Visible and near-infrared light emitting calix[4]arene-based ternary lanthanide complexes

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Abstract

In this article ternary lanthanide complexes consisting of a calix[4]arene unit and dibenzoylmethane (dbm) as the antenna are described. In the europium complex [(Eu)**2**]NO$_3$ two solvent molecules are still coordinated to the ion, making substitution of them by the dbm antenna possible. In the ternary complex of europium, an energy back-transfer process plays an important role. The photophysical properties of complexes of three near-infrared emitting lanthanide(III) ions were determined, i.e. ytterbium, neodymium, and erbium. These exhibit dbm-sensitized emission, with luminescent lifetimes comparable to those in other organic ligand systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Luminescence; Lanthanide complexes; Calix[4]arene complexes

1. Introduction

The design of molecular systems that combine binding abilities and photosensitizing properties for the construction of efficient photoluminescent lanthanide complexes continues to be an active area of research. The luminescence of such lanthanide complexes distinguishes itself from other fluorophores by its long luminescence lifetimes and narrow emission bands in the visible and near-infrared region [1]. These characteristics make them ideally suited for applications as fluorescent probes [2] and optical signal amplifiers [3]. With the development of polymers that are transparent in two standard wavelength regions around 1330 and 1550 nm that are used for optical data transport, there is a growing interest in polymer-based integrated optics [4]. Polymer-based optical components like splitters, switches, and multiplexers have already been developed [5]. For the development of a polymer-based optical amplifier for easy integration with the existing components, lanthanide ion complexes of neodymium (Nd^{3+}) and erbium (Er^{3+}) are ideally suitable as the optically active component because of their intra-4f transitions at 1330 and 1550 nm, respectively.

The encapsulation of the lanthanide ion in an organic ligand improves not only the processibility of lanthanide ions in organic matrices but also its optical properties, as the ligand shields the lanthanide ion from its environment. High frequency O–H and to a lesser extent C–H vibrations in the local environment of the lanthanide ion, play an important role in removing energy non-radiatively from the lanthanide excited state [6]. The long luminescent lifetimes of lanthanide ions are a result of the weakly allowed intra-4f transitions, which unfortunately also results in low absorption coefficients (typically 1–10 M^{-1} cm^{-1}). To increase the excitation efficiency, the luminescent state of a lanthanide ion can be populated via energy transfer from the triplet-excited state [7,8] of an organic antenna chromophore (the photosensitizer). The three main factors that govern the efficiency of this sensitization process are the antenna intersystem crossing quantum yield, the antenna–lanthanide distance, and the overlap

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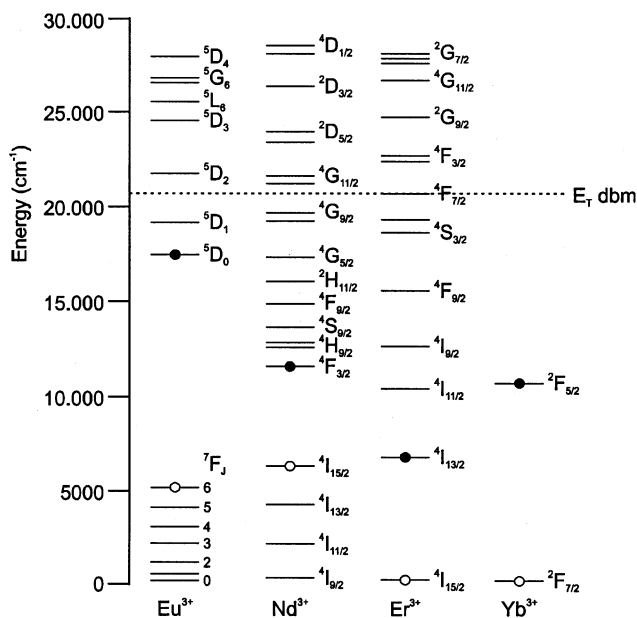*E-mail address:* f.c.j.m.vanveggel@ct.utwente.nl (F.C.J.M. van Veggel).

Fig. 1. Energy diagram of the 4f energy levels responsible for the lanthanide luminescence; a filled circle represents the lowest lumines-cent excited state, an open circle represents the highest non-lumines-cent state. Adapted from G. Stein, E. Würzberg, J. Chem. Phys. 62 (1975) 208.

properties of a β-diketonate (dibenzoylmethane (dbm)) [12,13] have been combined with the complexing prop-erties of the calix[4]arene-based ligand (see end of Sec-tion 4 for chemical structures.). The calix[4]arene-based ligand (H$_2$)2, is a derivative of the previously reported triacid-monoamide-calix[4]arene ionophores [14,15]. The lanthanide ion in the [(Ln)2]$^+$ complex is encapsu-lated by eight hard oxygen donor atoms: four ether oxygen atoms; two negatively charged carboxylate oxy-gens; and two amide oxygens. Coordination of the β-diketonate to the complexed lanthanide ion results in ternary complexes that are overall neutral.

The dbm antenna enables near-UV excitation up to 400 nm and possesses an efficient intersystem crossing process with an intersystem crossing yield of 0.90 [16]. The triplet energy of the sensitizer (20 600 cm^{-1}) and the 4f energy levels of lanthanide ions are depicted in Fig. 1.
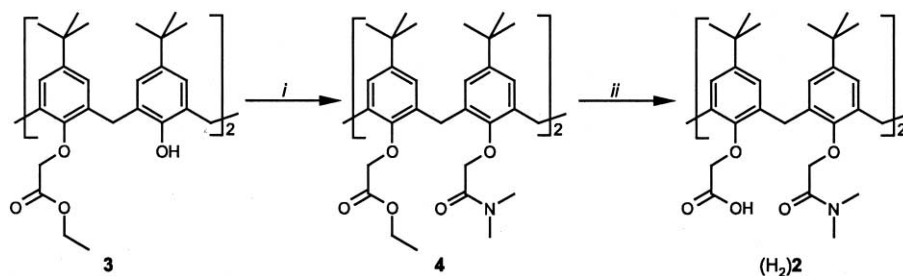
The gap of the emissive state of europium with the triplet state of the dbm antenna is relative small (4000 cm^{-1}) compared to the gap with the near-infrared emissive lanthanide ions: 9000 cm^{-1} (Nd^{3+}); 14 000 cm^{-1} (Er^{3+}); and 10 100 cm^{-1} (Yb^{3+}).

2. Results and discussion

2.1. Synthesis

The synthesis of the calix[4]arene-based ligand (H$_2$)2 starting from the diester calix[4]arene 3 is depicted in Scheme 1. Alkylation of the diester calix[4]arene 3 with 2-chloro-N,N-dimethylacetamide gave precursor 4 in 80% yield.

The ethylester moieties of 4 were hydrolyzed under basic conditions with K$_2$CO$_3$ in a water/methanol solu-tion in nearly quantitative yield. Complete hydrolysis was confirmed by the ^{1}H NMR spectra, in which the signals for the ethyl groups were absent, and by the IR spectrum in which a peak around 1750 cm^{-1} was observed for the carboxylic acids (ν_{COOH}). The corre-sponding lanthanide complexes were prepared by the addition of appropriate Ln(NO$_3$)$_3$ salt to a solution of

between the energy levels of donor and acceptor [9]. Recently, we have reported that triphenylene is a good sensitizer for Eu^{3+} and Tb^{3+} when they are encapsu-lated in a m-terphenyl-based [10] or a calix[4]arene-based [11] ligand carrying such an antenna (see end of Section 4 for chemical structures.). The triphenylene antenna was positioned relatively close to the lan-thanide ion via a spacer, but the antenna itself was not in direct contact with the ion. As a result the average distance between the encapsulated lanthanide ion and the triphenylene antenna was too large for a complete energy transfer. An optimization of the system would therefore be to introduce an antenna chromophore with chelating properties that coordinates directly with the lanthanide ion.

In this article we present the synthesis and a photo-physical study of ternary complexes of Eu^{3+}, Nd^{3+}, Er^{3+}, and Yb^{3+} in which the sensitizing and chelating

Scheme 1. Reagents and conditions: (i) 2-chloro-N,N-dimethylacetamide, CH$_3$CN, K$_2$CO$_3$, reflux, 80%; and (ii) K$_2$CO$_3$, methanol/water, 2h, reflux, 95%.
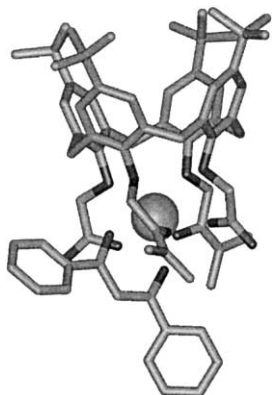
Fig. 2. Minimized structure of [(Eu)2]dbm obtained from gas-phase optimizations. The hydrogen atoms of the complex have been omitted for clarity.
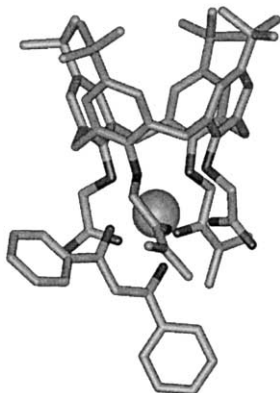

Fig. 3. The emission spectrum of [(Eu)2]NO$_3$ in methanol (10^{-4} M).

(H$_2$)2 in methanol in the presence of Et$_3$N as a base. The ternary [(Ln)1]dbm complexes were prepared by mixing 1 equiv. of the tetrabutylammonium salt of dbm and 1 equiv. of (Ln)1 in dichloromethane and subsequent workup to remove the salts. The [(Ln)2]NO$_3$ and [(Ln)2]dbm complexes have been identified by FAB MS and IR spectroscopy (see Section 4). The mass spectra show the expected 1:1:1 stoichiometry (ligand:Ln^{3+}:sensitizer) of the ternary complexes.

2.2. Molecular mechanics

Molecular mechanics was used to study the structure of the ternary complexes. The structure of [(Eu)2]dbm was minimized in the gas phase using the CHARMM force field [17]. The simulations show that the complexed Eu^{3+} ion is coordinated by 10 oxygen donor atoms (see Fig. 2). In the [(Eu)2]dbm complex all the eight donor atoms from the ligand, four phenol ether oxygens, two carboxylate oxygens, and two amide oxygens are coordinated to the lanthanide ion, in addition to the two oxygen donor atoms of the β-diketonate moiety.

2.3. Eu^{3+} luminescence

The influence of the metal coordinating functionalities of the calix[4]arene ligand and the dbm antenna on the photophysical properties of the complexed lanthanide ion has been investigated using Eu^{3+} as a model. Europium possesses well-known characteristics, indicative of the environment of the ion. Upon excitation at 287 nm of the calix[4]arene moiety of the precursor complex [(Eu)2]NO$_3$ in methanol, sensitized Eu^{3+} emission was observed corresponding to the $^5D_0 \rightarrow {}^7F_n$ transitions (see Fig. 3). The hypersensitive $^5D_0 \rightarrow {}^7F_2$ emission at 615 nm dominates the spectrum. The excitation spectrum of [(Eu)2]NO$_3$ (not shown) follows the absorption spectrum of the calix[4]arene moiety and has an additional small band at 393 nm corresponding to the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}.

The known sensitivity of Eu^{3+} luminescence towards quenching by the hydroxyl groups [18] of the solvent provides an experimental tool to estimate the degree of shielding by the ligand. An empirical relationship as given in Eq. (1) has been established by Horrocks et al. [19] and adapted by Parker and co-workers [20] that estimates the number of coordinated methanol molecules (n).

$$n = q(1/\tau_h - 1/\tau_d - k_{corr}) \tag{1}$$

where q is 2.1, τ_h is the luminescence lifetime of the complex in methanol-h$_1$ and τ_d the luminescence lifetime of the complex in methanol-d$_1$ (lifetimes in milliseconds), k_{corr} is a factor to correct for methanol molecules which coordinate in the second sphere and is 0.125 ms^{-1}. The time-resolved luminescence spectrum shows a mono-exponential decay with a luminescence lifetime of 0.39 ms. The luminescence lifetime in methanol-d$_1$ is significantly longer (0.75 ms), since –OD groups are much less efficient quenchers than –OH groups. Using Eq. (1), this experiment shows that 2.3 methanol molecules are coordinated to the complexed lanthanide ion in [(Eu)2]NO$_3$. This provides the space for a bidentate coordinating dbm antenna. The luminescent lifetimes of the ternary complex [(Eu)2]dbm in methanol and deuterated methanol were 0.058 and 0.061 ms, respectively, at room temperature. These low values are caused by an efficient energy back-transfer mechanism (vide supra) that makes the Horrocks equation inapplicable.

The emission and excitation spectra of the ternary complexes have been taken in dichloromethane as solvent. For comparison, the luminescence spectra of [(Eu)2]NO$_3$ in dichloromethane have also been taken. Upon excitation of the calix[4]arene moiety (λ_{exc} 300 nm) of [(Eu)2]NO$_3$ and the dbm antenna (λ_{exc} 360 nm) of [(Eu)2]dbm in dichloromethane (10^{-5} M), both luminescence spectra show the emission bands that correspond to the typical Eu^{3+} $^5D_0 \rightarrow {}^7F_n$ transitions (see Fig. 4).
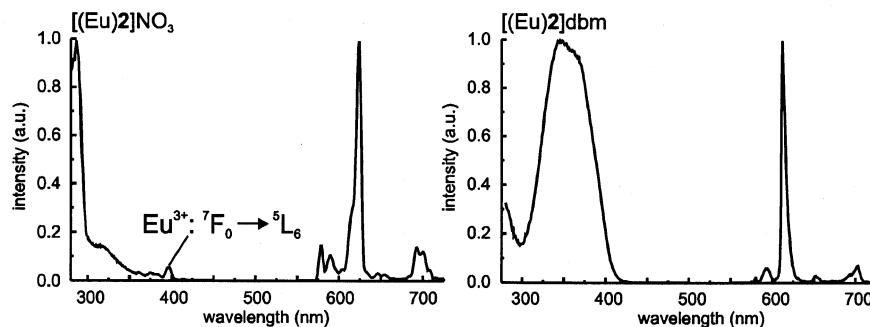
Fig. 4. The excitation and emission spectra of [(Eu)2]NO$_3$ (10^{-4} M) and [(Eu)2]dbm (10^{-5} M) in dichloromethane.

A single small peak is observed for the $^5D_0 \rightarrow {}^7F_0$ emission at 579 nm. Since the $^7F_0$ state is non-degenerate, the single peak indicates that there is only one Eu^{3+} species in solution on the millisecond timescale. The strongest emission corresponds again to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, which has shifted from 624 nm for [(Eu)2]NO$_3$ to 612 nm for [(Eu)2]dbm upon coordination of the dbm antenna. The intensity ratio of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition and the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is a measure of the symmetry of the first coordination sphere [21]. Distortion of the symmetry around the Eu^{3+} ion in general causes an intensity enhancement of the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition, while the $^5D_0 \rightarrow {}^7F_1$ emission intensity remains a constant. For the precursor complex [(Eu)2]NO$_3$ in methanol where the NO$_3^-$ anion is not coordinated to the complexed Eu^{3+} ion, the $^7F_2/^7F_1$ intensity ratio is 3.5. In dichloromethane, the $^7F_2/^7F_1$ intensity ratios of [(Eu)2]NO$_3$ and [(Eu)2]dbm are higher, 8 and 11, respectively, as a result of the coordination of the NO$_3^-$ anion and the dbm antenna to the Eu^{3+} ion.

The main difference between the excitation spectra of [(Eu)2]NO$_3$ and [(Eu)2]dbm is the presence of the broad band corresponding to the absorption spectrum of the dbm antenna, and thus proving that the Eu^{3+} luminescent state of [(Eu)2]dbm is populated via the antenna.

The efficiency of the overall sensitization process was established by determining the quantum yield of the sensitized emission, which was less than 0.01 for [(Eu)2]dbm. The low luminescence quantum yield can be explained by a thermally activated energy back-transfer process. This is quite feasible because the energy gap between the triplet excited state of dbm and the $^5D_1$ excepting state of Eu^{3+} is only 1600 cm^{-1}, which allows for a significant energy back-transfer within the millisecond lifetime of the lanthanide luminescence. The relatively short lifetime of [(Eu)2]dbm of 0.087 ms (in CH$_2$Cl$_2$) indeed implies that the luminescent $^5D_0$ state is depopulated probably via the $^5D_1$ state and subsequent energy back-transfer to the dbm antenna. Furthermore, cooling down of a sample in

methanol to 0°C doubled the luminescence intensity. For comparison, the luminescence lifetime of the Eu(dbm)$_3$ complex in an EPA solution (5:5:2 (v/v) ether/isopentane/ethanol) at room temperature is 0.15 ms with a luminescence quantum yield of approximately 0.01 [22].

2.4. Near-infrared Nd^{3+}, Er^{3+}, and Yb^{3+} luminescence

Dichloromethane-d$_2$ solutions (10^{-4} M) of the near-infrared emitting [(Ln)2]dbm complexes exhibit the typical line-like lanthanide emission upon excitation of the dbm antenna chromophore at 360 nm. At room temperature sensitized emission at 880 (not shown), 1060, and 1330 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ transition, respectively) for [(Nd)2]dbm, at 1540 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) for [(Er)2]dbm, and at 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) for [(Yb)2]dbm is observed (see Fig. 5). For all complexes the excitation spectrum closely follows the absorption spectrum of the dbm antenna which proves that excitation of the antenna is the main photophysical pathway that leads to Nd^{3+}, Er^{3+}, and Yb^{3+} luminescence.

Time-resolved luminescence measurements showed that the luminescence lifetimes of the complexes in CH$_2$Cl$_2$-d$_2$ are in the range of microseconds, with [(Yb)2]dbm having the longest lifetime (12.5 μs), followed by [(Er)2]dbm (1.3 μs), and [(Nd)2]dbm having the shortest lifetime (0.9 μs). These lifetimes are in accordance with luminescent lifetimes measured in other organic systems [23]. The low value of the lifetimes compared to the luminescent lifetimes of the ions in inorganic matrices is explained by the quenching of the luminescent state by high-frequency vibrations in the ligand and the solvent.

3. Conclusions

In ternary lanthanide complexes the properties of a calix[4]arene complex were combined with the sensitizing property of a β-diketone. This antenna is brought in
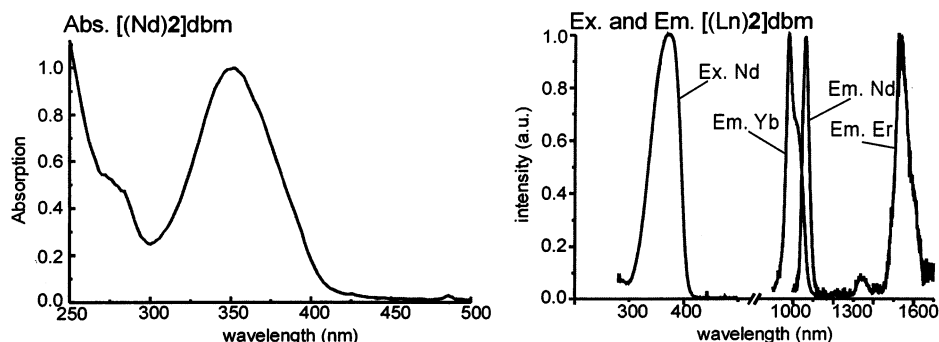
Fig. 5. The absorption spectrum of [(Nd)**2**]dbm (left spectrum) and the near-infrared excitation and emission spectra of [(Nd)**2**]dbm, [(Er)**2**]dbm, and [(Yb)**2**]dbm in dichloromethane-d$_2$ (right spectrum).

close contact with the lanthanide ion, giving rise to near-infrared emission of Yb^{3+}, Nd^{3+}, and Er^{3+}. Complexation and sensitized emission were further proven by the europium complex. In the sensitization process of Eu^{3+} by the dbm antenna an energy back-transfer mechanism plays an important role by deactivating the excited state of Eu^{3+}.

4. Experimental

4.1. Synthesis

Melting points were determined with a Reichert melting point apparatus and are uncorrected. Mass spectra were recorded on a Finnigan MAT 90 spectrometer using m-NBA (nitrobenzyl alcohol) as a matrix, unless stated otherwise. IR spectra were recorded with a Perkin–Elmer Spectrum BX FT-IR System using KBr pellets. Elemental analyses were performed on a Carlo Erba EA 1106 apparatus. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.7 MHz) spectra were recorded with a Bruker AC 250 spectrometer in CHCl$_3$-d unless stated otherwise, using residual CHCl$_3$ ($\delta = 7.26$ ppm) and CHCl$_3$-d ($\delta = 77.0$ ppm) as the internal standard, respectively. Triethylamine (Et$_3$N) was distilled in vacuo and stored over KOH. Acetonitrile and methanol were of analytical grade and were dried over molecular sieves (4 Å) prior to use. The Ln(NO$_3$)$_3$·5H$_2$O salts, dbm, and Bu$_4$NOH (1 M solution in methanol) were purchased from Aldrich and used without further purification. Diester calix[4]arene **3** was synthesized according to procedures given in the literature [24]. Standard workup involved washing the organic layers with water, drying over magnesium sulfate, filtration of the salts, and concentrating to dryness in vacuo.

4.1.1. 25,27-Bis(N,N-dimethylcarbonylmethoxy)-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,28-bis(ethoxycarbonylmethoxy) (4)

To a mixture of **3** (2.0 g, 2.4 mmol) and K$_2$CO$_3$ (0.84 g, 6.1 mmol) in acetonitrile (100 ml) was added 2-chloro-N,N-dimethylacetamide (0.65 g, 5.4 mmol) and the mixture was refluxed for 14 h. Subsequently, the reaction mixture was allowed to cool down to room temperature and was filtered. The filtrate was concentrated to dryness in vacuo. The residue was redissolved in CH$_2$Cl$_2$ (200 ml) and washed twice with 1 N HCl, followed by standard workup. The crude product was recrystallized from acetonitrile to give **4** as a white solid: yield 80%, m.p. 103–106°C. ^{1}H NMR (CHCl$_3$-d): $\delta = 6.87$ (s, 4H), 6.70 (s, 4H), 5.01–4.73 (m, 12H), 4.14 (q, 4H, $J = 8.45$ Hz), 3.23 (AB, 4H, $J = 12.7$ Hz), 3.07 (s, 6H), 2.98 (s, 6H), 1.28 (t, 6H, $J = 8.4$ Hz), 1.15 (s, 18H), 1.04 (s, 18H). ^{13}C NMR (CHCl$_3$-d): $\delta = 170.6$, 168.6, 153.5, 152.6, 144.9, 144.3, 133.5, 132.6, 126.0–124.0, 72.0, 70.8, 59.7, 36.0, 35.1, 33.2, 32.0–30.0, 13.5. FAB MS: $m/z = 991.9$ [(M + H)$^+$, calcd. 991.6]. Anal. Found: C, 72.11; H, 8.07; N, 2.99. Calc. for C$_{60}$H$_{82}$N$_2$O$_{10}$·0.40CH$_3$CN: C, 72.47; H, 8.32; N, 3.34% (the presence of CH$_3$CN in the sample was confirmed by the ^{1}H NMR spectrum of **4**, $\delta_{CH_3} = 1.98$ ppm).

4.1.2. 25,27-Bis(N,N-dimethylcarbonylmethoxy)-5,11,17,23-tetrakis(1,1-dimethylethyl)-26,28-bis(hydroxycarbonylmethoxy) ((H$_2$)2)

A mixture of **4** (2.0 g, 2.4 mmol) and K$_2$CO$_3$ (0.84 g, 6.1 mmol) in a 5:1 methanol/water solution (100 ml) was refluxed for 2 h. Subsequently, the solvents were removed in vacuo. The residue was redissolved in CH$_2$Cl$_2$ (200 ml) and washed twice with 1 N HCl, followed by standard workup. The crude product was recrystallized from acetonitrile to give (H$_2$)**2** as a white solid: yield 95%, m.p. 248–250°C. ^{1}H NMR (CHCl$_3$-d): $\delta = 7.14$ (s, 4H), 6.63 (s, 4H), 4.80 (s, 4H), 4.67 (AB, 4H, $J = 12.6$ Hz), 4.64 (s, 4H), 3.30 (AB, 4H, $J = 12.6$ Hz), 3.03 (d, 12H, $J = 4.2$ Hz), 1.33 (s, 18H), 0.87 (s, 18H). ^{13}C NMR (CHCl$_3$-d): $\delta = 169.2$, 166.5, 151.7, 149.8, 145.5, 144.3, 132.9, 130.5, 124.3, 123.8, 71.7, 70.8, 35.1, 34.5, 32.9–32.0, 30.0–28.9. FAB MS: m/z 935.6 [(M + H)$^+$, calc.: 935.5]. Anal. Found: C, 71.85; H, 7.86; N, 3.14. Calc. for C$_{56}$H$_{74}$N$_2$O$_{10}$: C, 71.92; H, 7.98; N, 3.00%.

4.1.3. General procedure for the preparation of the [(Ln)2]NO₃ complexes

To a solution of 0.05 mmol of the bisacid (H$_2$)**2** and 0.20 mmol of Et$_3$N in methanol (20 ml) was added 0.07 mmol of the lanthanide nitrate salt. The resulting solution was stirred for 2 h, after which the solvent was evaporated. The complex was redissolved in CHCl$_3$ and washed twice with water followed by standard workup. The [(Ln)**2**]NO$_3$ complexes were obtained as solids in quantitative yields. The complexes were characterized by FAB MS spectrometry (see Table 1) and IR spectroscopy. The [(Ln)**2**]NO$_3$ complexes gave similar IR spectra: A peak at 1640–1630 cm^{-1} ($\nu_{NC=O}$) with a shoulder around 1590–1600 cm^{-1} (ν_{COO}).

4.1.4. General procedure for the preparation of the calix[4]arene-based ternary complexes

The ternary complexes were prepared by stirring a dichloromethane solution (10 ml) of 0.030 mmol of the appropriate [(Ln)**2**]NO$_3$ complex, 0.030 mmol dbm, and 30 μl of a 1 M aqueous NBu$_4$OH solution for 1 h. Subsequently, dichloromethane was added (50 ml) and the organic layer was washed once with water, followed by standard workup. The ternary complexes were obtained as solids, and were characterized by FAB MS spectroscopy (see Table 1) and IR spectroscopy. The ternary [Ln]**2**]dbm complexes gave similar IR spectra: a peak at 1650–1640 cm^{-1} ($\nu_{NC=O}$ and $\nu_{C=O,\beta\text{-diketone}}$) and a peak at 1600 cm^{-1} (ν_{COO}).

4.2. Photophysical studies

Steady-state luminescence measurements in the visible region were performed with a Photon Technology International (PTI) Alphascan spectrofluorimeter. The samples were excited with a 75 W quartz–tungsten–halogen lamp followed by a SPEX 1680 double monochromator. The emitted light was detected at an angle of 90° by a Hamamatsu R928 photomultiplier,

and subsequently fed to a photon-counting interface. The absorptions of the samples were typically 0.1 at the excitation wavelength and the solvents were of spectroscopical grade. The overall luminescence quantum yield was determined relative to a reference solution of quinine sulfate in 1 M H$_2$SO$_4$ ($\phi = 0.546$), and corrected for the refractive index of the solvent [25]. Deaeration of the samples was performed by purging the solutions with argon for a duration of 10 min. Time-resolved luminescence measurements were performed with an Edinburgh Analytical Instruments FL900 system. The excitation source consisted of a pulsed Xe-lamp (μs-pulsed output). The luminescence signal was detected by a Hamamatsu R928 photomultiplier and fed to a time-to-amplitude converter and a multichannel analyzer (time correlated single photon detection).

Steady-state measurements in the near-infrared region, were performed with a PTI Alphascan spectrofluorimeter. The excitation light beam was modulated with a mechanical chopper at 40 Hz. The luminescence signal was detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques. Luminescence lifetime measurements in the near-infrared region (Edinburgh Analytical Instruments LP900 system) were performed by monitoring the luminescence decay after excitation with a 0.5 ns pulse of an LTB MSG 400 nitrogen laser ($\lambda_{exc} = 337$ nm, pulse energy 20 μJ, 10 Hz repetition rate). Decay signals were recorded using a liquid-nitrogen-cooled Ge detector with a time resolution of 0.3 μs. The signals were averaged using a digitizing Tektronix oscilloscope. All decay curves were analyzed by deconvolution of the measured detector response and could be fitted with mono-exponential curves. The detector response was obtained by recording the signal of the near-infrared fluorescent dye IR 140 in methanol, which has a fluorescence lifetime (less than 1 ns) that is much shorter than the detector response.

4.3. Molecular mechanics calculations

Initial structures as well as visualizations were carried out with QUANTA 97 [26]. The molecular mechanics calculation was run with CHARMM 24 [17]. Parameters were taken from QUANTA 97 and point charges were assigned with the charge template option in QUANTA. The parameters for Eu^{3+} were $\varepsilon = 0.050$ kcal mol^{-1} and $\sigma = 3.30$ Å [27]. The starting structures were minimized by ABNR (adopted-basis set Newton–Raphson) until the RMS on the energy gradient was ≤ 0.001 kcal mol^{-1} Å^{-1}. No cutoff on the non-bonded interactions was applied in the gas-phase minimizations of the complexes. A constant dielectric constant with an ε of 1 was used.

Table 1
Characterization of the ternary complexes by mass spectrometry (FAB)

Complex	Measured m/z	Calculated m/z
[(Eu)**2**]NO$_3$	1085.1 (M−NO$_3$)$^+$	1085.4
[(Eu)**2**]dbm	1331.5 (M+Na)$^+$	1331.5
[(Nd)**2**]NO$_3$	1076.5 (M−NO$_3$)$^+$	1076.4
[(Nd)**2**]dbm	1322.4 (M+Na)$^+$	1322.5
[(Er)**2**]NO$_3$	1100.7 (M−NO$_3$)$^+$	1100.4
[(Er)**2**]dbm	1347.0 (M+Na)$^+$	1346.7
[(Yb)**2**]NO$_3$	1106.7 (M−NO$_3$)$^+$	1106.5
[(Yb)**2**]dbm	1153.1 (M+Na)$^+$	1152.5
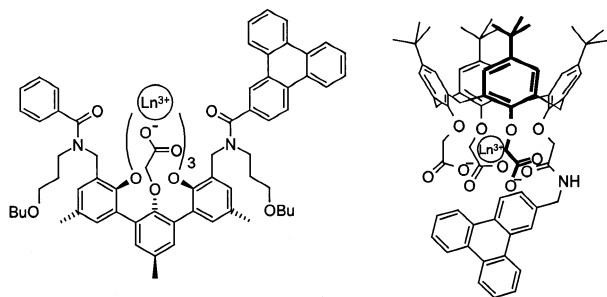
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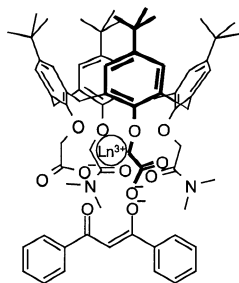
Chart 2.

Acknowledgements

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