

A Cation-Specific, Light-Controlled Transient Chromoionophore Based on a Benzothiazolium Styryl Azacrown Ether Dye

Igor K. Lednev, Ronald E. Hester, and John N. Moore*

Contribution from the Department of Chemistry, The University of York, Heslington, York YO1 5DD, U.K.

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Abstract: A benzothiazolium styryl azacrown ether dye (**1**) and its complexation with Ba²⁺ and Na⁺ cations in acetonitrile solution have been studied by UV-vis absorption and emission spectroscopy. *trans*-**1** is found to act as a normal chromoionophore for Ba²⁺ and Na⁺ at high concentration ($\geq 10^{-2}$ M) by complexation with the azacrown and as a light-controlled, transient chromoionophore specific for Ba²⁺ at low concentration (10^{-5} – 10^{-3} M). A quantitative analysis of the complexation and thermal reactions following photolysis has enabled a detailed mechanism to be proposed: *trans*-**1** photoisomerization produces *cis*-**1**, which is stabilized in the presence of Ba²⁺ by dual intramolecular complexation of the cation with both azacrown and sulfonate groups.

Introduction

Macrocyclic ionophores based on polyether derivatives have attracted much attention because of their selective affinity for cations^{1–6} and their application as functional units within supramolecular systems.^{7–11} The receptor and carrier characteristics of macrocyclic molecules enable metal or molecular ions to be recognized and transported and may facilitate the development of supramolecular ionic devices. Significant progress has been made in the development of sensing devices, with different types of response being available from ionophores with different functional properties, including ion-selective electrodes^{9,12–14} and optodes.^{9,15,16} The majority of ion and molecular sensors are based on specific interactions which result in easily recognizable changes in the sensor molecule, commonly observed via absorption, luminescence, or redox potential properties.^{6–9,17–21} A strong interaction between the ionophore and a dye is necessary to produce a strong optical response,

and this interaction may be either intermolecular^{22–24} or intramolecular, as for chromo- or fluoroionophores.^{25–30} Many chromo- and fluoroionophores which are sensitive to different ions have been investigated, mainly in solution^{17,26,29–45} but also

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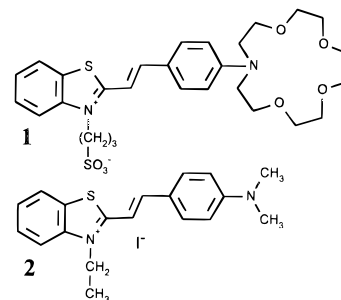
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in films.^{10,46–49} In chromoionophores, the color change usually occurs because of charge redistribution within the dye unit upon ion complexation,^{9,27} and the most dramatic and specific color changes have been found to occur when the ionophore and dye units share common atoms; for example, one or more heteroatoms of a crown ether ionophore may also form part of the π -conjugated system of a dye. The most promising examples of such compounds include monoazacrown ether derivatives in which the nitrogen heteroatom is within the π -conjugated system of a chromophore or fluorophore,^{26,28,37,39} and absorption and/or emission color changes have been studied for several styryl and azobenzene monoazacrown derivatives.^{26,29,30,33,34} In general, cation-specific color changes are observed on complexation in solvents of moderate polarity, but the sensitivity is not high. For example, the stability constant for complexation with alkali and alkaline-earth metal cations in acetonitrile is typically 2 or 3 orders of magnitude smaller for monoaza-15-crown-5 ether styryl dyes^{30,33,34} than for monoaza-15-crown-5 ether itself,⁵⁰ arising from the electron-withdrawing effect of the dye and the partial positive charge on the azacrown nitrogen atom which results.⁵¹

Macrocyclic molecules can be used as ion-selective carriers, and the development of triggered ion-capture, -release, and/or -transport devices is an important goal. For photoresponsive macrocyclic chromoionophores, it is possible to control the ion-binding and transport processes with light,^{9,52,53} forming the basis for photocontrolled ion-switching devices.^{7,54} The photocontrol of cation binding can be achieved by several different mechanisms, such as photoinduced structural change within the crown ether group or photocontrolled intramolecular coordination between a crowned cation and a pendant ionic group.⁵² The majority of such systems are based on the photoisomerization of chromophores, such as azobenzenes, thioindigos, and spiro-pyrans, or on the photodimerization of anthracene.^{19,52,55–58} In all of these cases, photolysis results in the formation of a new species with an affinity for cations which is different from that of the starting compound. One example is a benzothiazolium styryl dye containing a 15-crown-5 ether, which has been shown to have a higher stability constant for complex formation with alkaline-earth metal cations in the *cis*-isomer form.⁴⁰ This arises because the stabilizing effect of intramolecular coordination between the crowned cation and the negatively charged alkyl-sulfonate substituent of the benzothiazolium dye is possible only in the *cis*-isomer form.⁴⁰

Here we report studies of a benzothiazolium styryl dye (**1**), containing both an aza-15-crown-5 ether and an alkylsulfonate substituent, and its complexation with barium and sodium cations in acetonitrile solution. These studies demonstrate, remarkably, that the same chromoionophore may act as a sensor for barium ions in two different concentration ranges. While



the dye acts as a normal chromoionophore for Ba^{2+} and Na^{+} at high concentrations, it acts as a transient, cation-specific, light-controlled chromoionophore for Ba^{2+} at low concentrations. A detailed analysis of the kinetics of the *cis*–*trans* thermal isomerization reaction enables the stability constant for cation complexation with the *cis*-isomer formed on photolysis to be determined, and a five-state, quantitative reaction scheme is presented which summarizes the observations. These studies are relevant to the molecular design and development of sensitive cation-specific optical sensors and of photocontrolled ion-release systems.

Experimental Section

The synthesis of the *trans*-isomer of betaine 2-[2-[4-(4,7,10,13-tetraoxa-1-azacyclopentadecyl)phenyl]ethenyl]-3-(3-sulfopropyl)benzothiazolium (**1**) has been described previously.³⁹ 2-[4-(Dimethylamino)styryl]-3-ethylbenzothiazolium iodide (**2**), 1-(3-sulfopropyl)pyridinium hydroxide, sodium 9,10-anthraquinone-2-sulfonate, acetonitrile (anhydrous), potassium 4-sulfo-1,8-naphthalic anhydride (SNA), 1,8-naphthalic anhydride (NA), NaClO_4 , and $\text{Ba}(\text{ClO}_4)_2$ (all from Aldrich) were used as received.

A Hitachi U-3000 spectrophotometer was used to measure absorption spectra, using cells of 1, 5, or 10 cm pathlength. A 250 W Xe lamp (XENOPHOT HLX 64655) fitted with a 450 nm long-pass filter was used for sample photolysis. For the kinetic studies, the sample was photolyzed (ca. 1 min) and transferred immediately to the spectrometer, the lid was closed, and the absorbance at a fixed wavelength was measured as a function of time. A Shimadzu RF-150X spectrofluorimeter, with perpendicular sampling geometry, was used to measure the emission spectra; the sample was contained in a 1 cm pathlength cell, and the concentration chosen to give an absorbance of ca. 0.04 at the excitation wavelength. All measurements were made at room temperature (ca. 18 °C). The data were fitted using the SPSS statistical package, which allowed nonlinear regression analysis to be performed; fitted values are reported with uncertainties of $\pm 2\sigma$.

Results and Analysis

Cation Complexation with the Azacrown of *trans*-1. Acetonitrile solutions of *trans*-**1** and the model dye, *trans*-**2**, exhibited closely similar UV-vis absorption spectra, indicating that their electronic structures and spectral properties are determined principally by the dye group. The absorption spectrum of *trans*-**1** (ca. 4×10^{-6} M) in acetonitrile solution ($\lambda_{\text{max}} = 522$ nm) was found to change on addition of $\text{Ba}(\text{ClO}_4)_2$ at $> 10^{-3}$ M, as illustrated in Figure 1a,b, and a color change from dark pink to ochre was observed in forming this complex ($\lambda_{\text{max}} = 438$ nm). Such changes are typical of metal ion

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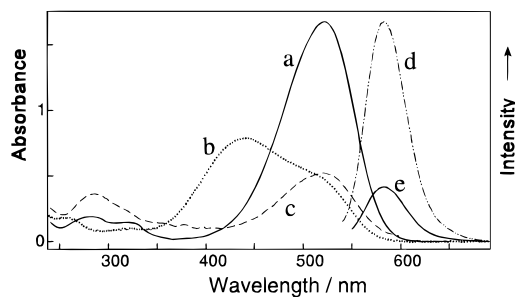


Figure 1. UV-vis absorption spectra of **1** (ca. 4×10^{-6} M) in acetonitrile solution: (a) in the absence of added barium salt, (b) in the presence of $\text{Ba}(\text{ClO}_4)_2$ (ca. 0.3 M), (c) after >450 nm photolysis in the presence of $\text{Ba}(\text{ClO}_4)_2$ (ca. 1×10^{-4} M). UV-vis emission spectra of **1** (ca. 1×10^{-6} M) on 520 nm excitation: (d) in the absence of added barium salt, (e) in the presence of $\text{Ba}(\text{ClO}_4)_2$ (ca. 1×10^{-4} M) and with nonattenuated fluorimeter lamp excitation.

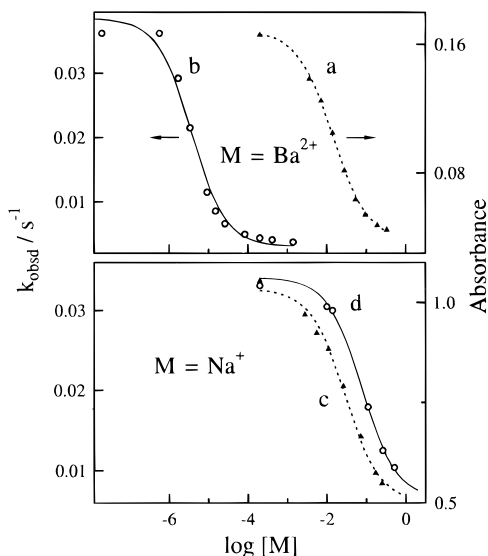


Figure 2. $\text{Ba}(\text{ClO}_4)_2$ concentration dependence of (a) the absorbance of **1** at 520 nm, fitted to eq 1, and (b) k_{obsd} , fitted to eq 8. NaClO_4 concentration dependence of (c) the absorbance of **1** at 520 nm, fitted to eq 1, and (d) k_{obsd} , fitted to eq 8.

complexation, and the concentration dependence of the absorbance, A , at a fixed wavelength fits well to eq 1, where A_0 and A_∞ are the absorbances at zero and infinite metal ion concentrations ($[M]$), respectively, indicating that 1:1 ligand-cation complexes are formed.²⁹ The stability constant for complex

$$A = (A_0 + A_\infty K[M]) / (1 + K[M]) \quad (1)$$

formation, K , was estimated to be $70 \pm 15 \text{ M}^{-1}$ (Figure 2a) and was found to be independent of the concentration of **1** within the range from 1×10^{-5} to 1×10^{-7} M. The large spectral changes indicate that the electronic structure of **1** is altered significantly on cation complexation. This can be attributed to coordination of Ba^{2+} to the azacrown ether and to the significant charge redistribution within the $\text{PhN}^+=\text{CC}=\text{CPhN}$ chromophore which results. The spectrum of **2** did not change on addition of Ba^{2+} , indicating that complexation does not occur in the absence of the azacrown ether.

The absorption spectrum of *trans*-**1** in acetonitrile was studied as a function of NaClO_4 concentration for comparison (Figure 3). The formation of a complex ($\lambda_{\text{max}} = 498 \text{ nm}$) between Na^+ and the azacrown of *trans*-**1** is evident from these spectra, and eq 1 was used to obtain $K = 35 \pm 10 \text{ M}^{-1}$ (Figure 2c). The long-wavelength absorption band of *trans*-**1** exhibited a smaller hypsochromic shift on complexation with Na^+ ($\Delta\lambda = 24 \text{ nm}$)

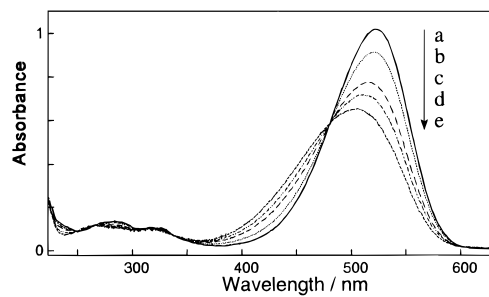


Figure 3. UV-vis absorption spectrum of **1** (ca. 2×10^{-5} M) in acetonitrile solution, in the presence of NaClO_4 at (a) 0, (b) 5.5×10^{-3} , (c) 2.6×10^{-2} , (d) 7.2×10^{-2} , and (e) 0.25 M.

than that on complexation with Ba^{2+} ($\Delta\lambda = 84 \text{ nm}$); the relative magnitude of these shifts is similar to those reported for metal cation complexation with aza-15-crown-5 ether groups within other styryl chromoionophores.^{9,26,29,33,51}

Cation Association with the Sulfonate Group. The sulfonate group within **1** provides a second possible site for cation association and this process must be considered in the quantitative study of such dyes. The possibility of Ba^{2+} and Na^+ association with the sulfonate group in acetonitrile solution has been investigated here by NMR, IR, and UV-vis absorption studies of **1** and other sulfonates. These studies are nontrivial because of the need to study the reaction at a sulfonate concentration lower than the cation concentration at which effective association occurs.

The NMR and IR techniques are relatively insensitive and require sulfonate concentrations of $>10^{-4}$ M, at which studies of *trans*-**1** are complicated by aggregate formation. NMR studies of *trans*-**1** (4×10^{-4} M), and IR studies of the sulfonate band of 1-(3-sulfopropyl)pyridinium hydroxide (3×10^{-4} M), both indicated a relatively high stability constant for $\text{Ba}^{2+}-\text{SO}_3^-$ association in acetonitrile of $K' > 3 \times 10^3 \text{ M}^{-1}$. UV-vis spectroscopy may be used at lower concentrations, but in this case the association is monitored indirectly; cation association with alkylsulfonates such as **1** does not result in changes in the UV-vis spectrum, and consequently, we have studied arylsulfonates which do show observable changes. A UV-vis study of sodium 9,10-anthraquinone-2-sulfonate (3×10^{-5} M) gave an approximate value of $K' = (3 \pm 2) \times 10^5 \text{ M}^{-1}$ for Ba^{2+} association in acetonitrile. After testing several other compounds, we have found the most useful arylsulfonate to be the potassium salt of 4-sulfo-1,8-naphthalic anhydride (SNA), and we have studied it along with its nonsulfonated analogue, 1,8-naphthalic anhydride (NA), for comparison.

The UV-vis absorption spectra of SNA and NA are different, as shown in Figure 4a,b. The addition of $\text{Ba}(\text{ClO}_4)_2$ at $>10^{-5}$ M to an acetonitrile solution of SNA (ca. 3×10^{-7} M) resulted in changes in the spectrum, and increasing the $\text{Ba}(\text{ClO}_4)_2$ concentration to 10^{-3} M resulted in a spectrum (Figure 4c) similar to that of NA. By comparison, the addition of $\text{Ba}(\text{ClO}_4)_2$ at $\leq 10^{-2}$ M did not affect the absorption spectrum of NA in acetonitrile; the spectrum showed very small changes only when the concentration of $\text{Ba}(\text{ClO}_4)_2$ was increased further to >0.05 M. These results indicate that the sulfonate group of SNA complexes with Ba^{2+} at a concentration of 10^{-5} – 10^{-4} M. Isosbestic points in the spectra would be expected for 1:1 complex formation, but these points were poorly defined; the changes in the spectrum were small and subject to error, but it is also possible that several different complexes form, including those involving perchlorate ions or additional SNA molecules. The dependence of the absorbance on Ba^{2+} concentration fits well to eq 1, which applies for the formation of only one

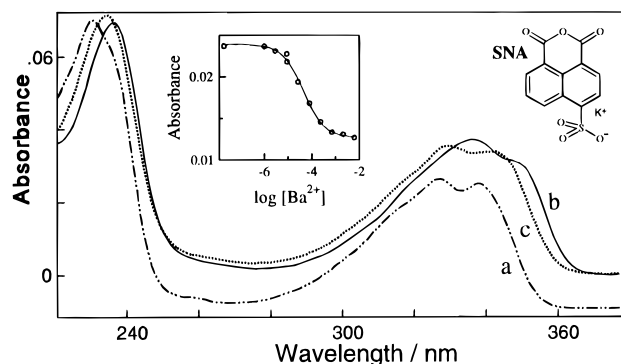


Figure 4. UV-vis absorption spectra of (a) NA (3×10^{-7} M) in acetonitrile (offset), (b) SNA (3×10^{-7} M) in acetonitrile in the absence, and (c) in the presence of Ba(ClO₄)₂ (6.9×10^{-4} M). Inset: Ba(ClO₄)₂ concentration-dependence of the absorbance of SNA at 354 nm, fitted to eq 1.

complex, giving $K' = (2.2 \pm 0.5) \times 10^4 \text{ M}^{-1}$ at 354 nm (Figure 4 inset) and $K' = (3 \pm 1) \times 10^4 \text{ M}^{-1}$ at 337 nm.

The addition of NaClO₄ at $\leq 10^{-2}$ M resulted in very small changes in the UV-vis absorption spectrum of SNA in acetonitrile and significant changes occurred only at NaClO₄ concentrations of ≥ 0.1 M. The absorption spectrum of SNA at [NaClO₄] = 1.3 M was found to be similar to that at [Ba(ClO₄)₂] = 7×10^{-4} M, but the interpretation of the data is complicated by the observation that the spectrum of NA also showed changes on addition of NaClO₄ at > 0.1 M; this may result from the association of Na⁺ cations with the oxygen atoms of the anhydride group. It may be concluded that the association constant for the interaction of the sulfonate group of SNA with Na⁺ in acetonitrile is $\leq 10^2 \text{ M}^{-1}$.

These studies of sulfonate-cation association indicate that any quantitative study of sulfonated dyes in acetonitrile requires this effect to be considered. This association occurs readily at low Ba²⁺ concentrations and, consequently, we have been able only to estimate lower limits for the K' values for alkylsulfonates, which would be the best models for **1**. The values we have obtained for arylsulfonates may be influenced by charge redistribution arising from the aromatic ring to which the sulfonate is directly attached, but nevertheless they serve as accessible models. Thus, for **1**, we conclude that the Ba²⁺-SO₃⁻ association constant is likely to be in the range of $K' = 10^4$ – 10^6 M^{-1} , while that for Na⁺-SO₃⁻ association is likely to be $K' \leq 10^2 \text{ M}^{-1}$.

Isomerization of 1. Styryl dyes photoisomerize readily, giving a distinct change in the UV-vis absorption spectrum, but this change often cannot be seen by eye because the *cis*-isomers usually are unstable at ambient temperature and rapidly revert to the *trans*-isomers in the dark.⁵⁹ The photoisomerization reactions of *trans*-**1** and **-2** in acetonitrile were studied by visible irradiation ($\lambda > 450$ nm) into the long-wavelength absorption band. Photoisomerization was observed, and the kinetics of the reverse *cis*-*trans* thermal isomerization were studied by measuring the time-dependence of the absorbance at a fixed wavelength (520 nm) after irradiation ceased. Color changes were not observed visually because of the rapid recovery times and the low concentration of the *cis*-isomer in the photostationary state. The kinetic data fit well to eq 2, where A_t is the absorbance at time t after irradiation ceased, A_0 and A_∞ are the initial and final absorbances, and k_{obsd} is the observed rate constant obtained from the fit. This analysis gave lifetimes ($1/k_{obsd}$) of ca. 26 and 10 s for *cis*-**1** and *cis*-**2**, respectively, in acetonitrile at room temperature.

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t) \quad (2)$$

The addition of Ba(ClO₄)₂ was found to increase the lifetime of *cis*-**1** substantially. The absorption spectra of **1** in acetonitrile solution containing Ba(ClO₄)₂ at 1×10^{-4} M were measured before (similar to Figure 1a) and ca. 1 min after irradiation (Figure 1c); the large change in the absorbance on irradiation resulted in a distinct color change from dark pink to light pink, attributable to a slower recovery time and a higher concentration of the *cis*-isomer in the photostationary state. The initial spectrum was found to recover fully in the dark, and the recovery kinetics were studied for **1** (5×10^{-7} M) in the presence of Ba(ClO₄)₂ at concentrations in the range of 1×10^{-6} – 2×10^{-2} M; all of the kinetic data fit well to eq 2 to give the observed rate constant, k_{obsd} , as a function of Ba²⁺ concentration (Figure 2b).

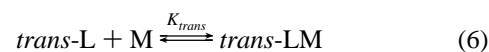
The lifetime of *cis*-**1** was measured as a function of the concentration of **1** in the range of 5×10^{-8} – 5×10^{-6} M, at two fixed Ba(ClO₄)₂ concentrations. The lifetime of *cis*-**1** was found to be independent of the chromophore concentration and to be 92 ± 4 and 258 ± 3 s for [Ba²⁺] = 1×10^{-5} and 5×10^{-4} M, respectively.

The lifetime of *cis*-**2** remained almost unchanged on addition of Ba(ClO₄)₂ up to a concentration of 0.16 M, indicating that the transient color change does not occur in the absence of azacrown and sulfonate groups. The lifetime of *cis*-**1** in acetonitrile was not affected by the addition of NaClO₄ at concentrations below 5×10^{-3} M, indicating that the effect is cation-specific, and the lifetime increased only at Na⁺ concentrations of $\geq 10^{-2}$ M (Figure 2d).

Fluorescence Measurements. The fluorescence spectra of **1** (10^{-6} M) in acetonitrile solution in the absence and presence of Ba(ClO₄)₂ (10^{-4} M) were measured in two different ways using a fluorimeter. In one case, the excitation beam (520 nm) was attenuated by ca. $\times 2000$ with a neutral-density filter and an iris; a small decrease of ca. 10–15% in the fluorescence intensity was found on addition of the barium salt. In the second case, the excitation beam was not attenuated and a large decrease of ca. 85% in the fluorescence intensity was observed on addition of the barium salt (Figure 1d,e). This effect was observed in < 1 min after exposure of the sample to the fluorimeter excitation beam. The profiles of the fluorescence spectra ($\lambda_{max} = 583$ nm) were similar in each case.

Discussion

All of the observations can be interpreted by a five-state scheme including *cis*- and *trans*-isomers and metal ion complexation with sulfonate and azacrown groups (Figure 5). The general scheme for the thermal back-reaction of *cis*-*trans* isomerization in the presence of metal ions in solution is given by eqs 3–6



where L is the ligand and M the metal cation, k_f and k_c are the rate constants of thermal *cis*-*trans* isomerization of **1** in free and cation-complexed forms, respectively, and K_{cis} and K_{trans} are the stability constants for complexation of *cis*- and *trans*-**1**,

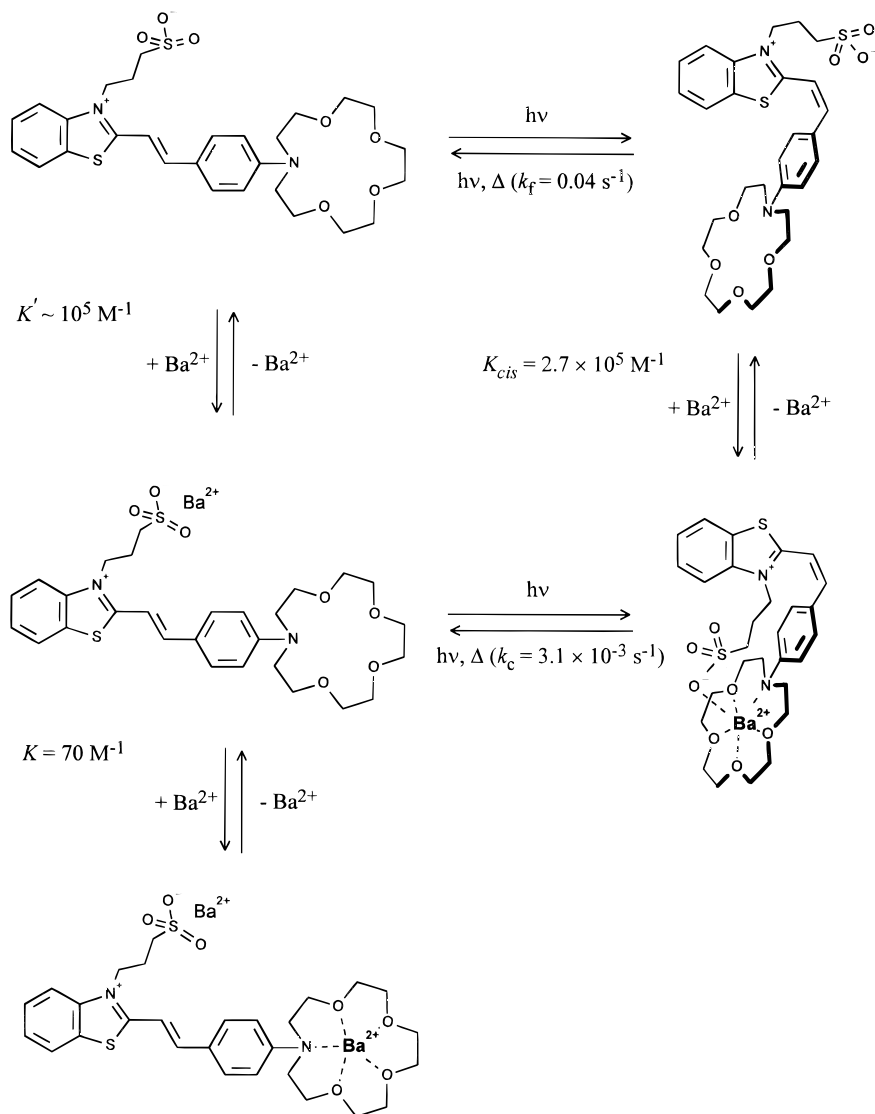


Figure 5. Proposed scheme for the photochemical ($h\nu$) and thermal (Δ) reactions of **1** in acetonitrile, in the presence of Ba^{2+} , along with stability constants and rate constants.

respectively, with the metal cation. The establishment of equilibria eqs 5 and 6 will occur more rapidly than the thermal isomerization reactions in eqs 3 and 4, and therefore the system is at equilibrium, from the viewpoint of complexation, at all times during the dark reactions in eqs 3 and 4. For this condition, and assuming that only a small fraction of the metal cations are complexed (i.e., that the concentration of free cations is essentially equal to the total concentration of the salt), the kinetic equation for the dark reaction is

$$[\text{cis-L}]^{\Sigma} = [\text{cis-L}]_0^{\Sigma} \exp(-k_{\text{obsd}}t) \quad (7)$$

where k_{obsd} is the observed rate constant, t is the time after photolysis ceased, $[\text{cis-L}]^{\Sigma} = [\text{cis-L}] + [\text{cis-LM}]$, $[\text{cis-L}]_0^{\Sigma} = [\text{cis-L}]^{\Sigma}$ at time $t = 0$, and

$$k_{\text{obsd}} = k_f/(1 + K_{\text{cis}}[\text{M}]) + k_c/(1 + 1/K_{\text{cis}}[\text{M}]) \quad (8)$$

Equation 7 indicates that the kinetics of thermal *cis*–*trans* isomerization are monoexponential at any concentration of metal cation; it may be rewritten as eq 2 to give the time-dependence of the experimentally observed absorbance. Equation 8 gives the observed rate constant as a function of cation concentration.

The data fit well to eq 8, as shown in Figure 2b,d for Ba^{2+} and Na^{+} , respectively. Fitted values of $K_{\text{cis}} = (2.7 \pm 1.0) \times$

10^5 M^{-1} , $k_f = (3.9 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$, and $k_c = (3.1 \pm 2.0) \times 10^{-3} \text{ s}^{-1}$ were obtained for Ba^{2+} . The fitted value of k_f is in agreement with the measured lifetime in the absence of Ba^{2+} , and k_c is an order of magnitude lower than k_f , indicating that the *cis*-isomer is stabilized by the presence of Ba^{2+} . This stabilization occurs at Ba^{2+} concentrations of 10^{-5} – 10^{-3} M , below those at which Ba^{2+} complexation with the azacrown of *trans*-**1** occurs but in the range where Ba^{2+} – SO_3^- association occurs. The fitted stability constant for *cis*-**1**– Ba^{2+} formation, $K_{\text{cis}} = 2.7 \times 10^5 \text{ M}^{-1}$, is within the range of $K' = 10^4$ – 10^6 M^{-1} estimated for Ba^{2+} – SO_3^- association, and this suggests that cation association with the sulfonate plays an important role in the stabilization mechanism. Barium–sulfonate ion association alone is most unlikely to stabilize the *cis*-isomer, and the most likely mechanism is the formation a “closed” *cis*-isomer form in which a “tail-biting” intramolecular Ba^{2+} cation bridge connects the alkylsulfonate and azacrown ether groups of **1** (Figure 5). This proposal is substantiated by earlier studies of benzothiazolium styryl dyes containing a 15-crown-5 ether group and a propylsulfonate chain.^{40,43} In this case, tail-biting intramolecular coordination was proposed to occur for the *cis*-isomer in the presence of alkaline-earth metal cations at low concentration. A strong hypsochromic shift of the dye absorption band was observed at low cation concentrations, and this

shift decreased substantially as the metal cation concentration was increased to give a spectrum which resembled that of the *cis*-isomer in the absence of metal cations: this change was attributed to the sulfonate associating preferentially with free metal cations in solution at high cation concentrations. The effects ascribed to this tail-biting interaction were not observed for an analogue with an ethyl rather than a propylsulfonate group pendant to the benzothiazolium dye.

The observation that k_{obsd} is independent of dye concentration is consistent with the occurrence of the reactions in eqs 3–6, and in accordance with eq 8, this indicates that K_{cis} also is independent of dye concentration. This suggests strongly that 1:1 **1**–Ba²⁺ complexes are formed at these Ba²⁺ concentrations (ca. 10⁻⁵–10⁻³ M), for which Ba²⁺ complexation with the azacrown of *trans*-**1** is not significant. This is consistent with the proposed structure of *cis*-**1**–Ba²⁺, and the observed dependence of k_{obsd} on Ba²⁺ concentration may be attributed to the concentration of associated Ba²⁺–SO₃⁻ groups present in solution prior to irradiation. This association effectively captures the Ba²⁺ cation in the *trans*-isomer form, for which intramolecular tail-biting is not possible, and facilitates the formation of the “closed” *cis*-isomer on photoisomerization.

Fitted values of $K_{cis} = 13 \pm 10 \text{ M}^{-1}$, $k_f = (3.4 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$, and $k_c = (6.6 \pm 5.0) \times 10^{-3} \text{ s}^{-1}$ were obtained for Na⁺. The fitted value of k_f again is in agreement with the measured lifetime in the absence of added salt, and again k_c is lower than k_f , indicating that the *cis*-isomer is stabilized by the presence of Na⁺. In this case, the *cis*-isomer is stabilized only at Na⁺ concentrations of >10⁻² M, above those at which Na⁺ complexation with the azacrown of *trans*-**1** occurs, and the fitted stability constant is also within the limit of $K' \leq 10^2 \text{ M}^{-1}$ estimated for Na⁺–SO₃⁻ association. Thus, the mechanism by which *cis*-**1** is stabilized by Na⁺ is not clear, although it is evidently quite different from that proposed for stabilization by Ba²⁺.

These complexation properties indicate that **1** acts as a normal chromoionophore for sodium and barium cations at $[M] \geq 10^{-2} \text{ M}$, through complexation with the azacrown ether. Compound **1** is insensitive to Na⁺ at lower concentrations. For Ba²⁺ at <10⁻³ M, **1** is insensitive to the presence of barium ions alone but the *cis*-isomer formed on visible photolysis is stabilized by dual intramolecular complexation of Ba²⁺ with both sulfonate and azacrown units, providing a color change which indicates the presence of Ba²⁺ cations in solution at 10⁻⁵–10⁻³ M. Species **1** is insensitive to visible photolysis alone because of the fast *cis*–*trans* thermal isomerization. Thus, **1** acts as a cation-specific, light-controlled transient chromoionophore, providing a transient visual sensor for Ba²⁺ cations only in the presence of both Ba²⁺ and light. The sensor returns to the starting state over ca. 10 min in the dark.

The fluorescence emission of **1** offers another probe of ion complexation. The decrease in the fluorescence intensity of **1**, in the presence of Ba²⁺ cations at 10⁻⁵–10⁻³ M and on irradiation by the full output of a fluorimeter lamp at 520 nm, may be attributed to the relatively high concentration of the stabilized *cis*-**1**–Ba²⁺ species formed in the photostationary state. These data are consistent with the occurrence of fluorescence from only the *trans*-isomer, and not the *cis*-isomer,

of **1**. Thus, **1** may be used with a fluorimeter to detect Ba²⁺ at low concentrations by comparison of the emission intensity with that of a sample of **1** in the absence of Ba²⁺; this technique, although giving a less distinct effect, is complementary to the probes of UV-vis absorption or color change.

It can be expected that the ion selectivity of this effect will be determined both by the association efficiency of different cations with the sulfonate group and by the strength of the additional complexation with the azacrown ether ring. The contrasting effectiveness of Ba²⁺ and Na⁺ cations in complexing *cis*- and *trans*-**1** reported here confirms this; while **1** acts as a normal chromoionophore for Na⁺, the weak association of this cation with the sulfonate group in acetonitrile renders it ineffective as a transient chromoionophore for sensing low concentrations of Na⁺. Preliminary studies of the stabilization of *cis*-**1** in the presence of different alkali and alkaline-earth metal cations in acetonitrile show that the selectivity rules are different from those predicted solely on the basis of the crown ether ring size/ion size effect; these results will be reported in full elsewhere.

The results presented here also are relevant to the development of photoionic molecular devices and may be described in this context.⁶⁰ Compound **1** may be considered as a device for two categories of photoionic signal processing. First, as a one-input/one-output functionality; the presence of Ba²⁺ at $\geq 10^{-2} \text{ M}$ (ionic input) results in a substantial photonic output change, observed as an increase in the visible transmittance. Second, as a two-input/one-output functionality; the presence of both Ba²⁺ at 10⁻⁵–10⁻³ M (ionic input) and visible irradiation (photonic input) are required to give a substantial photonic output change, observed again by an increase in the visible transmittance or by a decrease in the fluorescence intensity.

Conclusions

This study demonstrates that **1** may act as a light-controlled, transient chromoionophore which is specific and sensitive to metal cations at low concentration, in addition to acting as a normal chromoionophore for metal cations at high concentration. A detailed analysis of the complexation and kinetic data has enabled a quantitative understanding of the mechanism to be developed which will facilitate comparison with other molecules which may be designed to exhibit similar but different complexation and photochemical properties. Derivatives of **1** with different azacrown, dye, or functionalized alkyl chains may offer good opportunities for the design of molecules with different properties, and the approach described here for their quantitative study may be used to inform strategies for molecular design.

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