Photoswitchable molecular pincers: synthesis, self-assembly into sandwich complexes and ion-selective intramolecular [2+2]-photocycloaddition of an unsaturated bis-15-crown-5 ether

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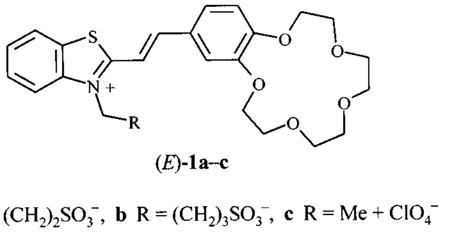
Bis-crown-containing styryl dyes (*E*,*E*)-**2a**,**b** having the structure and properties of molecular pincers were synthesised. In acetonitrile solution, dye (*E*,*E*)-**2b** is able to form intramolecular sandwich complexes with Ca^{2+} and Ba^{2+} cations. These complexes undergo *E*–*Z*-photoisomerisation and intramolecular stereoselective [2+2]-photocycloaddition to afford cyclobutane derivatives **6a**,**b**, whose structures were studied by ^1H NMR spectroscopy. Molecular-mechanics and semiempirical quantum-chemical calculations were performed to interpret experimental data.

Introduction

A rational molecular design of multicomponent structures obtained upon self-assembly[1–4] in solution, containing photosensitive units,[5–9] made it possible to create a series of simple photoswitchable molecular devices.[10–13] Previously we reported the synthesis of crown-containing styryl dyes (CSD).[14,15] The CSD of type (*E*)-**1a**,**b** are capable of forming supramolecular complexes containing two dye molecules and two metal cations. The self-assembly of the dimeric complexes was shown to be a unique tool for controlling regio- and stereoselectivity of [2+2]-photocycloaddition (PCA) of CSD.[16] Another photochemical reaction involving CSD complexes is a reversible *E*–*Z*-isomerisation. The resulting *Z*-isomers of CSD are able to form intramolecular anion-"capped" complexes in which the sulfo group of the *N*-substituent interacts with the metal cation located in the crown-ether cavity.[15] The anion-"capped" and dimeric complexes formed by CSD can be considered to be simple photoswitchable molecular devices, since their cation-binding ability dramatically changes on exposure to light,[17] *i.e.* the complex formation process can be controlled.



(*E*)-**1a–c**

a $R = (CH_2)_2SO_3^-$, **b** $R = (CH_2)_3SO_3^-$, **c** $R = Me + ClO_4^-$

Bis-crown ethers in which two macroheterocycles are linked by a relatively short chain are of special interest because they are pre-organised for the formation of intramolecular sandwich complexes. These compounds can form more stable complexes and exhibit higher cation-binding selectivity than their monocyclic analogues, due to the co-operative effect of the two crown-ether moieties.[18,19] We suggested that integration of two crown-containing styryl chromophores into one molecule by means of a polymethylene chain (spacer) would create conditions for a new type of self-assembly of photoresponsive supramolecular systems incorporating metal cations with large ionic radii.

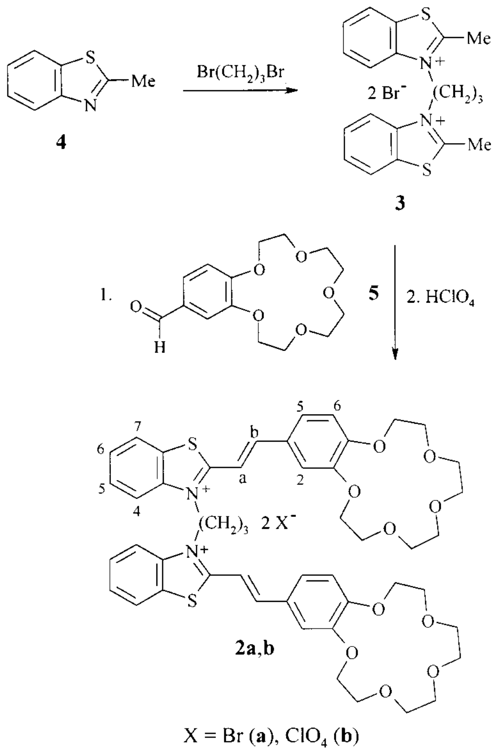
In this work, we describe the synthesis of a bis-crown-containing styryl dye (bisCSD) of the benzothiazole series **2b** and the results of a study of the complex formation of **2b** with large metal cations and of the intramolecular [2+2]-photocycloaddition of this dye. The CSD (*E*)-**1c**, the chromogen of which is identical to that of dye **2b**, was used as a reference compound.

Synthesis

CSD (*E*)-**1c** was prepared by the three-step procedure published previously.[20] The synthesis of bisCSD **2a**,**b** is presented in Scheme 1. A method for the synthesis of the bis-quaternary salt **3** has been described previously;[21] however, the target product was only formed in low yield (10%). In addition, in the study cited, no evidence for the structure of **3** was presented. We found that **3** can be synthesised in a satisfactory yield when a four-fold excess of 2-methylbenzothiazole (**4**) is employed.

Condensation of **3** with 4′-formylbenzo-15-crown-5 ether **5** in the presence of pyridine as base gave dye **2a** in addition to a cyanine dye side product, as determined by spectrophotometry. No cyanine dye was detected among the products of condensation of compounds **3** and **5** in acetic anhydride. In this case, the yield of **2a** was 47%. Diperchlorate **2b** was prepared in 94% yield by adding an excess of perchloric acid to an ethanolic solution of dibromide **2a**.

The purity of dyes (*E*)-**1c** and **2a**,**b** was analysed by reversed-phase HPLC using aqueous CH_3CN as eluent. The reversed-phase retention of crown ethers was found to be governed by a dual mechanism, because these compounds interact with both the nonpolar stationary phase and the accessible silanol groups



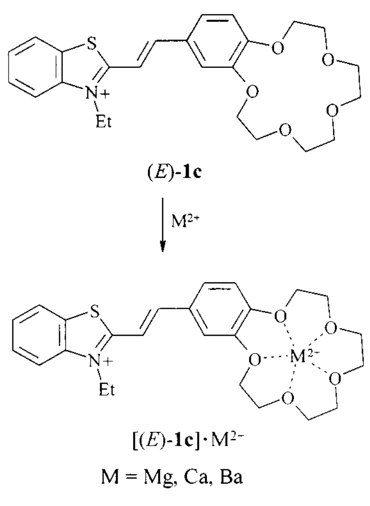
Scheme 1

on the silica surface.[22] In our studies, the silanophilic retention was obliterated by adding a silanol-masking agent (NaClO$_4$) to the eluent. In this case, the retention behaviour was mainly determined by the hydrophobic interaction, which accounts for the fact that the retention time of bisCSD **2a**,**b** (7.3 min) was longer than that of (*E*)-**1c** (5.6 min).

The structures of compounds **3** and **2a**,**b** were determined by two-dimensional (2D) ^{1}H NMR spectroscopy. According to the values of the vicinal spin–spin coupling constants found for the olefinic protons ($^3J_{trans}$ = 15.6 Hz), bisCSD **2a**,**b** have (*E*,*E*)-configuration.[23] The elemental analysis data agree with the proposed structures.

Complex formation

The addition of Mg, Ca, or Ba perchlorate to acetonitrile solutions of CSD (*E*)-**1c** resulted in substantial hypsochromic shifts of the long-wavelength absorption band. This observation indicates that these metal cations interact with the crown-ether moiety of the dye[13] (Scheme 2). Cation-induced hypsochromic effects were also observed for dye (*E*,*E*)-**2b**.



Scheme 2

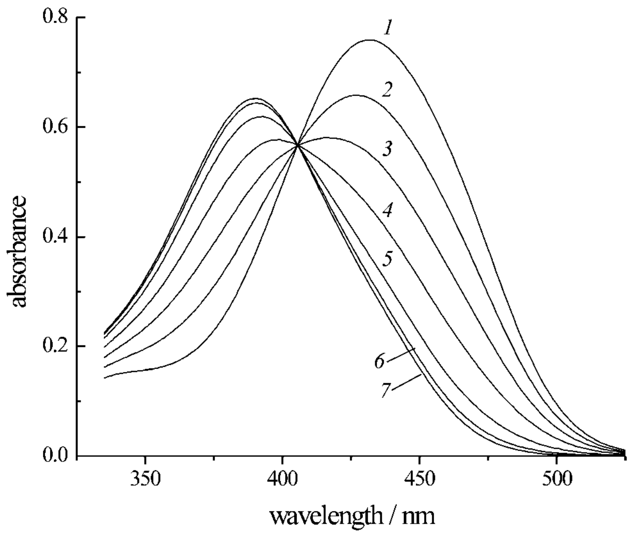


Fig. 1 Absorption spectra of (*E*,*E*)-**2b** (2 × 10^{-6} mol dm^{-3}) in CH$_3$CN in the absence (*1*) and in the presence (*2*–*7*) of Ba^{2+} ions at C_M/C_L = 0.24 (*2*), 0.47 (*3*), 0.70 (*4*), 0.92 (*5*), 1.13 (*6*), 10 (*7*). The calculated absorption spectrum of the complex [(*E*,*E*)-**2b**]·Ba^{2+} virtually coincides with curve *7*.

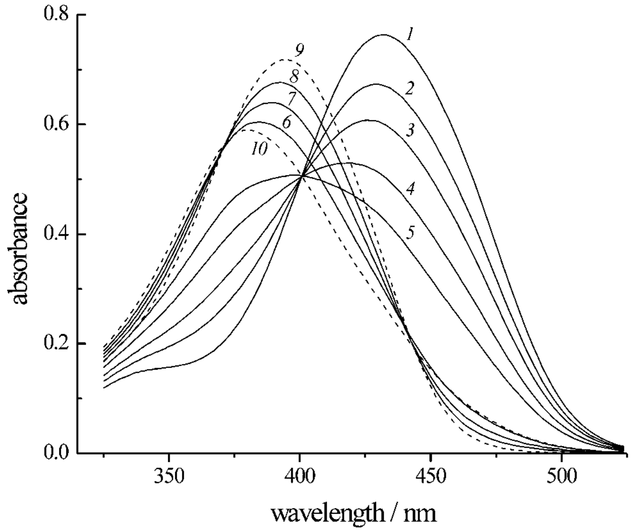


Fig. 2 Absorption spectra of (*E*,*E*)-**2b** (2 × 10^{-6} mol dm^{-3}) in CH$_3$CN in the absence (*1*) and in the presence (*2*–*8*) of Ca^{2+} ions at C_M/C_L = 0.4 (*2*), 0.8 (*3*), 1.6 (*4*), 2.7 (*5*), 42 (*6*), 140 (*7*), 400 (*8*). Curves *9* and *10* represent the calculated absorption spectra of the complexes [(*E*,*E*)-**2b**]·(Ca^{2+})$_2$ and [(*E*,*E*)-**2b**]·Ca^{2+} respectively.

For (*E*,*E*)-**2b** with Ba^{2+} (Fig. 1) and for (*E*)-**1c** with Ca^{2+} and Ba^{2+}, the variation of the concentration of metal cation in acetonitrile solution of the dye led to spectral changes typical of two-component systems. More complicated spectral changes occurred in the case of (*E*,*E*)-**2b** with Ca^{2+} (Fig. 2).

To determine the complexation stoichiometry and to estimate the stability constants of the complexes, sets of the absorption curves were analysed and reconstructed using matrix algebra methods.[24] For (*E*,*E*)-**2b** with Ca^{2+}, the spectrophotometric data were interpreted in terms of a complex formation model comprising two equilibria [eqns. (1) and (2)],

$$\mathrm{L} + \mathrm{M} \overset{K_1}{\rightleftharpoons} \mathrm{LM}, \quad K_1 = \frac{[\mathrm{LM}]}{[\mathrm{L}][\mathrm{M}]} \qquad (1)$$

$$\mathrm{LM} + \mathrm{M} \overset{K_2}{\rightleftharpoons} \mathrm{LM_2}, \quad K_2 = \frac{[\mathrm{LM_2}]}{[\mathrm{LM}][\mathrm{M}]} \qquad (2)$$

where L is a dye molecule, M is a metal cation, and K_1 is the complex stability constant. For (*E*)-**1c** with Ca^{2+} and Ba^{2+} and

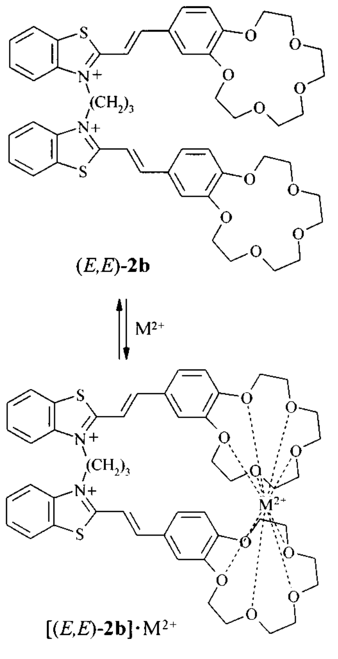
Table 1 Stability constants and positions of the long-wavelength absorption maxima for the complexes of dyes (*E*)-**1c** and (*E*,*E*)-**2b** with Ca^{2+} and Ba^{2+} ions[a]

Complex	log K_1	log K_2	λ/nm[a]	$\Delta\lambda$/nm[b]
[(*E*)-**1c**]·Ca^{2+}	4.78 ± 0.03	—	393	−37
[(*E*)-**1c**]·Ba^{2+}	4.39 ± 0.03	—	402	−28
[(*E*,*E*)-**2b**]·Ca^{2+}	5.68 ± 0.04	—	380	−52
[(*E*,*E*)-**2b**]·$(Ca^{2+})_2$	—	3.55 ± 0.03	395	−37
[(*E*,*E*)-**2b**]·Ba^{2+}	8.0 ± 0.1	—	390	−42

[a] CH_3CN solution, 25 °C; Et_4NClO_4 as supporting electrolyte. [b] $\Delta\lambda = \lambda_{max}(\text{complex}) - \lambda_{max}(\text{dye})$.

for (*E*,*E*)-**2b** with Ba^{2+}, the sets of concentration-dependent spectra were reconstructed in terms of a single equilibrium [eqn. (1)].

The stability constants and the positions of the absorption maxima for complexes of (*E*)-**1c** and (*E*,*E*)-**2b** with Ca^{2+} and Ba^{2+} ions are listed in Table 1. For (*E*,*E*)-**2b**, the stability constants of the 1 : 1 dye–metal complexes are significantly higher than those for (*E*)-**1c**. This can be attributed to the ability of bisCSD to form intramolecular sandwich complexes with Ca^{2+} and Ba^{2+} (Scheme 3).



M = Ca, Ba

Scheme 3

This increase in the stability constant is much more pronounced for Ba^{2+} than for Ca^{2+}, since the Ba^{2+} ion has a greater diameter and is more prone to form sandwich complexes with 15-crown-5 ethers.[25] A more detailed analysis of the complexation data for (*E*,*E*)-**2b** with Ca^{2+} and Ba^{2+} as well as with Mg^{2+} and Sr^{2+}, and the procedures used to estimate the stability constants will be reported elsewhere.

The changes of the absorption bands obtained for the 1 : 1 complexes of (*E*,*E*)-**2b** with Ca^{2+} and Ba^{2+} also support a sandwich structure of these complexes. For (*E*,*E*)-**2b**, the hypsochromic shift of the absorption maximum following the formation of 1 : 1 complexes is 14–15 nm larger than that for (*E*)-**1c**. In addition, the absorption bands of these complexes have a long-wavelength shoulder, which is clearly seen when comparing the spectra of the 1 : 1 and 1 : 2 dye–metal complexes of (*E*,*E*)-**2b** with Ca^{2+} (Fig. 2). Apparently, this is due to the splitting of the absorption band caused by intramolecular through-space interaction of the two identical chromophoric units which are closely located in the sandwich complex. This conclusion is supported by quantum-chemical calculations.

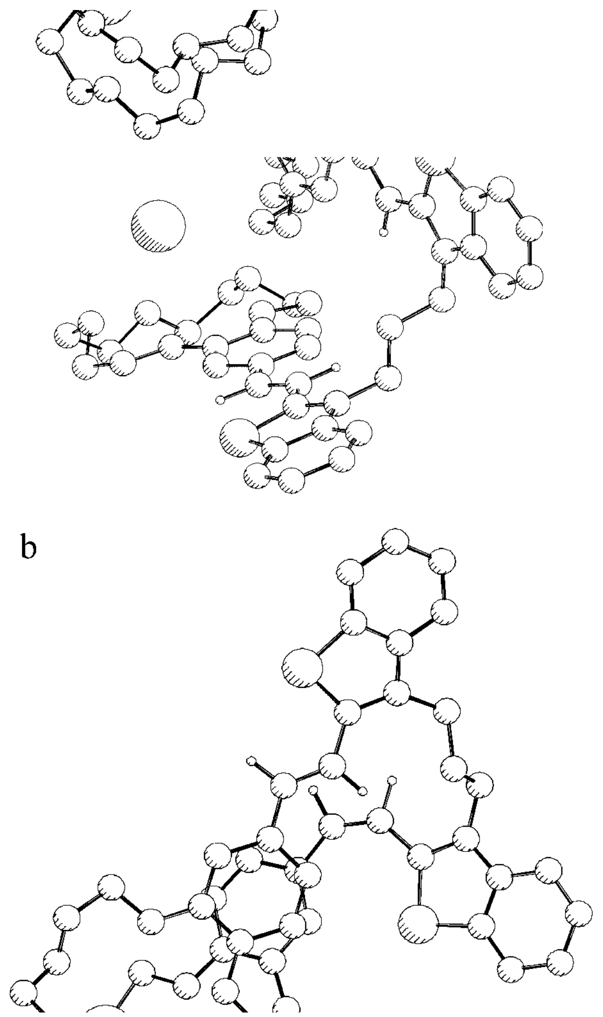


Fig. 3 Calculated spatial structures of [(*E*,*E*)-**2b**]·Ba^{2+} and [(*E*,*Z*)-**2b**]·Ba^{2+}.

Using the PCMODEL 3.2 program package, we constructed 3D models for the sandwich complex [(*E*,*E*)-**2b**]·Ba^{2+} (Fig. 3a) and for its open form in which the crown-ether moieties are separated by the maximum possible distance. In order to simplify the subsequent quantum-chemical calculations, the Ba^{2+} ions and the atoms of the crown-ether moieties, that do not contribute to the absorption of the chromophore, were excluded from the structures. The free valences thus formed were saturated by adding the appropriate number of hydrogen atoms. The energies of electron transitions in the resulting two conformations of the model bis-styryl dye were calculated by the semiempirical ZINDO/S quantum-chemical method with limited account of the configurational interactions. A similar calculation was carried out for the model styryl dye obtained from (*E*)-**1c** after excluding the atoms of the crown-ether moiety. All calculations were carried out with identical parameterisations of the method.

The long-wavelength electronic transition in the styryl dye model was found to occur at 422 nm. For the open conformation of the model bis-styryl dye, the band proved to be slightly split (425 nm, oscillator strength $f = 1.8$, and 435 nm, $f = 0.5$). Thus, the long-wavelength absorption band predicted for this conformation has a maximum at 425 nm and extends to longer wavelengths, which is due to a second, less intense electron transition. For the conformation corresponding to the sandwich complex, splitting of the absorption band was found to be much more pronounced (411 nm, $f = 2.0$, and 455 nm, $f = 0.47$). Hence, the predicted absorption band for this conformation should have a maximum at 411 nm and a noticeable shoulder at 455 nm.

Thus, the calculations carried out for the model bis-styryl dye indicate that the conformational changes that accompany the formation of the sandwich complex should lead to an additional shift of the absorption maximum to shorter wavelengths, which can be as large as 14 nm. The predicted magnitude of this shift is in good agreement with the experimental data obtained for (*E*,*E*)-**2b**. The additional shift of the absorption maximum is due to the specific changes in the spectrum of the bis-chromophore caused by interaction of the electronic oscillators of the two chromophore systems. In fact, the nearly parallel spatial arrangement of the chromophores, exactly facing each other in the sandwich complex, corresponds to the arrangement of molecules in *H*-aggregates, for which a hypsochromic shift of the absorption band also has been observed.[26] When two identical electronic oscillators are located close to each other, their in-phase and out-of-phase oscillations become energetically nonequivalent due to the correlation of the electron movement,[27] which results in a splitting of the absorption band. The closer the chromophores, the larger the splitting. In fact, the calculated splitting of the absorption band for the model bis-styryl dye conformation corresponding to the sandwich complex is four times larger than that for the open conformation of this dye.

Intramolecular [2+2]-photocycloaddition

The spontaneous assembly of bisCSD and metal cations with large ionic radii into sandwich complexes, which results in stacking and head-to-head alignment of unsaturated dye fragments, can become a new method for controlling the efficiency and stereoselectivity of intramolecular PCA with the formation of cyclobutanes. Therefore, we studied the effect of the metal ions on the photochemical behaviour of **2b** in acetonitrile solutions.

Irradiation of acetonitrile solutions of dyes (*E*)-**1c** and (*E*,*E*)-**2b** with 436 nm light of 4.7×10^{15} cm^{-2} s^{-1} intensity led to rapid changes in the absorption spectra, due to reversible *E*–*Z*-photoisomerisation. In both cases, a photostationary equilibrium between the geometric isomers was attained over a period of 1–2 min. On subsequent irradiation of these solutions for several hours, the absorption spectra did not change. A similar situation was observed for complexes of dye (*E*)-**1c** with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions and (*E*,*E*)-**2b** with Mg^{2+}. However, in the case of the Ba^{2+} complexes of bisCSD **2b**, prolonged photolysis of a photostationary mixture of the geometric isomers led to complete consumption of the dye (Fig. 4). The photolysates exhibited absorption spectra typical of the cyclobutane derivatives formed upon PCA of CSD of the benzothiazole series.[16,28]

The analysis of 2D COSY and NOESY NMR spectra of the PCA products showed the presence of two isomeric crown-containing cyclobutane derivatives **6a** and **6b** (Scheme 4) in 17:83 ratio.

The ^{1}H NMR spectrum of the cyclobutane protons in **6a** is described by a symmetrical spin system of the AA′BB′ type with the following set of vicinal spin–spin coupling constants: $^3J_{14} = {}^3J_{23} = 6.7$ and $^3J_{12} = {}^3J_{34} = 8.5$ Hz. Due to the spectral overlap, only the subspectrum of H(C-1) and H(C-2) protons was analysed (rms = 0.06 Hz) by assuming that $^3J_{34}$ is equal to $^3J_{12}$ and manually fitting the $^3J_{12}$ value. The resulting set of vicinal constants agrees well with the values $^3J_{trans} = 6.8$ and $^3J_{cis} = 9.0$ Hz, found by molecular-mechanics calculations for 1,2,3,4-tetraphenylcyclobutane with an arrangement of substituents similar to that in **6a**, after fast conformational averaging due to the low energy barrier.[29] For the crown-containing 1,2,3,4-tetrasubstituted cyclobutane studied previously, whose structure is also similar to that of **6a**, the vicinal spin–spin coupling constants are 7.61 and 10.29 Hz.[30] Apparently, the somewhat greater values compared to those found for **6a** are due to different internal dihedral angles in the cyclobutane rings.

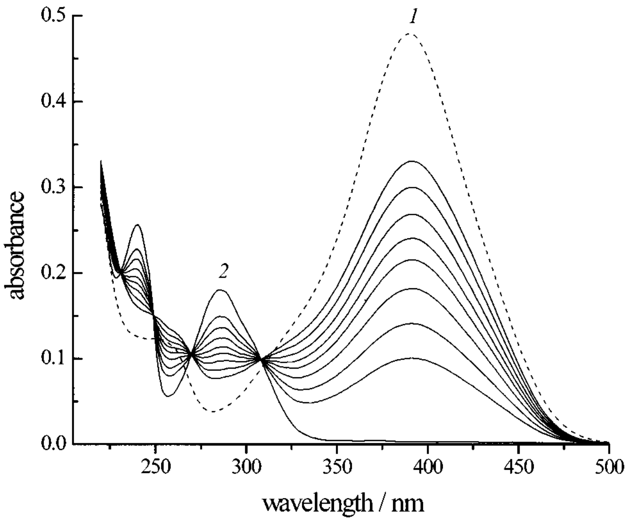
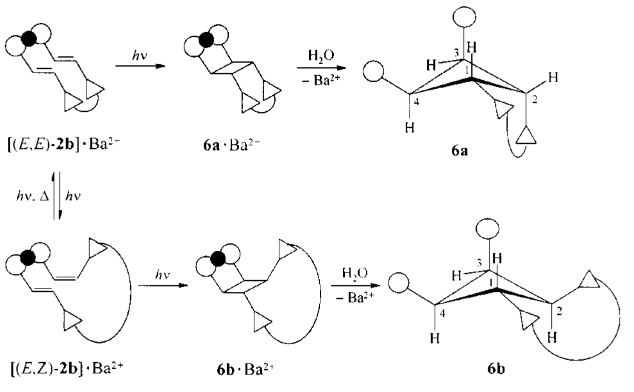
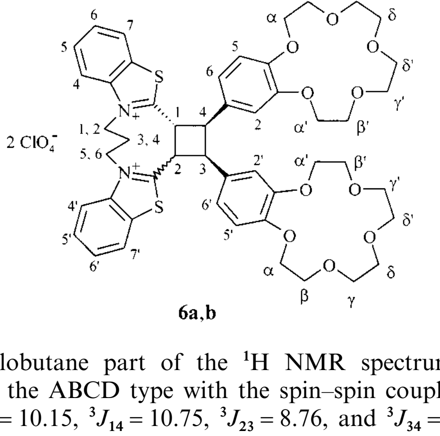


Fig. 4 Photolysis of (*E*,*E*)-**2b** (8.1×10^{-6} mol dm^{-3}) in CH_3CN solution containing $Ba(ClO_4)_2$ at a concentration of 1×10^{-4} mol dm^{-3}. The solution was irradiated with 436 nm light of 4.7×10^{15} cm^{-2} s^{-1} intensity. Curves *1* and *2* are spectra recorded before and after irradiation for 24 h respectively.



Notation. ○ is the benzo-15-crown-5-ether moiety; ▷ is the benzothiazole residue; ● is Ba^{2+}; ⌒ is $(CH_2)_3$

Scheme 4

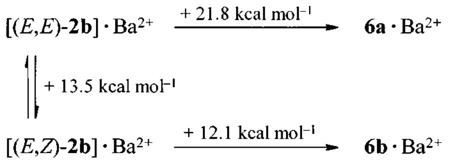


6a,b

The cyclobutane part of the ^{1}H NMR spectrum of **6b** belongs to the ABCD type with the spin–spin coupling constants $^3J_{12} = 10.15$, $^3J_{14} = 10.75$, $^3J_{23} = 8.76$, and $^3J_{34} = 9.97$ Hz found by iteration analysis. In principle, the intramolecular PCA of different geometric isomers of **2b** could give two different cyclobutane derivatives responsible for asymmetrical spectra of the ABCD type. Therefore, the ultimate conclusion about the structure of **6b** was based on the NOE observed between the cyclobutane protons H(C-2) and H(C-3), H(C-3) and H(C-4), and H(C-2) and H(C-4), indicating that these protons are located on one side of the cyclobutane ring (see Scheme 4). The theoretical vicinal coupling constants[31] calculated for the same isomer of 1,2,3,4-tetraphenylcyclobutane ($^3J_{12} = 10.91$, $^3J_{14} = 11.15$, $^3J_{23} = 9.11$, and $^3J_{34} = 9.46$ Hz) were very similar to those obtained in the experiment. It was also found that compound **6b** exists as an equilibrium mixture of two conformations in a ratio of approximately 7 to 3. At −10 °C, the spectrum of the minor conformation was essentially, but not completely, resolved. Although we were unable to analyse this spectrum thoroughly, exchange cross-peaks were detected in the NOESY spectra. However, the fact that the spin–spin coupling constants for the cyclobutane H(C-4) protons in the two conformations were nearly identical implied that this conformational equilibrium is not due to the cyclobutane ring inversion. In addition, the conformation of cyclobutane **6b** is stabilised by the second, newly formed, ring for which the diaxial fusion is energetically extremely unfavourable. Thus, the occurrence of two conformations is apparently due to the steric interaction between the benzocrown-ether moieties. In fact, the chemical shifts of the aromatic protons of the benzocrown-ether moieties in the two conformations of **6b** differed to a large extent. It is also noteworthy that the benzocrown-ether fragments in **6b**, like those in **6a**, occupy *cis*-positions; in both cases this is apparently predetermined by the sandwich structure of the preceding complexes with the Ba^{2+} ion. To date, this is the only example of PCA involving *cis*-CSD.

The quantum yield of the PCA involving the Ba^{2+} complex of **2b**, as calculated from the kinetics of the dye consumption, is about 0.001 (irradiation at 436 nm). The PCA reaction is photochemically reversible. Upon irradiation of cyclobutanes **6a**,**b** with 313 nm light, the initial dye **2b** was formed with a quantum yield of about 0.3. However, the total yield of **2b** was dependent on the conditions for the preparation of cyclobutanes **6a**,**b**. For samples obtained by prolonged irradiation with 436 nm light up to the complete consumption of the dye, the retroPCA yielded 85–90% of the initial dye (spectrophotometric monitoring). When the consumption of the dye in the PCA did not exceed 50%, the retroPCA resulted in full recovery of the dye. Reasons for this effect will be sought in future studies.

Fig. 3 and Scheme 5 present the results of a comparative theoretical analysis of the stereoselectivity of intramolecular PCA in sandwich complexes [(*E*,*E*)-**2b**]·Ba^{2+} and [(*E*,*Z*)-**2b**]·Ba^{2+}. The energetically most favourable conformations for these complexes (Fig. 3) and for the corresponding cyclobutanes **6a**·Ba^{2+} and **6b**·Ba^{2+} were determined with the PCMODEL 3.2 program using the MMX force field according to a previously described procedure.[17] For each of the conformations, the relative heat of formation was calculated (Scheme 5) (in relation to that of [(*E*,*E*)-**2b**]·Ba^{2+}, which was taken to be zero). For both complexes, cycloaddition is to a substantial extent an endothermic process, which partially accounts for the low quantum yield of PCA and the high quantum yield of the retroPCA.



Scheme 5

The spatial structures of [(*E*,*E*)-**2b**]·Ba^{2+} and [(*E*,*Z*)-**2b**]·Ba^{2+} (Fig. 3a and 3b, respectively) are most interesting. In [(*E*,*E*)-**2b**]·Ba^{2+}, the central C=C double bonds are separated by a distance of 5.7–7.1 Å, the planes of these bonds being nearly perpendicular to each other. This makes the PCA reaction unfavourable. In [(*E*,*Z*)-**2b**]·Ba^{2+}, the central C=C bonds are located at a distance of only 3.9–4.5 Å and their planes are nearly parallel to each other, explaining why PCA is favourable. A specific feature of the spatial structure of cyclobutane **6b**·Ba^{2+} is the *trans*-arrangement of the positively charged benzothiazolium residues in relation to the cyclobutane ring. As estimated by similar calculations, the alternative structure of **6b**·Ba^{2+} with *cis*-arrangement of the benzothiazolium residues and, correspondingly, with *trans*-arrangement of the crown-ether moieties in relation to the cyclobutane ring is 7.2 kcal mol^{-1} less favourable. Despite the fact that the total endothermic effect of the two-step cycloaddition, [(*E*,*E*)-**2b**]·Ba^{2+}→[(*E*,*Z*)-**2b**]·Ba^{2+}→**6b**·Ba^{2+}, is 3.8 kcal mol^{-1} larger than that for the one-step reaction, [(*E*,*E*)-**2b**]·Ba^{2+}→**6a**·Ba^{2+}, the specific features of the spatial structures of the sandwich complexes described above make the two-step pathway to **6b**·Ba^{2+} more favourable for the kinetic reasons.

This study demonstrates that bis-crown-containing styryl dyes can act as photoswitchable molecular pincers which are able to bind selectively the metal cations with large ionic radii *via* the formation of intramolecular sandwich complexes and, in addition, to produce a strong optical response. The stacking and the head-to-head alignment of the unsaturated dye fragments upon the sandwich complex-formation provide an opportunity for controlling the efficiency and stereoselectivity of intramolecular PCA. The results obtained in this study demonstrate that bisCSD-type molecules may be useful as structural units in the design of photoswitchable molecular devices.

Experimental

Synthesis

3,3′-Trimethylenebis(2-methylbenzothiazolium) dibromide (3). 1,3-Dibromopropane (0.18 cm^3, 1.8 mmol) was mixed with 2-methylbenzothiazole (1 cm^3, 7.8 mmol), and the mixture was heated for 6 h at 140 °C. The product was treated successively with boiling benzene, ether, and acetone and recrystallised from ethanol. The yield of **3** was 0.336 g (31%), mp 250 °C (lit.[21] 256 °C) (Found: C, 42.67; H, 4.52; N, 5.05. Calc. for $C_{19}H_{20}Br_2N_2S_2 \cdot 2H_2O$: C, 42.70; H, 4.53; N, 5.24%); δ_H([$^2H_6$]DMSO) 2.50† (2 H, m, CH_2), 3.33 (6 H, s, 2 CH_3), 5.12 (4 H, m, 2 CH_2N), 7.81 and 7.92 (4 H, 2 m, *J* 7.8, *J* 8.4, 2 H(C-5), 2 H(C-6)), 8.47 and 8.62 (4 H, 2 d, *J* 7.8, *J* 8.4, 2 H(C-7), 2 H(C-4)).

(*E*,*E*)-3,3′-Trimethylenebis{2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-15-yl)ethenyl]-1,3-benzothiazol-3-ium} dibromide (2a). *A*. Compounds **3** (0.173 g, 0.32 mmol) and **5** (0.41 g, 1.38 mmol) (lit.[32]) were added to acetic anhydride (5 cm^3). The reaction mixture was refluxed for 6 h and cooled, and 10 cm^3 of ether was added. The resulting precipitate was filtered off, washed with ether, refluxed with methanol (10 cm^3), and again filtered off. The yield of **2a** was 0.165 g (47%), mp 270–271 °C (Found: C, 53.47; H, 5.15; N, 2.43. Calc. for $C_{49}H_{56}Br_2N_2O_{10}S_2 \cdot 2H_2O$: C, 53.94; H, 5.55; N, 2.57%); δ_H([$^2H_6$]DMSO) 2.50† (2 H, m, CH_2), 3.65 (16 H, m, 8 CH_2O), 3.84 (8 H, m, 4 CH_2O), 4.19 (4 H, m, 2 CH_2O), 4.29 (4 H, m, 2 CH_2O), 5.48 (4 H, m, 2 CH_2N), 7.07 (2 H, d, *J* 8.4, 2 H(C-5) in benzocrown ether), 7.75 (2 H, d, 2 H(C-6) in benzocrown ether), 7.75 and 7.81 (4 H, 2 m, 2 H(C-5), 2 H(C-6) in benzothiazole), 7.89 (2 H, m, *J* 1.6, 2 H(C-2) in benzocrown ether), 8.14 (2 H, d, *J* 15.6, 2 H(C-a)), 8.25 (2 H, d, *J* 15.6,

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† The signals of the CH_2 protons are overlapped by [$^2H_6$]DMSO.

2 H(C-b)), 8.40 and 8.61 (4 H, 2 d, *J* 7.8, *J* 8.4, 2 H(C-7), 2 H(C-4) in benzothiazole).

B. Pyridine (4 cm^3) was added to a solution of **3** (0.173 g, 0.32 mmol) and **5** (0.20 g, 0.67 mmol) in anhydrous ethanol (5 cm^3). The reaction mixture was refluxed for 9 h in an argon stream, the solvent was evaporated, and the residue was washed with ether. The precipitate that formed was refluxed with methanol (10 cm^3) and filtered off. The yield of **2a** was 0.06 g (17%), mp 266–268 °C.

(*E*,*E*)-3,3′-Trimethylenebis{2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-15-yl)ethenyl]-1,3-benzothiazol-3-ium} diperchlorate (2b). Compound **2a** (0.025 g, 0.023 mmol) was dissolved with heating in methanol (5 cm^3), and 57% $HClO_4$ (0.040 cm^3, 0.336 mmol) was added. After cooling, the resulting precipitate was filtered off and washed with cold methanol. The yield of **2b** was 0.024 g (94%), mp 148–150 °C (Found: C, 54.06; H, 5.15; N, 2.16. Calc. for $C_{49}H_{56}Cl_2N_2O_{18}S_2$: C, 53.74; H, 5.16; N, 2.56%); δ_H([$^2H_6$]DMSO) 2.50† (2 H, m, CH_2), 3.65 (16 H, m, 8 CH_2O), 3.84 (8 H, m, 4 CH_2O), 4.18 (8 H, m, 4 CH_2O), 5.20 (4 H, m, 2 CH_2N), 7.09 (2 H, d, *J* 8.1, 2 H(C-5) in benzocrown ether), 7.60 (2 H, s, 2 H(C-2) in benzocrown ether), 7.61 (2 H, d, 2 H(C-6) in benzocrown ether), 7.78 and 7.85 (4 H, 2 m, 2 H(C-5), 2 H(C-6) in benzothiazole), 7.81 (2 H, d, *J* 15.6, 2 H(C-a)), 8.15 (2 H, d, *J* 15.6, 2 H(C-b)), 8.41 and 8.46 (4 H, 2 d, *J* 8.1, *J* 8.4, 2 H(C-7), 2 H(C-4) in benzothiazole).

Synthesis of cycloadducts 6a,b. A solution of compound **2b** (5.5 mg, 0.005 mmol) and barium perchlorate (1.7 mg, 0.0051 mmol) in 4 cm^3 of CH_3CN was irradiated in a quartz cell with 436 nm light until the dye was completely consumed (36 h, spectrophotometric monitoring). Then the solvent was evaporated *in vacuo*, and the dry residue was dissolved in 0.5 cm^3 of CD_3CN. Prior to the ^{1}H NMR measurement, about 10% (v/v) of H_2O was added to the solution.‡ Cyclobutane **6a** (content 17%). δ_H(CD_3CN + H_2O (10%)) 2.8 (2 H, m, H(C-3), H(C-4) in the trimethylene chain), 3.6–3.7 (16 H, m, 2 δ,δ′, γ,γ′-CH_2O), 3.6–3.8 (8 H, m, 2 β,β′-CH_2O), 3.90 (4 H, m, 2 α′-CH_2O), 4.11 (4 H, m, 2 α-CH_2O), 5.01 (2 H, m, $^3J_{32} = {}^3J_{41} = 6.7$ (0.07), $^3J_{34} = 8.5$, $^4J_{31} = {}^4J_{42} = -0.2$, H(C-3), H(C-4) in cyclobutane), 5.20 (2 H, m, H(C-2), H(C-6) in the trimethylene chain), 5.33 (2 H, m, H(C-1), H(C-5) in the trimethylene chain), 5.74 (2 H, m, $^3J_{14} = {}^3J_{23} = 6.7$ (0.07), $^3J_{12} = 8.5$, $^4J_{13} = {}^4J_{24} = -0.2$, H(C-1), H(C-2) in cyclobutane), 6.54 (2 H, br. s, 2 H(C-2) in benzocrown ether), 6.94 (2 H, d, *J* 8.3, 2 H(C-5) in benzocrown ether), 7.18 (2 H, d. d, *J* 8.4, *J* 2.0, 2 H(C-6) in benzocrown ether), 7.73 (2 H, m, *J* 8.1, *J* 7.2, *J* 0.7, 2 H(C-5) in benzothiazole), 7.84 (2 H, m, *J* 8.7, *J* 7.4, *J* 1.1, 2 H(C-6) in benzothiazole), 8.08 (2 H, br. d, *J* 8.0, 2 H(C-4) in benzothiazole), 8.19 (2 H, br. d, *J* 8.4, 2 H(C-7) in benzothiazole). Cyclobutane **6b** (content 83%) formed as an equilibrium mixture of two conformers in 7 : 3 ratio; the chemical shifts for the minor conformer are given in parentheses. δ_H(CD_3CN + H_2O (10%)) 2.85 (2 H, br. m, H(C-3), H(C-4) in the trimethylene chain), 3.6–3.7 (16 H, m, 2 δ,δ′, γ,γ′-CH_2O), 3.6–3.8 (8 H, m, 2 β,β′-CH_2O), 4.0–4.2 (8 H, m, 2 α,α′-CH_2O), 4.47 (1 H, br. m, H(C-6) in the trimethylene chain), 4.58 (1 H, br. m, H(C-2) in the trimethylene chain), 4.86 (1 H, m, $^3J_{34}$ 9.97 (0.07), $^3J_{32}$ 8.76 (0.07), cyclobutane H(C-3)), 4.91 (1 H, br. d, *J* 15.4, H(C-5) in the trimethylene chain), 5.01 (1 H, m, H(C-1) in the trimethylene chain), 5.27 (1 H, m, $^3J_{41}$ 10.75 (0.08), $^3J_{43}$ 9.97 (0.07), cyclobutane H(C-4)), 5.42 (1 H, m, $^3J_{21}$ 10.15 (0.07), $^3J_{23}$ 8.76 (0.07), cyclobutane H(C-2)), 5.58 (1 H, m, $^3J_{12}$ 10.15 (0.07), $^3J_{14}$ 10.75 (0.08), cyclobutane H(C-1)), 6.65 (6.69) (1 H, br. s, H(C-2) in benzocrown ether), 6.66 (7.05) (1 H, br. s, H(C-2′) in benzocrown ether), 6.82 (1 H, br. m, H(C-5) in benzocrown ether), 6.82 (1 H, br. m, H(C-6) in benzocrown ether), 7.02 (6.75) (1 H, br. m, *J* 8.2, H(C-5′) in benzocrown ether), 7.10 (6.95) (1 H, br. m, *J* 8.2, H(C-6′) in benzocrown ether), 7.80 (1 H, br. t, *J* 7.6, H(C-6′) in benzothiazole), 7.93 (1 H, br. t, *J* 7.6, H(C-6) in benzothiazole), 7.95 (1 H, br. t, *J* 7.3, H(C-5′) in benzothiazole), 8.05 (1 H, br. t, *J* 8.0, H(C-5) in benzothiazole), 8.14 (1 H, d, *J* 8.1, H(C-7′) in benzothiazole), 8.21 (1 H, d, *J* 8.7, H(C-4′) in benzothiazole), 8.32 (1 H, d, *J* 8.7, H(C-4) in benzothiazole), 8.39 (1 H, d, *J* 8.0, H(C-7) in benzothiazole).

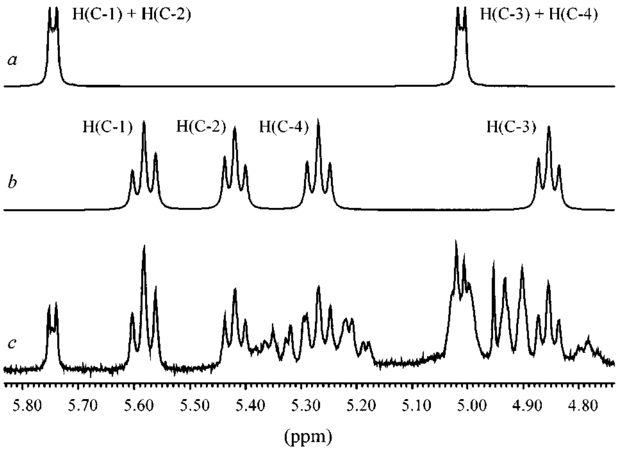

Fig. 5 Theoretical AA′BB′ (*a*) and ABCD (*b*) spectra and experimental (*c*) ^{1}H NMR spectra ("Bruker DRX-500", 500.13 MHz, $CD_3CN : H_2O = 9 : 1$, 300 K) of the cyclobutane protons in **6a**,**b**.

NMR spectroscopy

The ^{1}H NMR spectra of **2a**,**b** and **3** were recorded at 300 K in [$^2H_6$]DMSO on a Bruker DRX-500 spectrometer 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 samples of **6a**,**b** were dissolved in CD_3CN with addition of H_2O or D_2O. In the latter case, it was found that the cyclobutane protons at the carbon atoms linked to the benzothiazolium residues are quite acidic, which ultimately results in a proton–deuterium exchange as evident from the loss of ^{1}H NMR signals. The COSY and NOESY 2D spectra of **6a**,**b** were recorded using the standard Bruker pulse sequences (cosy45, noesytp) and processed using the XWINNMR program. The mixing time for the NOESY spectra was 700 ms, the delay between the experiments was 1.3–2 s, and the number of scans per experiment was 16–64. A total of 256–512 f1 points and 2048 f2 points were accumulated. The signals in the ^{1}H NMR spectrum of **6a**,**b** were assigned based on the NOEs obtained during the NOESY experiment. The cyclobutane subspectrum (Fig. 5) was analysed using the CALM iteration program. The CALM program is a version of the UEALTR program[33] adapted for personal computers (PC). The root-mean square deviation for the calculation was 0.07 Hz.

Chromatography

The HPLC system consisted of a Waters chromatograph with a 600E pump and an M 486 spectrophotometric detector (detection at 254 and 430 nm); a Separon C18 (a 250 × 4.6 mm) column was employed; a 4 : 1 MeCN–H_2O mixture containing 0.1 M of $NaClO_4$ was used as the mobile phase. The retention times at a flow rate of 1 cm^3 min^{-1} were 2 min for bisquaternary salt **3**, 5.6 min for dye **1**, and 7.3 min for dyes **2a**,**b**.

Spectrophotometry

Absorption spectra of **1c** and **2b** in anhydrous CH_3CN as a

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‡ Under these conditions, the crown-ether moieties are unable to form complexes with Ba^{2+} ions, which are strongly solvated by H_2O molecules.

function of the Ca^{2+} and Ba^{2+} concentration were obtained in a quartz cell of 5.5 cm pathlength maintained at 25 °C. The total concentration of metal cations (C_M) varied from 0 to 1×10^{-3} mol dm^{-3}. The total concentration of the dye was maintained constant ($C_L = 2 \times 10^{-6}$ mol dm^{-3}). In order to eliminate the influence of the variation of C_M on the equilibria of the possible reactions of the dye–metal complexes with the perchlorate ions,[34] 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 varied within a very narrow range (0.010–0.011 mol dm^{-3}).

Photochemical studies of **2b** were carried out in anhydrous CH_3CN in quartz cells of 1 cm pathlength at ambient temperature. The Ba^{2+} complex of **2b** was obtained in the presence of excess $Ba(ClO_4)_2$ (about 1×10^{-4} mol dm^{-3}). No supporting electrolyte was added. Solutions were irradiated with a glass-filtered 250W high-pressure Hg lamp. The light intensity was measured using a PP-1 cavity receiver, giving a total error in the quantum yield measurements of about 20%.

Solutions of dyes **1c** and **2b** and their complexes were prepared and used in red light. The absorption spectra were recorded on a Specord-M40 spectrophotometer attached to a PC. Magnesium, calcium, and barium perchlorates were dried *in vacuo* at 230 °C, and Et_4NClO_4 was dried at 40 °C. CH_3CN of spectroscopic grade was distilled over CaH_2 to remove traces of water.

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