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Study on monolayers of metal complexes of calixarenes and their luminescence properties

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Monolayers of complexes between trivalent lanthanide ions, alkali and alkaline earth metal ions and amphiphilic calix[n]arene derivatives ($n = 4, 6$) bearing acetic acid or hydroxamic acid groups are stable at the air-water interface. The pressure-area isotherms of the monolayers reflect the selectivity in metal ion recognition. Absorption, UV-reflection, excitation, and fluorescence emission spectra of Sm-, Eu-, Tb-, and Dy-complexes were measured in organic solutions and at the air-water interface. Quantum yields were determined for complexes in homogeneous solution. The emission spectra of the monolayers of some of the lanthanide complexes differ from those of the corresponding solutions and change at increasing surface pressure upon compression of the monolayer.

INTRODUCTION

Among the analytical methods applied for studying host-guest chemistry of cyclophanes and calixarenes in particular, molecular recognition by monolayers at the air-water interface is useful in the case of amphiphilic macrocyclic compounds as shown previously.^{1–11} At the air-water interface, the conformation of amphiphilic calixarenes is frozen due to hydrogen bond interactions with the water surface and the coordination properties may be expected to be similar to those of solutions below the coalescence temperature. Furthermore, the formation of 'sandwich'-complexes, which requires a face-to-face orientation, is hardly possible in monolayered assemblies. In the first part we describe the influence of pH, structure of ligands and nature of metal cations in the aqueous subphase on the pressure-area isotherms of

calixarene derivatives as well as their metal selectivity. The results are compared with those obtained earlier by means of solvent extraction as another heterogeneous system.^{12,13}

Recently, lanthanide complexes of calixarenes and their luminescence properties in particular^{14–19} gained interest because of their sufficient complex stability and extractability, a relationship between selectivity and structure of the host molecule, the formation of molecular assemblies with new properties, high fluorescence yields and possible applications, e.g. for analytical and biochemical purposes. In the second part of this work we describe the fluorescence properties of several complexes in organic solvents and at the air-water interface.

RESULTS AND DISCUSSION

Metal recognition by calixarene monolayers

Compounds **2A4**, **1A6**, **1B4**, **1B6**, and **1C3** form monolayers at the air-water interface with reproducible pressure-area (π -A) isotherms. With the hydrophilic head groups directed towards the water surface they are able to recognize guests, while the hydrophobic site is directed away from it and stabilizes the monolayer by hydrophobic interactions. Figure 1 shows typical π -A isotherms of **1B4** at various pH-values. The surface pressure at monolayer collapse (collapse pressure, π_c), the limiting molecular area at zero-pressure A_0 , and the molecular area at monolayer collapse A_c , are influenced by ionization and coordination of the head groups, governed by the composition of the aqueous subphase. At a pH above 9, the monolayer of **1B4** ($pK_a \approx 9$ of hydroxamic acid) is expanded due to the repulsion of the ionized head groups. This also destabilizes the monolayer, the collapse of which occurs at lower surface pressure. This

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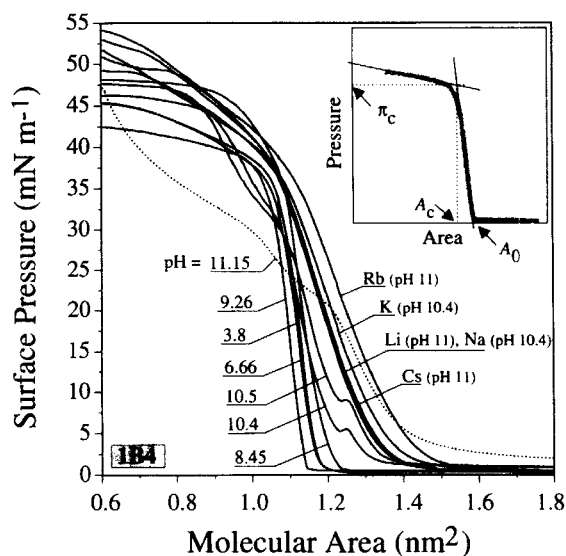


Figure 1 Typical pressure-area isotherms of **1B4** at various pH-values at 293 K. The subphase contains HNO_3 or $\text{N}(\text{CH}_3)_4\text{OH}$ and 50 mM alkali metal perchlorate if indicated.

effect is summarized in Figure 2, which shows the plot of collapse pressure π_c versus the pH of the subphase. Comparison between **1B4** and **1B6** shows that the destabilization at higher pH is more pronounced in case of the smaller calix[4]arene compared with the larger and more flexible calix[6]arene. This effect stems from stronger repulsive forces in **1B4** as well as different contributions from hydrogen-bonding interactions between the head groups. Previously, the stronger hydrogen-bonding interactions in calix[4]arenes in comparison with calix[6]arenes were established.²⁰ Correspondingly, the

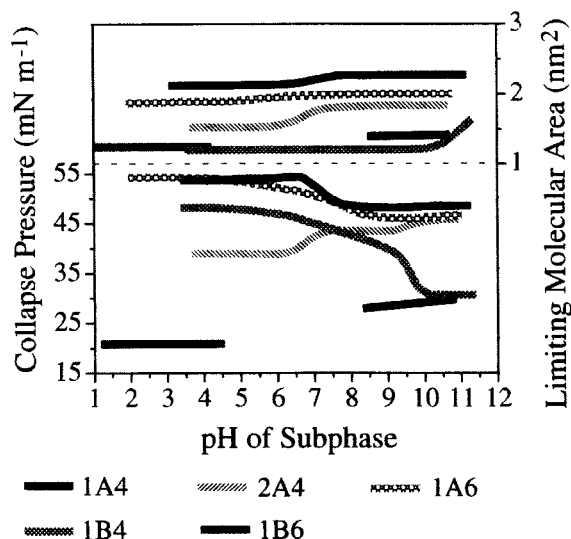


Figure 2 Surface pressure at collapse of monolayers (collapse pressure π_c) and extrapolated limiting area A_0 occupied by one molecule of calixarene as a function of the pH of the subphase at 293 K. Measurement points were interpolated and omitted for clarity.

limiting molecular area A_0 increases at higher pH (Figure 2). The increase in A_0 of **1B6** on a neutral subphase follows the decrease of π_c while the more rigid compound **1B4** has a constant limiting area up to pH 10. This difference is interpreted in terms of tighter hydrogen-bonds in **1B4** compared with **1B6**. At higher pH, dissociation and electrostatic repulsion take place leading to larger limiting areas for both **1B4** and **1B6**.

Figure 2 also includes the pH-dependent values of π_c and A_0 for compounds **1A4**, **2A4**, and **1A6**. The surface pressure at monolayer collapse π_c of **1A6** follows the trend of **1B6**, though A_0 only slightly increases within the investigated pH-range. Compound **1A4** showed a tendency to form domains at the air-water interface and was therefore substituted by **2A4** in the subsequent experiments. The more hydrophobic sites of **2A4** prevented the formation of domains and the resulting monolayer collapsed at surface pressures high enough to perform Langmuir-Blodgett depositions. In contrast to the other 3 compounds, the collapse pressure π_c of calix[4]arenes bearing acetic acid groups increases when the pH increases.

In the presence of lanthanide ions Ln^{3+} in the subphase, the π -A isotherms are influenced upon complex formation. Compound **2A4** with 4 negative charges recognizes lanthanides at a 2 mM level, as seen in Figure 3 from the change of collapse pressure π_c and limiting area A_0 . Sodium is recognized as well, the 5-fold excess of which strongly reduces the selectivity within the lanthanide series. The largest expansion in case of Eu^{3+} in the absence of Na^+ is consistent with the highest affinity toward Eu^{3+} during solvent extraction into toluene¹² with the very similar compound **1A4**: $\log K_{\text{ex}} = -3.3$ (Eu), -3.6 (Nd), -3.7 (Yb), -3.8 (Er), and -3.9 (La). However, the stoichiometry is different between the two systems: the ratio of calixarene to metal cannot exceed 1 in the monolayer, while a 'sandwich'-complex with a ratio of 2 is extracted in case of solvent extraction. The latter result was interpreted in terms of the high hydrophobicity achieved with a sandwich-structure, which is necessary for phase transfer. By extracting lanthanides with the more hydrophobic **2A4**, the stoichiometry is 1:1 as it is at the monolayer, but the selectivity is unchanged.¹³ From the selectivity of the monolayer it is concluded that the size of Eu^{3+} fits well the cavity of binding positions of calix[4]arene acetic acid derivatives. Furthermore, we suppose that dehydration of Ln^{3+} from the subphase occurs during complexation in the monolayer. The decreased selectivity of the monolayer of **2A4** in the presence of Na^+ differs from the solvent extraction system and is caused by different stoichiometric compositions.

Compound **1A6** shows a peak selectivity towards Nd^{3+} in weakly acidic medium, as seen from the change in collapse pressure and molecular area in Figure 3. Both compounds preferably bind light to medium lanthanides

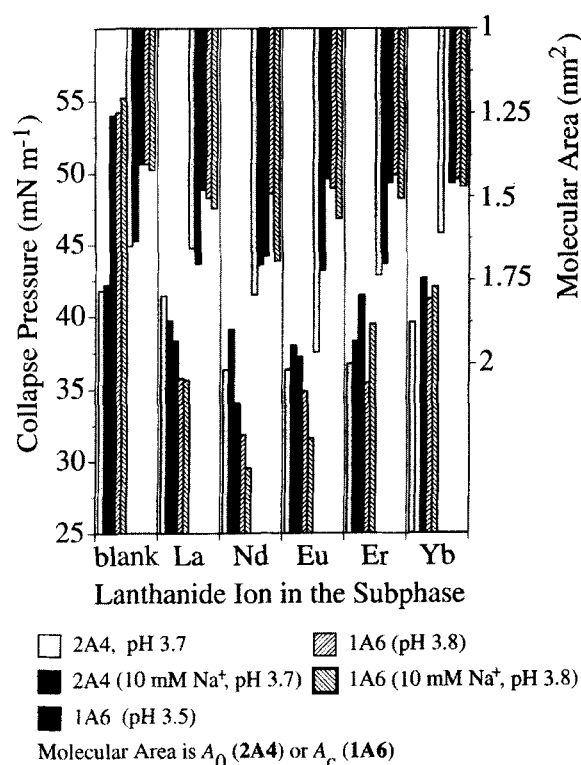


Figure 3 Collapse pressure π_c and molecular area of **2A4** and of **1A6** at different pH-values at 293 K. The subphase contains 2 mM $\text{Ln}(\text{ClO}_4)_3$, HNO_3 and additionally 10 mM NaClO_4 if indicated.

although the cavity size of **1A6** is larger compared with **2A4**. Therefore it is concluded that the lanthanides are not completely dehydrated during complex formation with **1A6**. This is in agreement with recent spectroscopic studies.¹⁷ In case of solvent extraction into chloroform, the highest affinity was observed for Nd^{3+} too, though the extracted species is again a 'sandwich'-complex: $\log K_{\text{ex}} = -0.9$ (Nd), -0.95 (Eu), -1.1 (La), and -1.6 (Er, Yb). In the presence of an excess of Na^+ , the selectivity at one and the same pH is increased in the monolayer system.

Figure 4 shows the fact that the π - A isotherms of **1C3** are influenced by Ln^{3+} at a 2 mM level at pH 3.8 even in the presence of a 5-fold excess of NaClO_4 . Surface pressure and molecular area are influenced to a greater extent by light and heavy lanthanide ions which indicates stronger binding compared with medium ones. This behaviour is opposite to that of the structurally related **1A6** and offers a possibility in lanthanide separation: The medium lanthanides can be purified from light and heavy ones by extraction with **1C3**, while they can be separated from the latter ones by using **1A4** or **2A4**. The selectivity order for **1C3** in the absence and the presence of Na^+ expressed as a change in π_c and A_c , is summarized in Figure 5. Collapse pressure and monolayer stability are largely influenced by Ln^{3+} , but almost not by Na^+ . The reason for this $\text{Ln}^{3+}/\text{Na}^+$ -selectivity is interpret-

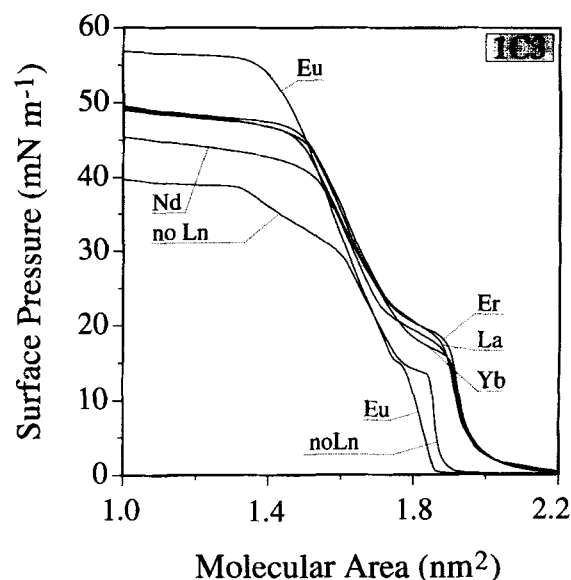


Figure 4 Pressure-area isotherms of **1C3** at 293 K and pH 3.8. The subphase contains 2 mM $\text{Ln}(\text{ClO}_4)_3$, HNO_3 , and 10 mM NaClO_4 .

ed as the favorite matching of the ion charges and the cavity size. On the other hand, the limiting area A_0 was almost constant in this series.

For **1B4**, the collapse pressure π_c is almost constant when 10 mM of lanthanide ions are added to the subphase at pH 4. This pH was chosen in order to avoid metal hydrolysis in the subphase. From earlier studies²⁰ on recognition of uranyl ion by **1B4** it was expected that lanthanide (Ln^{3+}) recognition takes place even at pH 3 to 4. However, the monolayer stability expressed as π_c was not influenced by Ln^{3+} . On the other hand, the limiting area A_0 shows a pronounced maximum in the presence of Tb^{3+} (Figure 5). The molecular area at collapse of the monolayer A_c was slightly higher for complexes of

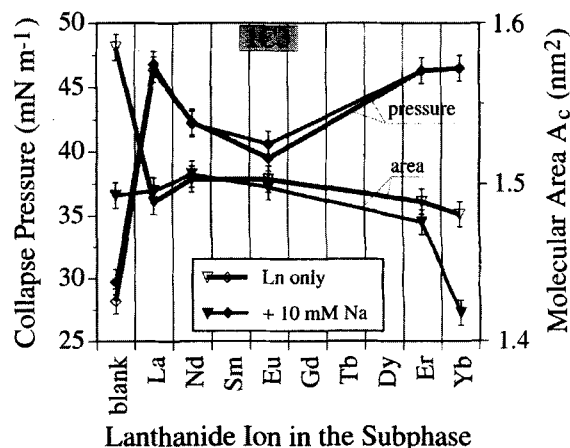


Figure 5 Plot of collapse pressure π_c and area per molecule at monolayer collapse A_c of **1C3** at pH 3.8. The subphase contains 2 mM $\text{Ln}(\text{ClO}_4)_3$, HNO_3 , and 10 mM NaClO_4 if indicated.

medium to heavy lanthanides compared with light ones indicating an interaction.

Since calixarenes bind alkali and alkaline earth metal ions as well, the influence of 50 mM MClO_4 or 0.1M $\text{M}(\text{ClO}_4)_2$ in the subphase on the π -A isotherms of **2A4**, **1A6**, and **1B4** was studied. The results are summarized in Figure 6. At pH 4, compound **1A6** shows a peak selectivity towards Rb^+ , indicated as a change in limiting area A_0 . This is different from **2A4**, the selectivity of which peaks at Na^+ at the same pH. The difference can be explained in terms of the different cavity size formed by the head groups of the two calixarenes. The peak selectivity of **2A4** towards Na^+ is due to the matching between the cavity size of the binding groups and the ionic diameter and therefore disappears at $\text{pH} > \text{pK}_a$, when the metal recognition no longer requires a cation exchange mechanism and all alkali metal ions are attracted electrostatically. Similarly, the Rb^+ -selectivity of **1B4** is reduced at $\text{pH} > \text{pK}_a$. However, the presence of metal ions at higher pH stabilizes the monolayer, because it reduces the electrostatic repulsion between the head groups of the amphiphile. In Figure 1, π -A isotherms of **1B4** depict this effect.

Spectroscopic properties of calixarenes complexed with trivalent Sm, Eu, Tb, and Dy.

For studying fluorescence spectra of lanthanide complexes, compound **1B4** with a high binding affinity due to its basicity and compound **2A4** with a well-established metal selectivity were chosen. The four above-mentioned lanthanides were used because of strong fluo-

rescence emission and a large difference between excitation and emission wavelengths. In order to prove that the monolayers of calixarene complexes exhibit the same UV-absorption spectra as in organic solutions, the UV-reflection spectrum of **1B4** on a subphase containing 10 mM Eu^{3+} was measured at various pH-values during compression of the monolayer. The reflectivity was constant above a surface pressure of 15 mN m^{-1} . Figure 7 depicts the UV-reflection spectra at 30 mN m^{-1} at pH 1, pH 3, and pH 5 as well as the absorption spectrum of 0.01 mM **1B4** mixed with 0.02 mM Eu^{3+} in acetonitrile. The latter concentration ratio was sufficient to achieve complete complexation as concluded from preliminary absorption measurements. The spectrum of the monolayer agrees with that of the solution.

Before studying the monolayer fluorescence, the UV- and fluorescence spectra in homogeneous solutions were characterized in order to determine absorbance, excita-

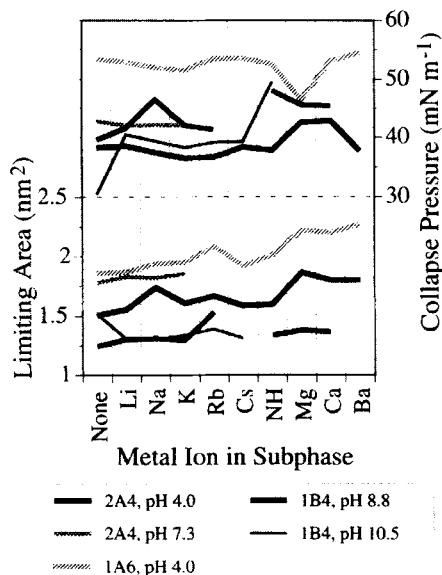


Figure 6 Influence of 50 mM mono- and bivalent metal perchlorates on the limiting areas A_0 of calixarenes at various pH-values. The subphase contains 50 mM MClO_4 ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) or 0.1 M $\text{M}(\text{ClO}_4)_2$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Ba}$). The pH was adjusted with HNO_3 or carbonate- (pH 8.8), phosphate- (pH 7.3) or $\text{N}(\text{CH}_3)_4\text{OH}$ buffer (pH 10.4).

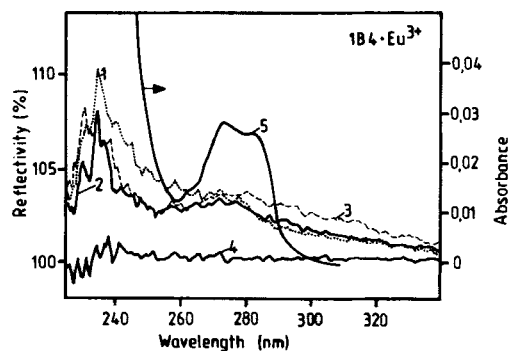


Figure 7 UV-Reflection spectra of the monolayer of **1B4** on a subphase containing 10 mM $\text{Eu}(\text{ClO}_4)_3$ at pH = 5, 3, and 1 (curve 1, 2, and 3 respectively). Curve 4 is a reference measured before spreading of **1B4** and curve 5 is the absorption spectrum of an acetonitrile solution of 0.01 mM **1B4** + 0.02 mM $\text{Eu}(\text{ClO}_4)_3$.

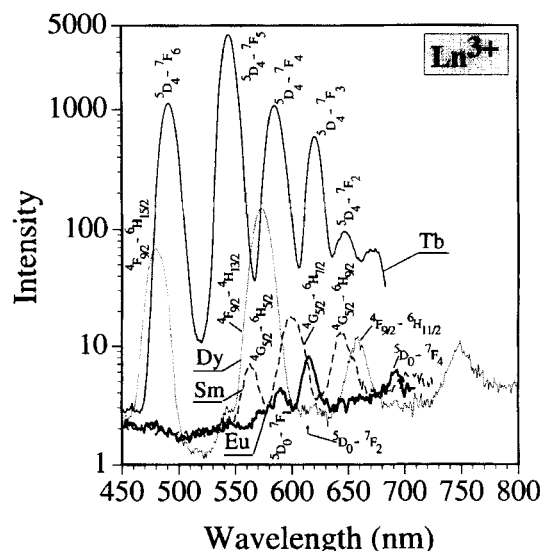


Figure 8 Fluorescence emission spectra of **1B4**-complexes with Ln^{3+} in acetonitrile solutions, excited at 274–275 nm. [**1B4**] = 0.01 mM, [Ln^{3+}] = 0.02 mM.

tion and emission wavelengths, quantum yield, stoichiometry, and kinetic effects. Figure 8 shows the fluorescence emission spectra of complexes of **1B4** with Ln^{3+} in acetonitrile upon excitation at 274–275 nm. The observed spectra agree with the emission spectra of Ln^{3+} -ions.^{21,22} The emission intensity was next measured in a series of 3 solvents and decreased due to increasing solvation of the metal ions and quenching of the fluorescence level by OH-vibrations²³ in the order: acetonitrile > methanol- d_1 > methanol. Quantum yields were determined in acetonitrile and methanol solutions at concentrations of 0.02 mM $\text{Ln}(\text{ClO}_4)_3$ and 0.01 mM calixarene. A two-fold excess of Ln^{3+} over ligand was sufficient to achieve a constant emission intensity. Calculations were performed by using aqueous standards (see experimental section) and the results are summarized in Table 1. A very high quantum yield is observed for Tb^{3+} indicating an efficient energy transfer and a stable complex to be formed. A low quantum yield for the Eu^{3+} -complexes is consistent with previous findings^{15,16} and caused by a deactivating charge-transfer band of Eu^{3+} below the triplet energy level of Ph-O-.^{16,24} The order in which the quantum yield decreases within the lanthanide series is the same for both compounds and governed by the matching of energy levels of donor and acceptor only. Fluorescence emission intensities of the complexes with **1B6** were considerably weaker compared with the calix[4]arene derivatives and therefore not studied in detail.

The stoichiometry of the Dy^{3+} -complex of **1B4** in acetonitrile was determined by means of the continuous variation method. The plot in Figure 9 reveals a 1:1-stoichiometry. In the subsequent monolayer studies one can therefore assume the same stoichiometric composition as in solution. The fluorescence intensity of the organic solutions of Tb^{3+} -complexes increased after mixing the sample and depended on the metal/ligand ratio and the water content (0 - 0.5% per volume). This kinetic effect was examined in detail with a 1 nm slit in the emission

Table 1 Calculated quantum yields ϕ^* and excitation wavelengths λ of the investigated Ln^{3+} -complexes in solution**

		<i>Sm</i>	<i>Eu</i>	<i>Tb</i>	<i>Dy</i>
1B4 ,	$\phi, \%$:	1.5	0	62	5.2
acetonitrile	λ, nm :	275	275	274	274
1B4 ,	$\phi, \%$:	0	0	32	1.7
methanol	λ, nm :	275		274	273
1A4 ,	$\phi, \%$:	0.6	0.02	58	3.12
acetonitrile	λ, nm :	275	275	274	274
error limits	\pm	20%	20%	5%	10%

*By integrating all emission peaks and using aqueous standards

**Absorbance: 0.02 to 0.04; solution: 0.01 mM calixarene + 0.02 mM $\text{Ln}(\text{ClO}_4)_3$

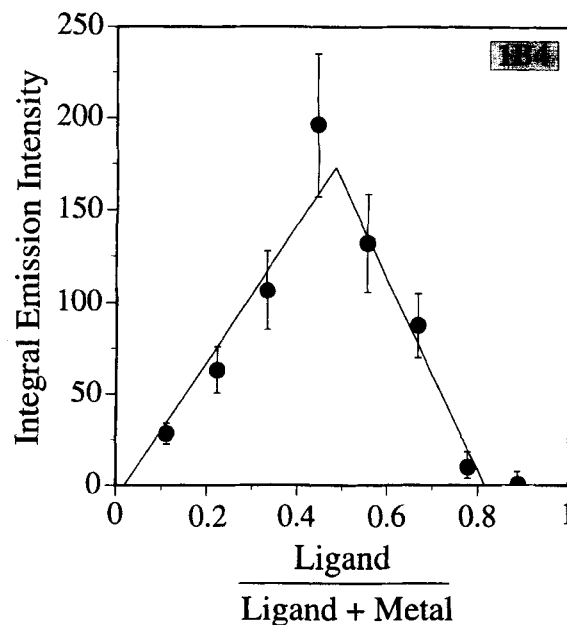


Figure 9 Continuous variation plot for acetonitrile solutions of **1B4** complexed by Dy^{3+} . Excitation at 275 nm, integral emission intensity at $16.58\text{--}21.77 \text{ kcm}^{-1}$, $[\text{metal} + \text{ligand}] = 0.045 \text{ mM}$.

path and the fine structure of the emission spectrum changed slightly during 2 hours (Figure 10). The spectral change is interpreted as removal of water molecules from the solvation shell of Dy^{3+} during complexation, where they quench the fluorescence emission. The absorption spectrum was constant during this time. A similar effect was observed with compound **1A4**. However,

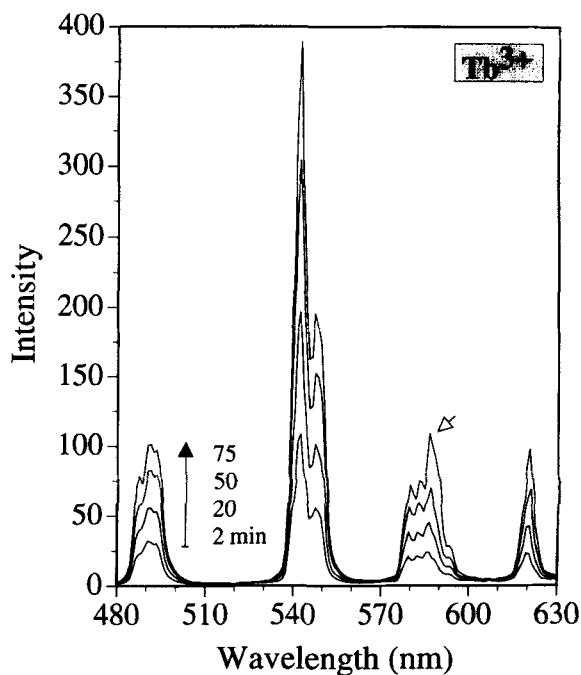


Figure 10 Kinetic effect of increasing fluorescence emission intensity in acetonitrile solutions of **1B4** (0.02 mM) containing $\text{Tb}(\text{ClO}_4)_3$ (0.02 mM, water 0.25 vol.%). The UV-absorption spectrum was constant. The arrow points at a changing fine structure.

no kinetic effects were observed at the air-water interface, where the emission intensity did not change with the time at constant surface pressure.

Fluorescence of calixarene monolayers

Fluorescence spectra of monolayers of **2A4** and **1B4** complexed with Sm^{3+} , Eu^{3+} , Tb^{3+} , and Dy^{3+} were measured at pH 4. Complexation was achieved by addition of 10 mM Ln^{3+} to the subphase. The complex formation equilibrium at the interface was reached immediately as proved by constant emission intensities.

Figure 11 depicts the emission spectrum of the monolayer of **1B4** complexed with Eu^{3+} . Only one peak at 590 nm is observed, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, which occurs through a magnetic dipole mechanism. When the pH of the subphase was decreased to pH 1.5 in order to ensure that hydroxo complexes have no influence, the spectral pattern did not change. It is different from the spectra of aqueous solutions of Eu^{3+} and of organic solutions of the same complex. The 590 nm peak in those spectra is less intense than the peak at 615 nm. However, a similar spectrum was observed for the solid perchlorate salt of the octakis(4-picoline *N*-oxide)-complex²⁵ of Eu^{3+} and examples of optical spectra of Eu^{3+} -ions in crystalline complexes,²⁵ dissolved complexes,²⁶ and doped glasses²⁷ demonstrated the influence of the ion's chemical environment. The same type of emission spectrum, but a lower fluorescence intensity is measured when a monolayer of **2A4** is used instead of **1B4**. The intensity of the peak at 590 nm increases during compression of the monolayer. This increase is much larger than the increase in packing density of the monolayer, the latter accounting for less than 20%. This observation may be explained by inclusion and desolvation of Eu^{3+} in the calixarene cavity due to increased surface pressure. With Sm^{3+} instead of Eu^{3+} , the complexes of which possess a

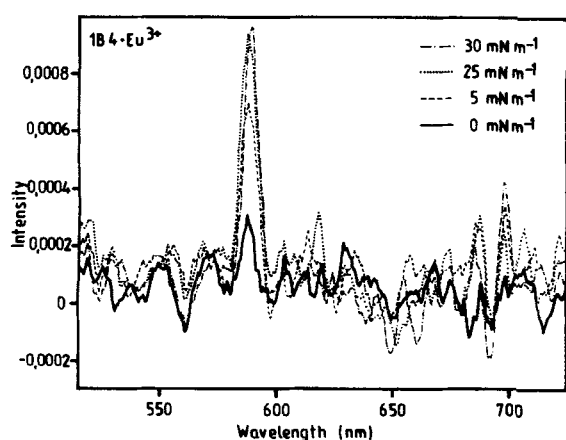


Figure 11 Fluorescence emission spectra of the monolayer of **1B4** complexed by Eu^{3+} at various surface pressures. Subphase: 10 mM $\text{Eu}(\text{ClO}_4)_3$ at pH 4. Depicted are the difference spectra (see Experimental).

higher quantum yield in organic solutions, we were unable to detect a fluorescence emission of the monolayer under the same conditions. From these results and from the selectivity of calix[4]arenes towards Eu^{3+} it is concluded that the binding of Eu^{3+} at the air-water interface at increased surface pressure leads to an improved energy transfer mechanism and increases the quantum yield. The fluorescence intensity at 25 mN m^{-1} was estimated by comparison with other monolayer spectra to be approximately 40% of Tb^{3+} complexed with **1B4** and 200% of Dy^{3+} complexed with **2A4**. The transferred LB-film of such a compressed monolayer should retain the spectral pattern and a subsequent study deals with this phenomenon.

In case of Tb^{3+} complexed with **1B4**, the intensity of the peaks at 486, 543, 580, and 620 nm increase during compression as shown in Figure 12. However, the peak at 543 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) increases more rapidly than the other peaks. At higher surface pressure the intensity ratio is similar to the ratio observed for the complex in organic solution and for the aqueous Tb^{3+} ion. This change in the intensity ratios indicates a change in coordination sphere, as shown for europium complexes.²⁶ It occurs with **1B4**, but not with **2A4**. The emission spectrum of the complex with **2A4** is depicted in Figure 13. The ratio between the peaks remains constant during compression, while the overall intensity increases. The different spectral behaviour may be explained in terms of a change in binding positions in the complex with **1B4** during compression. For example, the cavity size formed by the donor atoms may be reduced during compression and the metal ion moves to a different position that leads to a change in the energy transfer mechanism. During compression, a force ΔG is imposed on the monolayer. This value is about 29 kJ mol^{-1} in case of lanthanide complexes of **1B4** as estimated from integrating the reversed

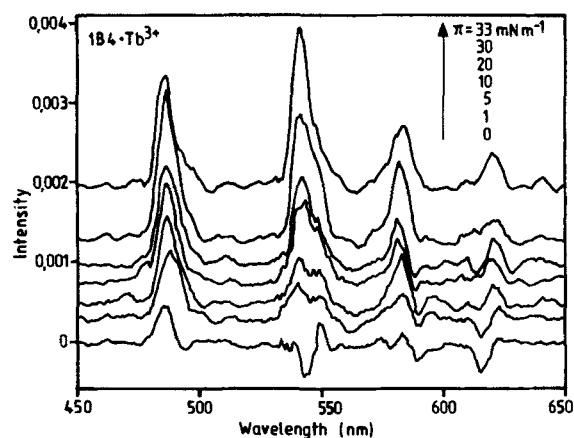


Figure 12 Fluorescence spectra of the monolayer of **1B4** complexed by Tb^{3+} in the subphase (10 mM, pH 4) at increasing surface pressure. The (difference) spectra are shifted to the top in the order of increasing pressure. The spectrum at zero mNm^{-1} was measured after spreading and before compression.

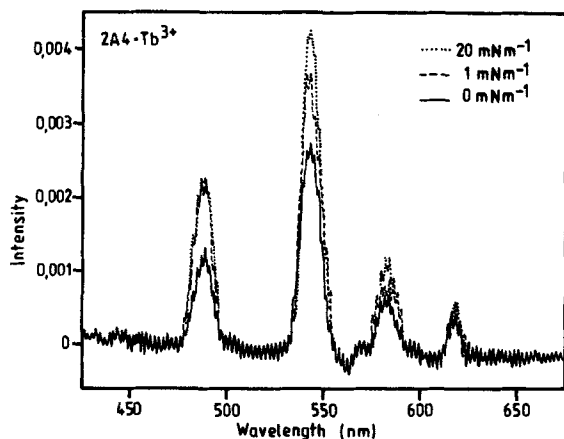


Figure 13 Fluorescence spectra of the monolayer of **2A4** complexed by Tb^{3+} at various surface pressures. Subphase: 10 mM $\text{Tb}(\text{ClO}_4)_3$, HNO_3 (pH 4).

π -A isotherm $f(x) = A(\pi)$. As shown previously,²⁸ a value in this range is sufficient to rearrange the binding positions in complexes at the air-water interface.

In case of Dy^{3+} , the complex with **2A4** exhibits a stronger fluorescence emission compared with **1B4**, different from the results in homogeneous solution. The spectrum of complexed **2A4** at various surface pressures is shown in Figure 14. The intensity of the peak at 476 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) strongly increases during compression, while the peak at 570 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) increases only slightly. However, the 570 nm peak shows a fine structure at increased surface pressure, typical for different co-existing complexes. If compound **1B6** is used to form an amphiphilic Dy^{3+} -complex instead, no fluorescence emission from the monolayer can be observed, which is interpreted in terms of inclusion of the hydrated metal ion¹⁷ leading to only a weak emission.

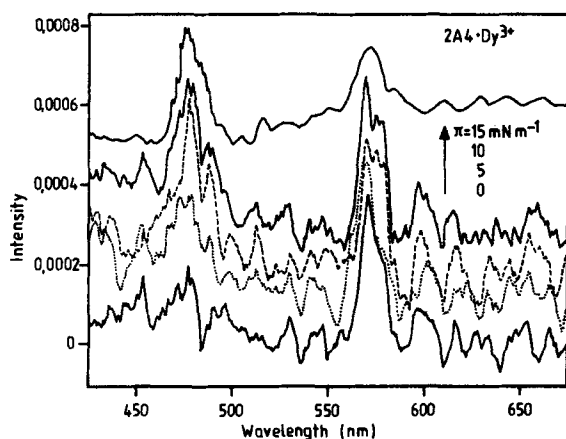
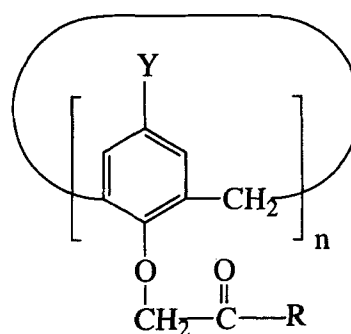


Figure 14 Fluorescence spectra of **2A4** complexed by Dy^{3+} (10 mM, pH 4) at various surface pressures π . The spectra are shifted to the top in the order of increasing π . At top: attenuated spectrum of directly excited, hydrated Dy^{3+} under the same conditions, observed as background from the subphase before subtracting the spectra.

In conclusion, the paper demonstrated that by use of calixarene assemblies at the air-water interface energy transfer from the calixarene as sensitizer to the encapsulated lanthanide ion takes place even in an aqueous environment and that the fluorescence emission spectra can be tuned by the surface pressure. Next studies deal with the energy transfer in monolayers from an amphiphilic sensitizer molecule placed in the vicinity of a second amphiphile that binds the lanthanide ion.

MATERIALS AND METHODS

The structure of the investigated calixarenes is shown in Scheme 1. Their synthetic route was described earlier.^{29–32,20} Monolayers were prepared by spreading a benzene:chloroform (4:1 v/v) solution on an aqueous subphase the pH of which was adjusted with nitric acid or phosphate-, carbonate-, or $\text{C}(\text{CH}_3)_3\text{OH}$ -buffer. Pressure-area (π -A) isotherms were measured at 293 K and a barrier speed of 0.4 mm s^{-1} with a computer-controlled



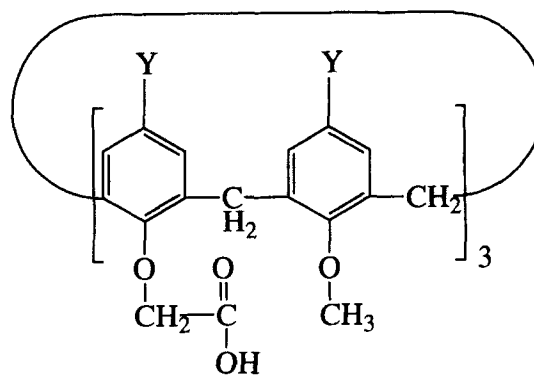
1A4: R = -OH, Y = *tert*-Butyl, n = 4

2A4: R = -OH, Y = *tert*-Octyl, n = 4

1A6: R = -OH, Y = *tert*-Butyl, n = 6

1B4: R = -N(H)-OH, Y = *tert*-Butyl, n = 4

1B6: R = -N(H)-OH, Y = *tert*-Butyl, n = 6



1C3: Y = *tert*-Butyl

Scheme 1

FSD-50 or an upgraded FSD-20 type (effective trough size 0.15 m × 0.47 m, volume 0.5 l) and a FSD-110 type (for spectroscopic measurements, 0.1 m × 0.18 m, 0.1 l) film balance (United System Integrators) on an air-suspended table in a clean-air zone according to the Wilhelmy-method. The spreading solvents were allowed to evaporate within 20 minutes. No kinetic effects concerning compressibility and spectra were observed after this time. Compound **1A4** turned out to form no reproducible monolayer because of aggregation, hence **2A4** which is more amphiphilic was used for π -A measurements instead. Water was filtered, ion exchanged and bidistilled (17.5 M Ω cm, Barnstead). Rare earth oxides (> 99.9%) were converted to perchlorate stock solutions of pH 3, the purity of which was confirmed by ICP-AES. All other solutions were freshly prepared.

UV-reflection spectra of monolayers during compression were measured with a computer-controlled MCPD-110 type spectrometer (Otsuka Electronics) equipped with a photodiode-array detector, a deuterium lamp, a filter (UV-18), slit (0.6 nm) and Y-shaped optical fibers (bundle of 8), one tip of which was vertically placed 2 mm above the air-water interface on a lift controlled by a FSD-21 lift controller with step motor. The detector was water-cooled and flushed with nitrogen. Fluorescence emission spectra of monolayers during compression were measured with the same instrument, equipped with a Xe-lamp, two separate fibers (the tips of both placed on the lift at an angle of 55° to each other), and filters. In the emission path, an Y-46 filter for Sm and Eu, and an L-38 filter for Tb and Dy were used with a 2.4 nm slit. In the excitation path, a UVD-33S filter plus a solution filter (UV-cell with conc. NiSO₄) were used as bandpass filter (230–340 nm) in order to minimize direct excitation of aqueous or of complexed Ln³⁺ by the light source. Filters and geometry were optimized for best signal:noise ratio at a measurement time of 32 s (4 scans). Constant measurement conditions were applied for all experiments, which were repeated at least once and were reproducible. The depicted spectra are the difference between the emitted light from the monolayer after spreading of the calixarene minus the emitted light from the subphase only (before spreading). The self-fluorescence of the subphase was eliminated by this way. A small part of the self-fluorescence light is absorbed in the monolayer. This absorption is not compensated and effects only small peaks near the baseline, which may turn negative. The amount of Ln³⁺ in the subphase for monolayer fluorescence measurements was 10 mM, a 2 mM level resulted in weak emission only which is a result of the dynamic equilibrium at the interface.

Fluorescence spectra in organic solvents (spectroscopic grade) were measured with a F-4500 spectrometer (Hitachi) at 298 ± 3 K by using 10 nm slits in both light paths if not stated otherwise, an L-38 filter in the emis-

sion path, and a 1 cm quartz cell. Typically, solutions were prepared by adding 0.04 ml of methanolic calixarene and 0.01 ml aqueous metal stock solutions to 4 ml of the organic solvent followed by aging (0.25% water). Absorption spectra of these solutions were recorded on a UV-2200 spectrometer (Shimadzu) at 298 K. Fluorescence quantum yields ϕ of the calixarene complexes were corrected for the emission of the free ions and calculated by using aqueous solutions of Ln(ClO₄)₃ as standards and literature values³³ of ϕ (Sm 0.16%, Eu 1.9%, Tb 8.4%, Dy 0.44%) at excitation wavelengths of 480, 394, 376, and 365 nm, respectively.

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