Short Communication

Photocontrol of Ca²⁺ complexation with an azacrown-containing benzochromene

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epoc ABSTRACT: The new azacrown-containing benzochromene **1a** was synthesized in order to study the effect of its reversible photochromic reaction on complex formation with Ca²⁺ in acetonitrile. It was found that both the initial chromene **1a** and its photoinduced merocyanine isomer **2a** are able to form 1:1 complexes with Ca²⁺, in which the metal cation coordinates to the crown ether moiety. The complexation causes strong spectroscopic shifts and leads to an increase in the dark lifetime of **2a**. The equilibrium constant for the 1:1 complexation decreases upon photoinduced ring-opening reaction (log K = 4.9 and 4.1 for **1a** and **2a**, respectively). Copyright © 2003 John Wiley & Sons, Ltd.
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KEYWORDS: azacrown-containing benzochromene; photocontrolled complexation; calcium cations; photomerocyanines; spectroscopic behavior; kinetics; ring-closure reaction

Crown ethers containing a photoresponsive unit are of current interest because of their potential applications as optical sensors for metal ions and as elements of photoswitchable molecular devices.[1] Several reversible photochemical reactions, such as geometric isomerism of azobenzene[2] and styryl compounds,[3] dimerization of anthracene[4] and photochromic reaction of spiro compounds,[5] have been employed to provide photocontrol over the metal ion-binding ability of crown ethers. The ring-opening reaction of chromenes[6] is another well-known photoreaction that could be used in photo-controlled metal-binding systems. Recently, the first representative of crown-containing chromenes has been reported,[7] and the photocontrolled binding of Pb²⁺ by a benzo-15-crown-5 ether-containing chromene was studied by electrochemical methods. This chromene was reported to bind Pb²⁺ in the dark, with dissociation of Pb²⁺ upon UV irradiation. However, no stability constants for metal complexes and no quantitative data

on the photochromic behavior of this crown chromene in the presence or absence of metal ions were published. Generally, despite the fact that a variety of photocontrolled metal-binding systems based on photoinduced bond cleavage have been investigated, there are very few quantitative reports on the stoichiometry and binding constants.[8]

Here we report the new azacrown-containing benzochromene **1a**, and describe the results of quantitative spectrokinetic studies of complexation of Ca²⁺ with **1a** and its photoinduced merocyanine isomer **2a** in acetonitrile. A convenient method for the measurement of complex stability constants for transient merocyanine forms of chromenes is proposed. The equilibrium constants for binding of Ca²⁺ to merocyanine forms of chromenes are reported for the first time.

The azacrown chromene **1a** and the reference compound **1b** were synthesized from the corresponding amino-substituted 1,1-diphenyl-prop-2-yn-1-ol and β-naphthol under acidic conditions and purified by column chromatography on silica gel. The synthesis of **1a** and **1b** will be published in detail elsewhere. Analytical data for **1a** and **1b** are given in the Supplementary Material.

Chromenes **1a** and **1b** in acetonitrile exhibited very similar UV–visible absorption spectra. The main spectroscopic feature distinguishing these compounds from chromene **1c** is the presence of additional absorption band with the maximum around 265 nm. The addition of

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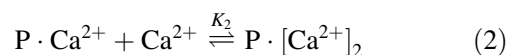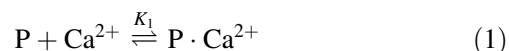E-mail: eushakov@icp.ac.ru.
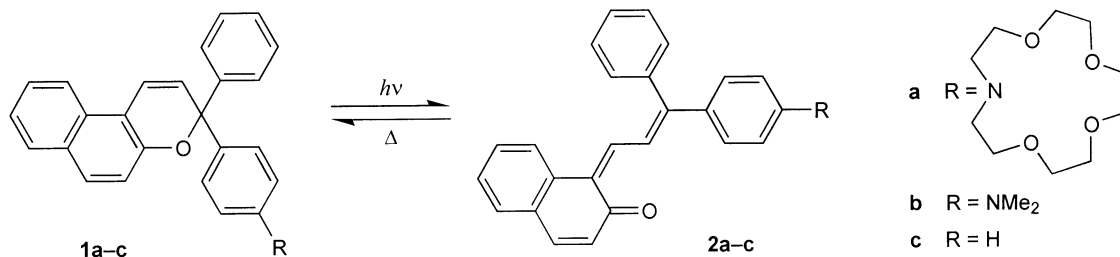
Ca(ClO$_4$)$_2$ to a solution of **1a** led to the disappearance of this band, indicating the binding of Ca^{2+} by the macrocyclic unit of **1a**. In contrast, the presence of Ca(ClO$_4$)$_2$ in a solution of **1b** even at a high concentration of 0.1 mol dm^{-3} had no effect on the absorption spectrum of **1b**. The absorption spectra of **1a** measured at various concentrations of added Ca(ClO$_4$)$_2$ (Fig. 1) were analyzed using a matrix modeling method.[9] This analysis provided evidence for the 1:1 complexation between **1a** and Ca^{2+} and allowed the corresponding complex stability constant to be estimated.

UV irradiation of **1a** in acetonitrile led to the appearance of a broad absorption band in the visible region, which is attributable to the merocyanine isomer **2a**. The dark (thermal) ring-closure reaction for **2a** occurred with the rate constant, k_d, of about 0.6 s^{-1}, to give the initial chromene. The spectrokinetic behavior of photomerocyanine **2b** was very similar to that of **2a**. No changes in the absorption spectra of **1a** and **1b** were observed after a few photochromic cycles.

Addition of large amounts of Ca(ClO$_4$)$_2$ led to a significant increase in the dark lifetime of photomerocyanines **2a** and **2b** and caused strong shifts in their absorption spectra, indicating that these compounds are able to bind Ca^{2+}. In order to study the complex formation of Ca^{2+} with the photomerocyanines, the absorption spectrum of **2a** (**2b**) in the photostationary equilibrium attained on irradiation of **1a** (**1b**) at 366 nm

and the rate constant of dark ring-closure reaction k_d for **2a** (**2b**) were measured as a function of the concentration, C_M, of added Ca(ClO$_4$)$_2$. In the subsequent analysis of these data, we assumed that the k_d values for the Ca^{2+}-complexed forms of **2a** and **2b** are much smaller than the corresponding rate constants of decomplexation reaction. The examination of a large collection of the kinetic data on cation–macrocycle interactions[10] showed that this assumption is very likely.

The dependence of k_d on C_M was interpreted in terms of the complexation model involving one equilibrium [Eqn. (1)] for **2b** and two equilibria [Eqns (1) and (2)] for **2a**.

$$P + Ca^{2+} \overset{K_1}{\rightleftharpoons} P \cdot Ca^{2+} \qquad (1)$$

$$P \cdot Ca^{2+} + Ca^{2+} \overset{K_2}{\rightleftharpoons} P \cdot [Ca^{2+}]_2 \qquad (2)$$

where P is the photomerocyanine and K_1 and K_2 are the complex stability constants. The values of stability constants were derived from non-linear fitting of the kinetic data (Fig. 2) to Eqn. (3) for **2b** or to Eqn. (4) for **2a**. The data were fitted using the corresponding functions in MATLAB. Equations (3) and (4) are derived for the corresponding complexation models, provided that [Ca^{2+}] = C_M, i.e. the concentration of uncomplexed
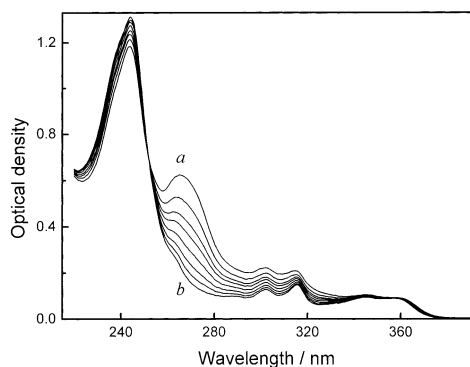

Figure 1. Absorption spectra of **1a** (2 × 10^{-5} mol dm^{-3}) in MeCN solution containing Ca(ClO$_4$)$_2$ at various concentrations ranging from (*a*) 0 to (*b*) 5 × 10^{-4} mol dm^{-3}
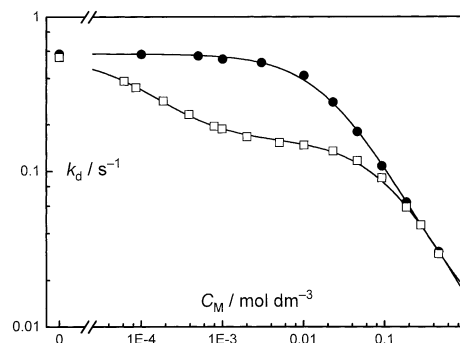
Figure 2. Rate constant of the dark ring-closure reaction for **2a** (squares) and **2b** (circles) in MeCN as a function of the Ca^{2+} concentration. The solid curves are from the fits to Eqn. (3) for **2b** or to Eqn. (4) for **2a**

Table 1. Stability constants for the complexes of **1a**, **2a** and **2b** with Ca^{2+}, and spectrokinetic data for **2a–c**[a]

	Log K[b]	$\lambda_{\max}$ (nm)	k_d (s^{-1})
1a·Ca^{2+}	4.9		
2a		543	0.56
2a·Ca^{2+}	4.1	440	0.16
2a·[Ca^{2+}]$_2$	1.0	507	≤0.01
2b		538	0.58
2b·Ca^{2+}	1.7	672	≤0.01
2c[c]		425	0.11

[a] In acetonitrile at $20 \pm 1\,°C$.
[b] For **2a**·[Ca^{2+}]$_2$, K is K_2 of Eqn. (2).
[c] Ref. 13.

Ca^{2+} is equal to the total concentration of Ca(ClO$_4$)$_2$:

$$k_d = \frac{k_{d1} + k_{d2}K_1 C_M}{1 + K_1 C_M} \quad (3)$$

$$k_d = \frac{k_{d1} + k_{d2}K_1 C_M + k_{d3}K_1 K_2 (C_M)^2}{1 + K_1 C_M + K_1 K_2 (C_M)^2} \quad (4)$$

where k_{d1}, k_{d2} and k_{d3} are the rate constants of dark ring-closure reaction for the pure components, i.e. P, P·Ca^{2+} and P·[Ca^{2+}]$_2$, respectively.

The C_M-dependent photostationary absorption spectra of **2a** and **2b** were analyzed using principal component analysis with self-modeling.[11] This analysis corroborated the supposed complexation models and provided the normalized absorption spectra of the Ca^{2+}-complexed forms of **2a** and **2b** (Supplementary Material, Fig. S1).

The results of spectrokinetic studies are presented in Table 1. Merocyanines **2a** and **2b** can be classified as integrated chromoionophores with an internal charge-transfer (ICT) excited state.[12] ICT-based chromoionophores bearing a cation-binding site at the electron-donor end of the chromophore are known to show cation-induced hypsochromic shifts in the absorption spectra. In contrast, when a cation receptor is integrated with the electron-acceptor terminus of the chromophore, interactions between the receptor and a metal cation induce bathochromic spectral shifts.

The formation of a weak 1:1 complex between **2b** and Ca^{2+} leads to a large bathochromic effect, indicating that the metal ion in the complex **2b**·Ca^{2+} coordinates to the oxygen atom of the *electron-acceptor* naphthalenone moiety of the merocyanine, as illustrated. This complexation results also in a very strong decrease in the rate constant of dark ring-closure reaction.

In contrast, the formation of a 1:1 complex between **2a** and Ca^{2+} leads to a large hypsochromic effect, suggesting that the Ca^{2+} ion in this complex interacts with the *electron-donor* moiety of the merocyanine, i.e. with the phenylaza-15-crown-5 fragment. For **2a**, the decrease in the rate constant of dark ring-closure reaction upon 1:1 complexation is less than in the case of **2b**. The 1:1 complex **2a**·Ca^{2+} shows the spectroscopic and kinetic properties close to those of the merocyanine form of **1c** (i.e. **2c**).[13]

The stability constant for the 1:1 complex **2a**·Ca^{2+} is almost one order of magnitude lower than that for the corresponding complex of **1a**. This is attributable to withdrawal of electron density from the phenylazacrown ether moiety upon opening of the pyran ring in **1a**.

In addition to the 1:1 complex, the photoinduced merocyanine **2a** is able to form a very weak 1:2 complex **2a**·[Ca^{2+}]$_2$ involving two Ca^{2+} ions. Judging from the spectrokinetic data, the 1:2 complex arises from the coordination of Ca^{2+} to the metal-free carbonyl oxygen in the 1:1 complex **2a**·Ca^{2+}.

In conclusion, the dimethylamino chromene **1b**, unable to bind Ca^{2+} in the dark, shows a small cation-binding ability upon UV irradiation, owing to the coordination of Ca^{2+} to the carbonyl oxygen in the photoisomer **2b**. In contrast, both the azacrown chromene **1a** and its photomerocyanine isomer **2a** are able to form 1:1 complexes with Ca^{2+}. In these complexes, the metal ion coordinates to the crown ether moiety. The photochromic ring-opening reaction of **1a** leads to a substantial decrease in the complex stability constant.
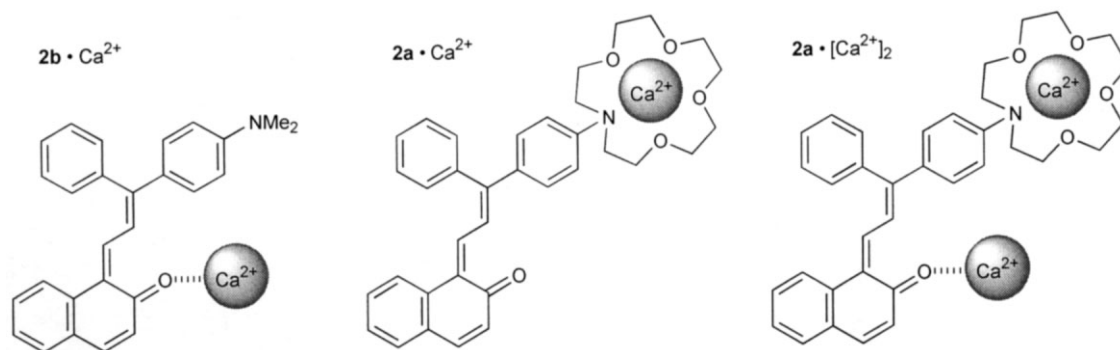
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REFERENCES

1. (a) Lehn J-M. *Supramolecular Chemistry*. VCH: Weinheim, 1995; (b) de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE. *Chem. Rev.* 1997; **97**: 1515–1566.
2. Shinkai S. In *Cation Binding by Macrocycles*, Inoue Y, Gokel GW (eds). Marcel Dekker: New York, 1990; 397–428.
3. Ushakov EN, Gromov SP, Buevich AV, Baskin II, Fedorova OA, Vedernikov AI, Alfimov MV, Eliasson B, Edlund U. *J. Chem. Soc., Perkin Trans. 2* 1999; 601–607.
4. Tucker JHR, Bouas-Laurent H, Marsau P, Riley SW, Desvergne J-P. *Chem. Commun.* 1997; 1165–1166.
5. (a) Inouye M, Noguchi Y, Isagawa K. *Angew. Chem., Int. Ed. Engl.* 1994; **33**: 1163–1166; (b) Kimura K. *Coord. Chem. Rev.* 1996; **148**: 41–61.
6. Van Gemert B. In *Organic Photochromic and Thermochromic Compounds. Volume 1: Photochromic Families*, Crano JC, Guglielmetti RJ (eds). Plenum Press: New York, 1999; 111–140.
7. Stauffer MT, Knowles DB, Brennan C, Funderburk L, Lin F-T, Weber SG. *Chem. Commun.* 1997; 287–288.
8. (a) Stephens MR, Geary CD, Weber SG. *Photochem. Photobiol.* 2002; **75**: 211–220; (b) Inouye M, Noguchi Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* 1994; **246**: 187–189; (c) Zhou J-W, Li Y-T, Song X-Q. *J. Photochem. Photobiol. A: Chem.* 1995; **87**: 37–42.
9. Ushakov EN, Gromov SP, Fedorova OA, Pershina YV, Alfimov MV, Barigelletti F, Flamigni L, Balzani V. *J. Phys. Chem.* 1999; **103**: 11188–11193.
10. Izatt RM, Pawlak K, Bradshaw JS, Bruening RL. *Chem. Rev.* 1991; **91**: 1721–2085.
11. Saltiel J, Sears DF, Choi J-O, Sun Y-P, Eaker DW. *J. Phys. Chem.* 1994; **98**: 35–46.
12. de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE, *Chem. Rev.* 1997; **97**: 1515–1566.
13. Delbaere S, Luccioni-Houze B, Bochu C, Teral Y, Campredon M, Vermeersch G. *J. Chem. Soc., Perkin Trans. 2* 1998; 1153–1157.