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Exceptionally Long-Lived Luminescence Emitted from Tb^{III} Ion Caged in an Ag^{I}–Tb^{III}–Thiacalix[4]arene Supramolecular Complex in Water

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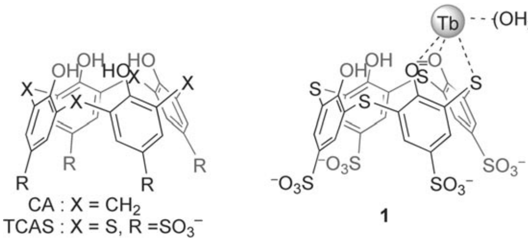
Abstract: The compositions and photophysical properties of luminescent ternary complexes of thiacalix[4]arene-*p*-sulfonate (TCAS), Tb^{III}, and Ag^{I} ions were determined. At pH 6, $Ag^{I}_2{\cdot}Tb^{III}_2{\cdot}TCAS_2$ formed. Moreover, at pH 10, in the presence of a 20-fold excess of Ag^{I} and a 50-fold excess of TCAS with respect to Tb^{III}, $Ag^{I}_2{\cdot}Tb^{III}{\cdot}TCAS_2$ formed as the main luminescent species. The structure of these complexes was proposed: two TCAS ligands are linked by two S–Ag^{I}–S linkages to adopt a double-cone supramolecular structure. Furthermore, each Tb^{III} ion in the former complex accepts O^-, S, O^- donation, whereas in the latter, the Tb^{III} center accepts eightfold O^- donation. The luminescence quantum yield (Φ) of $Ag^{I}_2{\cdot}Tb^{III}_2{\cdot}TCAS_2$ (0.16) was almost equal to that of $Tb^{III}{\cdot}TCAS$, but the luminescence lifetime τ of the former ($=1.09$ ms) was larger than that of the latter. For $Ag^{I}_2{\cdot}Tb^{III}{\cdot}TCAS_2$, the yield Φ ($=0.11$) was small, which is attributed to the low efficiency of photosensitization ($\eta = 0.11$). However, the τ value (4.61 ms) was exceptionally large and almost equal to the natural luminescence lifetime of Tb^{III} (4.7 ms), which is due to the absence of coordinating water molecules ($q = 0.1$). This is compatible with the proposed structure in which the Tb^{III} ion is shielded by a supramolecular cage that expels coordinated water molecules responsible for luminescence quenching.

Keywords: calixarenes · energy transfer · luminescence · silver · terbium

Introduction

Owing to its attractive features, such as long lifetime (≈600–1000 μs) and large Stokes shift (>200 nm), the sensitized emission of the lanthanide(III) ion (Ln^{III}) complexed with a light-absorbing ligand draws much attention in the field of bioanalysis, in which it can be applied to the luminescent labeling of biomolecules for the detection and imaging of biological tissues with high signal-to-background-noise ratios.[1–5] A key to obtaining long-lifetime emissions is ligand design by introducing a sufficiently large number of coordination sites to complete the first coordination sphere of the Ln^{III} center to act as a shield from coordinating water molecules, the OH stretching vibration of which readily quenches the excited state of Ln^{III}. A frequently used molecular scaffold for constructing such ligands is calix[4]arene (CA; Scheme 1), to which a wide variety of ligating and antenna functional groups have been covalently attached.[6] Contrary to the covalent approach of designing ligands, we recently found that thiacalix[4]arene-*p*-tetrasulfonate (TCAS) forms the luminescent Tb^{III} complex **1** (Scheme 1) by ligation of a bridging sulfur and its two adjacent phenoxide O donor atoms.[7] Notably, TCAS does not require auxiliary ligating or antenna groups. The luminescence quantum



Scheme 1. Structures of calixarenes and complex **1**.

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yield was reasonably high (0.15), but the luminescence lifetime was somewhat short (0.71 ms) due to a large number of coordinating water molecules (≈ 5). While studying the binding ability of the three sets of vacant O^-, S, O^- coordination sites of complex **1** toward soft metal ions, we unexpectedly found a Ag^I–Tb^{III}–TCAS ternary complex that had an exceptionally long luminescence lifetime (4.6 ms). Herein we report the composition and photophysical properties of the complex to shed light on the way in which coordinating water molecules are excluded by a supramolecular rather than a covalent manner.

Results and Discussion

Typical excitation and emission spectra of aqueous solutions containing Tb^{III}–TCAS binary and Ag^I–Tb^{III}–TCAS ternary components are shown in Figure 1. As was reported previously,[7] the binary system exhibits energy-transfer luminescence in the form of a broad excitation band at 313 nm arising from ligand-centered $\pi \rightarrow \pi^*$ transition and Tb^{III}-centered sharp emission bands at 488, 543, 583, and 618 nm assigned to transitions from $^5D_4$ to $^7F_6$, $^7F_5$, $^7F_4$, and $^7F_3$, respectively (Figure 1, ---). At pH 6.4, a complex was barely formed between TCAS and Tb^{III} ion (see below). However, with addition of an equimolar amount of Ag^I ion relative to Tb^{III} ion, luminescence from Tb^{III} was observed (Figure 1, -----). The difference in the excitation spectra of this and the binary system shows that a ternary luminescent species containing Ag^I was formed. At pH 10.0, the luminescence intensity increased and the excitation maximum shifted slightly toward shorter wavelengths (Figure 1, ——), which suggests a change in the composition of the ternary species.

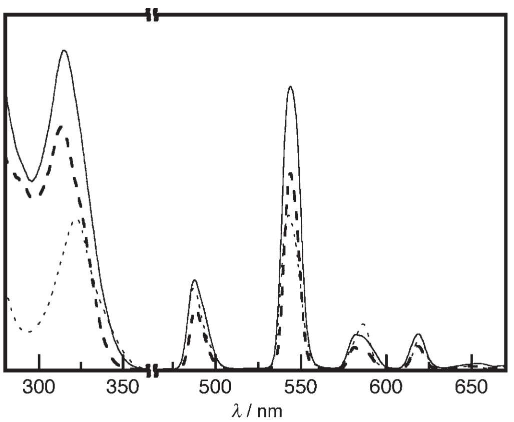


Figure 1. Typical excitation and emission spectra for the Tb^{III}–TCAS binary (---) and Ag^I–Tb^{III}–TCAS ternary systems (-----=pH 6.4, ——=pH 10.0). $[Tb^{III}]_T = 1.0 \times 10^{-6}$, $[Ag^I]_T = 0$ or 1.0×10^{-6}, $[TCAS]_T = 2.0 \times 10^{-6}$, $[buffer]_T = 2.0 \times 10^{-3}$ M, pH 6.4, 8.2, or 10.0, $\lambda_{ex} = 320$, $\lambda_{em} = 544$ nm.

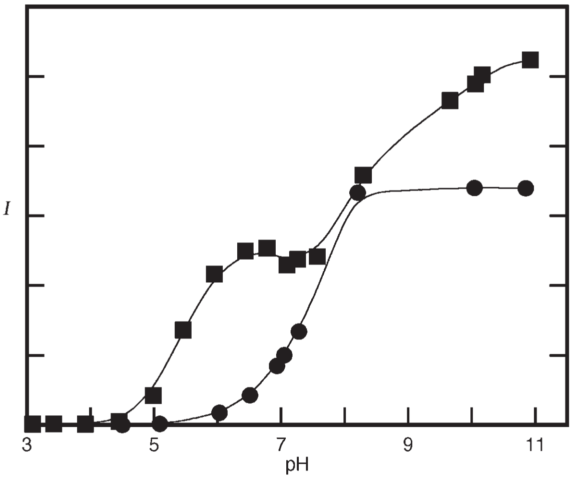


Figure 2. pH dependence of luminescence intensity for the Tb^{III}–TCAS binary (●) and Ag^I–Tb^{III}–TCAS ternary systems (■). The conditions are the same as those described for Figure 1.

Figure 2 shows the pH dependence of the luminescence intensity of bi- and ternary systems. The luminescence intensity of the binary system increased at pH 7.5 and reached a plateau at pH 8.0, which implies that the phenol OH group of TCAS dissociated to coordinate to Tb^{III}. By using the molar-ratio method (at pH 9.0), the luminescent complex was determined to be the 1:1 complex Tb^{III}·TCAS (**1**).[7] The electrospray ionization (ESI) mass spectrum of a solution containing complex **1** at pH 10.0 exhibited peaks assignable to $[Tb+4H+TCAS]^-$ at $m/z = 970.7144$ (see Supporting Information, Figure S1). In contrast to the binary system, the ternary system gave a two-step increase at pH 5.5 and 9, which indicates the presence of at least two types of luminescent species, the equilibria between which are pH-dependent. Molar-ratio analysis of the ternary system with various $[Ag^I]_T/[Tb^{III}]_T$ and $[TCAS]_T/[Ag^I]_T$ ratios at pH 6.5 (T = total) revealed the complex species to be Ag^I_i·Tb^{III}_i·$TCAS_i$ (in which i is an integer) (see Supporting Information, Figures S2 and S3). At pH 5.9, the ESI mass spectrum gave in-

Abstract in Japanese:

チアカリックス[4]アレーン-*p*-テトラスルホン酸(TCAS)が水溶液中でTb^{III}–Ag^I–TCAS三元錯体を自律的に形成することを見いだし，その組成と発光特性を調査した．エレクトロスプレーイオン化–質量分析法によりpH 6ではAg^I_2·Tb^{III}_2·$TCAS_2$錯体(**2**)が，pH 10ではTb^{III}に対し20倍量のAg^I，50倍量のTCASを共存させることでAg^I_2·Tb^{III}·$TCAS_2$錯体(**3**)が主な発光化学種として生成することがわかった．チアカリックス[4]アレーン金属錯体は多くの場合ダブルコーン型構造をとることから，同様に錯体**2**, **3**共に二つのTCASがS–Ag^I–S結合により架橋されたダブルコーン型構造を取ると考えた．さらに**2**ではそれぞれのTb^{III}イオンがTCASよりO^-,S,O^-配位を受け，**3**では両方のTCASから計8個のO^-配位を受けると考察した．錯体**2**の発光量子収率Φは0.16となり，二元錯体Tb^{III}·TCAS(**1**)の$\Phi = 0.15$とほぼ同等であったが，発光寿命τは1.09 msと錯体**1**の$\tau = 0.73$ msより長くなった．錯体**3**については$\Phi = 0.11$と小さく，これは光増感効率が0.11と低いためであった．一方発光寿命は$\tau = 4.61$ msと非常に大きく，Tb^{III}の自然発光寿命(4.7 ms)に匹敵した．Tb^{III}の失活に寄与する配位水分子数を測定したところ0.1となった．以上のことから錯体**3**においてTb^{III}は超分子かご型構造の中心に位置し，溶媒水分子から遮蔽されているため超長寿命性を持つと結論づけられる．

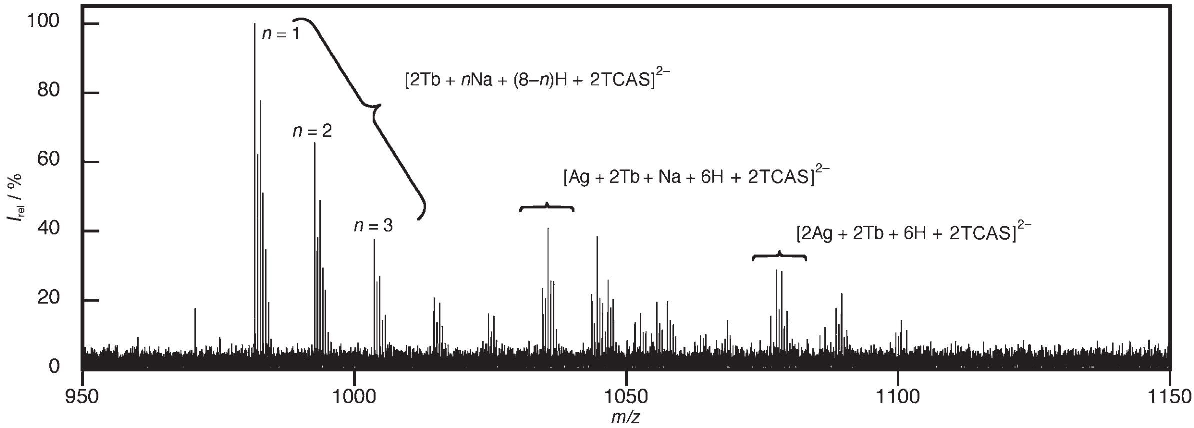


Figure 3. ESI mass spectrum of the Ag^I–Tb^{III}–TCAS ternary system at pH 6. $[TCAS]_T = [Ag^I]_T = [Tb^{III}]_T = 4\times10^{-6}$, $[CH_3COONH_4]_T = 5\times10^{-3}$ M, pH 5.9.

tense peaks at $m/z = 980$–1020 assignable to $[2Tb+nNa+(8-n)H+2TCAS]^{2-}$ ($n = 1$–3), 1030–1070 assignable to $[Ag+2Tb+Na+6H+2TCAS]^{2-}$, and, importantly, 1070–1100 assignable to a 2:2:2 complex, $[2Ag+2Tb+6H+2TCAS]^{2-}$ (Figure 3; see also Supporting Information, Figure S4). No significant peaks were observed at $m/z = 700$–950, over which $Ag^I{\cdot}Tb^{III}{\cdot}TCAS$ is expected to give peaks. On the whole, it is reasonable to conclude that the main species of the ternary system at pH ≈ 6 was $Ag^I_2{\cdot}Tb^{III}_2{\cdot}TCAS_2$ (**2**), part of which dissociated to give fragments such as $Tb^{III}_2{\cdot}TCAS_2$ and $Ag^I{\cdot}Tb^{III}_2{\cdot}TCAS_2$ during MS.

Under the conditions shown in Figures 1 and 2, the luminescence of the ternary system at pH 6.5 underwent single-exponential decay with a lifetime τ of 1.09 ms, which confirms that complex **2** was the major species at pH ≈ 6. On the other hand, the luminescence decay curve at pH 10 consisted of two components ($\tau = 4$ and 1 ms), which suggests that the ternary system produced two luminescent species. Hence, the concentration ratio of the solution that would give the single luminescent species was explored by changing the $[TCAS]_T/[Tb^{III}]_T$ and $[Ag^I]_T/[Tb^{III}]_T$ ratios (see Supporting Information, Tables S1 and S2). As a result, a single component with a 4-ms lifetime was obtained with $[Ag^I]_T/[Tb^{III}]_T/[TCAS]_T = 20{:}1{:}50$, whereby the majority of Ag^I ions should form a nonluminescent $Ag^I_4{\cdot}TCAS_2$ complex.[8] For ESI MS, an $[Ag^I]_T/[Tb^{III}]_T/[TCAS]_T$ ratio of 10:1:50 was chosen to avoid peaks from $Ag^I_4{\cdot}TCAS_2$, for which the ratio of species with 4-ms/1-ms lifetimes was 89:11 (see Supporting Information, Table S2). As shown in Figure 4, main peaks from $[2Ag+Tb+9H+2TCAS]^{2-}$ as well as accompanying peaks due to Na^+/H^+ exchange were obtained, but no other notable peaks were observed at $m/z = 800$–1200. From the above results, the component of long-lifetime emission was assigned to a 2:1:2 complex, $Ag^I_2{\cdot}Tb^{III}{\cdot}TCAS_2$ (**3**). The question now is, what is the structure of complexes **2** and **3**? In attempts to prepare single crystals of the ternary complexes for X-ray analysis, we recently obtained those of a 4:1:2 complex, $Ag^I_4{\cdot}Tb^{III}{\cdot}TCAS_2$ (**4**), rather than **2** or **3**, by slow diffusion of *N,N*-dimethylformamide (DMF) into a solution with an $[Ag^I]_T/[Tb^{III}]_T/[TCAS]_T$ ratio of 4:1:2. In a similar manner to metal complexes of thiacalix[4]arene with a multimetal core (Mn^{II}_4, Co^{II}_3, Cu^{II}_4, Zn^{II}_3, Hg^{II}_4, and Nd^{III}_4) sandwiched by

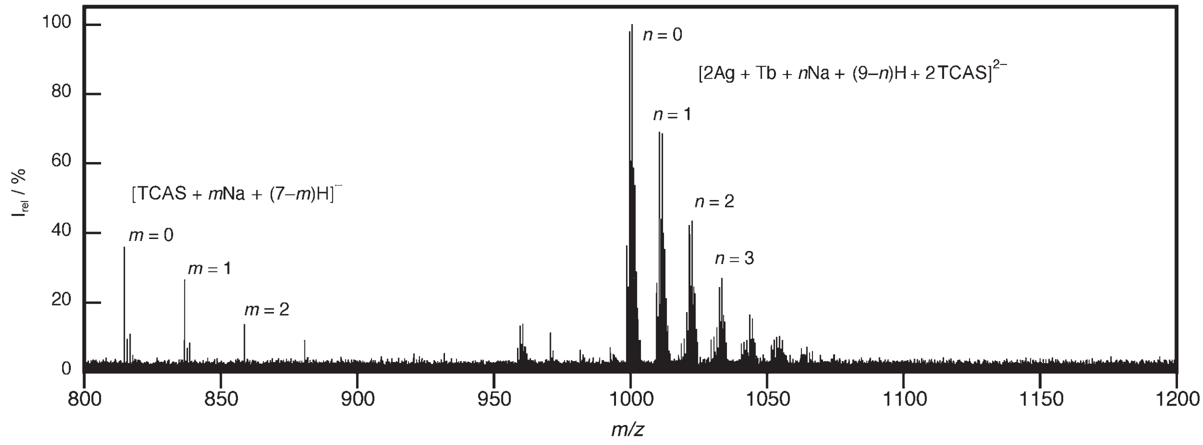


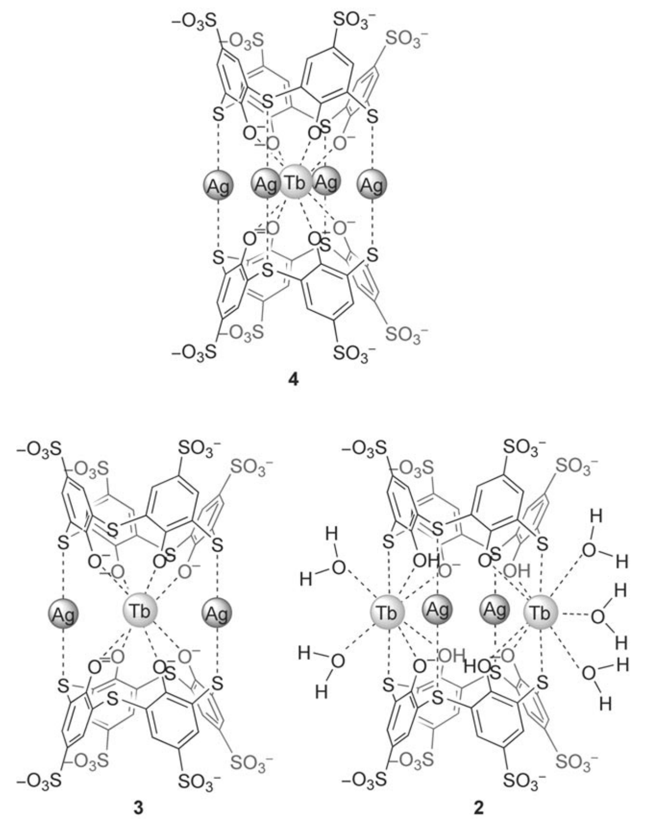
Figure 4. ESI mass spectrum of the Ag^I–Tb^{III}–TCAS ternary system at pH 10. $[TCAS]_T = 8\times10^{-6}$, $[Tb^{III}]_T = 4\times10^{-6}$, $[Ag^I]_T = 4\times10^{-5}$, $[(NH_4)_2CO_3]_T = 5\times10^{-3}$, $[NH_4OH]_T = 3\times10^{-2}$ M, pH 10.0.

two calixarene ligands,[9] complex **4** showed a typical double-cone shape, in which two thiacalix[4]arenes sandwich an $Ag^{I}_{4}Tb^{III}$ core by forming S–Ag^{I}–S and O–Tb^{III}–O bridges (Scheme 2).[10] An interesting feature of **4** is the coordination environment of Tb^{III}, which is surrounded by eight phenoxide O donors from TCAS. Although the composition is different, the structure of **4** suggests that **3** may adopt the same double-cone structure but with two silver bridges instead of four (Scheme 2). In an analogous manner, the structure of **2** is tentatively assigned as a double cone in which two TCAS molecules are bridged through the formation of two S–Ag^{I}–S linkages (Scheme 2). Furthermore, the Tb^{III} ion sits between two TCAS ligands and is coordinated to two O^-, S, O^- donor sets from each TCAS molecule.

Table 1. Photophysical properties of complexes **1**–**3** determined under N_2 atmosphere.

Complex	pH	ε [$M^{-1}cm^{-1}$]	λ_{ex} [nm]	Φ	τ [ms]	Φ_{Ln}	η	q[b]
Tb·TCAS[a] (**1**)	9.1	21700	314	0.15±0.02	0.73±0.01	0.16	0.98	4.84
Ag_2·Tb_2·$TCAS_2$ (**2**)	6.5	47200	323	0.16±0.02	1.09±0.01	0.23	0.68	2.38
Ag_2·Tb·$TCAS_2$ (**3**)	10.0	50800	318	0.11±0.01	4.61±0.05	0.98	0.11	0.08

[a] Photophysical properties for **1** were re-evaluated in this study to show good agreement with the results obtained in the previous study.[7] [b] For emission lifetimes in D_2O, see Supporting Information, Table S3.



Scheme 2. Double-cone-type complexes of TCAS.

Photophysical properties, such as luminescent quantum yield (Φ) and lifetime (τ), of complexes **2** and **3** were determined and compared with those of **1** re-evaluated in this study (Table 1). Luminescent quantum yield Φ is a product of the yields of the three steps involved in producing photoluminescence: intersystem crossing in TCAS (Φ_{ISC}), energy transfer from TCAS to Tb^{III} (Φ_{ET}), and terbium(III)-centered luminescence (Φ_{Tb}) [Eq. (1)].

$$\Phi = \Phi_{ISC}\Phi_{ET}\Phi_{Tb} \tag{1}$$

Φ_{Tb} can be calculated on the basis of [Eq. (2)], in which τ_0 is the natural luminescence lifetime of terbium(III) (4.7 ms) in water.

$$\Phi_{Tb} = \tau/\tau_0 \tag{2}$$

The value of Φ_{Tb} enabled us to calculate the sensitization efficiency η defined by [Eq. (3)].

$$\eta = \Phi_{ISC}\Phi_{ET} \tag{3}$$

Also, the number of coordinating water molecules (q) was estimated by using the Horrock equation [Eq. (4)], in which A_{Tb} is a constant (=4.19) for τ in milliseconds.[11]

$$q = A_{Tb}\left(\tau^{-1}_{\text{in}H_2O} - \tau^{-1}_{\text{in}D_2O}\right) \tag{4}$$

Needless to say, the re-evaluated values of Φ and τ for **1** agree well with those reported previously.[7] As can be seen, binary complex **1** gave a quantum yield Φ (=0.15) as large as that of complex **2**. Compared with the Φ values (0.002–0.20) of the Tb^{III} complexes of chemically modified CA in water,[6] the Φ value of **1** is relatively large. In terms of luminescence lifetime, **1** gave the smallest τ value among the complexes **1**–**3** owing to a large number of coordinating water molecules (q=4.8) responsible for quenching the excited state of the Tb^{III} center. Notably, the sensitization efficiency η was almost unity, which means that the efficiencies of triplet-state formation (i.e., Φ_{ISC}) and energy transfer (Φ_{ET}) are nearly unity to compensate for the quenching ability of the coordination environment of the Tb^{III} center in the excited state. As mentioned above, complex **2** had a luminescence quantum yield Φ almost similar to that of **1**. Although the two Tb^{III} centers of **2** doubles the chances of accepting triplet excited energy from TCAS, the sensitization efficiency η was smaller than that of **1**. This suggests that the efficiencies Φ_{ISC} and/or Φ_{ET} are small in **2**. The terbium(III) luminescence efficiency Φ_{Tb} of **2** was larger than that of **1** owing to the smaller q value (=2.4) in **2**. Notably, the Tb^{III} center of complex **2** has two or three coordinating water molecules, which agrees with the model of **2** depicted in Scheme 2. Thus, the Tb^{III} center of **2** was excited with less efficiency than that of **1** but was deactivated to a lesser extent to result in a similar Φ value. Complex **3** gave the smallest Φ and η values among the complexes, which suggests that the efficiencies for triplet-state formation and/or energy transfer were low. Surprisingly, the terbium(III) luminescence efficiency Φ_{Tb} was nearly unity. In other words, the luminescence lifetime ($\tau = 4.61$ ms) was as exceptionally large as that of the natural emission lifetime τ_0 ($=4.7$ ms), which can be rationalized by the fact that the estimated number of coordinating water molecules, q, is almost zero. This is compatible with the proposed structure of **3** (Scheme 2b): Tb^{III} is sandwiched between two TCAS ligands to accept eight O$^-$ donors that shield it from water molecules.

Conclusions

In summary, in the presence of Ag^{I} and Tb^{III} ions, TCAS gave ternary complexes $Ag^{I}_2 \cdot Tb^{III}_2 \cdot TCAS_2$ (**2**) and $Ag^{I}_2 \cdot Tb^{III} \cdot TCAS_2$ (**3**) at pH 6 and 10, respectively. Complexes **2** and **3** should be regarded as supramolecular complexes, because the soft Ag^{I} ion, the hard Tb^{III} ion, and TCAS with its multicoordinating sites synergistically built the complexes and provided longer luminescence lifetimes than the binary complex $Tb^{III} \cdot TCAS$ (**1**). Importantly, the exceptionally long lifetime of the Tb^{III}-centered emission of complex **3** is owed to the supramolecular cage that shields the Tb^{III} center from coordinating water molecules. Applications of the formation of supramolecular complexes **2** and **3** for the determination of Ag^{I} and near-infrared luminescence are now underway.

Experimental Section

Materials and Methods

The tetrasodium salt of thiacalix[4]arene-*p*-tetrasulfonate (TCAS) was prepared as described previously[7] and dissolved in deionized water to prepare the stock solution (5.0×10^{-3} M). Stock solutions of silver(I) and terbium(III) ions (0.01 M) were prepared by dissolving an appropriate amount of the nitrate (Kanto Chemical Co., Inc., Tokyo) in 0.01 M HNO_3. The pH buffers 2-morphorinoethanesulfonic acid (MES), *N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), 2-hydroxy-3-[4-(2-hydroxyethyl)-1-piperazinyl]propanesulfonic acid (HEPPSO), *N*-cyclohexyl-2-aminoethanesulfonic acid (CHES), and *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS) were purchased from Dojindo Laboratories, Kumamoto. Buffer solutions (0.5 M) were prepared by dissolving the buffer in water, adjusting the pH with HNO_3 or NaOH, and making the solution up to the appropriate volume with water. The pH ranges of the buffers used are as follows: MES/NaOH (pH 5.5–6.6), BES/NaOH (pH 6.6–7.5), HEPPSO/NaOH (pH 7.5–8.6), CHES/NaOH (pH 8.6–10.0), and CAPS/NaOH (pH 10.0–11.0). Doubly distilled water was used throughout this study.

The ternary complex species were prepared by simply mixing appropriate amounts of aqueous solutions of silver(I) nitrate, terbium(III) nitrate, TCAS, and buffer. Before the absorption, luminescence, and mass spectra were recorded, the sample solution was allowed to stand for 1 h at room temperature to ensure equilibration. Luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrometer under nitrogen atmosphere. Luminescence quantum yields were estimated as described previously.[7] ESI MS experiments were performed by using a Bruker APEX III Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Mass spectra were simulated with the program iMass for Mac OS X version 1.1.[12]

Acknowledgements

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[8] TCAS formed the 4:2 complex $Ag^{I}_4 \cdot TCAS_2$ at pH 5–11. The composition was confirmed by the molar-ratio method and ESI MS, the latter of which gave a main peak at $m/z = 1048.578$ assignable to $[4Ag + Na + 9H + 2TCAS + H_2O]^{2-}$.

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