

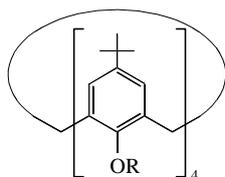
Some new properties of calixarenes: the luminescence of four lanthanide ions in calixarene complexes

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Complexes of Nd, Eu, Tb and Yb with a number of phenolic-type calix[4]arenes have been obtained and their spectral-luminescence properties investigated.

The luminescence properties of lanthanide ions (Ln^{III}) are of great interest because of the possibility of solving different biochemical and medical problems using Ln^{III} as labels.^{1,2} Calixarenes are a class of macrocyclic compounds which are able to encapsulate Ln^{III} quite efficiently.^{3–5} Moreover, Ln^{III} complexes with some calixarenes display luminescence properties.^{6–8} However, up to now of calixarene complexes exhibiting luminescence properties, only those of Eu^{III} and Tb^{III}, which are known to radiate in the visible region, have been reported. On the contrary, as we have already established, in Ln complexes with resorcinol-type calixarene, only Nd^{III} and Yb^{III} ions exhibit IR luminescence.⁹ In the present work complexes of Nd^{III}, Eu^{III}, Tb^{III} and Yb^{III} ions with phenolic-type calix[4]arenes (Figure 1), in which all the above-mentioned ions show luminescence, are investigated.



- 1 R = H
- 2 R = Me
- 3 R = CH₂-CH=CH₂
- 4 R = CH₂COOH
- 5 R = CH₂COOMe

Figure 1 The structures of the ligands studied.

The absorption band maxima of compounds 1–5[†] are situated in the UV-region (270–295 nm). In their Ln^{III} complexes[‡] there is a shift to longer wavelengths by 5–20 nm. The analogy between the absorption spectra of free ligands and the excitation spectra of their complexes with Ln^{III} (see Figure 2 for Nd^{III}) is established. This proves that an intramolecular ligand-to-metal energy transfer from the triplet (T) levels of ligands, which are situated at 20600–23500 cm⁻¹, to the resonance levels of Ln^{III}, which are situated at 17300 cm⁻¹ (⁵D₀, Eu^{III}), 20500 cm⁻¹ (⁵D₄, Tb^{III}), 11500 cm⁻¹ (⁴F_{3/2}, Nd^{III}) and 10300 cm⁻¹ (²F_{5/2}, Yb^{III}), takes place. The efficiency of this process can be explained by the fact that the molecular luminescence of free ligands, which is observed in the range of 450–550 nm, is significantly reduced in their complexes with Ln^{III}.

Table 1 The relative luminescence quantum yields (Φ) of the Ln^{III} ions in complexes with 1–5.^a

Compound	Φ/10 ³						
NdC1	0.8	EuC1	23.1	TbC1	10.0	YbC1	1.2
NdC2	0.9	EuC2	24.9	TbC2	120.1	YbC2	1.8
NdC3	0.6	EuC3	6.2	TbC3	17.2	YbC3	0.9
NdC4	1.8	EuC4	33.3	TbC4	37.4	YbC4	2.2
NdC5	0.7	EuC5	19.1	TbC5	31.9	YbC5	1.2

^a DMF solution, room temperature. Measured in correspondence with the most intense emission band (⁴F_{3/2} → ⁴F_{11/2}, λ 1060 nm for Nd^{III}; ³D₀ → ⁷F₂, λ 612 nm for Eu^{III}; ⁵D₄ → ⁷F₅, λ 545 nm for Tb^{III}; ²F_{5/2} → ²F_{7/2}, λ 980 nm for Yb^{III}).

The relative luminescence quantum yields (Φ)[§] of the Ln^{III} ions in complexes with 1–5 upon ligand excitation[¶] are presented in Table 1. It is clear that the highest values of Φ

[†] ¹H NMR spectra were recorded on a Bruker AM-250 spectrometer at an operating frequency of 250 MHz.

Synthesis. Compounds 2, 3 and 5 were prepared by refluxing (< 30 h) mixture 1 (1 mmol) with the corresponding alkyl halogenide and alkali metal carbonate in acetonitrile. The solvent was then removed. After addition of water with 5% HCl to the residue the product was extracted with CHCl₃, the extract was dried over anhydrous MgSO₄ and the solvent was removed. The crude product was purified by recrystallization. Using CH₃I (24 equiv.) in the presence of K₂CO₃ (40 equiv.) yielded 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(methoxy)-calix[4]arene 2. Yield 96% (recrystallized from CHCl₃-MeOH, 2:1). Mp 238 °C, R_f 0.47 (silica gel, hexane-CHCl₃, 4:3); m/z: 704 (M⁺, 100%), 377 (40), 177 (14), 175 (4), 160 (15), 148 (20); ¹H NMR ([²H₆]DMSO) δ: 1.18 (br. s, 36H, Bu^t), 3.37 (m, 12H, OCH₃), 3.6–3.9 (m, 8H, ArCH₂Ar), 6.93 (br. s, 8H, ArH); IR, ν/cm⁻¹ (CHCl₃): 2982, 2950, 2890, 2855, 1472, 1458, 1358, 1240, 1110, 1010, 865. Found (%): C, 81.69; H, 8.98. Calc. for C₄₈H₆₄O₄ (%): C, 81.83; H, 9.08.

When CH₂=CH-CH₂Br (50 equiv.) was used as the alkylating agent in the presence of K₂CO₃ (40 equiv.), 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(allyloxy)calix[4]arene 3 was obtained. Yield 90% (recrystallized from CHCl₃-MeOH, 2:1). Mp 228 °C, R_f 0.63 (silica gel, hexane-CHCl₃, 4:3); m/z: 808 (M⁺, 100%), 768 (29), 767 (35), 751 (21), 709 (31), 175 (47), 159 (20), 145 (20); ¹H NMR (CDCl₃) δ: 1.08 (s, 36H, Bu^t), 3.15 and 4.37 (d, 8H, ArCH₂Ar), 4.45 (d, 8H, OCH₂), 5.19 (d, 4H, CH₂=), 5.25 (d, 4H, CH₂=), 6.45 (m, 4H, CH=), 6.75 (s, 8H, ArH); IR, ν/cm⁻¹ (CHCl₃): 2970, 2930, 2890, 2845, 1600, 1475, 1445, 1415, 1360, 1295, 1180, 1110, 1000, 980, 910, 870. Found (%): C, 83.28; H, 8.85. Calc. for C₅₆H₇₂O₄ (%): C, 83.18; H, 8.90.

Using methyl bromoacetate (20 equiv.) in the presence of Na₂CO₃ (20 equiv.) gave 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(methoxycarbonylmethyl)oxy]calix[4]arene 5. Yield 96% (recrystallized from EtOH-MeCN, 2:1). Mp 200–204 °C, R_f 0.5 (silica gel, hexane-CHCl₃, 3:4); m/z: 936 (M⁺, 100%), 922 (20), 921 (25), 905 (58), 863 (26), 159 (20); ¹H NMR (CDCl₃) δ: 1.2 (s, 36H, Bu^t), 1.4 (s, 12H, COOCH₃), 3.18 (d, 4H, H_B, ArCH₂Ar), 4.89 (d, 4H, H_A, ArCH₂Ar, J_{AB} = 13 Hz), 4.75 (s, 8H, CH₂CO), 6.76 (s, 8H, ArH). Found (%): C, 71.68; H, 7.74. Calc. for C₅₆H₇₂O₁₂ (%): C, 71.81; H, 7.69.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(carboxymethyl)oxy]calix[4]arene 4 was obtained by basic hydrolysis of 5 in the system NaOH-EtOH-THF. The crude product was neutralized with HCl. This compound was recrystallized from CHCl₃-DMSO (1:2) and has characteristics consistent with the literature data.¹⁰

[‡] The complexes of Ln^{III} ions with compounds 1–5 were synthesized as described previously.⁹ From elemental analysis data the composition of Ln^{III} complexes with compounds 1–5 was equal to 1:1. The Ln^{III} content was determined by a complexometric method with Arsenazo III as indicator.

[§] The relative quantum yields of luminescence were determined according to a known method¹¹ with the standards Ru(bipy)₃ for Eu^{III} ion, quinine sulfate for Tb^{III} ion and Zn-tetraphenylporphyrin¹² for Nd^{III} and Yb^{III} ions.

[¶] The absorption spectra of ligand and complex solutions were recorded on Specord M-40 UV/VIS (Zeiss, Jena, Germany) and Lambda 9 UV/VIS/NIR (Perkin Elmer, Offenbach, Germany) spectrophotometers. Luminescence and excitation spectra were recorded on a SDL-2 spectrometer (Leningrad Optic-Mechanical Association, Russia). Luminescence was excited by a DKSEL-1000-5 xenon lamp.

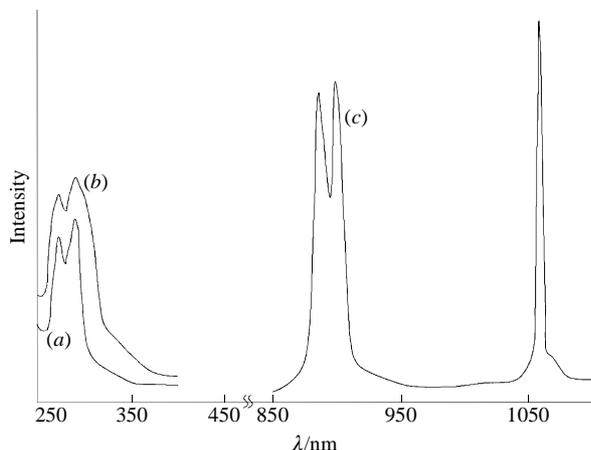


Figure 2 Absorption spectrum (a) of 1×10^{-4} mol dm^{-3} of **2**, excitation (b) and luminescence (c) spectra of 1×10^{-4} mol dm^{-3} of $\text{NdC}2$ in DMF at room temperature.

are for complexes with ligands possessing methoxy- and (methoxycarbonylmethyl)oxy- substituents. In this case, the T-level of **2**, which is equal to 20600 cm^{-1} , is the closest to the radiative level of Tb^{III} ($^5\text{D}_4$), which favours the most efficient ligand-to-metal energy transfer. The values of Φ for Nd^{III} and Yb^{III} ions are not as high as in complexes with other ligands, because of the large energy gap between the T-levels of the ligands and the radiative levels of these ions. This explains the non-radiative losses of excitation energy.

Thus, based on the data obtained, it is possible to conclude that phenolic-type calix[4]arene can be considered as suitable compounds for Ln^{III} ions to exhibit their metal-centered 4f-luminescence. This fact can be quite useful when solving some specific problems, such as bioanalytical problems.

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