Photophysics of *1,3-alternate* calix[4]arene-crowns and of their metal ion complexes: evidence for cation–π interactions in solution

Luca Prodi,*[a] Fabrizio Bolletta,[a] Marco Montalti,[a] Nelsi Zaccheroni,[a] Alessandro Casnati,*[b] Francesco Sansone[b] and Rocco Ungaro[b]

[a] *Dipartimento di Chimica "G. Ciamician" Università di Bologna, Via Selmi 2, I-40126, Bologna, Italy. E-mail: lprodi@ciam.unibo.it. Fax: +39-051-259456*
[b] *Dipartimento di Chimica Organica e Industriale, Università di Parma, Parco Area delle Scienze 17/A, I-43100, Parma, Italy. E-mail: casnati@ipruniv.cce.unipr.it. Fax: +39-0521-905472*

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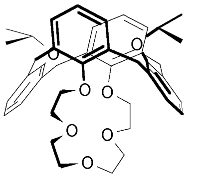
The photophysical properties of the family of calix[4]arene-crowns and of their metal complexes are reported here for the first time. Among different observed perturbations, addition of alkali metal ions causes monitorable, and sometimes pronounced, changes in fluorescence intensities and in the wavelength maxima of the hosts. All together, the observed results strongly suggest that the cation–π interactions play a major role in tuning the luminescence properties of the host. The utility of photoluminescence spectroscopy for the determination of association constants between calixarene derivatives and metal ions is also demonstrated.

Introduction

In recent years, calixarene-based ligands have received increasing attention because they can be obtained in good yields and with the required stereochemistry at the binding groups to function as receptors or as carriers.[1] They have been used in many fields, such as sensor technology,[2] extraction,[1b–e] membrane transport[3] and chromatography.[4] A very interesting class of host molecules, developed using a calixarene skeleton, is that composed of calix[4]arene-crown-*n* derivatives.[5,6] These macrobicyclic ligands possess high affinity and selectivity toward metal ions, in particular K^+ ($n = 5$)[5] and Cs^+ ($n = 6$)[6]; the highest selectivity has been obtained when the calixarene adopts the *1,3-alternate* conformation.

Among the different techniques used to monitor molecular recognition processes, photoluminescence spectroscopy certainly offers great advantages in terms of sensitivity and versatility. It can help to find solutions to many analytical problems in applications such as medical diagnostics, cell biology and environmental sciences, and also provides the possibility of monitoring analyte concentrations in real-time and real-space.[7–11] Luminescence spectroscopy is also very useful to obtain deeper insights into the molecular structure of the adducts[12] and good estimates of association constants,[13] even in very dilute solutions. In order to use ligands of known selectivity properties as chromoionophores, luminophores (chromophores) are usually introduced in suitable positions on the ligand skeleton. This has also been done in the case of calixarene ionophores, either of the podand type[14] or belonging to the class of calixcrowns.[15] Luminophore-functionalised calixarenes, however, have to be considered as new ionophores, since the structure and even the nature of the binding groups change with respect to those of the parent macrocycles. As a consequence, the selectivity observed in these cases is often not completely correlated with that of the class of compounds under investigation. One example is represented by the chromoionophore synthesised by McCarrick *et al.*[16] which is selective for lithium ions, whereas the parent calixarene usually binds more strongly to sodium. Especially for highly selective ligands such as the calix[4]arene crown ethers (crown-5 and crown-6), it would be highly desirable to detect the binding event without affecting the highly efficient ligand architecture and exploiting the calixarene itself as a chromoionophore. For this purpose, it becomes essential to know the photophysical properties of the ligands. In this paper we present a study on the intrinsic photophysical properties of 1,3-diisopropoxycalix[4]arene-crown-5 (**1**) and -crown-6 (**2**) in the *1,3-alternate* conformation and on their complexes with several metal ions. The results obtained evidence the possibilities offered by luminescence spectroscopy in the study of such an important class of synthetic receptors and disclose weak cation–π interactions.[17]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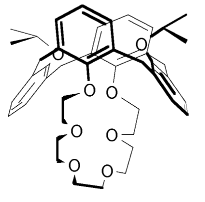
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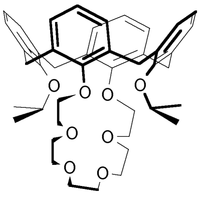
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Results and discussion

Absorption spectra

The absorption spectra of the hosts **1**–**3** in methanol (Table 1 and Fig. 1) are dominated by a band centred at *ca.* 270 nm, very similar in shape to those reported for methoxybenzene derivatives,[18] which by analogy can be assigned to a π–π* transition occurring in the aromatic rings of the calixarene. It is worth noting, however, that the intensity of such a band is lower than what might be expected from the algebraic sum of four 2,5-dimethylanisole (2,5-DMA) bands, indicating a degree of interaction (and/or a distortion from planarity) of the aromatic nuclei in the hosts. When complexation with an alkali metal ion occurs, a very small decrease in the intensity of such a band is observed for all the hosts,[5c,6b] together with a slight

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Table 1 Photophysical properties of the hosts **1**–**3**, of their metal ion complexes[a] in MeOH solutions at 25 °C

	Absorption		Luminescence		
Compound	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	τ/ns	I_{rel} [b]
2,5-DMA	275	1950	299	4.8	900
1	270	1600	309	0.7	100
1·Na$^+$	269	1550	317	1.4	235
1·K$^+$	269	1550	307	1.7	210
1·Rb$^+$	269	1550	308	0.5	55
1·Cs$^+$	270	1550	309	<0.4	19
1·Ag$^+$	257	3800	307	<0.4	14
2	270	1550	311	0.7	100
2·Na$^+$	[c]	[c]	[c]	[c]	[c]
2·K$^+$	269	1450	310	1.0	133
2·Rb$^+$	270	1500	307	0.5	67
2·Cs$^+$	270	1500	307	<0.4	35
2·Ag$^+$	271 (sh)	2500	302	<0.4	11
3	270	1600	310	0.7	100

[a] For metal ion complexes, the values have been obtained after addition of a sufficient amount of salt to ensure that more than 99% of the host is in its associated form. [b] The values reported in this column are the quantum yields relative to **1**. [c] No complexation observed.

modification of the band shape (Fig. 1 and Table 1). It is not possible, however, to make a correlation between the nature of the guest and the observed changes. Much stronger changes are instead observed when Ag$^+$ ions are added to a solution of **1** (Fig. 1) or **2** (Table 1), due to the appearance of a new absorption band, absent in the spectrum of the silver ion alone, almost covering the band of the host centred at 270 nm.

Room temperature fluorescence spectra

The fluorescence spectra of the hosts **1** and **2** obtained in methanol solutions at room temperature present a band centred at 310 nm. The corrected excitation spectrum obtained at this emission wavelength is nearly identical in shape to the absorption spectrum. The observed fluorescence band is slightly red-shifted, weaker in intensity and with a shorter excited state lifetime compared to that of 2,5-dimethylanisole (Table 1). Comparison of these data with those observed for other methoxybenzene derivatives, leads to the assignment of this band to a $^1\pi$–π^* transition occurring in the aromatic rings of the calixarene, although an interaction between the chromophoric units is evident from the observed decrease in the fluorescence intensity. Similar behaviour is also observed for the 1,3-diisopropoxycalix[4]arene-crown-6 (**3**) in the *cone* conformation.

Interestingly, as can be seen from Table 1 and Fig. 2, the addition of alkali metal ions causes monitorable, and sometimes pronounced, changes in fluorescence intensities and in the wavelength maxima of the hosts **1** and **2**. Contrary to what was observed for the absorption spectra, the fluorescence intensity of the alkali metal ion complexes follows a precise trend for both **1** and **2**, *i.e.* decreasing with increasing atomic number from Na$^+$ to Cs$^+$. It is interesting to note that the changes in fluorescence intensity upon metal ion complexation are greater for **1** than for **2**.

The observed behaviour of hosts **1** and **2** could, in principle, be explained by 3 different effects: (i) perturbation of the π-system due to cation–π interactions between the metal ion and the two aromatic rings facing the crown ether moiety, (ii) interaction of the phenolic oxygen atoms with the cation, and (iii) a change in the intersystem crossing efficiency due to the heavy-atom effect, introduced by the presence of the metal ion. The latter interaction cannot anyway be responsible for the majority of the observed changes, since it does not explain the increase in the fluorescence intensity and lifetime observed in some cases (*e.g.* **1**·Na$^+$, **1**·K$^+$, **2**·K$^+$ in Table 1). Furthermore, we did not observe any change in the lifetime of the phosphorescence at 77 K upon metal ion complexation, even for the heaviest ions. All these findings are not consistent with a pronounced heavy-atom effect.

In order to evaluate the single effect on the photophysics due to the phenolic oxygens involved in metal ion binding, we used compound **3** which, being in the *cone* conformation, allows the exclusion of cation–π interactions. No significant changes were observed in its luminescence, even in the presence of a large excess of cation. Moreover the addition of alkali metal ions to methanolic solutions of benzo-, naphtho-, and anthraceno-crown ethers,[19–21] as a general rule, causes only weak changes in the luminescence properties of the host, and they do not follow monotonic patterns. These obser-

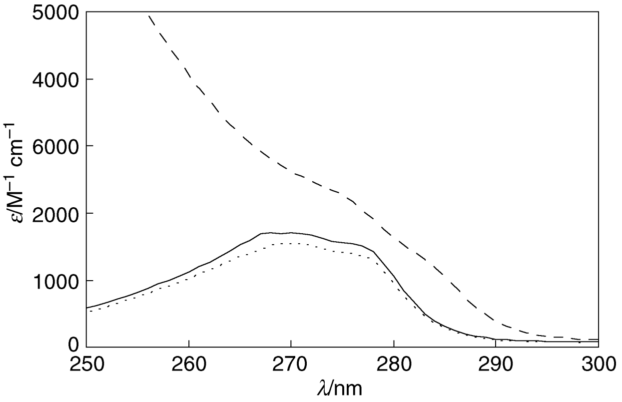

Fig. 1 Absorption spectra of the host **1** (——) and of its complexes with Ag$^+$ (– – –) and Cs$^+$ (· · ·) in methanol solution at 25 °C.

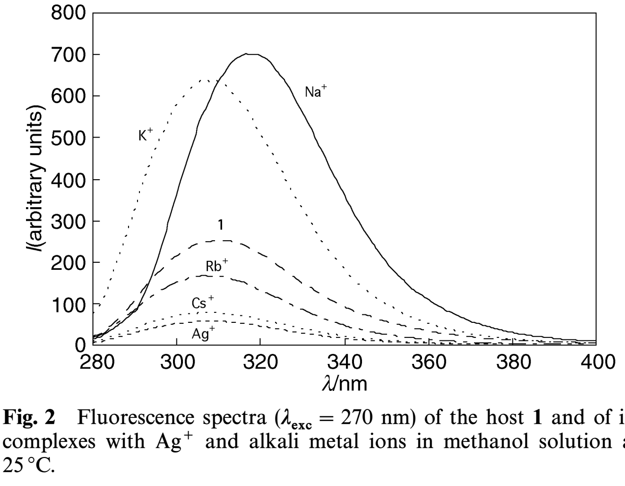

Fig. 2 Fluorescence spectra (λ_{exc} = 270 nm) of the host **1** and of its complexes with Ag$^+$ and alkali metal ions in methanol solution at 25 °C.

vations suggest that the involvement of the phenolic oxygen in cation binding cannot be expected to cause strong changes in fluorescence properties. Some changes could also come from the freezing of conformational mobility upon metal ion complexation. Although this effect could possibly cause a difference between the free ligands and their adducts, it cannot solely account for the remarkable differences observed among the various complexes.

On the other hand, the existence of cation–π interactions has already been demonstrated in calixarenes by various X-ray crystal structures,[6a,b,17,22] and by mass spectrometry.[23] Recently, a cation–π interaction has been also observed for a phenolic sidechain of a lariat crown ether.[24] Furthermore, the presence of a new absorption band for the complexes of **1** and **2** with silver ions clearly indicates a strong perturbation of the π-system caused by Ag^+ ions, thus suggesting the direct involvement of the two aromatic rings of the hosts facing the crown ether moiety. It is, in fact, well documented in the literature that silver ions are able to interact with aromatic systems,[25] which drastically changes their absorption and fluorescence spectra.[26] An influence of cation–π interactions on the absorption spectra of a calixarene ligand in the partial cone conformation has been recently proposed by Reinhoudt *et al.* for its Pb(II), Cu(II) and Cd(II) complexes.[27]

These findings are in agreement with the remarkable downfield shifts of the aromatic protons observed in the ^1H NMR spectra[6b] and very strong changes in the intensities (I_{rel}) and lifetimes (τ) of luminescence in the silver complexes with hosts **1** and **2**. Similar effects, although sometimes weaker, were also observed for those alkali cation complexes of **1** and **2** that have sufficiently high association constants (*i.e.* $>100\ M^{-1}$). The stronger perturbation on the absorption spectra observed with silver ions can be explained in our case by the important role played by the d-orbitals of the metal in this kind of interaction.[28]

It is interesting to note that the perturbation induced by the cation on the luminescence spectra of host **1** follows the order $Na^+ > K^+ > Rb^+ > Cs^+$, which is what would be expected on the basis of the electrostatic model of cation–π interactions.[28] Furthermore, this trend is the same as was observed for the radiative rate constant of a naphthalene crown ether in which the alkali metal cation lies near the face of the aromatic system.[29] Again, this trend has not been observed when, in analogous receptors, the ion is held at the side of the naphthalene chromophore.[29,30]

The above-mentioned results, taken together, lead us to believe that a major role in tuning the luminescence intensity of the host is played by the cation–π interaction between the metal ion and the two aromatic rings pointing towards the binding site.

As already mentioned, changes in the fluorescence intensity upon metal ion complexation are more important for **1** than for **2**; this could be due to the fact that in **1** the metal ions are in closer contact with the two aromatic rings pointing towards the binding site, increasing thereby the electronic interaction.

Binding constants

The observed changes in the luminescence properties of the hosts induced by complexation with metal ions are sufficiently strong to allow the determination of the association constants for almost all the complexes examined. The data obtained with fluorescence spectroscopy are in good agreement with those previously found from spectrophotometric and potentiometric measurements (Table 2). In addition, photoluminescence spectroscopy offers the advantage of being direct, sensitive and easy, allowing fast and accurate determination of association constants, even in very dilute solutions.[13]

Conclusions

We have shown here the photophysical properties of a very interesting class of host molecules, calix[4]arene-crown-*n* compounds, and of their complexes with silver and alkali metal ions. In particular, addition of alkali metal ions usually caused weak effects on the absorption spectra, but monitorable, and sometimes pronounced, changes in the intensity and wavelength maxima of the fluorescence bands of the hosts. The fluorescence quantum yields of complexes with alkali metal ions follows a precise trend for both **1** and **2**, *i.e.*, decreasing with increasing atomic numbers from K^+ to Cs^+. We have interpreted such changes as due to a cation–π interaction between the metal ion and the two aromatic rings pointing towards it. In addition, luminescence spectroscopy was demonstrated to be a suitable technique for the determination of association constants for such a class of host species and a possible tool to study cation–π interactions. To the best of our knowledge, this is the first study dealing with the photophysical properties of single calixcrowns.[15]

Experimental

Materials

1,3-Diisopropoxycalix[4]arene-crown-5 (**1**)[5b] and -crown-6 (**2**)[6b] in the *1,3-alternate* conformation and 1,3-diisopropoxycalix[4]arene-crown-6 (**3**)[6b] in the *cone* conformation were synthesised as reported in the literature. The solvent used was methanol UVASOL from Merck Co. without further purification. Sodium perchlorate, potassium hexafluorophosphate, rubidium chloride, caesium chloride and silver perchlorate were from Aldrich, of the highest purity available.

Equipment

Ultraviolet absorption spectra were recorded with a Perkin-Elmer lambda 16 spectrophotometer. Corrected emission and excitation spectra were obtained with a Perkin-Elmer LS50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ±5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D_2. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects[13] and phototube sensitivity were performed. A correction for differences in the refraction index was introduced, when necessary.

Measurement of binding constants with metal ions

Emission spectra were run on solutions of the host in methanol (3.0 ml of 1×10^{-4} M at 25 °C), by excitation of the solution at 270 nm. Aliquots of salt solution (10 μl of 1×10^{-2}

Table 2 Log *K* of hosts **1** and **2** with silver and alkali metal ions in methanol at 25 °C

	Na^+	K^+	Rb^+	Cs^+	Ag^+
1 This work[a]	2.4	$\geqslant 10$	6.6	4.8	5.4
Ref. 5*c*	2.6	$\geqslant 9$	6.8	5.07	5.87
2 This work[a]	<2	4.6	5.8	6.19	4.7
Ref. 6*b*	—	4.5	5.93	6.1	4.52

[a] The uncertainty associated with the *K* values is estimated to be ±10%.

M) were added and intensities recorded at the maximum of the emission band. Readings were then fitted to the relationship:

$$I_{\mathrm{corr}} = C_{\mathrm{H}}\phi_{\mathrm{H}} + C_{\mathrm{C}}\phi_{\mathrm{C}} \quad (1)$$

where C_{H} and C_{C} are the concentrations of uncomplexed and complexed crown, and ϕ_{H} and ϕ_{C} are proportionality constants between the corrected emission intensity (in arbitrary units) and the concentration of uncomplexed and complexed host, respectively.[31]

C_{C} satisfies the usual binding expression in eqn. (2), where M_{tot} is the total concentration of added metal ion.

$$C_{\mathrm{C}}^2 - [(C_{\mathrm{H}} + C_{\mathrm{C}}) + M_{\mathrm{tot}} + 1/K]C_{\mathrm{H}} + M_{\mathrm{tot}}(C_{\mathrm{H}} + C_{\mathrm{C}}) = 0 \quad (2)$$

Values for the equilibrium constants, K, were then obtained by simulation of the data with both K and ϕ_{C} as adjustable parameters, using a Newton–Raphson procedure to minimise the sum of the squares of the residuals.

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