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Biscrown fluoroionophores: has the dye conformation an influence upon the formation of sandwich complexes in the ketocyanine series?

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The effect of the sensor conformation upon cation recognition, and more precisely upon the formation of 2:1 (host-guest) sandwich complexes, was studied with three new fluoroionophores. These are symmetrical ketocyanine dyes substituted with two crown ethers. The first member of this series, 2,5-bis{[4-(*N*-aza-15-crown-5)-phenyl]methylene}cyclopentanone (**1**) has a planar and rigid structure. In compound **2**, 2,6-bis{[4-(*N*-aza-15-crown-5)-phenyl]methylene}cyclohexanone, the two phenyl groups both are twisted by 40° with respect to the core of the molecule. Compound **3**, 1,5-bis[4-(*N*-aza-15-crown-5)phenyl]penta-1,4-dien-3-one, displays possibilities of rotation about the carbonyl carbon quasi-single bond and was previously reported to exist in solution as a mixture of two conformers. For the sake of comparison, a monoazacrown dye of the cyclopentanone series (**4**) was also investigated. The behaviour of these dyes in acetonitrile in the presence of Ca^{2+} and Ba^{2+} perchlorates was studied by infrared spectroscopy, mass spectrometry, NMR and UV/vis absorption spectroscopy. The absorption data were fitted by taking into account three different stoichiometries and the corresponding association constants were calculated. Very stable 2:1 sandwich complexes were observed for all three symmetrical dyes, meaning that small twists and conformational variations of the sensors hardly affect the formation of such structures. The monocrown dye also leads to sandwich complexes, but the corresponding association constants were slightly weaker than for biscrown dyes.

Introduction

During the last two decades, considerable research interest has been devoted to the design of crown ether substituted chromophores. These compounds were mainly studied for their photochromic[1] and fluorescence[2] properties. Their affinity for a given cation depends on many factors, including the relative sizes of the cation and the macrocyclic cavity.[3] For instance, if the cation closely matches the crown ether cavity, complexes generally form in a 1:1 ratio. When the cation size exceeds that of the crown cavity, the cation can only partially fit and, as a result, can be accommodated by two crowns.[3a–e] If the crowns belong to two different molecules, these so-called sandwich complexes have a 2:1 host-guest stoichiometry. This type of assembly has been reported for monocrown dyes.[4] A more complicated situation occurs with structures that bear two crown ethers on the same dye. Two cases must be distinguished. In the first one, the crowns are in close proximity, or the molecule is flexible enough, so that the crowns can act in concert to bind a cation. It has long been established that the formation of sandwich complexes is strongly favoured when the crowns are linked by a spacer. In this case, the selectivity towards large cations is increased.[3c,4] This strategy has been widely exploited with photochromic biscrown ethers[1d–h] and tweezer-like biscrown fluoroionophores,[4e,5] which form *intramolecular* sandwich complexes with cations. In the second case, which is that of rodlike biscrown dyes,[6,7] the crowns lie at each extremity of the molecule. Intramolecular complexes cannot be formed, because the rigidity of the structure prevents the two crowns from cooperating in cation binding. However, rigid biscrown dyes can form *intermolecular* sandwich complexes. The distinct advantage of these compounds is that they can give multiple arrangements with cations. These range from discrete pairs of dyes, sandwiching one or two cations,[6a–d] to extended supramolecular architectures with a stairway structure.[7] This leads to original applications. For example, in the field of fluoroionophores, the formation of sandwich complexes is at the basis of an unusual photophysical mechanism for fluorescence sensing. The latter is described in terms of a self-assembling fluorescence enhancement (SAFE) process, due to the rigidification of the chromophore following cation binding.[7b] Besides, with photoreactive biscrown dyes, the supramolecular arrangement can be retained after photochemical reaction, thus generating nanomaterials, the properties of which could be directed by the size of the different cations employed.[7e]

The occurrence of sandwich complexes in rigid biscrown dyes is therefore of high interest. However, such complexes are not always detected and this has sometimes been attributed to slight deviations from planarity in the sensor molecule.[6f] This assumes that a close fit between the two sensors is a prerequisite for the formation of sandwich complexes. But very little is known about the factors that really govern this process. The aim of the present work is to analyse the extent to which conformation affects the ion-recognition properties and, more precisely, the formation of sandwich complexes.

To do so, a comparison was made between three biscrown dyes. Compound **1** (Scheme 1) is a rigid molecule, owing to its cyclopentanone core. It has been calculated, on the analogue bearing a diethylamino group instead of a crown ether, that the whole conjugated system is planar.[8] In contrast, sensor **2** is twisted. A calculation, also performed on the diethylamino analogue, revealed that the presence of the cyclohexanone residue causes steric hindrance so the two phenyl groups are at an angle of 40° with respect to the rest of the conjugated system.[8] Compound **3** exhibits another type of conformational difference. In this molecule, rotations may take place about the single bonds situated between the carbonyl

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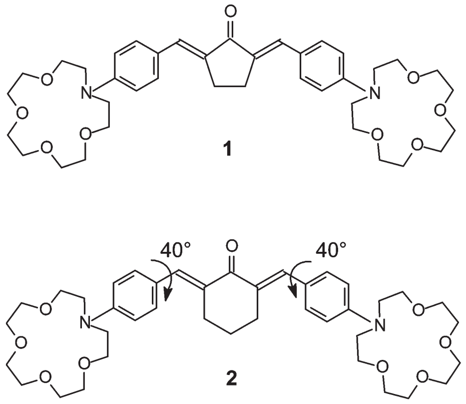


Scheme 1 Chemical structure of compounds **1** and **2**.

group and the ethylene groups. It was shown by infrared spectroscopy that **3** exists in solution as a mixture of two species,[8] identified as the s-*cis*,*cis* (11% in acetonitrile) and s-*cis*,*trans* (89%) conformers. The s-*cis*,*cis* conformer is planar, while in the s-*cis*,*trans* conformer the trans moiety is twisted by 30° with respect to the plane of the molecule (Scheme 2).

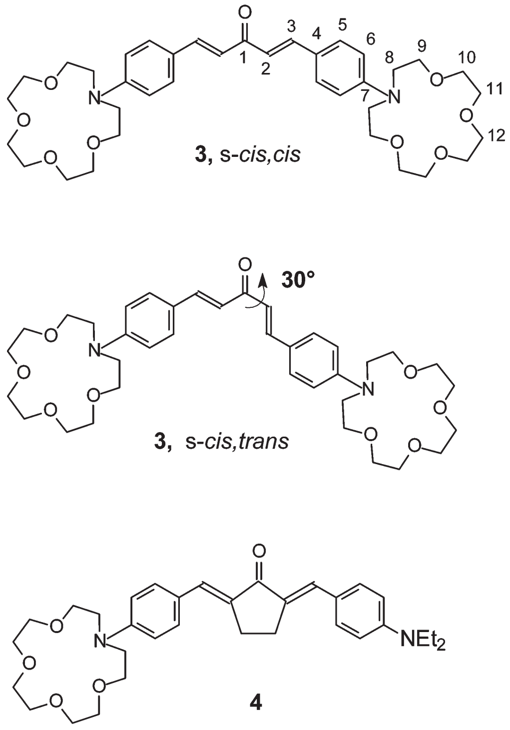
The three dyes were studied in acetonitrile, in the presence of calcium and barium perchlorates. For the sake of comparison, the coordination studies were also extended to a monoazacrown derivative, **4**, also shown in Scheme 2. Absorption spectroscopy allowed the direct determination of the stoichiometry and association constants with alkaline earth cations. Additional experiments by mass spectrometry, infrared spectroscopy and NMR were also carried out.

Results

Mass spectrometry

Mass spectrometry was used to provide evidence for the species that can be formed in the presence of cations. The electrospray technique of positive ionisation was employed. The spectrum of free dyes **1** to **4** (1.7×10^{-5} M) was recorded first, displaying the molecular peaks. Then calcium perchlorate (6.3×10^{-5} M) was added, leading to the appearance of some new peaks. These can be attributed to three different complexes: AM, A_2M and AM_2, where A is the organic dye and M the metal cation. The peaks obtained for all four compounds were assigned (Table 1).

In the molecules investigated, the crown ether is the preferred site of complexation. The AM species detected can thus be related to the insertion of a cation into one crown. The A_2M species corresponds to the formation of a sandwich complex, one cation being accommodated between the crowns of two different molecules. For dyes **1**–**3**, the AM_2 species corresponds to the complexation of the two crowns on the same molecule. It was unexpected to encounter an AM_2 species for unsymmetrical dye **4**, which bears only one crown. In this case, the species can be explained by the complexation of the crown at the same time as the direct interaction of another cation with the unsaturated system of the molecule. It should be recalled that cross-conjugated dibenzylideneacetone is a commonly used ligand for stabilising various metallic ions and a weak interaction could very well take place with alkaline earth cations.[9]



Scheme 2 Chemical structure of the rotational conformers of **3** and of the unsymmetrical compound **4**.

UV/vis absorption spectroscopy

The complexing behaviour of this type of sensor has already been investigated by us[6a] (for compound **3**) and by another team[10] (for compound **1** with Mg^{2+}), although no quantitative data has been reported in the last case. We showed that **3** (1×10^{-5} M) displayed strong variations of the spectrophotometric properties in the presence of alkaline earth cations up to 5×10^{-2} M in acetonitrile. This effect is qualitatively comparable to that observed here with compounds **1** and **2** in the presence of calcium and barium perchlorates. Upon cation addition, the intensity of the charge transfer (CT) band was dramatically reduced while a new band appeared at low wavelengths. Fig. 1 pictures the variations recorded for **1** with calcium perchlorate.

For compound **4**, the intensity of the CT band also decreased upon cation addition, but to a lesser extent, and this change was accompanied by the appearance of a new absorption band at around 550 nm. This effect is reminiscent of that already encountered for the diethylamino derivative of **3**. It was attributed to the interaction of alkaline earth cations with the unsaturated core of the ligand, which strengthens the electron-withdrawing character of the carbonyl group and therefore enhances charge transfer over the entire molecule.[6a]

In order to calculate the association constants, the absorbances *versus* cation concentration were analysed. The shape of the absorption spectrum varied strongly in the presence of cations and the maximum information was obtained by analysing the absorbance at different wavelengths. In our previous work, fitting was performed simultaneously on only four curves.[6a] In the present work, the analysis was performed simultaneously at 21 wavelengths, to obtain more reliable constants. Good fits were only obtained by taking into account the three different stoichiometries previously observed by mass spectrometry, that is AM, A_2M and AM_2, according to a model already established for **3** in our previous paper:[6a]

$$\mathrm{A} + \mathrm{M} \rightleftarrows \mathrm{AM} \quad K_1 = [\mathrm{AM}]/([\mathrm{A}][\mathrm{M}]) \tag{1}$$

$$\mathrm{AM} + \mathrm{A} \rightleftarrows \mathrm{A_2M} \quad K_2 = [\mathrm{A_2M}]/([\mathrm{AM}][\mathrm{A}]) \tag{2}$$

$$\mathrm{AM} + \mathrm{M} \rightleftarrows \mathrm{AM_2} \quad K_3 = [\mathrm{AM_2}]/([\mathrm{AM}][\mathrm{M}]) \tag{3}$$

The absorption data acquired for **1** and **2** were processed. The quality of the fit is illustrated in Fig. 1 for **1** in the presence of

Table 1 Assignment of the main peaks obtained by mass spectrometry for compounds **1** to **4** (1.7×10^{-5} M) in the presence of calcium perchlorate (6.3×10^{-5} M) in acetonitrile

m/z						
1	**2**	**3**	**4**	*z*	Related species	Symbol
695.5	709.3	669.3	549.5	1	$A + H^+$	A
833.5	847.4	807.5	687.4	1	$A + Ca(ClO_4)^+$	AM
1073.4	1085.3	1045.4	–	1	$A + Ca(ClO_4)^+ + Ca(ClO_4)_2$	AM_2
367.6	374.2	354.3	294.2	2	$A + Ca^{2+}$	AM
486.3	493.3	473.3	413.2	2	$A + Ca^{2+} + Ca(ClO_4)_2$ or $A + 2Ca(ClO_4)^+$	AM_2
714.7	728.6	688.5	568.7	2	$2A + Ca^{2+}$	A_2M

the calcium salt. The association constants obtained are given in Table 2.

For **3**, processing was performed on the UV/vis absorption data previously acquired[6a] as well as on new data. Association constants close to those published earlier were calculated for Ba^{2+}, but markedly different results were obtained in the case of Ca^{2+} (the constants were previously reported to be 4.8×10^2, 2.2×10^5 and 3.9×10^1 M^{-1} with Ba^{2+} and 1.5×10^4, 1.1×10^4 and 3.2×10^2 M^{-1} with Ca^{2+} for K_1, K_2 and K_3, respectively). False minima were probably attained in the case of Ca^{2+} when calculations were performed at only four wavelengths.

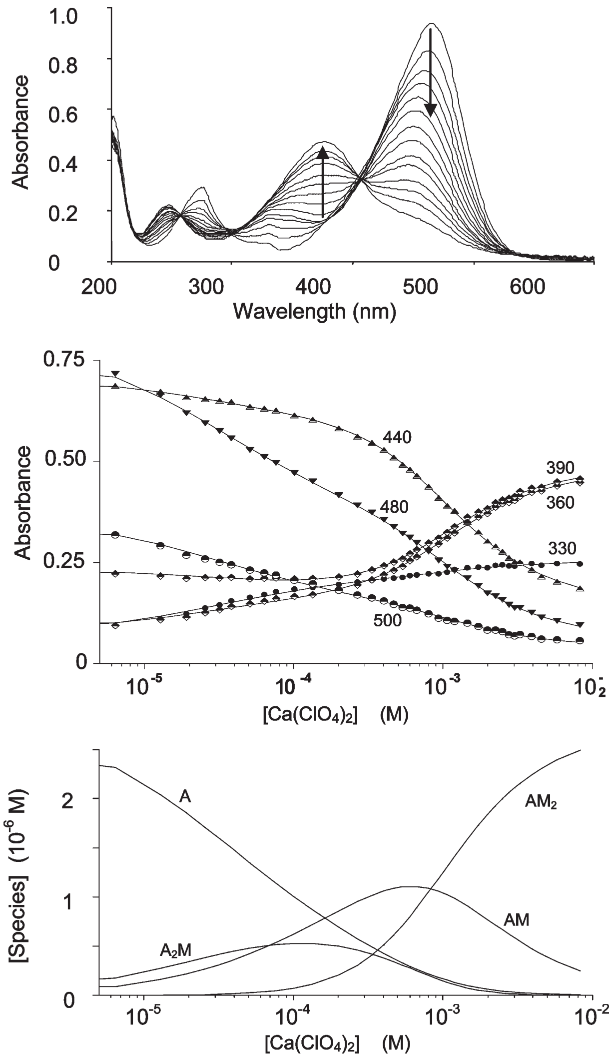


Fig. 1 Top: UV/vis absorption spectra for compound **1** (2.7×10^{-6} M) in acetonitrile before and after addition of calcium perchlorate. From top to bottom at 460 nm $[Ca(ClO_4)_2 \cdot 4H_2O] = 0$, 1.3×10^{-5}, 3.2×10^{-5}, 6.4×10^{-5}, 1.3×10^{-4}, 2.7×10^{-4}, 4.7×10^{-4}, 6.7×10^{-4}, 9.4×10^{-4}, 1.2×10^{-3}, 1.7×10^{-3}, 2.3×10^{-3}, 3.0×10^{-3} and 5.8×10^{-3} M. Cell path length = 5 cm. Arrows indicate increasing salt concentration. Middle: Data analysis of the absorbance *versus* cation concentration for six chosen wavelengths: λ_{abs} = 330, 360, 390, 440, 480 and 500 nm. The points are experimental data and the curves were calculated by fitting the data. A semi-logarithmic scale was used so that the quality of the fit to the points corresponding to low salt concentration can be assessed. Bottom: Calculated concentrations of the different species *versus* cation concentration.

Three stoichiometries were taken into account to describe the complexes formed with the dyes. However, the formation of A_2M_2 complexes must also be considered for dyes **1**–**3**. These will probably be indistinguishable from AM complexes by mass spectrometry. It was interesting to check, by simulation, their influence upon the UV/vis absorption data analysis.

The system used above provides a satisfactory fit by using the set of eqns. (1) to (3). Eqn. (4) was added to this system:

$$AM + AM \rightleftarrows A_2M_2 \quad K_{A_2M_2} = [A_2M_2]/[AM]^2 \quad (4)$$

The new model was used to process the absorption data acquired for dye **1**. The molar absorption coefficients ε of species AM, A_2M and AM_2 were set identical as before (see Experimental). For A_2M_2, $\varepsilon_{A_2M_2}$ value was taken equal to $2\varepsilon_{AM}$. For constant $K_{A_2M_2}$ taken equal to 10^4, it appeared that the concentration in A_2M_2 species would be 1.2×10^{-8} M, which is one hundred times less than the amount of AM_2 species formed at high cation concentrations. In these conditions, constant K_1 (6.3×10^3 M^{-1}) underwent a small change, constants K_2 and K_3 remaining unaffected. The residual error was identical. The quality of the fit was only poorer when $K_{A_2M_2}$ was higher than 10^5. This means that, in the range of concentrations used, only a very small amount of A_2M_2 complex can be formed, with very little consequence upon the constants of the other complexes.

Infrared spectroscopy

In the calculation performed to determine the association constants for **3**, the conformational equilibrium was not taken into account. However, the possibility that the presence of ions causes isomerisation of the starting material must be

Table 2 Association constants of species AM, A_2M and AM_2 with cations in acetonitrile, determined by processing the absorption data. The estimated error for the values of the constants was from 10 to 20%

	K_1/M^{-1}	K_2/M^{-1}	K_3/M^{-1}
1 + Ca^{2+}	6.2×10^3	8.4×10^5	1.2×10^3
2 + Ca^{2+}	1.1×10^4	6.1×10^5	1.8×10^3
3 + Ca^{2+}	5.3×10^3	4.2×10^5	1.0×10^3
4 + Ca^{2+}	1.2×10^4	1.4×10^4	1.4×10^1
1 + Ba^{2+}	7.7×10^2	8.1×10^5	4.6×10^2
2 + Ba^{2+}	1.6×10^3	1.0×10^6	5.0×10^2
3 + Ba^{2+}	7.2×10^2	2.0×10^5	1.8×10^2
4 + Ba^{2+}	2.7×10^3	2.0×10^4	6.8×10^0

considered. To do so, an infrared spectroscopy study of **3** was undertaken. As previously reported, the IR spectrum of **3** displays a split C=O band. The peaks observed at 1660 and 1641 cm^{-1} in acetonitrile were assigned to the s-*cis*,*cis* (11%) and s-*cis*,*trans* (89%) rotational conformers, respectively, the relative proportions of which were deduced from the area under the bands after deconvolution.[8] An additional IR study of **3** (1.2×10^{-2} M) in the presence of calcium and barium perchlorates up to a concentration of 5×10^{-2} M was carried out in this work. The addition of salt induced no observable modification in the relative intensity of the two C=O bands. It can thus be deduced that the equilibrium between the two conformers was not altered, even at high salt concentrations. In these conditions, the association constants reported for **3** can be regarded as a combination of the constants corresponding to the two rotational conformers.

It may be argued that the dye concentration used for IR measurements was higher than that used for determining the association constants by UV/vis absorption spectroscopy. However, it was shown by simulation that every equilibrium studied by UV/vis absorption spectroscopy was also spanned by IR spectroscopy. The model used for processing the absorption spectroscopy data, and the constants obtained from this fitting, were employed to calculate the concentrations of the different species in solution. At the lowest Ca^{2+} perchlorate concentration used for IR measurements (5×10^{-3} M), the A_2M species accounted for 83%, the remaining 17% being mostly the free dye. At the maximum Ca^{2+} concentration, the A_2M and AM species were present in minor proportions while the percentage of AM_2 complex reached 89%. For comparison, at the maximum salt concentration used in UV/vis spectroscopy, the AM_2 complex only accounted for 79% of the total species present in solution.

^1H and ^{13}C NMR spectroscopy

Unlike AM and AM_2 complexes, the sandwich complex A_2M can display different geometries. The two extreme cases are that in which the two dye molecules are entirely superimposed and that where only the crowns involved in complexation are superimposed. Additional information concerning the structure of this complex was sought on compound **3** using NMR spectroscopy. ^1H and ^{13}C NMR spectra were recorded for solutions of **3** (5.9×10^{-3} M) in CD_3CN, in the presence (2.7×10^{-3} M) and in the absence of calcium perchlorate. It was calculated that in the presence of the salt, the free dye accounted for 8.8% and complex A_2M for 90.8% of the total species, complexes AM and AM_2 being found in negligible amounts. Most of the protons underwent no variation in their chemical shift upon cation addition. Only the protons of the aromatic ring situated close to the amino group, which appeared at 6.7 ppm for the free dye, were deshielded by 0.2 ppm in the presence of calcium perchlorate. The methylene protons of the crown, close to the nitrogen atom, were also slightly shifted downfield by 0.1 ppm. This confirms that an interaction with the cation occurred in the crown.[11] However, it must be noticed that the shifts observed are weak compared to those reported for the 1:1 complexes of other monoaza-15-crown-5 dyes.[12] One possibility is that another effect counterbalances the low-field shift due to conventional complexation. This effect could be the high-field shift of the aromatic protons due to intermolecular shielding of two phenyl crown ether moieties.[11] More significant variations were observed for the carbon chemical shifts and, above all, the signals corresponding to the aromatic and ethylenic carbons disappeared (Table 3). This last feature may indicate molecular aggregation.[13] It can reasonably be assumed that an interaction is taking place between the two organic dyes, that is the signalling moieties are superimposed, at least partially, in the sandwich complex.

Table 3 ^{13}C chemical shifts for **3** (5.9×10^{-3} M) in the presence (2.7×10^{-3} M) and in the absence of calcium perchlorate in CD_3CN

Carbon	**3**	**3** + $Ca(ClO_4)_2$
C1	189.1	190.1
C2	122.1	–
C3	143.2	–
C4	123.5	–
C5	131.1	131.4
C6	112.8	–
C7	150.7	151.7
C8	53.5	53.6
C9–12	71.6	71.1
	71.0	70.9
	70.4	70.1
	69.1	69.3

Discussion

All four of the dyes investigated form various complexes with alkaline earth cations, the interaction taking place essentially with the crown ether units. For the symmetrical dyes **1**–**3**, the AM, A_2M and AM_2 complexes are formed by insertion of the cations into the crown ethers. No direct interaction of the cation with the dye's unsaturated system was detected in the UV/vis absorption spectrum. In contrast, the red-shift in the absorption spectrum of unsymmetrical dye **4** at high salt concentration indicates that such a direct interaction does take place. Our data processing technique allows the UV/vis spectrum of each species to be reconstructed. For the symmetrical dyes, the absorption spectrum of the AM_2 species is normally blue-shifted with respect to that of A, due to the reduction of the conjugated electron system.[14] For **4**, the absorption spectrum of AM_2 was red-shifted. This confirms that in the case of AM_2 complexes formed with **4**, the crown is occupied by one cation, while a second cation interacts with the unsaturated system. This is in line with the mass spectrometry results. Regarding the formation of A_2M_2 complexes, the simulation revealed that these assemblies are not formed for the symmetrical dyes, or only in very small amounts, at the concentrations used in this work. However, these complexes could very well appear for other concentrations. Regarding compound **4**, these A_2M_2 species cannot form, because the sensor bears only one crown.

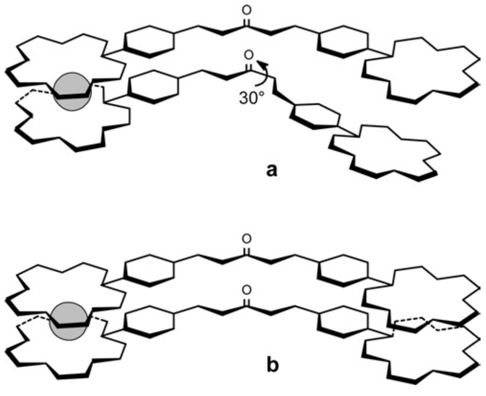
The stability of the complexes is given by the association constants, calculated from the UV/vis absorption data. These association constants must be discussed very carefully. It must be kept in mind that processing the data with three species being taken into account is a difficult task. It is obvious that the set of constants obtained may differ from one experiment to another and depend on the number and choice of wavelengths taken into account. Therefore, very small variations between the constants cannot seriously be considered as significant. However, some general trends can be noted.

Constant K_1 corresponds to the AM complex, that is the insertion of one cation into one crown. Among the three symmetrical dyes, it was slightly higher for compound **2**. It could be that in **2**, the involvement of the donor amino group in the conjugated system is weakened by the phenyl ring twist. The higher availability of the nitrogen electron pair for complexation may thus explain the better binding performance of this compound. It can also be noted that constant K_1 is quite comparable for unsymmetrical compound **4** and for the biscrown dyes. This is in line with the fact that for biscrown dyes the K_1 constant refers to the formation of the 1:1 complex and not to that of the 2:2 complex.

Constant K_2 is the one that focuses our attention. It corresponds to the formation of the sandwich complex A_2M. A striking result here is the high value found for the K_2 constants, meaning that the sandwich complexes are very stable in every case. This is understandable for Ba^{2+}, a bulky cation (diameter 2.68 Å)[15] known to favour this type of complex. However, it is surprising to find such stable complexes with Ca^{2+} salts. Actually, the diameter of the Ca^{2+} cation (1.98 Å)[15] closely fits the aza-15-crown-5 cavity (1.7–2.2 Å).[3a] In these conditions, very stable AM complexes could be expected.[16] The literature reports that for various fluoroionophores built from aza-15-crown-5, the spectrophotometric data has been satisfactorily fitted by considering only the formation of the AM complex in the presence of calcium salts.[2g,17] However, Izatt's team has reported that this crown has a propensity to form sandwich complexes with Ca^{2+} in methanol, with a K_2 constant rivalling with K_1 in magnitude.[18] In the present work, constant K_2 was up to three orders of magnitude higher than K_1. Therefore, it is likely that the chromophore linking the crowns is a key factor for forming A_2M sandwich complexes. The NMR study detected stacking, which occurs when the two sensors become arranged around the cation. This stacking could contribute to the stabilisation of these complexes.

Very little difference was found between the K_2 constants obtained for the three symmetrical dyes. This confirms that the dyes exhibit similar complexing behaviour. Small deviations from planarity, such as the twists encountered for **2**, have minor effects on the formation of these complexes. The K_2 constants found for **3** are slightly lower than for the other analogues, in particular with barium salts. This can be explained as follows. It has already been mentioned that both receptor molecules are probably superimposed in the sandwich complex. Matching must be optimal with molecules that display identical conformations. However, a solution of **3** is a mixture that contains 89% of the s-*cis*,*trans* rotational conformer and 11% of the s-*cis*,*cis* conformer.[8] Of the total A_2M complex formed, it can be calculated that, statistically, almost 20% is a hybrid composed of an s-*cis*,*cis* molecule and an s-*cis*,*trans* molecule. In these complexes, the sensors only partly overlap [Scheme 3(a)]. Consequently, they are not well stabilised by stacking. Matching should be far better, for example, when the complex is formed between two molecules of the s-*cis*,*cis* conformer of **3** [Scheme 3(b)]. The formation of hybrid s-*cis*,*trans*/s-*cis*,*cis* complexes with reduced stability can explain that a lower association constant was found in the presence of the rotational conformer mixture. However, the effect on the association constants is weak. It cannot be compared to examples where conformational changes affect the binding site and have considerable influence upon the binding properties.[19]

It can also be noted that the least stable A_2M complexes are encountered for unsymmetrical compound **4**. It is difficult to explain why this compound is less efficient than the biscrown sensors in forming sandwich complexes. It could be interesting to see if this trend is confirmed for other pairs of mono- and biscrown structures.



Scheme 3 Schematic representation of A_2M complexes formed between (a) one s-*cis*,*cis* and one s-*cis*,*trans* rotational conformer of compound **3** and (b) two s-*cis*,*cis* conformers.

Constant K_3, which is related to AM_2 complexes, is the smallest of the three constants, irrespective of the compound and the salt used. For the symmetrical dyes, this constant corresponds to the insertion of a cation into each of the crowns. It can be observed here that in most cases the K_3 value is about one quarter that of K_1. This situation is characteristic of independent complexation of two binding sites on the same ionophore. This result can be compared with that obtained for other biscrown systems, which exhibit negative or positive cooperation effects.[6j,k–20] Regarding unsymmetrical compound **4**, the AM_2 constant is low. As said above, it corresponds to the complexation of the crown and to the direct interaction of a second cation with the unsaturated system. It is easily understandable that the latter interaction is much weaker than complexation in a crown ether.

Conclusions

In summary, no major differences in binding efficiency were observed here between the three symmetrical dyes. In particular, it was shown that subtle geometrical changes in the sensor core, due to the existence of rotational isomers or to small twists, do not impede the formation of very stable sandwich complexes, at least in this series of dyes. It seems that only *discrete* sandwich complexes, that is isolated pairs of dyes, were obtained here, strongly stabilised by stacking between the chromophores. It could be interesting to know more about the factors that govern the formation of sandwich complexes, and more specifically, which allow transition from 2:1 host-guest triads to extended aggregates. It is clear that rigid rodlike biscrown systems offer great potential for sensing applications and nanotechnologies, and deserve to be better known and more widely used.

Experimental

Materials and methods

Spectroscopic grade acetonitrile (Merck) was used for absorption and fluorescence measurements. Alkaline earth perchlorates [$Ca(ClO_4)_2 \cdot 4H_2O$; $Ba(ClO_4)_2$] were from Aldrich and used as received. All compounds were prepared by the method of Olomucki and Le Gall.[21]

Infrared spectra were obtained with a Perkin Elmer 1760-X Infrared Fourier Transform spectrometer using CaF_2 cells of 100 μm path length. The mass spectra were obtained on simple quadrupole mass spectrometers (Perkin Elmer Sciex API 100 and Waters Q-TOF Ultima) using electrospray as the ionisation mode. The infusion rate was 5 μL min^{-1}. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers operating at 200 and 400 MHz, respectively. UV/vis absorption spectra were recorded on a Hewlett–Packard 8452 A diode array spectrophotometer, using cuvettes of 5 cm optical path length for dyes **1**–**3** and 1 cm cuvettes for **4**. The microanalyses were obtained with an EA1110 elemental analyser from CE Instruments.

Syntheses

Dyes **1**, **2** and **3** were obtained by condensation of formylated *N*-phenylaza-15-crown-5 with cyclopentanone, cyclohexanone and acetone, respectively, in ethanol in the presence of aqueous NaOH at room temperature. The oily product obtained was purified on preparative silica plates, using 95% ethanol as eluent, and extracted with dichloromethane to remove traces of silica. The synthesis and characteristics of 1,5-bis[4-(*N*-aza-15-crown-5)phenyl]penta-1,4-dien-3-one (**3**) have been reported in a previous work.[6a] Compounds **1** and **2** were a gift from Dr. V. G. Pivovarenko (Kiev University) and were checked for purity. The characteristics of **1**, 2,5-bis{[4-(*N*-aza-15-crown-5)phenyl]methylene}cyclopentanone, have been described elsewhere.[10a]

(2,6-Bis{[4-(*N*-aza-15-crown-5)phenyl]methylene}cyclohexanone) (2). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.8 (m, 2H, C–CH_2–CH_2), 2.9 (t, $J = 5.0$ Hz, 4H, C–CH_2–CH_2), 3.6 (m, 32H, CH_2–O_{crown}), 3.7 (t, $J = 6.5$ Hz, 8H, CH_2–N_{crown}), 6.6 and 7.4 ($2 \times$ d, $J = 8.8$ Hz, 8H, Ph), 7.7 (s, 2H, CH=C). IR (KBr pellet) ν/cm^{-1}: 1652 (conjugated C=O), 1590 (C=C), 1160 (C–N), 1125 (C–O–C), 820 (*para*-substituted Ph). MS (ESI+): $m/z = 708$ (M^+). Anal. calcd for $C_{40}H_{56}N_2O_9$: C 67.77; H 7.95; N 3.95; found: C 67.11; H 8.03; N 3.85.

2-[4-(*N*-Aza-15-crown-5)phenylmethylene]-5-[4-(diethylamino)-phenylmethylene]cyclopentanone (4). Cyclopentanone was firstly reacted with one equimolar amount of diethylaminobenzaldehyde, yielding 2-{[4-(diethylamino)phenyl]methylene}cyclopentanone, which was purified by sublimation. Then, this compound was condensed with an equimolar amount of *p*-formyl-*N*-phenylaza-15-crown-5 ether and purified on preparative silica plates, using 50:50 toluene–dioxane as the eluent, and dichloromethane to extract the dye from the silica. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.2 (t, $J = 7.0$ Hz, 6H, CH_3), 3.1 (s, 4H, CH_2 cyclopentanone), 3.4 (q, $J = 7.0$ Hz, 4H, CH_2–CH3), 3.6–3.7 (m, 16H, CH_2–O_{crown}), 3.8 (t, $J = 6.3$ Hz, 4H, CH_2–N_{crown}), 6.72 and 7.52 ($2 \times$ d, $J = 8.8$ Hz, 4H, Ph), 6.73 and 7.53 (d, $J = 8.9$ Hz, 4H, Ph), 7.52 (s, 2H, CH=C). IR (solid, in diamond cell) ν/cm^{-1}: 1679 (conjugated C=O), 1587 (C=C), 1171 (C–N), 1128 (C–O–C), 816 (*para*-substituted Ph). MS (ESI+): $m/z = 549.5$ $[M+H]^+$. Anal. calcd for $C_{33}H_{44}N_2O_5$: C 72.23; H 8.08; N 5.10; found: C 71.50; H 7.78; N 5.09.

Data analysis

The absorption experimental data were processed on an HP 9000 series 710 workstation. The equilibrium equations are as follows:

$$K_1[A][M] - [AM] = 0 \qquad (5)$$

$$K_2[AM][A] - [A_2M] = 0 \qquad (6)$$

$$K_3[AM][M] - [AM_2] = 0 \qquad (7)$$

The two concentrations [M] and $[AM_2]$ can be written as a linear combination of the other concentrations with the help of the mass conservation equations:

$$[M] = [M]_0 - [AM] - [A_2M] - 2[AM_2] \qquad (8)$$

$$[AM_2] = [A]_0 - [A] - [AM] - 2[A_2M] \qquad (9)$$

in which subscript 0 refers to initial concentrations. Therefore, only three independent variables [A], [AM] and $[A_2M]$ remain in the three equilibrium eqns. (5), (6) and (7). In this system of equations, concentrations C_i were related to absorbance A using Beer–Lambert's law: $A = l\Sigma(\varepsilon_i C_i)$ where ε_i is the molar absorption coefficient of species i and l is the optical path-length. The system was then numerically solved using an iterative method. The equilibrium constants were refined in order to improve the fit between the model and the experimental data. The residual error was calculated as being equal to:

$$1/n \sum_n \left(A_{\text{calculated}} - A_{\text{measured}}\right)^2 \qquad (10)$$

with n being the number of experimental points. The method used has been extensively described in a previous paper.[22]

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