Φ_T and η_{ET} are dependent on the ligand, whereas k_0 is not.[3]

Thus, it is concluded that calix[4]arene frameworks having X = S and SO_2 provide a better environment to retain the excited energy of the Tb^{3+} ion for a longer time. On the other hand, the one with X = S is suitable to form a Tb^{3+} complex with a higher luminescence quantum yield.

Conclusion

We have shown here that replacement of the bridging CH_2 by S and SO_2 provided calix[4]arenetetrasulfonate (**1**) with higher potential as a ligand for energy-transfer luminescence with respect to complexation and photophysical properties. Firstly, the thia and sulfonyl analogues have higher complexation ability toward Tb^{3+} owing to the higher acidity of the phenolic OH groups as well as to the ligation of the bridging groups S or SO_2. Secondly, the thia analogue formed a Tb^{3+} complex with a longer emission lifetime and a larger quantum yield, whereas the sulfonyl analogue formed one with a longer emission lifetime. Nevertheless the replacement of the bridging group of **1** by S and SO_2 afforded better ligands for energy-transfer luminescence; further improvement of the luminescent performance may be possible by introducing functional groups into the lower rim of thiacalix[4]arenetetrasulfonate (**2**) and dioxothiacalix[4]arenetetrasulfonate (**3**) to expel coordinated water molecules from the Tb^{3+} ion. In this line, construction of luminescence devices by modification of **2** and **3** is now underway.

Experimental

Equipment

Mps were taken using a Yamato MP-21 apparatus and are uncorrected. Fast atom bombardment mass spectra were recorded on a JEOL JMS-SX102A spectrometer using Xe as a bombarding atom and diethanolamine as a matrix. IR spectra were recorded on a Shimadzu IR-460. ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or CH_3CN as an external standard and D_2O as the solvent. UV absorption spectra were measured by use of a Shimadzu UV-2500PC. Corrected luminescence spectra and emission decay curves were measured by a Hitachi F-4500 spectrofluorimeter, the instrumental function of which was initially measured by use of

rhodamine and an optical scatterer. The pHs of the solutions were measured by a Horiba D-14 with an S8720 electrode.

Materials

Calix[4]arenetetrasulfonate pentasodium salt (**1**) was purchased from Sugai Chemie Inc. (Wakayama, Japan) and recrystallized from water–acetone mixture before use. Each calix[4]arene-tetrasulfonate (**1**, **2**, or **3**) was dissolved in deionized water and a stock solution was prepared (5.0×10^{-3} M). The stock solutions of lanthanide ions (0.01 M) were prepared by dissolving an appropriate amount of the nitrates (Kanto Chemical Co., Inc., Tokyo) in 0.01 M HNO_3. Before use, it was diluted to the desired concentration with 0.01 M HNO_3 solution. The pH buffers 2-morpholinoethanesulfonic acid (MES), piperazine-1,4-bis(ethane-2-sulfonic acid) (PIPES), 2-hydroxy-3-[4-(2-hydroxyethyl)piperazin-1-yl]propanesulfonic acid (HEPPSO), N-cyclohexyl-2-aminoethanesulfonic acid (CHES), and N-cyclohexyl-3-aminopropanesulfonic acid (CAPS) were purchased from Dojindo Laboratories, Kumamoto. Buffer solution (0.5 M) was prepared by dissolving the buffer in water, followed by adjustment of the pH by HNO_3 or NaOH and making up to the appropriate volume with water. The pH ranges where buffers were used are as follows: glycine–HNO_3 (pH 2.5–3.5), acetic acid–NaOH (pH 4.0–5.0), MES–NaOH (pH 5.5–6.0), PIPES–NaOH (pH 6.5–7.0), HEPPSO–NaOH (pH 7.5–8.5), CHES–NaOH (pH 9.0–10.0), and CAPS–NaOH (pH 10.5–11.0). Deionized water provided by Daiwa Chemical (Sendai, Japan) was used throughout this study.

Synthesis of tetrasodium 25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene-5,11,17,23-tetrasulfonate (2). The procedure reported previously[21] was slightly modified as follows. A mixture of p-$tert$-butylthiacalix[4]arene 5[12,13] (10.0 g, 13.9 mmol) and conc. H_2SO_4 (100 cm^3) was heated at 90 °C for 24 h. After cooling in an ice–water bath for 10 min, the mixture was filtered to recover precipitates, which were then dissolved in 50 cm^3 H_2O and filtered to remove unchanged thiacalix[4]arene. Addition of NaCl to the filtrate gave a precipitate of the crude product (9.7 g, 77%). Triturating with ethanol (30 cm^3) and recrystallization from water afforded an essentially pure sample of the tetrasulfonate **2** (8.7 g, 69%). Mp decomp. at 390 °C; ν_{max}/cm^{-1} 3450 (OH), 1046, 1193 (SO_3); δ_H (from DSS, 400 MHz, D_2O) 8.04 (s, 8H, ArH); δ_C (from CH_3CN, 400 MHz, D_2O) 118.32, 132.14, 132.82, 158.03 (Ar).

Pentasodium 25,26,27-trihydroxy-28-oxido-2,2,8,8,14,14,20,20-octaoxo-2,8,14,20-tetrathiacalix[4]arene-5,11,17,23-tetra-sulfonate (3). *Route 1: Oxidation of thiacalix[4]arenetetra-sulfonate (2).* To the powder of **2** (200 mg, 0.22 mmol) were added a solution of 30% H_2O_2 (1 cm^3, 9.9 mmol) and CF_3COOH (2 cm^3, 26.0 mmol). After the mixture was stirred well for 8 h at ambient temperature, acetone was added to precipitate the crude product. Recrystallization from acetone–water followed by filtration and drying *in vacuo* gave an essentially pure sample of **3** (187.7 mg, 81%).

Route 2: Sulfonation of p-tert-butyldioxothiacalix[4]arene (7). After a mixture of p-$tert$-butyldioxothiacalix[4]arene[15] (**7**, 187.0 mg, 0.22 mmol) and chlorosulfonic acid (10 cm^3) was kept stirred at 120 °C for 36 h and at 140 °C for another 24 h, the reaction mixture was carefully poured into ice–water mixture (*ca.* 20 cm^3 total) to give a precipitate. The crude product (170.5 mg) was then collected by filtration, dissolved in 10 cm^3 water, and refluxed for 12 h. After cooling to ambient temperature, the solution was filtered through Omnipore JH (0.45 μm, Millipore) to remove undissolved residues. To the filtrate was added NaCl to salt out crude product, which was then collected by filtration, and dried *in vacuo* to give essentially pure **3** (166.1 mg, 72%).

Samples of compound **3** isolated by the above mentioned

procedures were characterized by atomic absorption analysis to be a pentasodium salt in which one out of the four phenolic OH groups releases its proton (*cf.* Fig. 1). Mp > 360 °C; FAB MS *m/z* 1030 (M−Na)⁻, 1052 (M−1)⁻, (M as pentasodium salt of **3**); ν_{max}/cm⁻¹ 3464 (OH), 1045, 1199 (SO₃); δ_H (from DSS, 400 MHz, D₂O) 8.32 (s, 8H, ArH); δ_C (from CH₃CN, 400 MHz, D₂O) 128.89, 134.29 (Ar).

Crystallography

Single crystals of dioxothiacalix[4]arene **3** suitable for X-ray analysis were prepared by slow diffusion of ethanol vapor into an aqueous solution of pentasodium salt of **3**.

Data were collected on a Rigaku/MSC Mercury CCD using Mo-Kα radiation ($\lambda = 0.71069$ Å) at a temperature of −93 °C. A total of 900 oscillation images were collected. A first sweep of data was done using ω scans from −77.0 to 103.0° in 0.40° steps, at $\chi = 45.0°$ and $\Phi = 0.0°$ with an exposure rate of 60.0 s/°. A second sweep of data was done at $\chi = 45.0°$ and $\Phi = 90.0°$ under the same conditions. The detector swing angle was 13.0°. The crystal-to-detector distance was 40.0 mm. Data were corrected for Lorentz-polarization effects and using the empirical absorption method (trans. factors: 0.7856–0.9199). The structure was solved by the direct method and refined by the full-matrix least-squares method. All hydrogen atoms of **3** were located from D-maps, which were fixed in the refinement. All calculations were performed using the software package teXsan (v. 1.10).[35] Crystal data and parameters of refinement for **3** are summarized in Table 2. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference number 154914. See http://www.rsc.org/suppdata/p2/b0/b009151k/ for crystallographic files in .cif or other electronic format.

Table 2 Crystal data and structure refinement for [C₂₄H₁₁O₂₄S₈Na₅·EtOH]·9H₂O

Formula	C₂₆H₃₅Na₅O₃₄S₈
M	1262.97
Colour, shape	Colorless, prism
Crystal size/mm	0.15 × 0.20 × 0.25
Crystal system	Monoclinic
Space group	*P*2₁/*n* (No. 14)
a/Å	11.9774(9)
b/Å	25.096(1)
c/Å	14.9633(5)
β/°	90.4770(4)
V/Å³	4497.5(4)
Z	4
D_{calc}/g cm⁻³	1.865
F(000)	2584
T/K	180
μ(Mo-Kα)/cm⁻¹	5.56
$2\theta_{max}$/°	55.0
Measured reflections	36087
Independent reflections	9574 ($R_{int} = 0.033$)
Observed reflections	7401 ($I_0 > 3.0\sigma(I_0)$)
Number of variables	655
R, R_w	0.057, 0.065
GOF	1.01
ρ_{max},ρ_{mix}/eÅ⁻³	0.45, −0.66

Spectral measurements

Into a volumetric flask are pipetted appropriate amounts of Tb³⁺ solution, calix[4]arene (**1**, **2**, or **3**) solution, and pH buffer solution. After being made up with water, the mixture was shaken and allowed to stand for 1 h at room temperature to allow complexation. Before measuring absorption, emission and excitation spectra, nitrogen gas was bubbled for 1 min to purge dissolved oxygen.

Luminescence lifetimes

Luminescence decay curves of complex solutions were measured by excitation pulse at each λ_{Ex} (given in Table 3) at 24 °C. The raw data were fitted by a linear regression curve, eqn. (3), to

$$\ln(I) = \ln(I^0) - \frac{t}{\tau} \qquad (3)$$

obtain lifetime τ (see Table 1), where *I* and I^0 are emission intensities at 345 nm at *t* = *t* and 0, respectively.

Quantum yield

The luminescence quantum yield (Φ) was determined by a comparison method[32] using quinine sulfate ($\lambda_{Ex} = 366$ nm, $\Phi = 0.546$ in 0.5 M H₂SO₄)[33] as standard under N₂ atmosphere.

Luminescence intensity. Corrected emission spectra of complexes and quinine sulfate were measured with a spectral band path of 10 nm at 24 °C (see Table 3 for components and conditions). The emission intensity (I_{Tb}) was estimated by use of a built-in integration program in the F-4500 spectrometer. Briefly, the *x*-axes of the corrected emission spectra were converted from wavelength [nm] to wavenumber [cm⁻¹], then all the emission bands were integrated from 14286 to 22222 cm⁻¹ to estimate I_{Tb} (Table 3). The emission intensity of quinine, I_Q, as standard was measured similarly (integration between 14286 and 28571 cm⁻¹).

Molar absorption coefficient. Absorption spectra of the complexes and quinine sulfate solutions, the compositions of which are the same as in the caption of Fig. 6, were measured at 24 °C. Then the absorbance (*A*) at the λ_{Ex} was read to calculate the molar absorption coefficient (ε, see Table 3) by eqn. (4)

$$A = \varepsilon cl \qquad (4)$$

where *c* is [Tb³⁺]$_{Total}$ or quinine concentration, and *l* is the optical path length for sample solution (1 cm).

Estimation of the quantum yields. Introducing optical parameters listed in Table 3 into eqn. (5)[32] gives quantum yields of Tb³⁺ complexes as given in Table 1

$$\Phi = \Phi_Q \left(\frac{I_{Tb}}{I_Q}\right)\left(\frac{I_{Ex.Tb}}{I_{Ex.Q}}\right)\left(\frac{\varepsilon_Q}{\varepsilon_{Tb}}\right)\left(\frac{c_Q}{c_{Tb}}\right) \qquad (5)$$

Table 3 Composition of sample solutions and optical parameters obtained[a]

	L$_{Total}$/M	Tb$_{Total}$/M	pH	λ_{Ex}/nm	I_{Tb}[b]	ε/dm³ mol⁻¹ cm⁻¹
Tb³⁺·(**1**)₂	2.0 × 10⁻⁶	2.0 × 10⁻⁷	12.1	290	1203 ± 15	1.85 × 10⁴
Tb³⁺·**2**	4.0 × 10⁻⁶	2.0 × 10⁻⁷	9.6	314	1890 ± 25	2.29 × 10⁴
Tb³⁺·**3**	1.0 × 10⁻⁶	2.0 × 10⁻⁷	6.6	330	2221 ± 24	3.28 × 10⁴
Quinine	1.0 × 10⁻⁶	—	—[c]	366	4932	2.94 × 10³

[a] All measurements were done at 24 °C under nitrogen atmosphere. [b] Emission intensity estimated by integration of the corrected emission spectra through wavenumbers from 14,286 to 22,222 cm⁻¹. For quinine, I_Q was estimated similarly from 14,286 to 28,571 cm⁻¹. [c] Measured in 0.5 M H₂SO₄ solution.

where $(I_{Ex,Tb}/I_{Ex,Q})$ is the ratio of the intensity of excitation radiation for Tb^{3+} complex and quinine at each λ_{Ex}, which should be unity; hence the spectrofluorimeter has been corrected.

Acknowledgements

References

1 J.-C. G. Bünzli and G. R. Choppin, *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, 1989.
2 M. P. O. Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruel, J. W. Hofstraat, F. A. J. Geurts and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2141.
3 D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613.
4 N. Sato, I. Yoshida and S. Shinkai, *Chem. Lett.*, 1993, 1261.
5 J.-C. G. Bünzli, P. Froidevaux and J. M. Harrowfield, *Inorg. Chem.*, 1993, **32**, 3306; C. G. Bünzli, *J. Phys. Chem.*, 1994, **98**, 532; J.-C. G. Bünzli, F. Ihringer, P. Dumy, C. Sager and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1998, 497; L. J. Charbonniere, C. Balsiger, K. J. Schenk and J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.*, 1998, 505.
6 N. Sabbatini, M. Guardigli, A. Mecati, V. Balzani, R. Ungaro, E. Ghidini, A. Casnati and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1990, 878.
7 A. Casnati, C. Fischer, M. Guardigli, A. Isernia, I. Manet, N. Sabbatini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1996, 395.
8 N. Sabbatini, A. Casnati, C. Fischer, R. Girardini, M. Guardigli, I. Manet, G. Sarti and R. Ungaro, *Inorg. Chim. Acta*, 1996, **252**, 19.
9 N. Sato and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 1993, 621.
10 F. J. Steemers, H. G. Meuris, W. Verboom, D. N. Reinhoudt, E. B. Tol and J. W. Verhoeven, *J. Org. Chem.*, 1997, **62**, 4229.
11 M. P. O. Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. van Beelen, J. W. Hofstraat, F. A. J. Geurts and D. N. Reinhoudt, *Chem. Eur. J.*, 1998, **4**, 772.
12 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.
13 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron*, 2000, **56**, 1437.
14 N. Iki, N. Morohashi, F. Narumi and S. Miyano, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1597.
15 N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari and S. Miyano, *Tetrahedron Lett.*, 1998, **39**, 7559.
16 N. Morohashi, N. Iki, A. Sugawara and S. Miyano, *Tetrahedron*, 2001, **57**, 5557.
17 N. Iki, N. Morohashi, C. Kabuto and S. Miyano, *Chem. Lett.*, 1999, 219.
18 *cf.* The X-ray crystal structures of transition metal complexes with **6** and **7** show the same coordination mode. N. Morohashi, N. Iki, T. Kajiwara, T. Ito and S. Miyano, *Chem. Lett.*, 2001, 66. See also ref. 19.
19 T. Kajiwara, S. Yokozawa, T. Ito, N. Iki, N. Morohashi and S. Miyano, *Chem. Lett.*, 2001, 6.
20 S. Shinkai, K. Araki, T. Tsubaki, T. Arimura and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2297.
21 N. Iki, T. Fujimoto and S. Miyano, *Chem. Lett.*, 1998, 625.
22 J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr and R. L. Vincent, *Nature*, 1991, **349**, 683.
23 C. Kabuto, N. Iki, K. Koyama and S. Miyano, to be submitted.
24 See supplementary material for the emission spectra.
25 H. Matsumiya, Y. Terazono, N. Iki and S. Miyano, to be submitted.
26 The L : Tb^{3+} ratios for **2** and **3** were also determined to be 1 : 1 by a continuous variation method. See supplementary material.
27 A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 2000, **53**, 895.
28 These coordination modes are different from those of the sulfonato complexes of **1** in which the SO_3^- group coordinates to the metal ion, as shown in the crystallographic studies by Atwood *et al.* This is not surprising because the pH conditions for formation of the complexes are different; under acidic conditions as used for the crystallization, the dissociation of phenolic OH is suppressed and the SO_3^- group is responsible for coordination. See, for example, A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H. Zhang and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1361; J. L. Atwood, G. W. Orr, N. C. Means, F. Hamada, H. Zhang, S. G. Bott and K. D. Robinson, *Inorg. Chem.*, 1922, **31**, 603; G. W. Orr, L. J. Barbour and J. L. Atwood, *Science*, 1999, **285**, 1049.
29 In the following photophysical measurement, use of 5- to 20-fold excess of calix ligands ensured quantitative formation of each complex. Therefore, the contribution of aqua/hydroxo species of Tb^{3+} to the luminescence was negligible.
30 W. D. Horrocks and D. R. Sudnick, *Acc. Chem. Res.*, 1981, **14**, 384.
31 It should be noted that the *q* value is not necessarily an integer. See the discussion in ref. 3.
32 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
33 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 234.
34 *cf.* Shinkai *et al.* reported that the Φ value of $Tb^{3+} \cdot (\mathbf{1})_2$ was 0.13[4].
35 Molecular Structure Corporation, Rigaku Corporation (1999). TeXsan Single Crystal Structure Analysis Software. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. Rigaku, 3-9-12 Akishima, Tokyo, Japan.