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Sandwich-Type Complexes of Alkaline-Earth Metal Cations with a Bisstyryl Dye Containing Two Crown Ether Units

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The formation of complexes between a bisstyryl dye containing two benzo-15-crown-5 ether groups, **2**, and Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions was studied in acetonitrile solution by using a spectrophotometric approach. In contrast to its monostyryl analogue **1**, which shows a rather low cation-binding selectivity, the bisstyryl dye **2** selectively binds the Sr^{2+} and Ba^{2+} ions because of formation of intramolecular sandwich complexes. Alkaline-earth metal cations induce substantial blue shifts of the absorption maximum of **1** and **2**, particularly in the case of sandwich complex formation. The emission behavior of **1** and **2** and their Ba^{2+} complexes in acetonitrile solution has also been studied. In both cases, complex formation leads to a blue shift of the fluorescence maximum and a decrease in the emission quantum yield. The fluorescence decay is monoexponential for the complex of **1** and biexponential for that of **2**. The longer-lived fluorescence component, which corresponds to the lower-energy band in the steady-state spectrum, is assigned to an intramolecular excimer state.

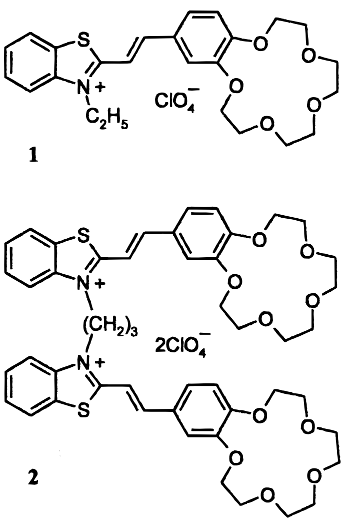
Introduction

Chromo- and fluorogenic crown ether derivatives are of considerable interest because of their application as optical sensors for alkali and alkaline-earth metal cations[1−6] and as functional units of photoswitchable ionic devices.[6−9] Combination of a crown ether with a styryl compound yields molecular systems where the styryl moiety can provide the chromo- and fluorogenic properties as well as the switching function,[7] the latter being related to either *trans*−*cis* isomerization or [2+2]-cycloaddition photoreactions, which are typical of styryl compounds.[10]

Most of the known macrocyclic chromo- and fluoroionophores with a styryl moiety[1,11−20] were designed by using a common principle, namely, by combining a macrocycle (usually, *N*-phenylaza- or benzocrown ether) with a chromophore so that both functional units share some critical atoms. The chromophore unit with an internal charge-transfer (ICT) excited state is used to produce a strong optical response to the cation−macrocycle interaction.[5] The crown-containing styryl dye **1**,[12] Chart 1, is an example of an integrated ICT-based chromoionophore.

Crowned styryl compounds may show significant cation-induced changes in the absorption and/or fluorescence spectra.[11−20] However, most of them have rather low cation-binding ability and poor selectivity within the series of alkali or alkaline-earth metal cations. The introduction of the sulfo group into the *N*-alkyl substituent of **1** results in a considerable increase in the ability of the dye to bind alkaline-earth metal cations[21] and photochemical control of the complex formation,[13] but the cation-binding selectivity remains poor.

CHART 1



1

2

Bis(crown ether) derivatives, in which two crown ether moieties are linked by a flexible aliphatic chain, in some cases form more stable complexes with metal cations and show a higher cation-binding selectivity compared to the monocyclic analogues.[22] This is due to the ability of bis(crown ethers) to form intramolecular sandwich-type complexes with particular cations whose size is larger than the cavity size of the crown ether ring. Recently we have developed procedures for the synthesis of bisstyryl dyes containing two crown ether units.[23,24] It was suggested that the biscrowned dyes may show not only improved cation-binding selectivity, but also specific optical

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response due to cation-induced intramolecular stacking of the dye units and "rigidification" of the dye skeleton.[25]

In this paper, we report a comparative study of the complex formation of bisstyryl dye **2** and its monostyryl analogue **1**, Chart 1, with alkaline-earth metal cations in anhydrous acetonitrile. Spectrophotometric data in conjunction with matrix algebra methods were used to determine the complexation stoichiometry, to calculate the stability constants, and to obtain the absorption spectra of the complexes. The effect of metal ion size on the complex stability constants was analyzed. Steady-state and time-resolved luminescence spectroscopies have provided evidence for the occurrence of intramolecular stacking in the case of the Ba^{2+} complex of the bisstyryl dye.

Experimental Section

Materials. Crown-containing dyes **1** and **2** were synthesized according to previously described procedures.[24,26] Anhydrous magnesium and barium perchlorates (Aldrich) were used as received. Calcium and strontium perchlorates (Aldrich) were dried in vacuo at 230 °C. Tetraethylammonium perchlorate, Et_4NClO_4, was dried in vacuo at 40 °C. Acetonitrile of spectroscopic quality was distilled with CaH_2 to remove traces of water.

Stability Constants and Spectroscopy. The complexation stoichiometry and the complex stability constants were derived from spectrophotometric data with the help of matrix algebra methods.[27,28] The spectrophotometric data represented a set of 12−16 absorption spectra (30000−18000 cm^{-1} in 80 cm^{-1} increments) obtained from acetonitrile solutions with a constant total concentration of the dye ($C_L = 4 \times 10^{-6}$ and 2×10^{-6} mol dm^{-3} for **1** and **2**, respectively) and a variable total concentration of the metal perchlorate (C_M, ranging from 0 to 1×10^{-3} mol dm^{-3}). To eliminate the influence of the variation of C_M on the equilibria of the reactions between the dye−metal complexes and the perchlorate ions,[21] the total concentration of ClO_4^- in the solutions was maintained constant (0.01 mol dm^{-3}) by the use of the supporting electrolyte Et_4NClO_4. The ionic strength of the solutions was varied within a very small range (0.010−0.011 mol dm^{-3}).

Dye solutions were prepared and used in red light. Absorption spectra were recorded on a Specord-M40 spectrophotometer interfaced with a PC XT. The measurements were carried out at 25.0 ± 0.2 °C in a matched jacketed cylindrical quartz cell of 5.5 cm path length. The inner surface of the quartz cell was modified by hydrophobic groups.[21]

Fluorescence spectra were recorded on a Spex-Fluorolog-2 fluorimeter at ambient temperature using quartz cells of 1 cm path length. A calibrated 45 W quartz−halogen tungsten filament lamp by Optronic Laboratories was used as a standard for the correction of the phototube response. Emission quantum yields Φ_s were computed by using $[Ru(bpy)_3]Cl_2$ as a reference standard ($\Phi_r = 0.028$ in air-equilibrated water),[29] and according to eq 1,[30] where s and r stand for sample and reference standard,

$$\frac{\Phi_s}{\Phi_r} = \frac{D_r n_s^2 A_s}{D_s n_r^2 A_r} \qquad (1)$$

respectively, D is the absorbance (taken as ≤0.1) at the selected excitation wavelength, n is the refractive index of the solvent, and A is the integral intensity of the corrected fluorescence spectrum on an energy scale. The uncertainty in emission quantum yields was within 20%.

TABLE 1: Absorption Spectroscopy Data for Dyes 1, 2, and Their Complexes[a]

species	λ_{max}/nm	$\Delta\lambda$/nm[b]	$\epsilon_{max} \times 10^{-4}$/($dm^3$ mol^{-1} cm^{-1})
1	430		4.07
1·Mg^{2+}	392	−38	3.88
1·Ca^{2+}	393	−37	3.88
1·Sr^{2+}	397	−33	3.90
1·Ba^{2+}	402	−28	3.93
2	432		6.90
2·Mg^{2+}	400	−32	5.96
2·$(Mg^{2+})_2$	394	−38	6.79
2·Ca^{2+}	380	−52	5.33
2·$(Ca^{2+})_2$	395	−37	6.48
2·Sr^{2+}	380	−52	5.24
2·Ba^{2+}	390	−42	5.92

[a] Acetonitrile solution at 25 °C. [b] Difference between λ_{max} for the complexed and free forms of the dye.

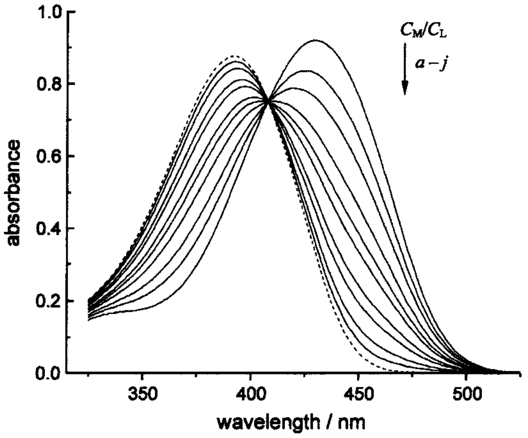


Figure 1. Absorption spectrum of dye **1** ($C_L = 4.1 \times 10^{-6}$ mol dm^{-3}) in acetonitrile solution as a function of the concentration of Ca^{2+} ions: C_M/C_L = 0 (a), 0.88 (b), 1.76 (c), 3.48 (d), 5.18 (e), 6.85 (f), 12.1 (g), 17.4 (h), 37.9 (i), 86.4 (j). The dashed curve is the calculated spectrum of the complex **1**·Ca^{2+}.

Deconvolution of fluorescence spectra on an energy scale, $I(\nu)$, was carried out using the symmetric and asymmetric Gaussian functions (eqs 2 and 3, respectively), where B is the Gaussian bandwidth at half-intensity.

$$I(\nu) = I_{max} \exp\{-2.7726(\nu_{max} - \nu)^2/\nu_{max}{}^2/B^2\} \qquad (2)$$

$$I(\nu) = I_{max} \exp\{-2.7726(\nu_{max} - \nu)^2(\nu/\nu_{max})^2/B^2\} \qquad (3)$$

The picosecond time-resolved fluorescence spectrometer was based on a Nd:YAG laser, a spectrograph, and a streak camera; details are reported elsewhere.[31] Excitation was at 355 nm, with an energy of 1 mJ/pulse. Time profiles were averaged over 40 wavelength channels (ca. 15 nm). Analysis was performed on 512 data points by using standard iterative nonlinear procedures and according to a single-exponential decay or to a combination of exponentials. The overall time resolution was 20 ps, and the uncertainty was within 10%. Time-resolved spectra were constructed by integration of the signal falling within selected time channels of the streak images.

Results

Absorption Spectra and Complex Stability Constants. Long-wavelength absorption maxima and extinction coefficients for **1**, **2**, and their complexes with alkaline-earth metal cations in anhydrous acetonitrile are given in Table 1. The absorption spectra of **1** and **2** as a function of the concentration of Ca^{2+} ions are shown in Figures 1 and 2, respectively. Dyes **1** and **2** exhibit very similar absorption profiles in the 200−500 nm region; a minor difference is in a very small red shift (∼2 nm)

TABLE 2: Stability Constants for Complexes of Alkaline-Earth Metal Cations with Dyes 1 and 2[a]

	$C_L \times 10^6$/(mol dm^{-3})	C_M/C_L	$\beta \times 10^2$ [b]/(mol dm^{-3})	log K_1	log K_2	s_D[c]
1·Mg^{2+}	4.08	0−200	1.0−1.1	5.23 ± 0.03		0.0010
1·Ca^{2+}	4.10	0−200	1.0−1.1	4.78 ± 0.03		0.0008
1·Sr^{2+}	4.14	0−200	1.0−1.1	4.43 ± 0.04		0.0014
1·Ba^{2+}	4.07	0−200	1.0−1.1	4.39 ± 0.03		0.0012
2·Mg^{2+}	2.19	0−400	1.0−1.1	5.97 ± 0.06	4.38 ± 0.05	0.0008
2·Ca^{2+}	2.22	0−400	1.0−1.1	5.68 ± 0.04	3.55 ± 0.03	0.0011
2·Sr^{2+}	2.17	0−1.2	1.0	8.5 ± 0.2		0.0009
2·Ba^{2+}	1.84	0−1.2	1.0	8.0± 0.1		0.0008

[a] Acetonitrile solution at 25 °C; supporting electrolyte Et_4NClO_4. [b] Ionic strength of the solution. [c] Total residual error for the reconstruction of the absorption spectra.

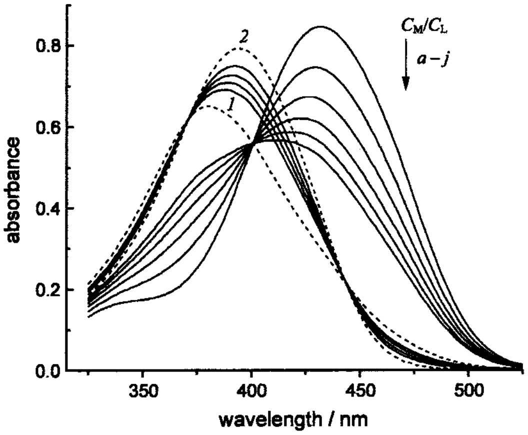


Figure 2. Absorption spectrum of dye **2** ($C_L = 2.22 \times 10^{-6}$ mol dm^{-3}) in acetonitrile solution as a function of the concentration of Ca^{2+} ions: C_M/C_L = 0 (a), 0.390 (b), 0.777 (c), 1.16 (d), 1.54 (e), 1.92 (f), 91.0 (g), 135 (h), 221 (i), 387 (j). The dashed curves are the calculated spectra of the complexes **2**·Ca^{2+} (1) and **2**·(Ca^{2+})$_2$ (2).

and a slight broadening of the long-wavelength portion of the absorption band of dye **2**. This indicates that the through-space interaction between the two chromophoric units of **2** is weak. Addition of alkaline-earth metal salt to an acetonitrile solution of **1** or **2** leads to a strong hypsochromic shift of the long-wavelength absorption maximum, which may be explained by a significant charge redistribution within the chromophoric unit of the dye upon interaction of the crown ether group with the metal cation. Cation-induced hypsochromic effects are typical of integrated ICT-based chromoionophores bearing the ion-binding site at the electron-rich end of the chromophore unit.[2]

To assess the number, *k*, of absorbing components in the dye−metal system, the factor analysis[27] was applied to the absorbance matrix consisting of the absorption spectra obtained at different concentrations of the metal cation (see the Supporting Information for details). For **1** with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} as well as for **2** with Sr^{2+} and Ba^{2+}, it was found that $k = 2$. For dye **2** with Mg^{2+} and Ca^{2+}, the factor analysis provided $k = 3$. The complexation models involving one equilibrium (eq 4) and two equilibria (eqs 4 and 5) were assumed for the systems with $k = 2$ and 3, respectively. In eqs 4 and 5, L is the dye molecule, M is the metal cation, and K_1 and K_2 are the complex stability constants.

$$L + M \underset{}{\overset{K_1}{\rightleftharpoons}} LM \tag{4}$$

$$LM + M \underset{}{\overset{K_2}{\rightleftharpoons}} LM_2 \tag{5}$$

The experimental absorbance matrixes were reconstructed in terms of the corresponding complexation model by using the parametrized matrix modeling methods,[27,28] as detailed in the Supporting Information. For all of the dye−metal systems, the reconstruction gave very small residual errors, s_D (Table 2), indicating that the complexation models hold. The calculated values of log K_1 and log K_2 together with their uncertainties are given in Table 2. The calculated spectra of the Ca^{2+} complexes of dyes **1** and **2** are shown in Figures 1 and 2, respectively.

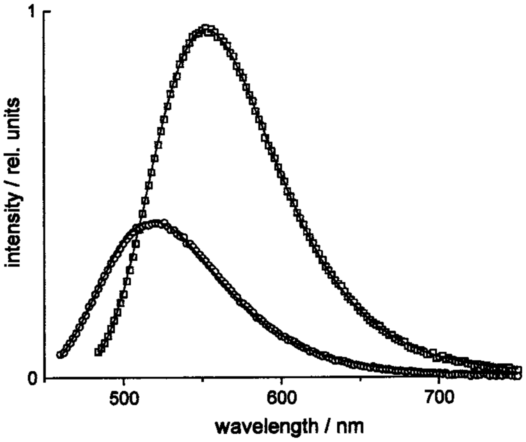


Figure 3. Fluorescence spectra of dye **1** (1.9×10^{-5} mol dm^{-3}, λ_{exc} = 295 nm) in acetonitrile solution: in the absence of metal salt (squares), in the presence of $Ba(ClO_4)_2$ (0.01 mol dm^{-3}, circles). The spectra are corrected for nonlinearity of instrumental response. Solid curves are fits to the asymmetric Gaussian function.

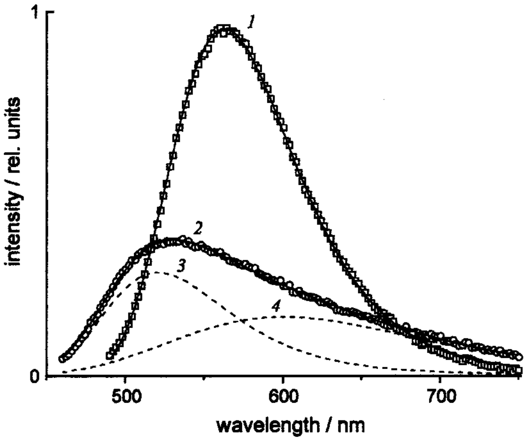


Figure 4. Fluorescence spectra of dye **2** (9×10^{-6} mol dm^{-3}, λ_{exc} = 291 nm) in acetonitrile solution: in the absence of metal salt (squares), in the presence of $Ba(ClO_4)_2$ (2×10^{-5} mol dm^{-3}, circles). Curve 1 is from the fit to the asymmetric Gaussian function. Curve 2 is obtained by using asymmetric (3) and symmetric (4) Gaussian profiles.

Fluorescence. The fluorescence spectra of dye **1** and its Ba^{2+} complex in acetonitrile solution are shown in Figure 3. The corresponding spectra for dye **2** are shown in Figure 4. The fully complexed forms of the dyes were obtained at $Ba(ClO_4)_2$ concentrations of 0.01 and 2×10^{-5} mol dm^{-3} for **1** and **2**,

TABLE 3: Steady-State and Time-Resolved Fluorescence Spectroscopy Data for Dyes 1, 2, and Their Ba^{2+} Complexes[a]

species	ν_{max}/cm^{-1} (λ/nm)	$\Delta\nu_{1/2}$/cm^{-1} [b]	Φ_{fl}[c]	τ_1/ps[d]	τ_2/ps[d]
1	18 100 (552)	2980	0.0063	65	
1·Ba^{2+}	19 280 (519)	3280	0.0031	35	
2	17 770 (563)	2910	0.0051	70	
2·Ba^{2+}	18 860 (530)	4990	0.0031	40	1400

[a] Acetonitrile solution at ambient temperature. [b] Fluorescence band width at half-intensity. [c] Emission quantum yield. [d] Fluorescence lifetime.

respectively. The excitation wavelength was chosen at iso-absorbing points for the free dye and its Ba^{2+} complex (295 and 291 nm for **1** and **2**, respectively). No changes in the shape of the fluorescence curves occurred on varying the excitation wavelength in the 280−450 nm region.

Fluorescence data for free dyes **1** and **2** and for their Ba^{2+} complexes are collected in Table 3. The fluorescence band maximum of **2** is red-shifted (11 nm), and the emission quantum yield is lower (ca. 20%) compared to that of **1**. Both dyes showed monoexponential fluorescence decays. The formation of the complex of dye **1** with Ba^{2+} leads to a strong hypsochromic shift of the fluorescence band and a decrease in the emission quantum yield. The fluorescence decay of this complex is purely monoexponential with a lifetime (35 ps) shorter than that for the free dye (65 ps).

The formation of the complex of dye **2** with Ba^{2+} also leads to a hypsochromic shift of the fluorescence maximum and a decrease in the emission quantum yield. In this case, however, the fluorescence intensity in the long-wavelength region of the spectrum increases markedly and the fluorescence spectrum can be fitted by two Gaussian bands (Figure 4 and Table 4). Definite evidence for two-component fluorescence of the Ba^{2+} complex of **2** is provided by time-resolved fluorescence experiments. The fluorescence decay shows a biexponential behavior (Table 3 and Figure 5): the lifetime of the fast component is very close to that of the Ba^{2+} complex of **1**, and that of the slow component is considerably longer than the fluorescence lifetime of the free dye (1.4 ns and 70 ps, respectively). The inset of Figure 5 shows the time-resolved spectrum taken in the time interval 1.6−5.9 ns, where the contributed emission by the faster component is over, together with the spectral shape of the prompt component. The band is quite broad, with a maximum around 600 nm. This is in agreement with the steady-state fluorescence data and with the results of the deconvolution analysis illustrated in Figure 4.

Discussion

In the experimental conditions used, the interaction of alkaline-earth metal cations with the benzo-15-crown-5 ether group of the reference dye **1** results in the formation of the 1:1 dye−metal complexes exclusively. As compared to unsubstituted benzo-15-crown-5 (B15C5), dye **1** shows a much lower ability to bind the metal cations. For example, the value of log K_1 for the Mg^{2+} complex of **1** is nearly two units lower than that for the corresponding complex of B15C5 (log $K_1 = 7.3$, acetonitrile, $Mg(ClO_4)_2$, $T = 22$ °C).[21] The low stability of the dye complexes may be due to electronic factors, viz., the electron-withdrawing effect of the benzothiazolium residue of the dye and the electrostatic repulsion between the positively charged dye molecule and the metal cation.

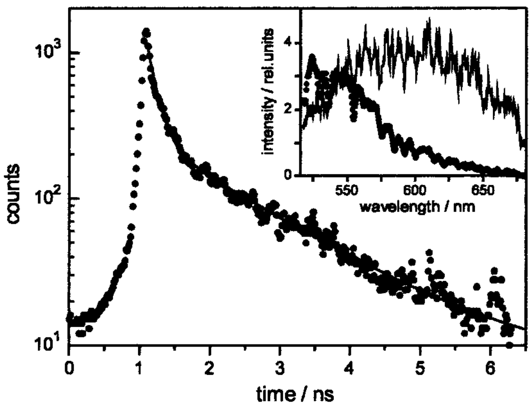


Figure 5. Fluorescence decay of dye **2** (1×10^{-5} mol dm^{-3}) in the presence of $Ba(ClO_4)_2$ (2×10^{-5} mol dm^{-3}), as measured at 600 nm. The fitting analysis (solid line) according to a biexponential decay gave $\tau_1 = 40$ and $\tau_2 = 1.4$ ns. The inset shows the normalized spectra of the fast (circles) and slow (solid line) components taken between 0 and 500 ps and between 1.6 and 5.9 ns, respectively.

For dye **1**, the complex stability constant increases in the series from Ba^{2+} to Mg^{2+}, Table 2, indicating that the cavity size of the crown ether group of the dye is best fitted to the size of the Mg^{2+} ion. The stability constant seems to increase with increasing hypsochromic shift of the long-wavelength maximum ($\Delta\lambda$) in the absorption spectrum (Table 1). The binding selectivity of **1** for Mg^{2+} over the other alkaline-earth metal cations is rather low, presumably because of the strong solvation of the doubly charged cations in acetonitrile. This unfavorable effect of the solvation against complex stability increases with decreasing ionic radius of the metal cation, as expected from the increase in solvation energy. Dye **1** is known to undergo photoinduced *trans*−*cis* isomerization with a quantum yield of ca. 0.4 (acetonitrile, ambient temperature),[32] and this reaction is likely to be responsible for the observed fast fluorescence decay and low emission quantum yield found for **1** (Table 3).

For the chromoionophores with an ICT excited state, such as dye **1**, the emission spectrum can be much less affected by cation complexation than the absorption spectrum.[5] This phenomenon, which has been observed, for example, with crowned merocyanine dye DCM[11] and with an azacrown-containing styryl dye,[20] is due to a disruption of some critical coordination bonds in the excited state. In the case of dye **1**, a significant blue shift of the fluorescence band upon complexation with the Ba^{2+} ion indicates that no recoordination reaction occurs during the lifetime of the excited state.

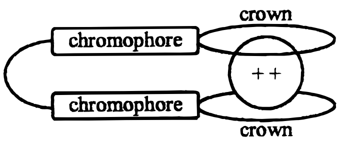
For the bisstyryl dye **2**, the stability constants of the 1:1 dye−

TABLE 4: Deconvolution of the Fluorescence Spectrum of the Ba^{2+} Complex of Dye 2

	Gaussian[a]	
parameter	asym + asym	asym + sym
ν_{max}/cm^{-1} (λ/nm)	19 185 (521) + 16 374 (611)	19 205 (521) + 16 647 (601)
B/cm^{-1} [b]	3405 + 4172	3388 + 5137
$\int I(\nu)$/rel units[c]	0.675 + 0.325	0.560 + 0.440

[a] Eqs 2 and 3 were used to describe the symmetric and asymmetric Gaussian bands, respectively; the fits to a linear combination of two asymmetric Gaussian bands and to a linear combination of high-energy asymmetric and low-energy symmetric Gaussian bands gave nearly the same residual errors. [b] Gaussian band width at half-intensity. [c] Integral intensity of the fluorescence spectrum.

CHART 2



metal complexes are higher than those for dye **1** by a factor of 5.5, 7.9, 1.2 × 10^4, and 4.1 × 10^3 for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively (Table 2). A dramatic increase in the stability constant in the case of Sr^{2+} and Ba^{2+} is attributable to the ability of **2** to form the intramolecular sandwich complexes, Chart 2, with the metal cations whose size is larger than the cavity size of the crown ether groups in the dye molecule. An intramolecular sandwich structure may be assumed also for the complex **2**·Ca^{2+} since the equilibrium constant K_2 for the reaction of this complex with a second Ca^{2+} ion is much lower (by a factor of 135) than the constant K_1 (Table 2).

For the complexes **2**·Ca^{2+}, **2**·Sr^{2+}, and **2**·Ba^{2+}, the cation-induced hypsochromic shifts of the absorption maximum, $\Delta\lambda$, are significantly larger than those for the corresponding complexes of dye **1** (Table 1). These enhanced shifts are likely to be due to the stacking of the chromophoric units in the sandwich complexes. It is known[33] that parallel (H-type) dye aggregates show absorption band maxima at shorter wavelengths when compared to the monomer. According to approaches based on exciton theory,[34] distortion of the parallel structure of the aggregates leads to band splitting. In many cases, the weaker, lower-energy band is unresolved. For example, in the case of dimers of some azo dyes[35] and tetramers of a styryl dye containing an alkylsulfonate substituent,[20] the red-shifted band is a shoulder of the blue-shifted band. We believe that the spectral pattern observed for the intramolecular sandwich complexes of **2** can be understood by a similar approach. Figure 2 enables us to compare the spectra of **2**·Ca^{2+} and **2**·$(Ca^{2+})_2$. One sees that the absorption band of **2**·Ca^{2+} has the maximum at shorter wavelength and shows a long-wavelength shoulder. In the complex **2**·$(Ca^{2+})_2$, the stacking of chromophoric units is not allowed because of electrostatic repulsion between the bound Ca^{2+} ions, and the profile of the absorption band of this complex is similar to that of the complex **1**·Ca^{2+} (Figure 1).

The two-component fluorescence found for the Ba^{2+} complex of **2** can also be explained in terms of an intramolecular cation-induced stacking of chromophoric units because the component with the broader and red-shifted spectrum is reminiscent of an excimer-type emission.[36] Formation of such a type of intermolecular excimers is controlled by diffusion processes, and would normally be disfavored in our case in view of the low concentration employed and the short-lived emission of the initially excited monomer, but might become possible within the **2**·Ba^{2+} complex.

One can notice that the value of $\Delta\lambda$ for the complex **2**·Mg^{2+} is lower than the corresponding values for the complexes **2**·$(Mg^{2+})_2$ and **1**·Mg^{2+} (Table 1). This suggests that the crown ether group of one of the chromophoric units in **2**·Mg^{2+} is not significantly coupled with the metal cation. In turn, this assumption seems to be in conflict with the fact that the stability constant for **2**·Mg^{2+}, despite the twice positive charge of the dye molecule, is higher than that for **1**·Mg^{2+} (Table 2), suggesting a sandwich structure also for complex **2**·Mg^{2+}; a significant difference in the stability constants K_1 and K_2 for the complexation of **2** with Mg^{2+} also counts in favor of a sandwich structure. This apparent discrepancy might be reconciled by noting that to form an intramolecular sandwich complex, the small Mg^{2+} ion must partially come out of the crown cavity so that the chromophoric units in this hypothetical complex would be less affected than in the case of **2**·$(Mg^{2+})_2$ and **1**·Mg^{2+}.

Conclusions

The presence of two crown-containing styryl components within the same molecule leads to a chromoionophoric system with improved functionality. Compared to its monomeric analogue **1**, the bisstyryl dye **2** shows higher affinity for alkaline-earth metal cations, significantly improved cation-binding selectivity, and enhanced optical response to the interaction with metal cation. The changes in cation-binding properties are related to the ability of the bisstyryl dye to form intramolecular sandwich complexes. The enhanced hypsochromic shifts of the absorption maximum observed for the Sr^{2+} and Ba^{2+} complexes of the bisstyryl dye, as well as the appearance of long-lived emission in the case of the Ba^{2+} complex, indicate the occurrence of intramolecular stacking in the bichromophoric system upon complex formation.

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Supporting Information Available: Matrix algebra methods applied to the treatment of spectrophotometric data and absorption spectra of **2** in anhydrous MeCN as a function of the concentration of Mg^{2+}, Sr^{2+}, and Ba^{2+} ions. This information is available free of charge via the Internet at http://pubs.acs.org.

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