

# Crown-containing styryl dyes: cation-induced self-assembly of multiphotochromic 15-crown-5 ethers into photoswitchable molecular devices



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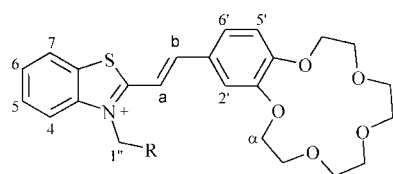
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The *s*-conformations of *trans*-**1b–e** were studied by <sup>1</sup>H NMR spectroscopy in CD<sub>3</sub>CN solution. It was shown that in *trans*-**1b–e** intramolecular ion pairs between the SO<sub>3</sub><sup>−</sup> group and the positively charged nitrogen atom of the benzothiazolium residue are formed. In the case of *trans*-**1a** no ionic association was observed. The complex formation of the *trans*- and *cis*-isomers of crown-containing styryl dyes with Mg<sup>2+</sup> in CH<sub>3</sub>CN was studied spectrophotometrically. The anion-“capped” complexes formed by the *cis*-isomers were found to be more stable than the complexes formed by the corresponding *trans*-isomers. The stability constants of the complexes formed by the *cis*-isomers depend markedly on length and type of the *N*-substituent. Data from PM3 quantum-chemical calculations were used for the interpretation of some experimental data.

## Introduction

Certain conditions must be fulfilled for a successful development of photoswitchable molecular devices.<sup>1–5</sup> The actual compounds must have the capability of self-organisation at the molecular level (self-assembly),<sup>6–8</sup> giving supramolecular structures with a desirable architecture, and allow a photochemical control of their properties. Synthesis of multiphotochromic complexes susceptible to various types of molecular photo-switching is of prime importance in this respect.

Previously, we developed a procedure for the synthesis of crown-containing styryl dyes (CSD).<sup>9</sup> The CSD of type *trans*-**1c–f** (Scheme 1) proved to be the most promising among these



*trans*-**1a–f**

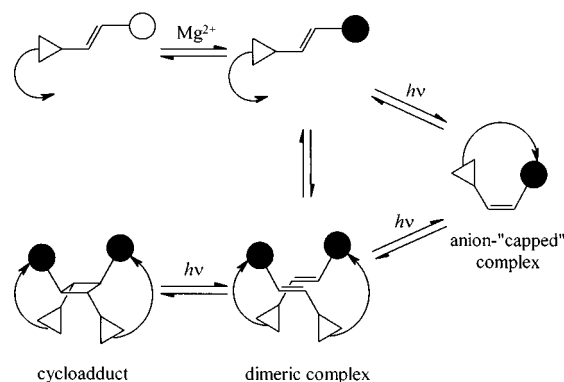
**a** R = Me + ClO<sub>4</sub><sup>−</sup>, **b** R = CH<sub>2</sub>SO<sub>3</sub><sup>−</sup>, **c** R = (CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub><sup>−</sup>, **d** R = (CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub><sup>−</sup>,

**e** R = *o*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>−</sup>, **f** R = *p*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>−</sup>

Scheme 1 Crown-containing styryl dyes.

compounds. These CSD are able to form anion-“capped” complexes (Scheme 2) upon *trans*–*cis*-photoisomerization owing to the interaction of the sulfo group of the *N*-substituent (spacer) with a metal cation in the crown-ether cavity.

Studies of CSD in solution have shown that in the presence of metal cations, the *trans*-isomers of these molecules can exist as self-organised pairs according to the *anti*-“head-to-tail” pattern<sup>10,11</sup> (Scheme 2). The self-assembly of the dimeric



Notation. ○ is the benzo-15-crown-5 ether moiety;  
● is the benzo-15-crown-5 ether moiety with Mg<sup>2+</sup>;  
▷ is the benzothiazole residue;  
◁ is (CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub><sup>−</sup>, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>−</sup>

Scheme 2

complexes comprising two *trans*-**1c,d** molecules and two metal cations can become a unique tool for controlling the regio- and stereoselectivity of [2+2]-photocycloaddition (PCA) of CSD.<sup>12–14</sup> It is noteworthy that neither *trans*-**1a–f** without alkaline earth metal cations nor complexes of *trans*-**1a** with Mg<sup>2+</sup>, Ca<sup>2+</sup>, or Ba<sup>2+</sup> undergo PCA even in saturated solutions. The change from spacers with flexible polymethine chains to *N*-substituents in which the sulfo group is rigidly arranged in space, makes it possible to influence the efficiency of these photochemical reactions and also to change the route of transformation of CSD.<sup>15</sup>

The anion-“capped” and dimeric complexes are the simplest photoswitchable molecular devices, since their ability to bind metal cations substantially changes on exposure to light, *i.e.* the complex-formation process can be controlled.<sup>10,12,15–17</sup>

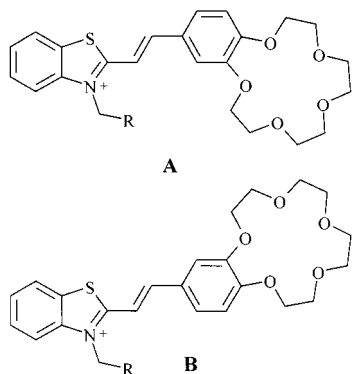
A rational design of photoswitchable molecular devices from CSD and metal ions requires a more detailed study of the regularities of their self-assembly into the anion-“capped” and dimeric complexes. In particular, we were interested in elucidating the influence of the CSD structure and how the nature and the length of the *N*-substituent could affect the self-assembly mechanism and stability of the molecular devices based on these molecules.

Therefore, we studied the structures of CSD *trans*-**1b–f** by <sup>1</sup>H NMR spectroscopy and the complex formation of these compounds with Mg<sup>2+</sup> ions by absorption spectroscopy. The effect of the *trans*-*cis*-isomerization of CSD on the complex formation is also presented. Dye *trans*-**1a** containing no sulfo group in the *N*-substituent was used as a convenient reference compound.

## Results and discussion

### NMR studies

As judged by the spin–spin coupling constants for olefinic protons, <sup>3</sup>*J*<sub>*trans*</sub> = 15.6–16.0 Hz,<sup>18</sup> CSD **1a–f** in CD<sub>3</sub>CN solution have the *trans*-configuration. Analysis of the NOESY spectra of dyes *trans*-**1b–e** in a CD<sub>3</sub>CN–D<sub>2</sub>O mixture showed that these dyes exist as an equilibrium mixture of two conformers **A** and **B** (Scheme 3) with different arrangements of the crown-ether moiety and that species **A** is dominating in all cases.



Scheme 3 *s*-Conformations of crown-containing styryl dyes.

A similar predominance of conformer **A** in CD<sub>3</sub>CN solution was also found for (*trans*-**1a**)·Mg<sup>2+</sup>. The higher stability of form **A** and its complexes with Mg<sup>2+</sup> ions was confirmed by theoretical calculations (see below) and also by X-ray diffraction data obtained for a dye of similar structure.<sup>19</sup>

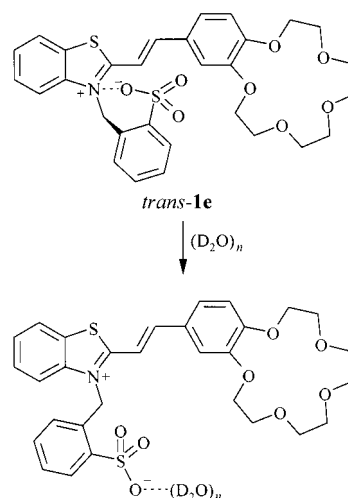
Dyes *trans*-**1b–f** were poorly soluble in CD<sub>3</sub>CN, apparently due to intermolecular and intramolecular electrostatic interactions, which are typical of betaines. The solubility markedly increased upon the addition of D<sub>2</sub>O. In principle, the sulfo group in *trans*-**1b–e** can form both intramolecular and intermolecular ion pairs (IntraIP and InterIP, respectively) with the positively charged nitrogen atom of the benzothiazolium residue, whereas the *p*-sulfo group in *trans*-**1f** can be involved only in InterIP. Upon an increase in the ratio of D<sub>2</sub>O (W) to CD<sub>3</sub>CN (A), one should expect the formation of a solvent-separated IntraIP or even complete dissociation of the IntraIP, due to the strong solvation of the sulfo group (Scheme 4).

In fact, as the W:A ratio varied from 1:100 to 1:3.4 for *trans*-**1e** (Fig. 1) and to 1:8.3 for *trans*-**1c,d**, the chemical shifts of the H(2') protons of the benzocrown-ether moiety and the H(a) proton continuously decreased by 0.35–0.43 ppm (Table 1) and by 0.29–0.34 ppm, respectively. No chemical shift changes were observed for *trans*-**1a** while the W:A ratio increased, *i.e.* in this case, no ion pair between the ClO<sub>4</sub><sup>−</sup> ion and the positively charged nitrogen atom of the benzothiazolium residue was formed.

Table 1 <sup>1</sup>H NMR chemical shifts (δ, ppm) of *trans*-**1e** at different D<sub>2</sub>O:CD<sub>3</sub>CN volume ratios at 40 °C

Protons	D <sub>2</sub> O:CD <sub>3</sub> CN					Δδ <sup>a</sup>
	1:100	1:20	1:11	1:6	1:34	
<b>Benzothiazole</b>						
H(4)	8.51	8.40	8.34	8.24	8.17	0.34
H(5)	7.85	7.83	7.81	7.79	7.77	0.08
H(6)	7.76	7.74	7.72	7.72	7.69	0.07
H(7)	8.29	8.28	8.27	8.26	8.21	0.08
<b>Sulfobenzyl</b>						
H(3'')	7.96	7.96	7.95	7.94	7.92	0.04
H(4'')	7.20	7.22	7.24	7.23	7.25	−0.05
H(5'')	7.08	7.11	7.12	7.13	7.13	−0.05
H(6'')	6.62	6.64	6.63	6.61	6.59	0.03
CH(1'') <sub>2</sub> N	6.49	6.50	6.48	6.46	6.42	0.07
<b>CH=CH</b>						
H(a)	8.30	8.13	8.03	7.95	7.87	0.43
H(b)	7.98	8.02	8.04	8.04	8.03	−0.05
<b>Benzocrown ether</b>						
H(2')	7.87	7.73	7.66	7.58	7.52	0.35
H(5')	6.89	6.91	6.91	6.92	6.92	−0.03
H(6')	7.24	7.28	7.29	7.29	7.29	−0.05

<sup>a</sup> Δδ is the overall change in the chemical shift (the difference between the second and the sixth columns).



Scheme 4

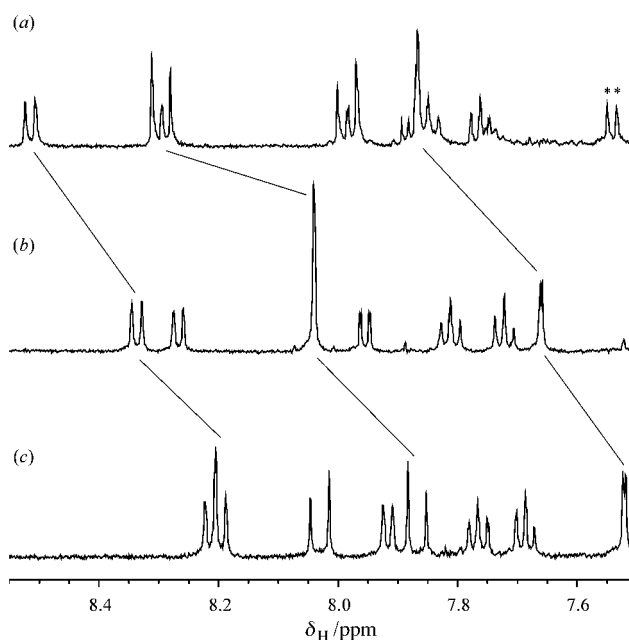
Analysis of the spatial structures of *trans*-**1b–e**, as predicted by quantum-chemical PM3 calculations (Fig. 2 and Table 2), showed that these protons are likely to fall into the sulfo group deshielding region, which could result in an increase in their chemical shifts. When a solvent-separated IntraIP is formed or when the IntraIP completely dissociates, the distance between the sulfo group and the above protons increases. This should weaken or eliminate the deshielding effect, as was actually observed in the experiment.

In the case of *trans*-**1b**, the addition of D<sub>2</sub>O (W:A is up to 1:2.5) decreased the chemical shift of the H(a) proton by 0.37 ppm, whereas the displacement of the signal for the H(2') proton was only 0.11 ppm. Apparently, the orientation of the sulfo group of the *N*-substituent is unfavourable for the H(2') proton of the benzocrown-ether moiety to be effectively deshielded.

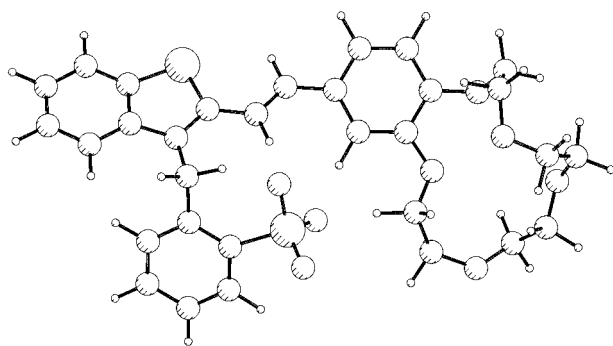
In the case of *trans*-**1b,e**, larger amounts of D<sub>2</sub>O are needed to attain the maximum change in the chemical shifts of the H(a) and H(2') protons, suggesting that the sulfo groups in these dyes are less prone to form hydrogen bonds with D<sub>2</sub>O than those in *trans*-**1c,d**. Some difference is also noticed between *trans*-**1b–d** and *trans*-**1e**. In the case of *trans*-**1e**, the chemical

**Table 2** PM3 calculated distances ( $R$ ) from the  $\text{SO}_3^-$  groups to the hydrogen atoms, the nitrogen atom, or the magnesium ion, dihedral angles ( $\tau$ ) between the benzothiazolium residue and the benzene ring of the crown-ether moiety in *trans-1b-f* and (*trans-1b-f*) $\cdot\text{Mg}^{2+}$ , and differences between the energies of formation for the complex and the free dye molecule ( $E_2 - E_1$ ) for CSD *trans-1b-f*

Compound	$R/\text{\AA}$						$\tau/\text{deg}$	$E_2 - E_1/\text{kcal mol}^{-1}$
	$\text{SO}_2\text{O}^- \cdots \text{N}^+$	$\text{SO}_2\text{O}^- \cdots \text{H}(1'')$	$\text{SO}_2\text{O}^- \cdots \text{H}(a)$	$\text{SO}_2\text{O}^- \cdots \text{H}(2')$	$\text{SO}_2\text{O}^- \cdots \text{H}(a)$	$\text{SO}_2\text{O}^- \cdots \text{Mg}^{2+}$		
<i>trans-1b</i>	3.9	2.7	1.8	1.8	1.9		17.5	
( <i>trans-1b</i> ) $\cdot\text{Mg}^{2+}$	3.7	2.4	1.8	1.8	1.7	5.2	22.8	264.81
<i>trans-1c</i>	3.5	1.8	1.8	1.8	1.8		13.3	
( <i>trans-1c</i> ) $\cdot\text{Mg}^{2+}$	3.7	1.8	1.8	1.8	1.7	5.2	23.5	258.94
<i>trans-1d</i>	3.6	1.7	1.7	2.3	2.6		-8.2	
( <i>trans-1d</i> ) $\cdot\text{Mg}^{2+}$	3.7	1.7	1.8	1.8	1.7	5.2	36.9	255.81
<i>trans-1e</i>	3.6	1.7	1.8	1.8	1.8		28.3	
( <i>trans-1e</i> ) $\cdot\text{Mg}^{2+}$	3.7	1.8	1.7	1.8	1.7	5.2	36.5	259.18
<i>trans-1f</i>	7.0	6.9	5.2	4.5	3.1		29.0	
( <i>trans-1f</i> ) $\cdot\text{Mg}^{2+}$	6.8	7.1	4.2	3.8	2.7	4.1	108.5	256.96



**Fig. 1** Dependence of the  $^1\text{H}$  NMR spectra of *trans-1e* in  $\text{CD}_3\text{CN}$  (A)- $\text{D}_2\text{O}$  (W) on the solvent ratio (by volume): A/W = 100 (a), 11 (b), 3.4 (c) at  $T = 40^\circ\text{C}$ . The straight lines show the change in the chemical shifts of H(4), H(a), and H(2'). The peaks marked by \* correspond to impurities.



**Fig. 2** Spatial structure of *trans-1e* calculated by the quantum-chemical PM3 method.

shift of H(4) in benzothiazole gradually decreased by a substantial value (up to 0.34 ppm) upon the addition of water. Apparently, the large chemical shift of this proton (8.51 ppm) in an ion pair is due to the fact that it falls into the region of deshielding of the benzene ring of the *o*-sulfofenyl group (Fig. 2).

In the case of *trans-1f*, unlike *trans-1b-e*, none of the proton chemical shifts underwent similar changes upon an increase in the W:A ratio, which might imply that formation of an IntraIP

is not possible. The validity of this hypothesis was confirmed by the results of the PM3 calculations (Table 2), according to which the distance between the  $\text{SO}_3^-$  group and the H(2') and H(a) atoms in *trans-1f* is much longer than the corresponding distances in other CSD. On the contrary, the formation of InterIP in *trans-1f* in the solid phase is quite possible. This was supported by solid-state  $^{13}\text{C}$  NMR data (CP MAS), where the C-13 lines in the spectrum of *trans-1f* were much broader than those in the spectrum of *trans-1e*. Although the quantitative analysis of the line widths is quite a complicated task, it showed that these dyes have different intermolecular interactions, which might be a result of the formation of the InterIP for *trans-1f* and IntraIP for *trans-1e* in the solid phase.

#### Quantum-chemical calculations

In order to perform a detailed interpretation of the experimental results, we carried out comparative analysis of the structures of *trans-1b-f* and (*trans-1b-f*) $\cdot\text{Mg}^{2+}$  (Scheme 5) using the semiempirical PM3 quantum-chemical method with geometry optimization. The key geometric and energy parameters from the calculations are presented in Table 2.

It was found that the *N*-substituent sulfo group in (*trans-1b-f*) $\cdot\text{Mg}^{2+}$  is located between the positively charged nitrogen atom in the benzothiazolium residue and the  $\text{Mg}^{2+}$  cation; in the case of *N*-sulfoalkyl and *N*-(*o*-sulfofenyl) substituents, the  $\text{SO}_3^-$  group is arranged substantially closer to the nitrogen atom (3.5–3.9 Å) than to  $\text{Mg}^{2+}$  (5.2 Å), whereas with the *N*-(*p*-sulfofenyl) substituent, it is located much closer to the  $\text{Mg}^{2+}$  cation (4.1 Å) than to the nitrogen (6.8–7.0 Å). These distances change only slightly upon complexation of the dyes.

The  $\text{SO}_3^-$  group oxygens in *trans-1b,c,e* and (*trans-1b,c,e*) $\cdot\text{Mg}^{2+}$  have short distances (1.7–1.8 Å) to three hydrogen atoms: H(a) of the double bond, H(2') of the benzene ring, and H(a) of the crown-ether moiety. In addition, the  $\text{SO}_3^-$  group in *trans-1c,e* is in close vicinity to the H(1'') atom of the *N*-substituent. A specific feature of the structure of *trans-1e* (Fig. 2) is that the H(4) atom of the benzothiazolium residue lies in the plane of the benzene ring being a part of the *N*-(*o*-sulfofenyl) substituent and is arranged close to this ring, which should strongly influence the NMR chemical shift of this proton. Indeed, the deshielding effect of the aromatic ring was observed for H(4) in our experiments (8.17–8.51 ppm, Table 1).

In the case of *trans-1d*, the  $\text{SO}_3^-$  group is located close to two hydrogen atoms: H(1'') of the *N*-substituent and H(a) of the double bond. In addition, this group in (*trans-1d*) $\cdot\text{Mg}^{2+}$  proves to have short distances to two more hydrogen atoms, the benzene-ring H(2') and crown-ether H(a) atoms.

In *trans-1f* and (*trans-1f*) $\cdot\text{Mg}^{2+}$ , the  $\text{SO}_3^-$  group is more distant from all of the hydrogen atoms. Only in the case of (*trans-1f*) $\cdot\text{Mg}^{2+}$ , the planarity of the chromophore is strongly distorted, whereas in other dyes and their complexes, the chromo-

phores are distorted relatively slightly; this distortion becoming somewhat more pronounced upon complex formation.

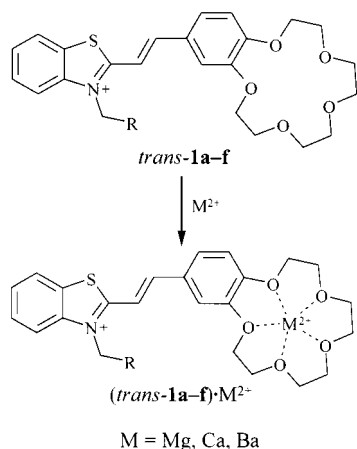
The results of the PM3 calculations are in good agreement with the experimental  $^1\text{H}$  NMR data obtained for dyes **trans-1c-f** (Table 1), in spite of the level of the calculations. To a large extent, this justifies the theoretical approach chosen for the structure analysis of the compounds in question.

The complex formation of **trans-1b** is 5.6–9 kcal mol $^{-1}$  less favourable than that of dyes **trans-1c-f** (Table 2), which may correspond to a difference of 2 log  $K$  units. However, we are actually equating the differences between the energies of complexation calculated for vacuum to the differences between the free energies of complexation in solution, which is generally not correct and can be justified only for compounds having very close structures, which are solvated and complexed in similar fashions. Apparently, in our case, this condition is fulfilled.

In fact, the order of increasing stability for 1:1 complexes of the dyes, **trans-1b** < **trans-1e** < **trans-1c** < **trans-1f** < **trans-1d**, predicted by calculations (Table 2) is completely matched by the sequence of variation of the experimental  $K$  values for (**trans-1b-f**) $\cdot\text{Mg}^{2+}$  (Table 3). As shown below, the effective stability constant  $K$  may contain a contribution from dimerization of the complexes. The agreement between theory and experiment indicates that this contribution due to dimerization is likely to be insignificant.

#### Complex formation of *trans*- and *cis*-isomers of CSD

The addition of Mg, Ca, or Ba perchlorates to solutions of CSD **trans-1a-f** in  $\text{CH}_3\text{CN}$  led to substantial hypsochromic shifts of the long-wavelength absorption band in the electronic spectra, indicating that the metal cations interact with the crown-ether moiety of the dye $^{5,15}$  (Scheme 5).



Scheme 5

Fig. 3 and 4 show the concentration dependence of the absorption spectra of  $\text{Mg}^{2+}$  complexes of **trans-1e,f**. The violation of Beer's law for both systems can be explained by assuming the occurrence of a dimerization equilibrium for the complexes in question (Scheme 2). The PCA reaction proceeding in dilute solutions of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  complexes of **trans-1e** confirmed the dimerization hypothesis. $^{15}$

It was found that the formation and dissociation of dimeric complexes are relatively slow processes. After dilution of a concentrated solution of the complexes and thorough stirring (for ~15 s), pronounced changes in the absorption spectrum of the dilute solution occurred over a period of 40–60 s. This effect allowed us to determine the wavelength at which the extinction coefficients of the 1:1 and 2:2 complexes (per one dye molecule) are equal. By bringing the recorded spectra to the known isosbestic point, we minimized the accidental errors in the concentration of the complexes (the maximum concentration correction did not exceed 1.5%).

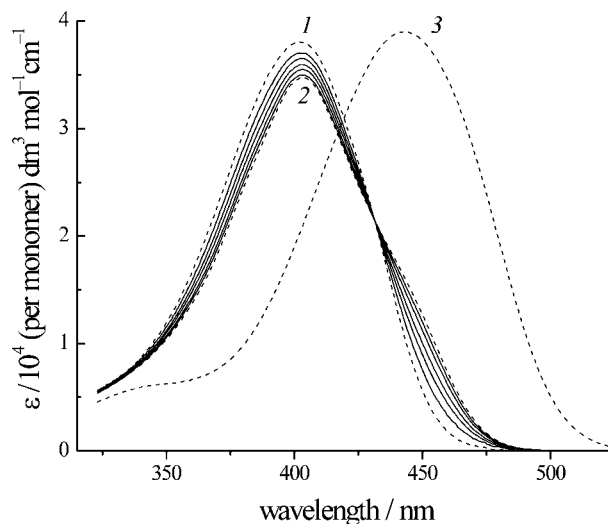


Fig. 3 Concentration dependence of the absorption spectrum of the  $\text{Mg}^{2+}$  complexes of **trans-1e** in  $\text{CH}_3\text{CN}$  ( $C_L$  varied from  $8.0 \times 10^{-7}$  to  $9.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ;  $C_M = C_L + 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ). Curves 1, 2 are the calculated spectra for (**trans-1e**) $\cdot\text{Mg}^{2+}$  (1) and [(**trans-1e**) $\cdot\text{Mg}^{2+}$ ] $_2$  (2); curve 3 is the spectrum of **trans-1e** without  $\text{Mg}^{2+}$  ions.

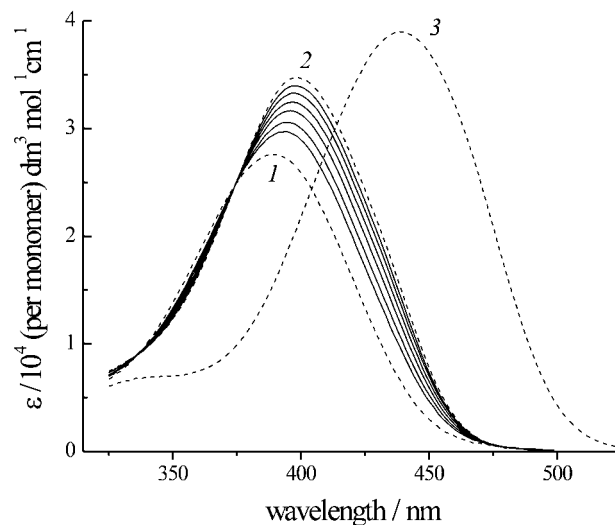
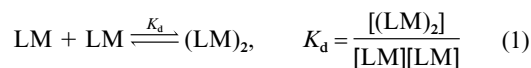


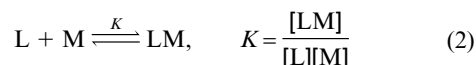
Fig. 4 Concentration dependence of the absorption spectrum of the  $\text{Mg}^{2+}$  complexes of **trans-1f** in  $\text{CH}_3\text{CN}$  ( $C_L$  varied from  $8.0 \times 10^{-7}$  to  $9.2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ;  $C_M = C_L + 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ). Curves 1, 2 are the calculated spectra for (**trans-1f**) $\cdot\text{Mg}^{2+}$  (1) and [(**trans-1f**) $\cdot\text{Mg}^{2+}$ ] $_2$  (2); curve 3 is the spectrum of **trans-1f** without  $\text{Mg}^{2+}$  ions.

To estimate the dimerization constants, the sets of absorption curves were reconstructed (Experimental) using the dimerization equilibrium (1), where L is the molecule of a *trans*-CSD,



M is the  $\text{Mg}^{2+}$  ion, and  $K_d$  is the dimerization constant. Both for **trans-1f** and **trans-1e**, total residual error for the reconstruction,  $\sigma_D$ , did not exceed an acceptable value of 0.002 (Experimental), indicating that the dimerization model holds. The calculated absorption spectra of the (**trans-1e,f**) $\cdot\text{Mg}^{2+}$  and [(**trans-1e,f**) $\cdot\text{Mg}^{2+}$ ] $_2$  complexes are shown in Fig. 3 and 4, and the  $K_d$  values are listed in Table 3.

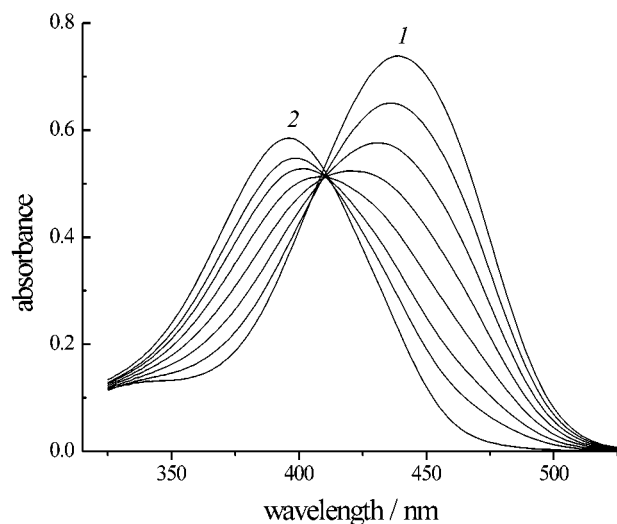
In order to estimate the ability of CSD to bind  $\text{Mg}^{2+}$  ions, the dependence of the absorption spectra of **trans-1e,f** on the concentration of these ions was studied (Experimental and Fig. 5). The sets of absorption curves were reconstructed using a simplified complex formation model, eqn. (2).



**Table 3** Stability constants for the  $\text{Mg}^{2+}$  complexes of *trans*- and *cis*-isomers of CSD **1a–f** in  $\text{CH}_3\text{CN}$  at 25 °C

Compound	$\log K$	Ionic strength/ $\text{mmol dm}^{-3}$	$\log K_d$	Ionic strength/ $\text{mmol dm}^{-3}$
B15C5 <sup>a</sup>	7.3	1.0	—	—
<i>trans</i> - <b>1a</b>	4.7	1.0	—	—
<i>trans</i> - <b>1b</b>	6.1	1.0	—	—
<i>trans</i> - <b>1c</b>	7.1	1.0	5.5	1.1–1.2
<i>trans</i> - <b>1d</b>	7.6	1.0	>6.5	1.1–1.2
<i>trans</i> - <b>1e</b>	6.7	1.0	5.5	1.1–1.2
<i>trans</i> - <b>1f</b>	7.3	1.0	5.7	1.1–1.2
<i>cis</i> - <b>1c</b>	9.4	1.1	—	—
<i>cis</i> - <b>1d</b>	10.3	1.1	—	—
<i>cis</i> - <b>1e</b>	7.3	1.1	—	—
<i>cis</i> - <b>1f</b>	10.0	1.1	—	—

<sup>a</sup> Benzo-15-crown-5 ether.



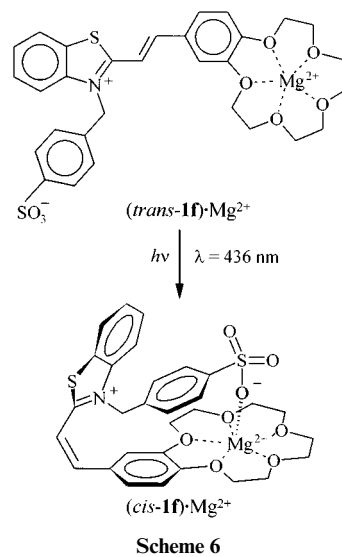
**Fig. 5** Dependence of the absorption spectrum of *trans*-**1f** ( $C_L = 3.4 \times 10^{-6} \text{ mol dm}^{-3}$ ) in  $\text{CH}_3\text{CN}$  on the concentration of  $\text{Mg}^{2+}$  ions.  $C_M$  ranged from 0 (**1**) to  $7.5 \times 10^{-6} \text{ mol dm}^{-3}$  (**2**).

For both dyes, the residual error for the reconstruction ( $\sigma_D = 0.005$  and  $0.007$  for *trans*-**1e,f** respectively) was markedly higher than the total experimental error for absorbance,  $\sigma_D \leq 0.002$ . This is not surprising since this model does not allow for the dimerization of the complexes. Furthermore, the dyes, like *trans*-**1e,f**, in the presence of small amounts of alkaline-earth metal perchlorates ( $C_M/C_L < 0.5$ ) may also form the complexes  $L_nM$  ( $n = 2-4$ ), which were detected in our previous study for an analogue of *trans*-**1c** containing an *N*-phenylaza-15-crown-5 ether moiety instead of the benzo-15-crown-5 ether fragment.<sup>20</sup>

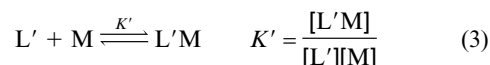
Thus, the parameter  $K$  obtained upon the modelling is not the real stability constant. It can instead be referred to as the “effective stability constant”. Apparently, this value can be used to compare the ability to bind  $\text{Mg}^{2+}$  ions in the series of *trans*-**1a–f** having similar structures. The  $K$  values were calculated using only the long-wavelength part of the absorption spectra (460–495 nm) in which the extinction coefficients of complexes of various types are apparently small compared to those of free CSD.

It was found previously that CSD **1e,f** in  $\text{CH}_3\text{CN}$  solutions undergo *trans*–*cis* isomerization upon irradiation with visible light, and the resulting *cis*-isomers form anion-“capped” complexes with  $\text{Mg}^{2+}$  (Scheme 6).<sup>15</sup>

The stability constants for these complexes were determined by the method of competing reactions,<sup>21</sup> using benzo-15-crown-5 ether (B15C5) as the competing ligand (Experimental). The complex formation of the *cis*-isomers in the presence of B15C5 was described by the reaction scheme involving eqn. (2) and (3),



**Scheme 6**



where  $L'$  is B15C5. The  $K$  value was calculated using the known  $K'$  value (Table 3). The results obtained are presented in Table 3.

In previous studies,<sup>16,21</sup> the  $K$  and  $K_d$  values for *trans*-**1a–d**, B15C5 and *cis*-**1c,d** were determined under different conditions (temperature, ionic strength of the solutions, concentration ranges of the reactants). To accurately compare the complexing ability over the whole series of CSD, we carried out new measurements for these compounds under conditions similar to those applied to CSD **1e,f** (Experimental). The constants  $K$  were estimated using the procedures described above. The  $K_d$  values for the  $\text{Mg}^{2+}$  complexes of *trans*-**1c,d** were determined by an original photochemical procedure,<sup>21</sup> since for these compounds, the differences between the absorption spectra of the 1:1 and 2:2 complexes were negligible. For *trans*-**1b**, we did not find reliable evidence for the existence of dimeric complexes with  $\text{Mg}^{2+}$  over the studied range of reactant concentrations. We failed to measure the stability constant for the  $\text{Mg}^{2+}$  complexes of *cis*-**1b**. However, the data obtained here confirmed the previous conclusion that *cis*-**1b** is unable to form an anion-“capped” complex.<sup>16</sup>

The data on complex formation of *trans*-**1a–f**, B15C5 and *cis*-**1c–f** with  $\text{Mg}^{2+}$  ions are summarized in Table 3. The effective stability constant  $K$  for *trans*-**1a** is about 400 times smaller than that for B15C5. This can be explained by two factors—the electron-withdrawing influence of the benzothiazolium residue in *trans*-**1a** and the electrostatic repulsion between the positively charged dye molecule and the metal cation. The introduction of highly electron-withdrawing substituents (for instance,  $\text{NO}_2$ ) into the B15C5 molecule is known to decrease the stability constants of its complexes with metal cations by not more than an order of magnitude.<sup>22</sup> Hence, the electrostatic factor makes a substantial contribution to the decrease in the stability of *trans*-**1a** complexes.

When a sulfo group is introduced in the *N*-substituent of a CSD, the positive charge is counterbalanced, and the effective stability constant for *trans*-**1b** increases by more than an order of magnitude. An increase in the length of the sulfoalkyl spacer increases the effective stability constant, the  $K$  value for *trans*-**1d** being approximately twice that for B15C5. It should be noted that the parameter  $K$  may be markedly greater than the stability constant for 1:1 complexes because it contains a contribution from dimerization of the complexes. Therefore, the higher  $K$  value found for *trans*-**1d** compared to that for B15C5 and *trans*-**1c** is apparently due, among other reasons, to the enhanced tendency of (*trans*-**1d**)· $\text{Mg}^{2+}$  to dimerize.

On passing from an *ortho*- to *para*-sulfo benzyl spacer, the effective stability constant  $K$  increases by a factor of more than 6, whereas the dimerization constant  $K_d$  changes only slightly. Thus, the increase in  $K$  is mostly due to the increased stability of the 1:1 complexes, which apparently is caused by the decrease in the average distance between the sulfo group and the metal cation (Table 2).

The stability constants for the  $Mg^{2+}$  complexes of *cis*-**1c–f** are substantially larger than those for the complexes formed by the corresponding *trans*-isomers. In the case of **1d,f**, this ratio of the constants is as high as 500. This is due to the fact that the sulfo group in the *cis*-form of the dye molecule and the  $Mg^{2+}$  ion located in the crown ether cavity are linked by an intramolecular coordination bond. The change in the electronic structure of the chromophore following the transition into the *cis*-configuration can also make some contribution to the magnitude of the constant. Thus, in the case of an analogue of the cationic dye **1a** which has an *N*-phenylaza-15-crown-5 ether moiety instead of the benzo-15-crown-5 ether group, the stability constant for the  $Ca^{2+}$  complex of the *cis*-isomer is about 2.5 times greater than that for the complex formed by the *trans*-isomer.<sup>23</sup>

The anion-“capped” complexes (*cis*-**1d**)· $Mg^{2+}$  are the most stable among similar complexes formed by other CSD, because they apparently possess the least strained spatial structure owing to the presence of the flexible and rather long sulfo butyl spacer. For the *cis*-isomers, the influence of the spacer structure on the complex stability is much more pronounced than for the *trans*-isomers. This refers most of all to CSD with conformationally rigid spacers. The ratio of the stability constants of the anion-“capped” complexes (*cis*-**1f**)· $Mg^{2+}$  and (*cis*-**1e**)· $Mg^{2+}$  is about 500.

## Conclusions

The crown-containing styryl dyes show an ability to form with metal cations supramolecular complexes of various structure, stoichiometry and stability. Irradiation with visible light may induce dramatic changes both in the structure and stability of the complexes, thus providing the possibility to control the complex formation process. The *trans*-isomers of CSD are capable of self-assembling into dimeric complexes, and the photoinduced *cis*-isomers may form more stable anion-“capped” complexes. The properties of CSD as light-controlled ionophores and their ability to form supramolecular complexes may be markedly affected by varying the structure of a spacer containing a sulfo group. A detailed analysis of the structure and complexation of CSD demonstrates the possibility of assembling photoswitchable molecular devices with different properties from these molecules and metal cations.

## Experimental

### Synthesis

The synthesis of *trans*-**1a–f** was described previously.<sup>15,16,24</sup> The anion-“capped” complexes of *cis*-**1c–f** were obtained photochemically<sup>15,16</sup> (purity  $\geq 99\%$  for *cis*-**1f** and  $\geq 97\%$  for *cis*-**1e**). Acetonitrile (for spectrophotometry,  $\lambda \geq 197$  nm) was distilled over  $CaH_2$  to remove traces of water.  $Mg(ClO_4)_2$  and  $Et_4NClO_4$  were dried *in vacuo* at 230 and 40 °C, respectively.

### NMR Spectroscopy

$^1H$  NMR spectra were recorded at 25 and 40 °C in  $CD_3CN$  on Bruker DRX-500 and Bruker AMX2-500 spectrometers operating at 500.13 MHz for protons. The chemical shifts were measured with an accuracy of 0.01 ppm, and spin–spin coupling constants were determined with an accuracy of 0.1 Hz. The 2D NOESY spectra of *trans*-**1b,d,e** were measured using the TPPI technique. The mixing time was 700 ms, the delay between

scans was 1 s, and the number of scans was 16 or 32 (per each  $t_1$  point). A total of 512  $t_1$  points and 2048  $t_2$  points were accumulated. Zero-filling over the indirect coordinate  $t_1$ , the squared sinusoidal filter with a  $\pi/2$  shift along  $t_1$ , and the Lorentz–Gaussian filter along  $t_2$  were used before the Fourier transformation. The signals in the  $^1H$  NMR spectra of *trans*-**1b,d,e** were assigned based on nuclear Overhauser effects (NOE) obtained from the NOESY experiment.

### Stability constants

The stability constants for the complexes of *trans*- and *cis*-isomers of CSD **1e,f** with  $Mg^{2+}$  ions were determined in anhydrous  $CH_3CN$  at 25 °C by spectrophotometric methods (the spectral parameters for both isomers and their complexes were reported previously).<sup>15</sup>

In the case of *trans*-isomers, two procedures were used: *i*) Absorption spectra were recorded for solutions with identical total dye concentration ( $C_L = 3.4 \times 10^{-6}$  mol  $dm^{-3}$ ) and variable total  $Mg^{2+}$  concentration ( $C_M$ , ranging from 0 to  $7 \times 10^{-5}$  mol  $dm^{-3}$ , 12 solutions, a cell of 5.5 cm pathlength). *ii*) Absorption spectra were recorded for solutions with variable dye concentration ( $C_L$ , ranging from  $8 \times 10^{-7}$  to  $9 \times 10^{-5}$  mol  $dm^{-3}$ , 10 solutions, cells of 5.5, 1, and 0.2 cm pathlengths); in this case the total  $Mg^{2+}$  concentration was  $C_M = C_L + 1.0 \times 10^{-4}$  mol  $dm^{-3}$ . This concentration of  $Mg^{2+}$  ions ensured complete binding of the dye. In order to eliminate the influence of the variation of  $C_M$  or  $C_L$  on the equilibria of the possible reactions between the complexes and perchlorate ions,<sup>21</sup> the total concentration of  $ClO_4^-$  was maintained constant ( $1.0 \times 10^{-3}$  mol  $dm^{-3}$ ) in both cases by adding  $Et_4NClO_4$  as the supporting electrolyte. The ionic strength of the solutions varied only slightly,  $(1.0–1.2) \times 10^{-3}$  mol  $dm^{-3}$ .

To estimate the complex stability constants from the spectrophotometric data, we applied the parameterized matrix modelling method.<sup>25,26</sup> This method provides the simultaneous estimation of stability constants and absorption spectra of complexes. A set of concentration-dependent absorption spectra is reconstructed with a complex formation model. The model holds, if the total residual error for the reconstruction ( $\sigma_D$ ) does not exceed the experimental error. The total experimental error for absorbance was evaluated with simple systems like  $B15C5 + Mg^{2+}$  and *trans*-**1a** +  $Mg^{2+}$ ,  $\sigma_D \leq 0.002$ .

The stability constants for the complexes of *cis*-**1e,f** were determined by the competing reaction method.<sup>21</sup> In this case, the optical density ( $\lambda = 430$  nm, 1 cm cell) was measured for solutions containing a dye ( $2.5 \times 10^{-5}$  mol  $dm^{-3}$ ),  $Mg(ClO_4)_2$  ( $5.0 \times 10^{-5}$  mol  $dm^{-3}$ ), and a competing ligand the concentration of which varied from 0 to 0.1 mol  $dm^{-3}$  (7 solutions).  $B15C5$ , which does not absorb visible light, was used as the competing ligand. The total concentration of the  $ClO_4^-$  ions was maintained at the same level as in the experiments with *trans*-isomers (by adding  $Et_4NClO_4$ ). The ionic strength of the solutions was  $1.1 \times 10^{-3}$  mol  $dm^{-3}$ . The procedure for data processing has been described in a previous publication.<sup>21</sup>

The absorption spectra were obtained on a Specord-M40 spectrophotometer interfaced with a PC XT. The spectra were recorded using quartz cells maintained at a constant temperature; the inner surface of the cells was modified by hydrophobic groups. The experiments were carried out in red light.

### Quantum-chemical calculations

PM3 calculations were done with HyperChem.<sup>27</sup>

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