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Abstract: The synthesis is described of a series of calix[4]arenes with three different sensitizer chromophores ("antennas") attached to the lower rim via a short spacer. In the Eu³⁺ and Tb³⁺ complexes of these calixarenes, photoexcitation of the antenna can induce lanthanide emission via intramolecular energy transfer. Although the higher energy of the Tb³⁺ luminescent state makes it more difficult to sensitize than in the case of Eu³⁺, especially a triphenylene antenna is found to have strong sensitizing ability toward not only Eu³⁺ but also Tb³⁺, allowing excitation of the lanthanide with wavelengths extending to 350 nm.

Introduction

Time-resolved immunoassay systems based on delayed luminescence become valuable analytical tools for in vitro diagnostics, replacing the use of radiolotope-labeled species. The complexation of Eu³⁺ and Tb³⁺ ions in suitable ligands yields highly luminescent species which can be used as probes for a variety of such applications. Cryptand-type ligands containing 2,2'-bipyridine (bpy) and/or 3,5'-bisquinolinyle-2,2'-dioxide (bq₂₂) combine the shielding effect (complexation effect) and the sensitizer ("antenna") moiety of the pendant groups.

In addition to many other applications calixarenes are suitable building blocks for ionophores for trivalent cations. Although Eu³⁺ ions are commonly used as probes in time-resolved luminescence systems, Tb³⁺ ions appear more attractive because of a higher intrinsic quantum yield. Sabbatini et al. have shown that the Tb³⁺ complex of a p-tol-butylicalix[4]arene tetracetamide shows a high luminescence quantum yield (0.2) and a long luminescence lifetime (1.5 ms). The luminescence quantum yield could even be improved when one of the side groups was replaced by a sensitizer group (phenacyl or diphenacylcarbonyl) or when the calixarene skeleton was functionalized at the upper rim with phenyl groups, the resulting biphenyls serving as sensitizers. However, such Tb³⁺ complexes are not attractive for immunoassay systems because of their overall charge. Besides the small effect on the quantum yield by introducing one or more sensitizers in the ligand, the excitation wavelength is normally around 270–300 nm. For the application in time-resolved immunoassay systems, the most preferable excitation wavelength is however >330 nm, which allows the use of standard optics.

Recently we reported the synthesis of calixarene derivatives, containing three carboxylic acid groups, which form overall neutral complexes with lanthanide cations. It was demonstrated that the lanthanide ion was effectively shielded from the solvent and that functionalization of the carboxamide side chain did not disturb the shielding efficiency. We found that excitation of a pyridine chromophore, attached to this side chain, gives rise to energy transfer to the complexed lanthanide ion but that the excitation wavelength (λ = 280 nm) and efficiency of energy transfer are rather low.

In the present paper, we report the synthesis and luminescence characteristics of bochared and neutral Eu³⁺ and Tb³⁺ complexes of calixarene derivatives substituted with three carboxylic ester (9d,e) and acid groups (10a–d), respectively, and one aromatic sensitizer group: naphthalene, phenanthrene, or triphenylene. Especially with triphenylene, long-wavelength (up to 350 nm) excitation of both Eu³⁺ and Tb³⁺ can be achieved.

Results and Discussion

Synthesis. The key step in the synthesis of the ionophores 10a–d (Chart 2) comprises reaction of calix[4]arene triester monooxamic chloride 8¹ with the amino-substituted sensitizers 9,1-(aminomethyl)naphthalene (11), 9-(aminomethyl)phenanthrene (12), 12(N-(2-methylthiophenyl)propylamine (7), and 2-(aminomethyl)triphenylene (6) (Chart 1). 9-(Aminomethyl)phenanthrene (12) was prepared in a yield of 73% by reduction of 11.

References

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Chart 1

Figure 1. Energy scheme for the absorption-energy transfer-luminescence process. Depicted are the main luminescent energy levels (\(\tilde{E}_0\) for Eu\(^{3+}\) and \(\tilde{E}_0\) for Tb\(^{3+}\)).

Table 1. FAB Mass Spectral Data of Complexes Eu(10a–d) and Tb(10a–d)

<table>
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<th>measd</th>
<th>calcld</th>
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</tr>
<tr>
<td>Tb(10a)</td>
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<td>1176.2</td>
</tr>
<tr>
<td>Eu(10b)</td>
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<tr>
<td>Tb(10b)</td>
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<td>1226.2</td>
</tr>
<tr>
<td>Eu(10c)</td>
<td>1184.2*</td>
<td>1184.3</td>
</tr>
<tr>
<td>Tb(10c)</td>
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</tr>
<tr>
<td>Eu(10d)</td>
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</tr>
<tr>
<td>Tb(10d)</td>
<td>1318.1</td>
<td>1318.4</td>
</tr>
</tbody>
</table>

*\(M^* - 2\text{CO}_2\)

9-cyanophenanthrene with B\(_2\text{H}_6\) in THF. Despite the low selectivity between the 1- and 2-positions in aromatic substitution reactions of triphenylene,\(^{15}\) triphenylene-2-carboxaldehyde (2) can be prepared from triphenylene (1) and bis(chloromethyl)ether/TICl in 78% yield. The \(^{1}H\) NMR spectrum shows a singlet at 9.10 ppm for the H-1 hydrogen atom which proves the functionalization of the 2-position. Reductive amination of 2 with \(\pi\)-propylamine/NaCNBH\(_3\) in THF afforded \(\tilde{N}\)-(2-methyltrithiophenyl)propylamine (7) in 96% yield. Reduction of triphenylene-2-carboxaldehyde (2) with B\(_2\text{H}_6\) in THF afforded 2-(hydroxymethyl)trithiophene (3) in 91% yield. Reaction of 3 with PbBr\(_2\) gave 2-(bromomethyl)trithiophene (4) in 94% yield. A subsequent Gabriel reaction of 4 afforded phthalimide 5, after which protection with hydrazine monohydrate, yielded in 94% the desired 2-(aminomethyl)trithiophene (6). Reaction of monoacid chloride 8 with the aminomethyl-substituted compounds 6, 7, 11, 12 and the hydroxymethyl-substituted compound 3 afforded the triester monoamido calix[4]arenes 9a–c and the tetraester 9d, respectively, in 78–83% yield upon recrystallization of the crude reaction mixture. Mild hydrolysis of the ester bonds in preference to the amide bond in compounds 9a–c, using K\(_2\text{CO}_3\) in refluxing MeOH–H\(_2\text{O}\) (5:1) gave the triacid monoamido derivatives 10a–d in 76–81% yield. The \(^{1}H\) NMR spectra of these derivatives show two characteristic AB systems for the methylene hydrogens, indicating the cone conformation and a 2:1:1 ratio of the tert-butyl groups of the calix[4]arene. The corresponding Eu(III) and Tb(III) complexes Eu(10a–d) and Tb(10a–d) were prepared by refluxing a solution of the calix[4]arene triacid monoamides 10a–d in acetonitrile in the presence of EuCl\(_3\) or TbCl\(_3\), triethyl orthoformate, and triethylamine as a base. FAB-MS spectra of the complexes show an intense signal corresponding to [ligand + lanthanide cation] (Table 1).

**Luminescent Properties.** Recently we reported\(^{14}\) the effective solvent shielding of lanthanide ions in overall neutral complexes with calix[4]arene triacetates. Excitation of a pyridine side chain chromophore gives energy transfer to complexed lanthanide ions, a phenomenon also observed by others.\(^{10,12}\) for other types of aromatic chromophores attached to calixarenes. Such an attached chromophore can in principle function as an "antenna" that allows the excitation of the lanthanide luminescence at wavelengths where neither the lanthanide ion nor the complexing calixarene display significant absorption. This is of particular importance if such complexes are employed as luminescent markers. Applications require excitation at relatively long wavelengths as transmitted by regular optics and produced by standard (UV) light sources. These requirements set a lower limit of ~350 nm to the wavelength of the excitation light, which is close to, for example, one of the Hg or N\(_2\) emission lines (335 and 337 nm, respectively), but longer wavelengths (e.g., 365 nm (Hg) or 354 nm (Nd/YAG third harmonic)) would be preferred. The antenna chromophores currently available for calixarene–lanthanide complexes absorb very weakly or not at all above 320 nm (i.e., ~31 250 cm\(^{-1}\)). From Figure 1 the limitations inherent in designing efficient antenna systems absorbing at longer wavelength can be derived. If we assume that the antenna sensitizer displays a single-triplet energy gap (\(\tilde{E}_{\text{exc}} - \tilde{E}_0\)) of at least 5000 cm\(^{-1}\), which appears a lower limit for \(n\)-systems,\(^{17}\) and that its triplet energy must be at least 3500 cm\(^{-1}\) above the main luminescent state of the lanthanide ion to make energy transfer fast and irreversible, the long wavelength absorption edge (\(\tilde{E}_0\)) of the antenna cannot be much above 346 nm for Tb\(^{3+}\) or above 385 nm for Eu\(^{3+}\) complexes. It thus appears that, although especially for Tb\(^{3+}\) the margins are narrow, there is room for extending the absorption of antenna chromophores that operate along the triplet mechanism depicted in Figure 1 into a more useful region than presently available.

In order to test this hypothesis we have compared the luminescent properties of the complexes of which the synthesis was (15) We prepared the starting triester monoamido calix[4]arene via a slight modification to what has been reported earlier: Acetic acid (4.0 mL, 100%) and nitric acid (6.7 mL, 65%) were added to a vigorously stirred solution of p-tert-butylcalix[4]arene tert-butyl ester\(^{20}\) (2.0 g) in CHCl\(_3\) (100 mL). The solution was stirred for 45 min followed by standard workup. After recrystallization from methanol, the triester monoamido calix[4]arene was obtained in a yield of 91%, mp 166–167 °C (lit.\(^{18}\) 89%, mp 166–169 °C). (a) Böhmer, V.; Vogt, W.; Harris, S. J.; Raymond, G. L.; Collins, B. M.; Deasy, M.; McKervey, M. A.; Owens, M. J. Chem. Soc., Perkin Trans. 1 1990, 431. (b) Barrett, G.; Böhmer, V.; Ferguson, G.; Galagher, J. F.; Harris, S. J.; Leonard, R. G.; McKervey, M. A.; Owens, M.; Tapadia, M.; Vierengel, A.; Vogt, W. J. Chem. Soc., Perkin Trans. 2 1992, 1555. (c) Gons, F. H.; Kamounn, P. S.; Mirti, A. Y. Tetrahedron 1979, 35, 2927. (16) Murov, S. L.; Carmichael, L.; Hug, G. L., Eds. Handbook of Photochemistry; Marcel Dekker, Inc.: New York, 1993.
studied the effect of variation in the bridging group between antenna and calixarene as well as of other calixarene side chains. Interestingly very strong effects of such structural changes were observed. Calixocene Eu(10c) is a homologue of the naphthalene and phenanthrene systems discussed above, and its behavior may be taken as evidence for the high efficiency of triphenylene as an antenna chromophore as compared to other aromatic species. However, small structural variations have a dramatic effect on the efficiency, In [Eu(9e)]^{3+}, with an n-propyl group at the bridging amido-nitrogen and with three ethyl ester groups instead of the three carboxylates, the sensitizing action of the antenna group is lost virtually completely. Saponification of the ester groups (Eu(10d)) partly restores the antenna effect as does “substitution” of the n-propylcarboxamide by an ester moiety ([Eu(9d)]^{3+}), the latter modification being more productive than the former and in fact producing the most effective system in the series.

The results obtained for various Tb^{3+} complexes (monitored at the appropriate wavelength (545 nm) are compiled in Figure 4. In this case not only naphthalene but also phenanthrene turns out to be quite inefficient in sensitizing the Tb^{3+} luminescence as compared to triphenylene.

It appears likely that this is mainly due (see Table 2) to the relatively low triplet energy of the former two chromophores as compared to that of the luminescent state of Tb^{3+} (see Figure 1) which makes energy transfer slower and/or reversible. With triphenylene as an antenna significant Tb^{3+} luminescence can be induced up to \( \lambda_{\text{exc}} = 350 \text{ nm} \), i.e., at wavelengths extending to the absorption edge of the antenna (see Figure 2). As with Eu^{3+}, strong structural influences on the efficiency of the antenna effect are observed. Again, the ligand with an n-propyl group at the amide-nitrogen atom ( Tb(16d)) performs rather poorly, while both [Tb(9d)]^{3+} and [Eu(10c)] display high activity, with again [Tb(9d)]^{3+} being the most effective.

The data presented above appear to validate the mechanism depicted in Figure 1, from which it was predicted that triphenylene should be able to sensitize the luminescence of both Eu^{3+} and Tb^{3+}, while with phenanthrene, the latter should be marginal in view of energetic considerations. This means that especially triphenylene must be considered as a highly efficient antenna chromophore that allows population via near-UV excitation of the luminescent state of not only Eu^{3+} but also Tb^{3+}. This is of considerable interest because the inherent luminescence quantum yield of complexed Tb^{3+} ions is in general much higher (~0.03–0.4) than that of Eu^{3+} ions (~0.001–0.3).19

On the other hand, the data presented above clearly show that optimization of the antenna function in calixarene–antenna/ Ln(III) systems requires rather strict structural control. The quantum yield of lanthanide luminescence resulting from antenna excitation can be expressed by eq 1:

\[
\phi_{\text{tot}} = \phi_{\text{ant}} \phi_{\text{et}} \tau
\]

\( \phi_{\text{tot}} \) stands for the intersystem-crossing efficiency of the antenna, \( \phi_{\text{et}} \) stands for that of the energy transfer step (including the possible effects of reversibility), while \( k_t \) and \( \tau \) are the radiative rate constant and the luminescence lifetime of the lanthanide ion.

In Table 3 luminescence lifetimes of the present lanthanide complexes with a triphenylene antenna chromophore are compiled as measured in methanolic solution. While especially for the Eu^{3+} complexes a significant structure dependence of \( \tau \) is observed, the differences are much smaller than and

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A strong indication for the correctness of this assumption was obtained by studying the effect of oxygen on the antenna-sensitized luminescence. While the luminescence decay time of the lanthanide is essentially oxygen insensitive (see Table 3), the intensity of this luminescence as elicited by 300-nm excitation of the antenna chromophore is dramatically enhanced by deoxygenation for many of the complexes studied (see Table 4 and Figure 5). This clearly indicates that in those cases energy transfer is slow and/or reversible so that a significant fraction of the $S^*$ species are trapped by oxygen quenching instead of contributing to the population of the luminescent state of the lanthanide.

Figure 5. Relative luminescence intensities of Eu** (A) and Tb** complexes (B) (λem = 615 and 545 nm, respectively) before and after deoxygenation (λex = 300 nm). The emission intensities of [Eu(94d)]** and [Tb(94d)]** in air-saturated solution were arbitrarily set to 100.

Figure 6. Corrected emission spectra of [Eu(94d)]** (--) and [Tb(94d)]** (---) in CH3OH at room temperature, λex = 300 nm.

Table 4. Ratios of Lanthanide Luminescence Intensity in CH3OH after (λex=300 nm) and before (λex=300 nm) Deoxygenation.

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<td>[Tb(94d)]**</td>
<td>0.96</td>
</tr>
<tr>
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<td>Tb(10d)</td>
<td>2.30</td>
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</table>

Concluding Remarks

The data presented above demonstrate that calix[4]arenes/Ln(III) complexes can be extended with antenna chromophores, enabling excitation of both Eu** and Tb** luminescence at wavelengths extending to at least 350 nm. Especially a triphenylene antenna chromophore was found to display very effective sensitizing properties. Clearly more work is required to optimize the properties (e.g., water solubility) of the present complexes, as well as to enhance the long-wavelength absorptivity of the triphenylene chromophore in order to produce calix[4]arenes/Ln(III) complexes with properties suitable for practical applications in biosensors.

Experimental Section

Synthesis. General Procedure. Melting points were determined with a Reichert melting point apparatus and are uncorrected. 1H NMR and 13C NMR spectra were recorded on a Bruker AC 250 spectrometer in CDCl3 with Me4Si as the internal standard unless stated otherwise. FAB-MS (fast atom bombardment mass spectrometry) and electron impact (EI) spectra were obtained using a Finigan MAT 90 spectrometer. In the first case m-nitrobenzyl alcohol was used as a matrix. CH2Cl2 was distilled from CaCl2 and stored over molecular sieves. Tertahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl, whereas N,N-dimethylformamide (DMF), toluene, and hexanes (mixed isomers) were dried on 4 Å molecular sieves. All reactions were carried out under an argon atmosphere. Chromatographic separations mentioned were performed on silica gel 60 (Si60) (E. Merck, particle size 0.040–0.063 mm, 230–400 mesh). Triphenylene (1), 1-tolaniimethyl)naphtalene (11), and 9-cyanonaphthalene (13) were purchased from Aldrich. The presence of solvent in the analytical samples was confirmed by 1H NMR spectroscopy. All reactions were carried out in an argon atmosphere. Standard workup means that the organic layers were finally washed with water, dried over magnesium sulphate (MgSO4), filtered, and concentrated in vacuo.

Triphenylene-2-carboxaldehyde (2). To a solution of triphenylene (1) (1.0 g, 4.38 mmol) and freshly distilled TICl3 (1.65 g, 8.70 mmol) in dry CH2Cl2 (75 mL) was added dropwise bis(chloro)ethoxy ether (2.5 g, 21.7 mmol) at 0 °C. The reaction was stirred at room temperature for 3 h, whereupon again TICl3 (1.65 g, 8.70 mmol) and bis(chloro)ethoxy ether (2.5 g, 21.7 mmol) were added. After the mixture was stirred for another 3 h, the reaction was quenched by the addition of 2 M HCl (100 mL). The organic layer was washed with 2 M HCl (2 × 100 mL), followed by standard workup. The crude reaction product was crystallized from CH2Cl2/methanol to obtain an orange/brown colored solid: yield 78%; mp 147–148 °C; 1H NMR δ 12.63 (s, 1 H), 9.10 (s, 1 H), 8.9–8.5 (m, 5 H), 8.11 (d, 2 H, J = 8.4 Hz), 7.9–7.5 (m, 4 H); 13C NMR δ 192.2 (s); mass spectrum (EI) m/e 156.1 (M+, calcd 156.3). Anal. Calcd for C16H13O2: C, 88.42; H, 6.49. Found: C, 88.14; H, 6.49.

2-(Hydroxymethyl)triphenylene (3). To a solution of 2 (0.50 g, 1.95 mmol) in dry THF (75 mL) was added Bz2THF (3 mL, 1.0 M solution) at 0 °C. The cooling bath was removed, and the solution was stirred for 2 h at room temperature. 1.0 M NaOH (75 mL) was added, followed by standard workup. The product was triturated with CH2Cl2 to give pure 3: yield 93%; mp 151–152 °C; 1H NMR δ 8.9–8.5 (m, 7 H), 7.9–7.5 (m, 6 H), 4.95 (s, 2 H), 1.90 (br s, 1 H); 13C NMR δ 61.0 (t); mass spectrum (EI) m/e 258.0 (M+, calcd 258.3), 220.0 (M–COCH3). Anal. Calcd for C16H12O2: C, 86.39; H, 5.58. Found: C, 86.21; H, 5.15.

2-(Bromomethyl)triphenylene (4). To a solution of 3 (0.50 g, 1.94 mmol) in toluene (75 mL) was added PBr3 (0.79 g, 2.90 mmol) at room temperature. The solution was stirred for 2 h at 50 °C. NaOH (0.1 M, 75 mL) was added, and the organic layer was washed with saturated NaHCO3 (2 × 50 mL), followed by standard workup. The product was obtained as a white solid: yield 94%; mp 137 °C; 1H NMR δ 8.8–8.5 (m, 6 H), 7.8–7.6 (m, 5 H), 4.76 (s, 2 H); 13C NMR δ 33.9 (t); mass spectrum (EI) m/e 320.0 (M+, calcd 320.0), 241.0 (M–Br + H). Anal. Calcd for C16H13Br: C, 71.05; H, 4.08. Found: C, 71.02; H, 5.53.

2-(Phthalimidomethyl)triphenylene (5). To a solution of 4 (0.50 g, 1.56 mmol) in DMF (25 mL) was added potassium phthalimide (0.23 g, 1.72 mmol). The solution was stirred overnight at 40 °C. The solvent was removed in vacuo and the residue dissolved in CH2Cl2 (50 mL) and washed with 0.1 M NaOH (3 × 50 mL). The product was obtained as a white solid in a quantitative yield: mp 212–213 °C; 1H NMR δ 8.8–8.5 (m, 6 H), 7.9–7.8 (m, 9 H), 5.09 (t, 2 H); 13C NMR δ 168.1 (s), 41.9 (t); mass spectrum (EI) m/e 387.1 (M+, calcd 387.1). Anal. Calcd for C20H14N2O2: C, 82.93; H, 4.45; N, 3.58. Found: C, 82.86; H, 4.28; N, 3.57.
General Procedure for the Preparation of Complexes Eu(10a–d) and Tb(10a–d). The lanthanide salts Eu(III)Cl₃·6H₂O and Tb(III)Cl₃·6H₂O (1.1 equiv) and the drying agent triethyl orthoformate (5 drops) were first dissolved in acetonitrile and heated under reflux for 2 h. Triethylamine (3 equiv) and the calixarene tricarboxylic derivative 10a–d (1 equiv) were added, and reflux was continued for another 2 h. The solution was concentrated to dryness. Chloroform (150 mL) and H₂O (100 mL) were added, and the organic layer was concentrated in vacuo. The Eu(III) and Tb(III) complexes were obtained in quantitative yields and have mp’s > 300 °C. All complexes gave satisfactory elemental analyses. The mass spectral data are summarized in Table 1.

Procedure for the Preparation of Complexes [Eu(9d,e)]⁺⁺ and [Tb(9d,e)]⁺⁺. The lanthanide complexes [Eu(9d,e)]⁺⁺ and [Tb(9d,e)]⁺⁺ were prepared by reaction of the ligand (9d,e, 1 equiv) with the lanthanide salt (Eu(NO₃)₃·5H₂O or Tb(NO₃)₃·5H₂O, 1 equiv) in spectrograde methanol. The resulting solutions of the complexes were immediately used for the luminescence measurements.

Luminescence Measurements. Absorption spectra were recorded on a Varian Cary 3 UV-visible spectrophotometer.

Continuous emission spectra were recorded on a Spex Fluorolog 2 spectrofluorometer. Figure 6 gives representative results of such spectra.

Where indicated, deoxygenation was achieved by purging with argon. Time-resolved emission spectra were obtained using a Lumonics EX700 XeCl excimer laser (308 nm) as excitation source. The resulting luminescence was observed by a gated diode array detector coupled to an EG & G OMA III data handling system. Spectra were averaged over 100 shots to improve the signal to noise ratio. From these spectra luminescent lifetimes were calculated by fitting the integrated signal in time. MonoeXponential decay was observed in all cases.

Acknowledgment. The research described in this paper was supported by the Technology Foundation (S.T.W.), Technical Science Branch of the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available. Table listing elemental analyses of Eu(III) and Tb(III) complexes of 10a–d (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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