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Photophysics of Calix[4]biscrown-Based Ditopic Receptors of Caesium Containing One or Two Dioxocoumarin Fluorophores

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The ditopic receptors Calix-COU1 and Calix-COU2 consist of a calix[4]biscrown containing one or two dioxycoumarin fluorophores, respectively, inserted into the crown. They can form 1:1 and 2:1 (metal:ligand) complexes with caesium ions. The photophysical properties of the 1:1 complexes can be explained by (i) cation tunneling through the tube-shaped cavity (composed of the four phenyl rings) of the calix[4]biscrown, (ii) photodisruption of the interaction between the bound cation and the oxygen atoms belonging to both the coumarin moiety and the crown, (iii) photoinduced motions of the cation.

KEY WORDS: photophysics; caesium molecular sensor; coumarin; calix[4]arene.

INTRODUCTION

Photophysical studies of complexes between fluorescent receptors and cations provide a better understanding of cation-control of photoinduced processes. This is of interest not only from the fundamental point of view, but also such investigations are expected to help us in the design of more efficient fluorescent molecular sensors in terms of both selectivity and magnitude of cation-induced changes in fluorescent properties [1].

In the present paper, the photophysics of ditopic receptors of caesium ion, Calix-COU1 and Calix-COU2, is reported (Fig. 1). These compounds consist of a calix[4]biscrown-6 ether with a dioxycoumarin fluorophore inserted into one of the crown (Calix-COU1) or in both crowns (Calix-COU2). The synthesis and the binding properties of these ditopic receptors were described in a previous paper [2]; we confirmed the excellent selectivity of calix[4]biscrowns for caesium ion over sodium ion, as previously demonstrated [3]. This is of great interest for applications in nuclear toxicology.

In Calix-COU1 and Calix-COU2, a photoinduced charge transfer can occur in the coumarin between the two oxygen atoms linked to the phenyl moiety and the carbonyl group. When a fluorophore undergoes photoinduced charge transfer, a bound cation at proximity of the electron-withdrawing group enhances the charge transfer, which results in a red shift of the fluorescence spectrum with respect to that of the free ligand. In contrast, when a bound cation is close to the electron-donating group, the fluorescence spectrum is, in most cases, only slightly blue-shifted because the charge transfer reduces the electron density on the electron-donating atoms whose coordination strength is thus reduced. Photodisruption of the interaction between the cation and the electron-donating atoms can even occur.

Photodisruption has been indeed observed in "crowned" fluorophores in which a bound cation is in interaction with the nitrogen atom of an azacrown conjugated with an electron-withdrawing group [4–6]. The case of DCM-crown, an azacrown-linked merocyanine, is of particular interest: in the complex with a strontium ion,

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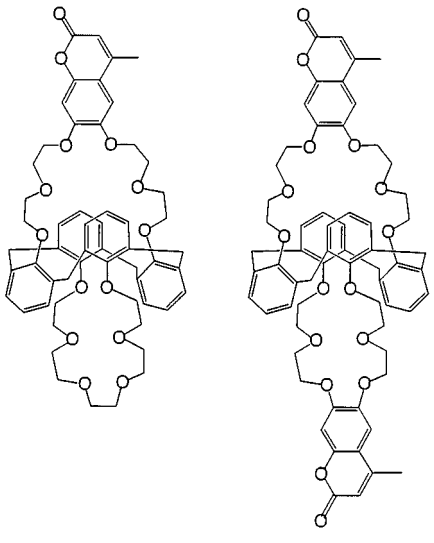


Fig. 1. Structure of Calix-COU1 and Calix-COU2.

photodisruption of the cation interaction is followed by a release of the cation from the crown, as demonstrated by subpicosecond pump-probe experiments [7].

Photodisruption of the interaction between a bound cation and coordinating oxygen atoms linked to a phenyl ring has also been observed in ditopic receptors like benzocoronands [8].

In the present work, special attention will be paid to the photodisruption of the interaction between a bound caesium ion and the oxygen atoms linked to the phenyl moiety of the coumarin in Calix-COU1 and Calix-COU2 with possible consequences in terms of cation motion within the 1:1 complex.

EXPERIMENTAL

The synthesis of Calix-COU1 and Calix-COU2 was described in the previous paper [2]. Absolute ethanol from SDS (spectrometric grade) was used as a solvent for absorption and fluorescence measurements. Caesium acetate from Aldrich was vacuum dried over P_2O_5 prior to use.

UV visible absorption spectra were recorded on a Varian Cary 5E spectrophotometer. Corrected emission spectra were obtained on a SLM -Aminco 8000C spectrofluorometer.

Global analysis of the evolution of the whole fluorescence spectra was performed with SPECFIT Global Analysis System V3.0 for 32-bit Window System. This software uses singular value decomposition and nonlinear regression modelling by the Levenberg-Marquardt method [9].

Time-resolved fluorescence experiments were carried out by multifrequency phase-modulation fluorometry using a SPEX Fluorolog3-tau3 equipped with a Pockel's cell. POPOP in cyclohexane (1.12 ns) was used as a reference solution. Fluorescence was detected through a Schott GG375 cut off filter at 375 nm. The phase and modulation data were analyzed by GLOBALS software (Globals Unlimited, University of Illinois at Urbana-Champaign, Laboratory for Fluorescence Dynamics).

All measurements were carried out at 20°C.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of Calix-COU1 and Calix-COU2 and their changes upon addition of Cs^+ were reported in the previous paper [2]. Cs^+ binding induces very slight changes in the absorption spectra but a very significant fluorescence quenching together with a blue shift of the fluorescence spectra. These effects were interpreted in terms of perturbation by a bound cation of the photoinduced intramolecular charge transfer from the coumarinic oxygen atoms to the carbonyl group [2].

Analysis of the evolution of the whole fluorescence spectra by means of the SPECFIT programme provided the stability constants of the 1:1 and 2:1 complexes (log $K_{11} = 6.9$, log $K_{21} = 3.91$ for Calix-COU1; log $K_{11} = 6.48$, log $K_{21} = 3.81$ for Calix-COU2) [2]. These constants show that (i) the complexation of a second cation is made more difficult by the presence of a bound cation owing to electrostatic repulsion (anticooperative binding), (ii) the affinity of a cation for the crowns does not significantly depend on whether it contains a coumarin moiety or not.

The SPECFIT programme can also provide the fluorescence spectra of the 1:1 and 2:1 complexes. The fluorescence spectra of Calix-COU1 and Calix-COU2 together with those of their 1:1 and 2:1 complexes with Cs^+ are shown in Fig. 2.

In the present paper, special attention is paid to time-resolved fluorescence experiments that were carried out by the multifrequency phase-modulation technique. The fluorescence decays of free Calix-COU1 and Calix-COU2 in ethanol were found to be a single exponential with a lifetime equal to 2.05 ± 0.02 ns. Upon addition of Cs^+, the decay becomes nonexponential.

A global analysis of the phase-modulation data obtained for four concentrations of Cs^+ (using the GLOBALS software)—with two decay times independent of the Cs^+ concentration—failed. A global analysis with a sum

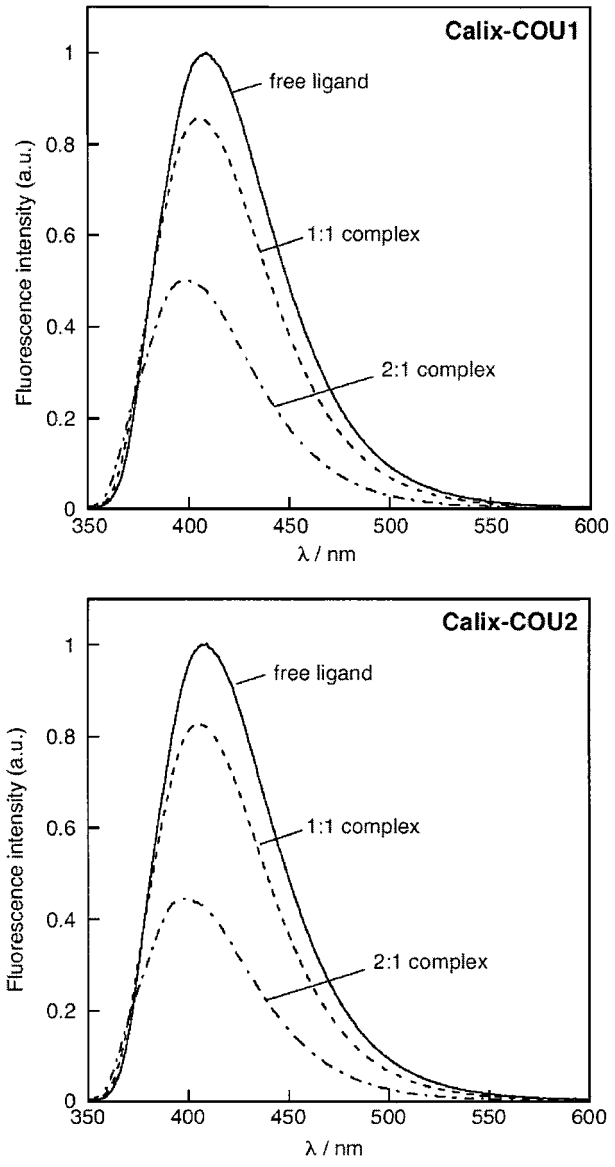


Fig. 2. Corrected fluorescence spectra of Calix-COU1 (top) and Calix-COU2 (bottom) and their 1:1 and 2:1 complexes with Cs^+ in ethanol calculated from the titration data analysis using the SPECFIT programme.

of three exponentials was then attempted with one of the decay times fixed to be the lifetime of the free ligand, i.e. 2.05 ns, and the two other decay times restricted to be independent of the concentrations (Tables I and II). The global chi-squared values and the curve fits were found to be satisfactory (Figs. 3 and 4).

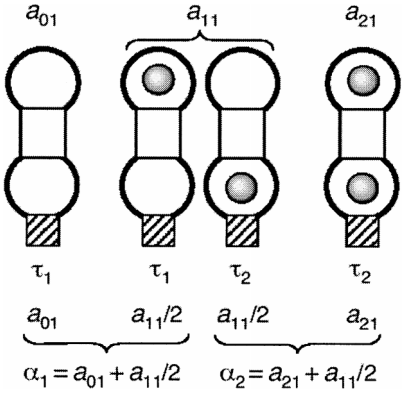
The short decay time whose amplitude increases when increasing the ratio R = [cation]/[ligand] is assigned to the lifetime of the coumarin moiety that is in interaction with Cs^+ in the 2:1 complex. It is more difficult to interpret the intermediate decay time.

Interpretation of the time-resolved experiments requires the knowledge of the relative proportions of the ligand, the 1:1 and 2:1 complexes (denoted a_{01}, a_{11}, a_{21}, respectively) for a given ratio R = [cation]/[ligand]. These proportions, that are derived from the stability constants of the complexes, are provided by the SPECFIT programme. The distribution curves of the species are shown in Figs. 5 and 6.

The time-resolved data will now be tentatively interpreted in light of several models. The case of Calix-COU1 will be examined first. For the sake of clarity, we turn first our attention to the case where the 1:1 complex is almost solely present (94%), i.e. for $R = 1.5$.

Model 1

Assumptions: (i) a cation bound to the crown deprived of coumarin has no effect on the lifetime of the coumarin inserted in the other crown; (ii) the lifetime of a coumarin moiety in vicinity of a bound cation is the same in the 1:1 and 2:1 complexes (Scheme 1).

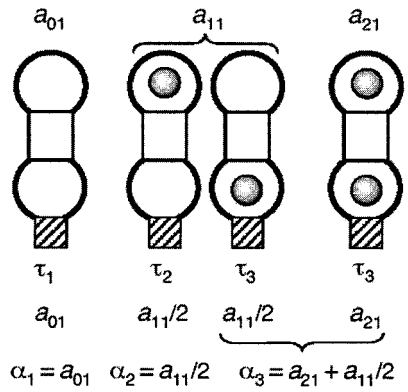


Scheme 1

In this model, the fluorescence spectrum of the 1:1 complex is expected to be half sum of the spectrum of the free ligand and that of the 2:1 complex. Figure 1A clearly shows that this is not true. Moreover, the fluorescence decay would be a sum of two exponentials, whereas three exponential terms are required to obtain a satisfactory fit.

Model 2

Assumptions: (i) a cation bound to the crown deprived of coumarin has an effect on the lifetime of the coumarin inserted in the other crown; (ii) the lifetime of a coumarin moiety in interaction with a bound cation is the same in the 1:1 and 2:1 complexes (Scheme 2).



Scheme 2

A triple exponential decay is expected.

$$I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3) \quad \text{with} \quad \Sigma\alpha_i = 1$$

where τ_1 is the lifetime of a coumarin moiety in the free ligand, τ_2 is the lifetime of a coumarin moiety that is not in interaction with a bound cation in the 1:1 complex, and τ_3 is the lifetime of a coumarin moiety in interaction with Cs^+ in the 1:1 and 2:1 complexes.

The expected preexponential factors that express the relative proportions of the fluorescent species are related to the relative proportions of the free ligand and its complexes by:

$$\alpha_1 = a_{01}$$

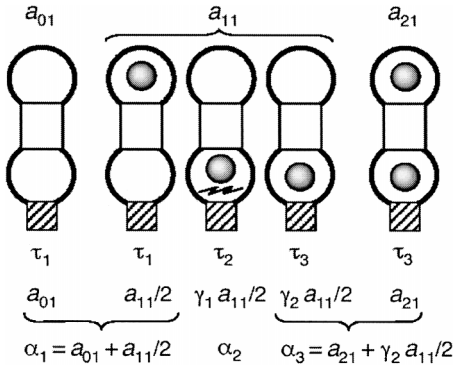
$$\alpha_2 = a_{11}/2$$

$$\alpha_3 = a_{21} + a_{11}/2$$

For $R = 1.5$, the expected values are then $\alpha_1 = 0.03$, $\alpha_2 = 0.47$, $\alpha_3 = 0.50$. These values are not consistent with the experimental values that are equal to 0.15, 0.60, 0.25, respectively (see Table I). These discrepancies show that both assumptions of this model are not valid.

Model 3

Assumptions: (i) a cation bound to the crown deprived of coumarin has no effect on the lifetime of the coumarin inserted in the other crown; (ii) the lifetime of a fraction of the coumarin moieties that are in vicinity of a bound cation in the 1:1 complex is not the same as in the 2:1 complex (Scheme 3).



Scheme 3

The second assumption results from a possible photodisruption of the interaction between a bound cation and the two oxygen atoms linked to the phenyl moiety of the coumarin. In fact, photoinduced charge transfer occurs from these two oxygen atoms to the electron-withdrawing carbonyl group of the coumarin. The charge transfer upon excitation reduces the electron density on those oxygen atoms. As recalled in the introduction, such a photodisruption has been previously reported in various compounds. According to our previous investigations, this process does not exceed a few tens of picosecond [4,7], i.e. it occurs at a time scale much shorter than the excited-state lifetime. The decay time of the coumarin moities that undergo photodisruption is expected to be closer to the lifetime of the coumarin moieties in the free ligand.

In contrast to the 1:1 complex, the 2:1 complex is expected to undergo much less photodisruption (if any)

Table I. Global Analysis of Time-Resolved Fluorescence Data for Calix-COU1 (1.1×10^{-5} mol L^{-1}) in Ethanol in the Presence of Cs^+

$[Cs^+]$ mol L^{-1}	R^a	τ_1 ns	α_1	τ_2 ns	α_2	τ_3 ns	α_3	χ_r^{2b}	Global χ_r^{2b}
1.1×10^{-5}	1	2.05	0.19	1.64	0.59	0.76	0.22	0.82	0.94
1.7×10^{-5}	1.5	2.05	0.21	1.64	0.60	0.76	0.25	0.50	
2.77×10^{-4}	14	2.05	0.08	1.64	0.51	0.76	0.55	1.42	
1.1×10^{-3}	63	2.05	0.00	1.64	0.38	0.76	0.78	1.02	

Note. The decay time τ_1 is fixed to the value of the free ligand lifetime.

[a] $R = [Cs^+]/[\text{Calix-COU1}]$.

[b] Standard deviations for phase shift and modulation ratio: $\sigma_\Phi = 0.2^\circ$, $\sigma_m = 0.002$.

Table II. Global Analysis of Time-Resolved Fluorescence Data for Calix-COU2 (5.42×10^{-6} mol L^{-1}) in Ethanol in the Presence of Cs^+

$[Cs^+]$ mol L^{-1}	R^a	τ_1 ns	α_1	τ_2 ns	α_2	τ_3 ns	α_3	χ_r^{2b}	Global χ_r^{2b}
1.1×10^{-5}	2.03	2.05	0.24	1.55	0.57	0.70	0.20	1.53	1.01
1.7×10^{-5}	3.03	2.05	0.17	1.55	0.64	0.70	0.20	0.72	
2.77×10^{-4}	50	2.05	0.08	1.55	0.50	0.70	0.42	0.87	
1.1×10^{-3}	200	2.05	0.00	1.55	0.37	0.70	0.63	0.93	

Note. The decay time τ_1 is fixed to the value of the free ligand lifetime.
[a] $R = [Cs^+]/[\text{Calix-COU2}]$.
[b] Standard deviations for phase shift and modulation ratio: $\sigma_\Phi = 0.3^\circ$, $\sigma_m = 0.003$.

because the repulsion between the two cations is expected to force them to remain close to the coumarin moieties.

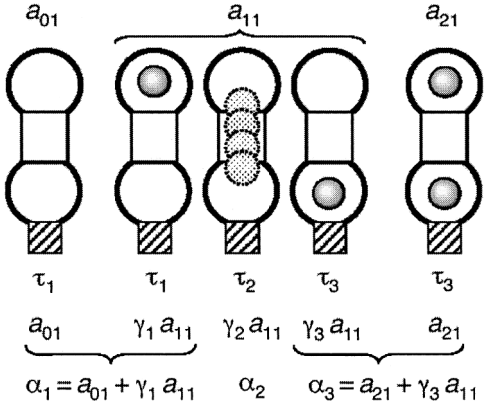
Among the coumarin moieties that are in vicinity of a bound cation in the 1:1 complex, let γ_1 be the fraction of them that undergo photodisruption. One has

$$\alpha_1 = a_{01} + a_{11}/2 \quad \alpha_2 = \gamma_1 a_{11}/2 \quad \alpha_3 = a_{21} + \gamma_1 a_{11}/2$$

For $R = 1.5$, the experimental values $\alpha_2 = 0.60$, and $a_{11} = 0.94$ are not consistent with these equations because they lead to $\gamma_1 > 1$.

Model 4

Assumptions: (i) A cation bound to the crown deprived of coumarin has no effect on the lifetime of the coumarin inserted in the other crown; (ii) in the 1:1 complex, there are various possible locations of the cation due to tunneling of the cation through the tube-shaped cavity linking the two crowns (Scheme 4).



Scheme 4

The second assumption is based on the fact that tunneling of caesium ion through the tube-shaped cavity of a calix[4]biscrown was indeed reported to be detectable with ^1H NMR spectroscopy at room temperature [10] in spite of a theoretical study predicting a relatively high barrier for the oscillation of caesium ion along the π-tube [11]. Moreover, it was shown that a cation can be stabilized by cation-π interaction in the tube-shaped cavity composed of four phenyl rings [12].

In the 1:1 complexes, let γ_1 and γ_3 the fractions of them in which the coumarin moiety has the same lifetime as in the free ligand and in the 2:1 complex, respectively. In the remaining fraction γ_2, the coumarin moieties have an intermediate lifetime which must be considered as an average because the lifetime is expected to depend on the cation-coumarin distance. The following relations are thus obtained:

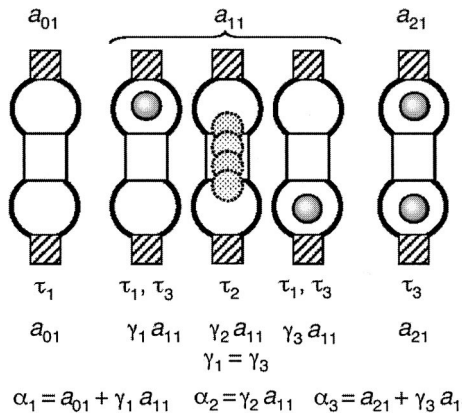
$$\alpha_1 = a_{01} + \gamma_1 a_{11}$$
$$\alpha_2 = \gamma_2 a_{11}$$
$$\alpha_3 = a_{21} + \gamma_3 a_{11}$$

From the experimental values of α_1, α_2, α_3, and a_{01}, a_{11}, a_{21}, for $R = 1.5$, one obtains $\gamma_1 = 0.13$, $\gamma_2 = 0.64$, $\gamma_3 = 0.23$.

In Table III the values of γ_1, γ_2, γ_3 are reported for the three first concentrations of Cs^+ at which the 1:1 complex is predominant (condition required to obtain reliable values of $\gamma_1, \gamma_2, \gamma_3$). In view of the difficulty to recover lifetimes that differ by a factor of 1.25 and the corresponding preexponential factors, the values of γ_1, γ_2, γ_3 can be considered as independent of R within experimental errors, which shows that model 4 is consistent with experimental data of Calix-COU1.

The data of Table II for Calix-COU2 can then be processed in a similar way according to Scheme 5 from which the following relations are obtained

$$\alpha_1 = (2a_{01} + 2\gamma_1 a_{11})/2 = a_{01} + \gamma_1 a_{11}$$
$$\alpha_2 = 2\gamma_2 a_{11}/2 = \gamma_2 a_{11}$$
$$\alpha_3 = (2a_{21} + 2\gamma_1 a_{11})/2 = a_{21} + \gamma_3 a_{11}$$
$$\gamma_1 = \gamma_3$$



Scheme 5

The values of γ_1, γ_2, γ_3 (Table IV) are reasonably independent of R within experimental errors. The values of γ_1 and γ_3 are found to be similar as expected. Moreover, γ_2 has nearly the same value for Calix-COU1 and Calix-COU2. These observations further support the validity of Model 4.

The values of γ_2 is larger than 0.5, which means that, in the complex 1:1, the probability to find the cation somewhere between the two crowns when deexcitation occurs is higher than the probability to find it within the crowns. This can be explained by two additional causes: (i) in a fraction of the 1:1 complexes, the cation is not located in the crowns at the instant of excitation because of tunneling; (ii) in another fraction of the 1:1 complexes, the cation that is in interaction with a coumarin moiety at the instant of excitation is photodisrupted from its oxygen anchors upon excitation and is thus very rapidly pushed owing to the repulsion from those oxygen atoms, as a result of the intramolecular charge transfer. Then, the question arises as to further displacement of the cation. Photoejection of the cation from the

Table III. Fractions a_{01}, a_{11}, a_{21}, γ_1, γ_2, γ_3 for Calix-COU1 (see Scheme 4)

R^a	a_{01}	a_{11}	a_{21}	γ_1	γ_2	γ_3
1	0.15	0.84	0.01	0.05	0.70	0.25
1.5	0.03	0.94	0.03	0.13	0.64	0.23
14	0	0.53	0.47	0.15	0.70	0.15

[a] $R = [Cs^+]/[\text{Calix-COU1}]$.

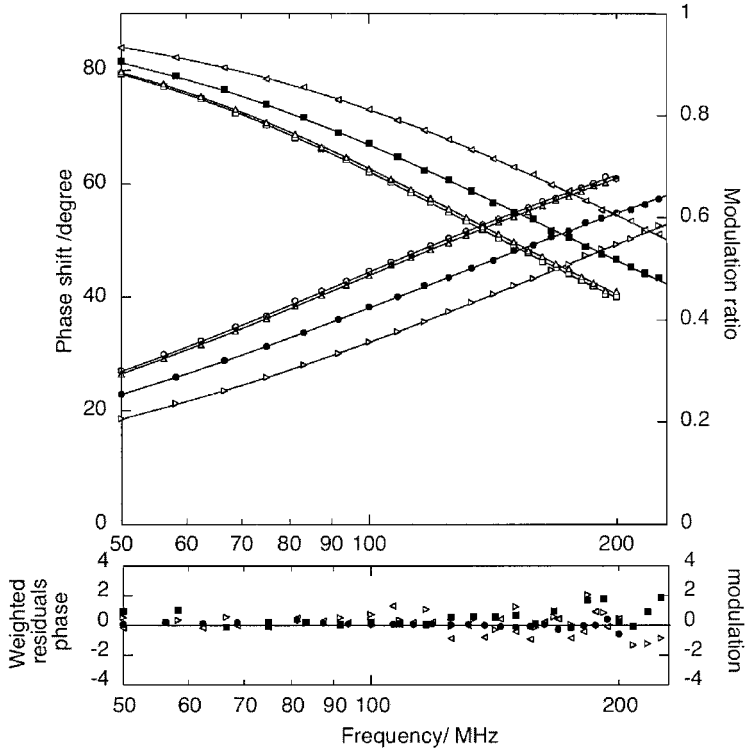


Fig. 3. Phase and modulation data obtained with Calix-COU1 at various concentrations of Cs^+. The solid lines represent the best fits obtained by global analysis of the data. $R = 1$ (○, □), 1,5 (△, ▽), 14 (●, ■), 63 (▷, ◁).

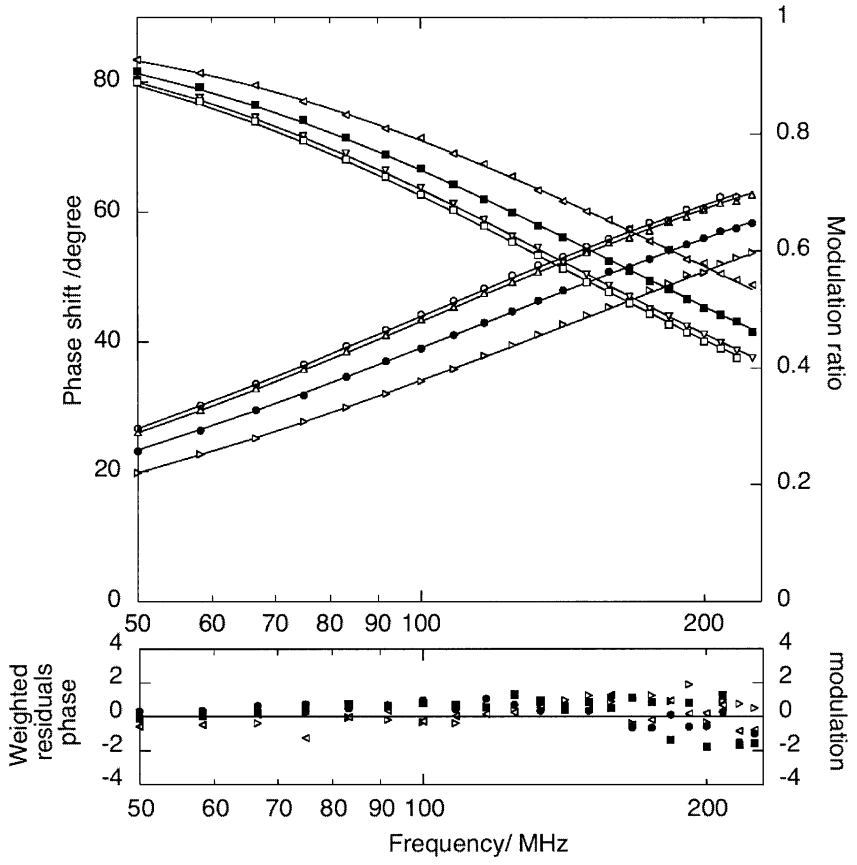


Fig. 4. Phase and modulation data obtained with Calix-COU2 at various concentrations of Cs^+. The solid lines represent the best fits obtained by global analysis of the data. $R = 2.03$ (○, □), 3.03 (△, ▽), 50 (●, ■), 200 (▷, ◁).

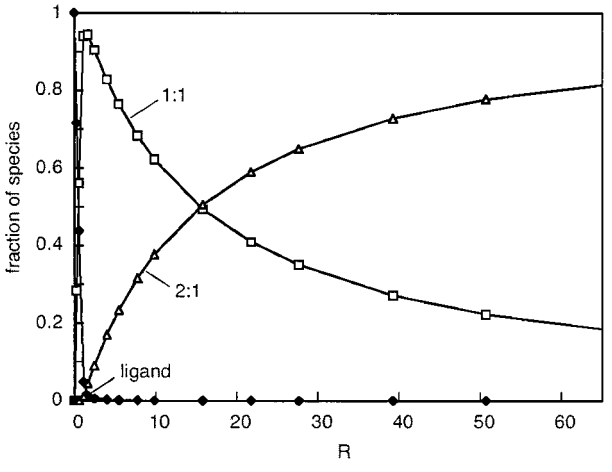


Fig. 5. Distribution curves of Calix-COU1 (1.1×10^{-5} M) and its 1:1 and 2:1 complexes with Cs^+.

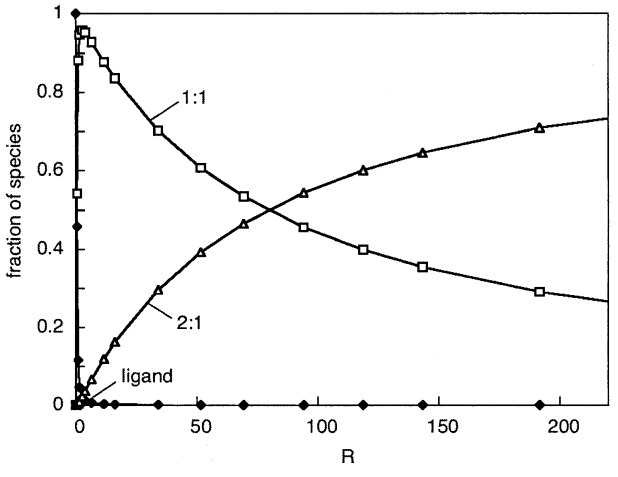


Fig. 6. Distribution curves of Calix-COU2 (5.6×10^{-6} M) and its 1:1 and 2:1 complexes with Cs^+.

Table IV. Fractions a_{01}, a_{11}, a_{21}, γ_1, γ_2, γ_3 for Calix-COU2 (see Scheme 5)

R^a	a_{01}	a_{11}	a_{21}	γ_1	γ_2	γ_3
2.03	0.03	0.96	0.01	0.22	0.59	0.19
3.03	0.02	0.96	0.02	0.16	0.67	0.19
50	0	0.62	0.38	0.13	0.81	0.07

[a] $R = [Cs^+]/[\text{Calix-COU2}]$.

crown appears to be less likely than a motion towards the tube-shaped cavity where it could be stabilized by cation-π interaction. The cation might even go to the opposite crown.

In conclusion, the present work confirms the possibility of cation motions through the tube-shaped cavity of calix[4]biscrowns, and shows that these motions can be partly induced by light via coumarin excitation.

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