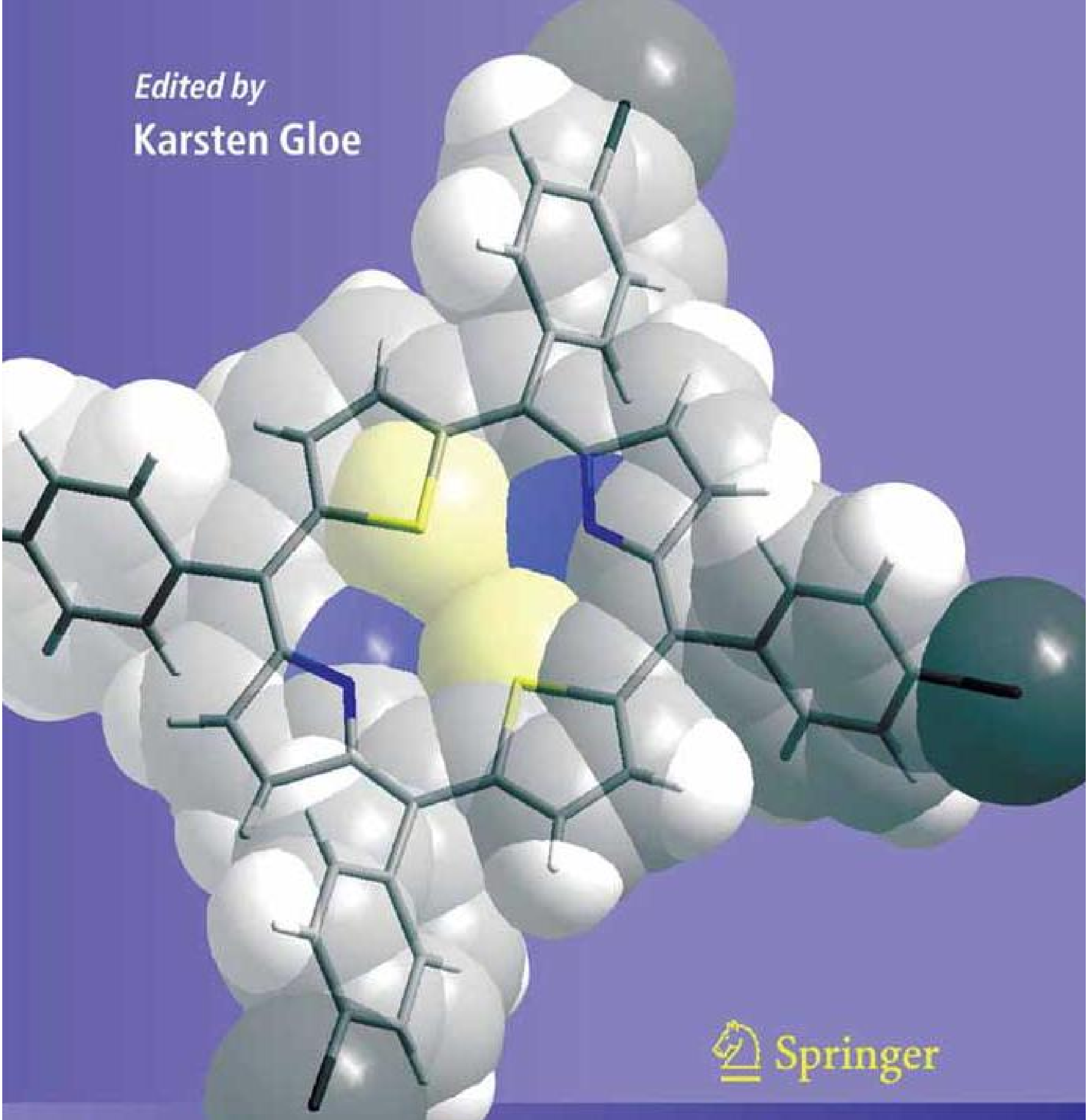
MACROCYCLIC CHEMISTRY

Current Trends and Future Perspectives

Edited by

Karsten Gloe



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The front cover illustration depicts the X-ray structure of 5,10,15,20-(4-bromophenyl)-21,23-dithiaporphyrin obtained by S. Stute and T. Söhnel, TU Dresden.

The image on the back cover and in the preface shows the logo of the ISMC 2005 in Dresden designed by Cornelia Kreiß, TU Dresden.

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15.
MACROCYCLIC SYSTEMS WITH PHOTOSWITCHABLE FUNCTIONS

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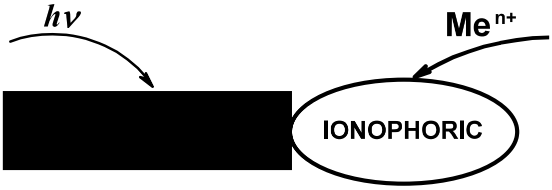
1. Introduction

Photochromism is a reversible transformation of a single chemical species between two states, the absorption spectra of which are clearly different, the transition in at least one direction being induced by electromagnetic radiation [1]. The widest and most important group of the photochromic system is based on electrocyclic reactions [2,3]; a few have been commercially successful (polymer-based photochromic eyewear, novelty items and security printing inks). Several other photochromic systems based on *E,Z-isomerization*, cycloaddition reaction, electron or proton transfer have potential industrial applications [4].

Photochromic macrocyclic compounds constitute a new class of artificial receptors in which the recognition of metal cations induces a conformational change in the receptor framework accompanied by signalling (coloration). In addition, since binding of cations is sensitive to the ligand environment, the binding constant can be controlled effectively by employing photochromic systems which change in the light [5,6].



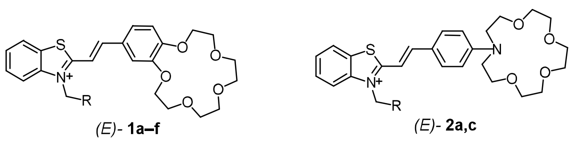
This review surveys our studies devoted to the photoswitchable molecular receptors based on photochromic crown ethers. Photochromic systems described in the review may be classified into three groups according to the reaction types: *E,Z-isomerization*, [2+2]-photocycloaddition reactions and electrocyclic reaction. It has proved the groups to be an especially suitable basis for photochromic systems, and promising for the industrial applications.

Karsten Gloe (ed.), Macrocyclic Chemistry: Current Trends and Future Perspectives, 235–252.

It is known from literature that several reversible photochemical reactions, such as geometric isomerism of azobenzene [7], electrocyclic reaction of dihydroindolizines, fulgides and diarylethylenes with heterocyclic groups [8-10], dimerization of anthracene [11], and photochromic reaction of spirocompounds [12] have been also employed to provide photocontrol over metal-ion binding ability of crown ethers.

2. Macrocyclic Systems with Ability for *E,Z*-isomerization

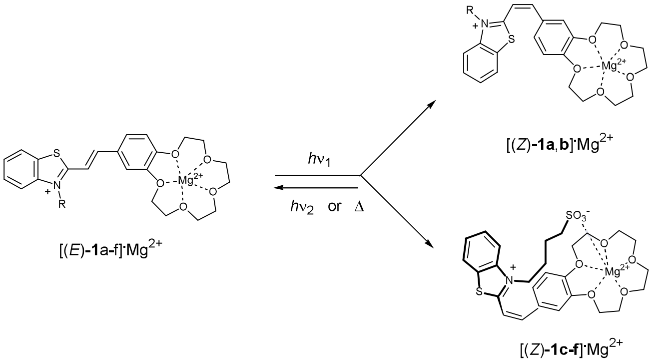
It was found that the linking of styryl dye fragment to benzocrown ether results in novel photochromic compounds CESD (Crown Ether Styryl Dyes) possessing interesting physico-chemical properties (Scheme 1) [13]. The dyes are intensively colored and show significant hypsochromic shifts upon complexation with alkaline earth metal cations in acetonitrile solution. Reversible photochemical reaction *E,Z-isomerization* is observed for both dyes and their complexes.



a: R = Me (anion ClO_4^-), **b**: R = $(CH_2)_2SO_3^-$, **c**: R = $(CH_2)_3SO_3^-$, **d**: R = $(CH_2)_4SO_3^-$,
e: R = *o*-$CH_2C_6H_4SO_3^-$,**f**: R = *p*-$CH_2C_6H_4SO_3^-$

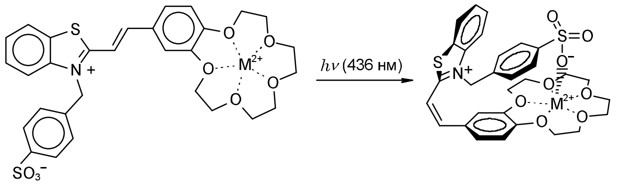
Scheme 1

The CESD **1c-f** with terminal sulfo group are able to form anion-“capped” complexes (Scheme 2) upon *E,Z*-photoisomerization owing to the interaction of the sulfo group of the *N*-substituent (spacer) with a metal cation in the crown-ether cavity. However, the dates obtained that the *Z*-isomer of **1a,b** is unable to form an anion-“capped” complex [14].



Scheme 2

It should be noted that the influence of the spacer structure on the stability of the complexes is much more pronounced in the case of *Z*-isomers. This refers most of all to CESD **1e,f** with conformationally rigid spacers. The ratio of the stability constants of the anion-“capped” complexes [(*Z*)-**1f**]·Mg^{2+} and [(*Z*)-**1e**]·Mg^{2+} is about 500 (Scheme 3) [15,24].



$[(E)\text{-}\mathbf{1f}]\cdot Mg^{2+}$ $[(Z)\text{-}\mathbf{1f}]\cdot Mg^{2+}$

Scheme 3

The *E,Z-isomerization* of the styryl dyes **2c** containing aza-15-crown-5 ether moiety is characterized by great hypsochromic shifts, equal to 170 nm, of the spectrum of $[(Z)\text{-}\mathbf{2c}]\cdot Ca^{2+}$ with respect to the spectrum of $[(E)\text{-}\mathbf{2c}]\cdot Ca^{2+}$ (see Figure 1). Apparently, it can be explained by the fact that in anion-“capped” complex the molecule of dye acquires a twisted conformation with marked disruption of the conjugation in the chromophoric system. When (*E*)-**2a** is converted into the *Z*-form, the stability of complex increases approximately 2.5 fold. On going from the cationic dye **2a** to the betaine **2c**, stability of the complexes formed by *Z*-isomer increases by more than three orders of magnitude [16].

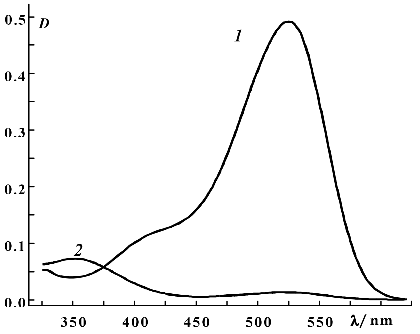
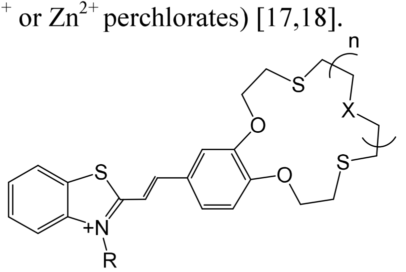


Figure 1. Absorption spectra of CESD **2c** in MeCN ($C_L = 1.0\times10^{-5}$mol L^{-1}) in the presence of $Ca(ClO_4)_2$ at C_M/C_L = 100; E-isomer (1); E-Z-photosteady (2) state formed on exposure to light with a wavelength of 546 nm and intensity of ~ $1\cdot10^{16}cm^{-1}s^{-1}$.

Styryl dyes CESDs **3a-e, 4a-e** incorporating thiacrown ether moieties exhibit a strong preference for the formation of complexes with heavy metal salts (Hg^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} or Zn^{2+} perchlorates) [17,18].



3a-e	**4a-e**
R = Me (ClO_4^-);	R = $(CH_2)_4SO_3^-$;
3a: n= **0**;	**4a**: n= **0**;
3b: n= **1, X** = O;	**4b**: n= **1, X** = O;
3c: n= **2, X** = O;	**4c**: n= **2, X** = O;
3d: n= **3, X** = O;	**4d**: n= **3, X** = O;
3e: n= **2, X** = S	**4e**: n= **2, X** = S

Scheme 4

Exposure of (*E*)-**3a-e, 4a-e** in MeCN solutions in the presence of Hg^{2+} or Pb^{2+} to visible light, leads to UV-Vis spectral changes typical of *E,Z*-isomerization [18]. The behaviour of complexes $[(E)\text{-}\mathbf{4a\text{-}d}]\cdot Hg^{2+}$ is analogous to that previously described for the $[(E)\text{-}\mathbf{1c}]\cdot Mg^{2+}$ complex, whose *Z*-isomer is anion-“capped”. Observed long absorption band (LAB) shifts of 50-70 nm on complexation of (*Z*)-**4a-d** with Hg^{2+} are consistent with diminished conjugation between the three moieties comprising the

CESD chromophore, due to the pronounced departure from planarity that accompanies formation of anion-“capped” complexes. Enhanced stability due to intramolecular coordination in the anion-“capped” [(*Z*)-**4c**]·Hg^{2+} complexes are reflected in the stability constants in Table 1 (K_c/K_t equals 10 for **4c**·Hg^{2+} and 15 for **4c**·Pb^{2+}) and causes sharp decelerations of their dark *Z* → *E* isomerizations. The saturated coordination capacity of Hg^{2+} in complex [(*E*)-**4e**]·Hg^{2+} explains why its *Z* isomer does not form an anion-“capped” complex. For the *Z* isomers of CESDs **4a-d** no spectral evidence of anion-“capped” complex formation could be found when Cd^{2+}, Ni^{2+} or Zn^{2+} was substituted for Pb^{2+} or Hg^{2+}. As expected, based on the theory of “hard” and “soft” acids and bases, the strength of the coordination bond between Cd^{2+}, Ni^{2+} or Zn^{2+} and the SO_3^- group appears to be to small to stabilize the Z isomer [19,25].

TABLE 1: Equilibrium Constants for Pb^{2+} and Hg^{2+}Complex Formation with CESDs

Complex	log *K*	Complex	log *K*
(E)-**3b**·Hg^{2+}	15.9(1)[a]; 15.7(1)[b]	*(E)*-**4b**·Hg^{2+}	18.0(1)[b]
(E)-**3c**·Hg^{2+}	18.2(1)[a]; 18.0(1)[b]	*(E)*-**4c**·Hg^{2+}	19.8(1)[b,c]
(E)-**3c**·Pb^{2+}	5.61(2)[b]	*(E)*-**4c**·Pb^{2+}	7.57(3)[b]
(E)-**3e**·Hg^{2+}	21.0(1)[a]	*(E)*-**4e**·Hg^{2+}	20.7(1)[b]
BDT12C4[e]·Hg^{2+}	22.7(2)[a,d]	*(Z)*-**4c**·Hg^{2+}	20.8(1)[b,c]
BDT15C5[e]·Hg^{2+}	18.0(1)[a]	*(Z)*-**4c**·Pb^{2+}	8.75(3)[b]
BDT18C6[e]·Hg^{2+}	19.5(1)[a,c]		
BDT18C6[e]·Pb^{2+}	7.26(2)[b]		

[a] These values were determined polarographically for 0.01 M solution of Et_4NClO_4 in MeCN at 20 °C; values in parentheses are uncertainties in the last significant figure shown. [b] These values were determined spectrophotometrically in MeCN at 20 °C; values in parentheses are uncertainties in the last significant figure shown. [c] These values were taken from ref 19. [d] For complex 2 ligand : 1 metal. [e] BDT12C4 –benzodithia-12-crown-4; BDT15C5 – benzodithia-15-crown-5; BDT18C6 – benzodithia-18-crown-6.

Substantial changes are observed in the ^1H NMR spectra when a solution of [(*E*)-**4c**]·Pb^{2+} is exposed to visible light (Figure 2). In the novel photoproduct, the spin-spin coupling constants for the olefinic proton signals at 6.70 and 7.52 ppm were 12.2 Hz, which implied the formation of [(*Z*)-**4c**]·Pb^{2+}. In the *Z*-isomer, the signals of aromatic protons of the benzocrown ether moiety and of the olefinic protons shift upfield, while the benzothiazole proton signals shift downfield relative to those of [(*E*)-**4c**]·Pb^{2+}. The pronounced spectral difference between the two photoisomers is due to the substantial conformational rearrangement induced by the formation of the anion-“capped” complex. The formation of this complex enforces a twisted conformation on the chromophore, resulting in a distortion of the conjugated system and concentration of the positive charge in the benzothiazole fragment of the molecule. The greatest changes were found for the chemical shifts of the H(a) and H(2’) protons, which is apparently due to the fact that the protons fall into the areas of shielding of the benzothiazole fragment and the double C=C bond [20].

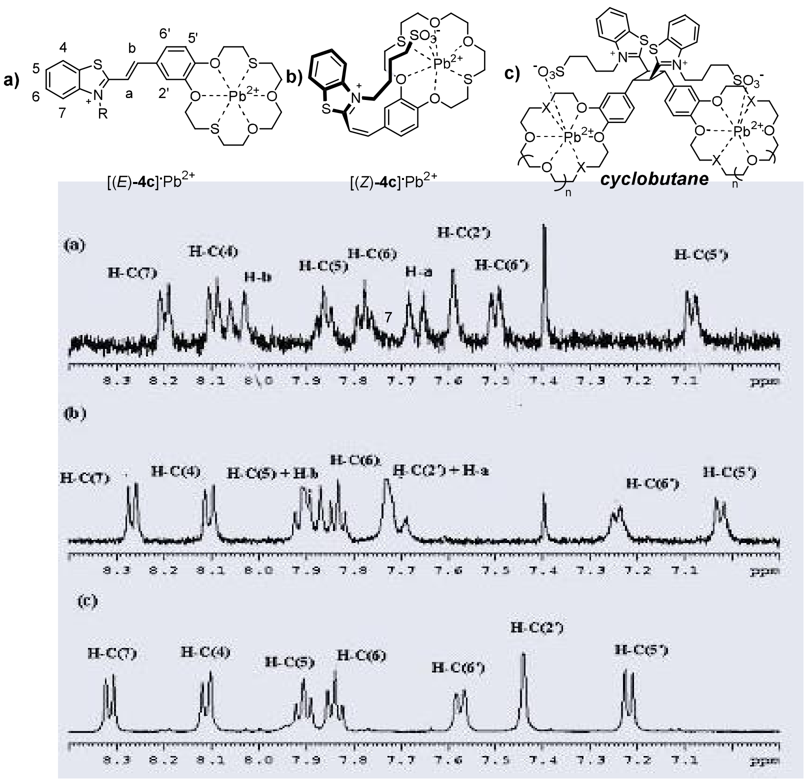


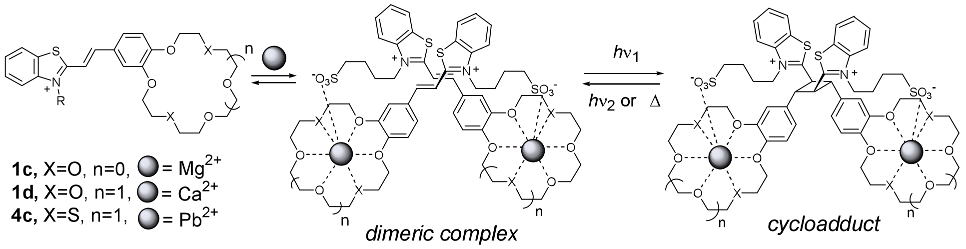
Figure 2. ^{1}H NMR spectra of the complexes [(E)-**4c**]·Pb^{2+}(a), [(Z)-**4c**]·Pb^{2+}(b) and cyclobutane (c) ($C_L = 1\times10^{-3}$ M; $C_{Pb}{}^{2+} = 5\times10^{-3}$ M) in CD_3CN at 50°C.

Thus, the CESD with anionic terminal substituent are able of anionic "capping" complex formation during the irradiation and thus to achieve photochemical control over binding of metal cations.

3. Macrocyclic Systems with Ability for [2+2]-Photocycloaddition Reaction

A promising tool for controlling the regio- and stereoselectivity of photocycloaddition reaction (PCA) as well as the efficiency may be provided by assembling alkenes into a supramolecular structure with pre-organization of reactants such that the spatial arrangement of molecules would be favorable for the formation of only one cyclobutane isomer in a high yield.

This idea was realized using crown ether styryl dyes (CESD) **1c,d, 4c** (Scheme 1,4). The compounds **1c,d, 4c** having betaine structures form supramolecular dimers with a crossed arrangement of molecules (*anti*-head-to-tail) in the presence of ions, due to the intermolecular interaction between the sulfo group of one of the molecules and a ion located in the crown-ether cavity of the other molecule [20,21]. It was shown that photoirradiation of solutions of dimer results in stereospecific PCA giving only one of the 11 possible derivatives of cyclobutane, which is expected in conformity with the concerted superficial (s,s) addition of the reactants (Scheme 5) [22,23]. It is noteworthy that neither (*E*)-**1c,d, 4c** without metal cations nor complexes of (*E*)-**1a,b** with Mg^{2+}, Ca^{2+}, Ba^{2+} undergo PCA even in saturated solutions.



Scheme 5

Transition from spacers with flexible polymethine chains to *N*-substituents in which the sulfo group is rigidly arranged in space (CESD **1e,f)**, makes it possible to influence the efficiency of these photochemical reactions and also to change the route of transformation of CESD [15,24]. Thus, upon irradiation with UV light reversible [2+2]-photocycloaddition reaction takes place only in case of styryl dye **1e** with *ortho*-sulfobenzyl substituent.

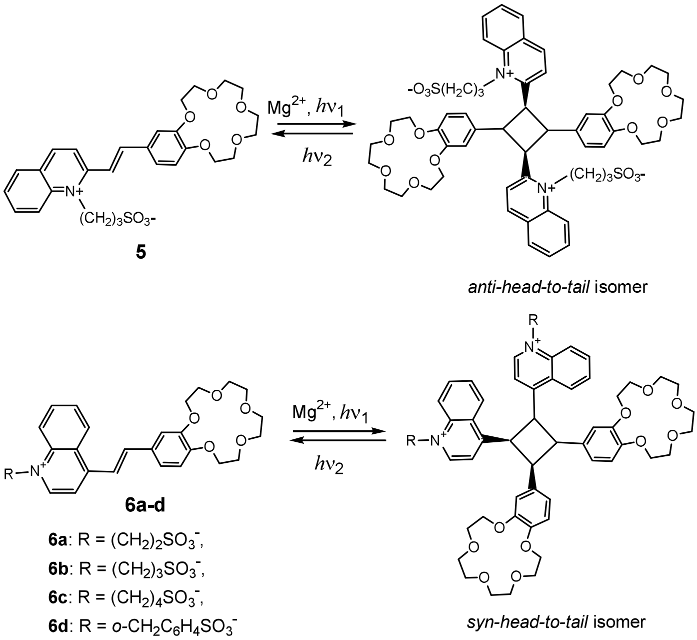
The single [2+2]-photocycloadduct obtained by irradiating thiacrown-containing dye **4a-e** in the presence of either Pb^{2+} or Hg^{2+} was assigned the cyclobutane structure (see figure 2c). The quantum yield of photodimer formation is substantially more efficient in the presence of Pb^{2+} than in the presence of Hg^{2+} (Table 2) [20,25]. The efficiency of cycloadduct formation depends strongly on the size and S/O ratio of the crown ether moiety. It is not known at present whether the quantum yield difference is due to a) a more favorable orientation of the dye units dimeric complex, b) a longer excited state lifetime dimeric complex and/or c) a higher dimeric complex concentration as a result of stronger Pb^{2+}/SO_3^- than Hg^{2+}/SO_3^- coordination bonds.

TABLE 2: Photodimerization Quantum yields of the Hg^{2+} and Pb^{2+} Complexes of CSDs (E)-4a–e[a]

Complex	$10^4\,\varphi_{PCA}$
[*(E)*-**4a**]•Hg^{2+}	1.3
[*(E)*-**4b**]•Hg^{2+}	28
[*(E)*-**4c**]•Hg^{2+}	1.3
[*(E)*-**4c**]•Pb^{2+}	10
[*(E)*-**4d**]•Hg^{2+}	0.79
[*(E)*-**4e**]•Hg^{2+}	-

[a] Excitation intensity = 2.3 x 10^{-6} einstein/(s L); ligand concentrations were 4.0 x 10^{-5} M, and $Pb(ClO_4)_2$, and $Hg(ClO_4)_2$ concentrations were 7.0 x 10^{-5} and 4.1 x 10^{-5} M, respectively, in acetonitrile.

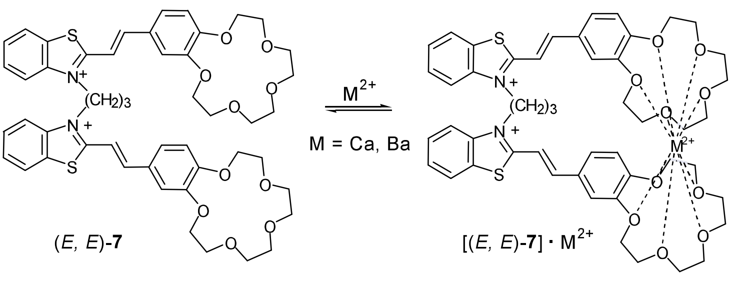
Isomeric chromogenic 15-crown-5-ethers of the quinoline series **5** and **6** were shown to undergo PCA in acetonitrile to give cyclobutane derivatives only in the presence of $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ [26,27]. The modification of the benzocrown-ether position from 2 to 4 appears to change in principle the PCA route (Scheme 6). The overall quantum yield in the PCA of **5**·Mg^{2+} was 0.0007. In the case of the PCA of **6**·Mg^{2+}, the high quantum yield (0.13) was found, which indicates that the degree of dimerization of the complexes of this dye remains rather high even in a very dilute solution and that the spatial structure of dimeric complexes is probably rather favourable for PCA.



Scheme 6

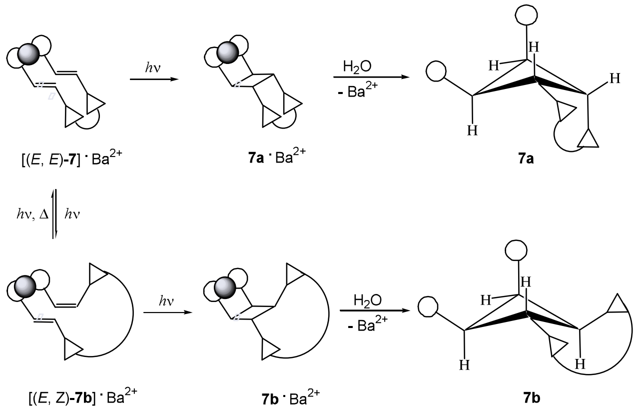
The structure of the spacer has a significant effect on the efficiency of photocycloaddition reaction of **6a-d** [27]. The PCA quantum yield is of 0.20 (**6a**), 0.13 (**6b**), 0.073 (**6c**) and 0.024 (**6d**) (irradiation at 436 nm). The reaction is photochemically reversible. Upon irradiation of the cycloadducts with 313 nm light, the initial dyes are formed with a quantum yield ranging from 0.02 to 0.01.

Bis-crown-containing styryl dye (*E,E*)-**7** having the structure and properties of molecular pincers has been synthesized. In acetonitrile solution, dye (*E,E*)-**7** is able to form intramolecular sandwich complexes with Ca^{2+} and Ba^{2+} cations (Scheme 7) [28,29].



Scheme 7

The analysis of 2D COSY and NOESY NMR spectra of the PCA products showed the presence of two isomeric crown-containing cyclobutane derivatives **7a** and **7b** in 17 : 83 ratio (Scheme 8).

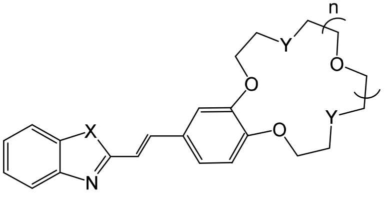


Notation. ○ is the benzo-15-crown-5-ether moiety; ▷ is the benzothiazole residue;

● is Ba^{2+}; ⌒ is $(CH_2)_3$

Scheme 8

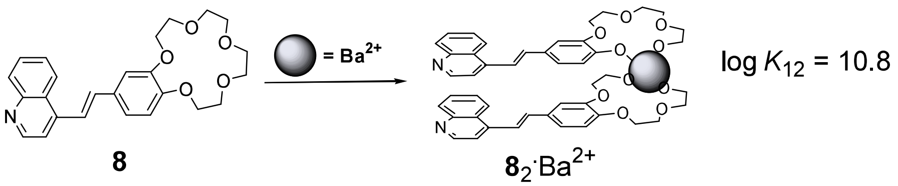
Recently, synthesis and investigation of stilbene analogues containing a crown ether fragment were developed [30,31] (Scheme 9).



X = S, O, CH=CH, Y = O, S, n=0-3

Scheme 9

The alkaline earth metal cations with a large diameter (Sr^{2+}, Ba^{2+}) and benzo-15-crown-5 stilbene derivatives are characterized by the formation of the 2 : 1 sandwich-type complexes (Scheme 10). In the case of Ba^{2+} the sandwich complex possesses the highest stability. According to the NMR studies and X-ray analysis of the sandwich complex of **8**, molecules of dye are arranged in a “head-to-head” stacking.



Scheme 10

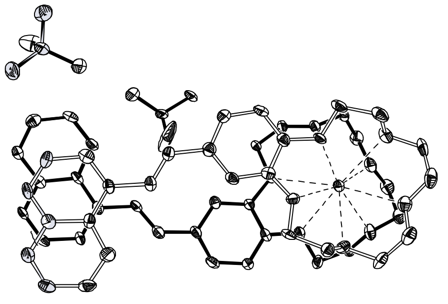
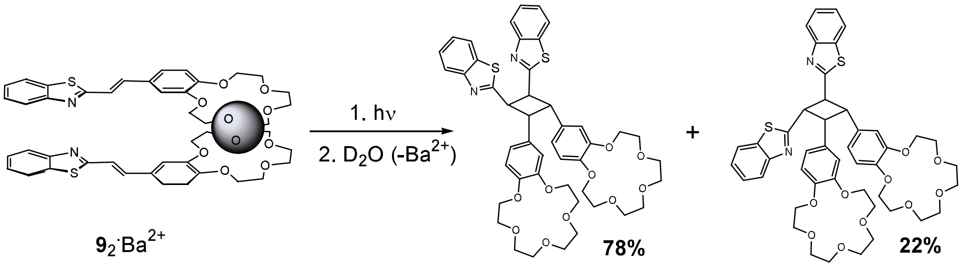


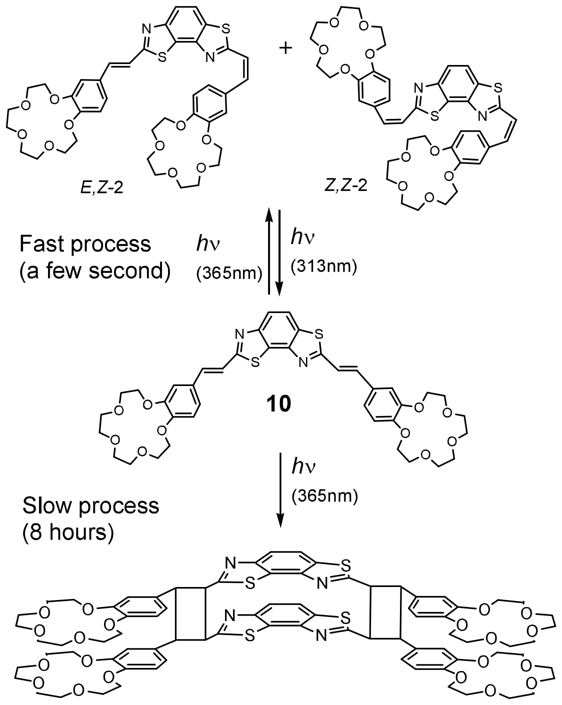
Figure 3. X-Ray structure of the $[\mathbf{8}_2{\cdot}Ba^{2+}](ClO_4^-)_2$ *complex*

In the sandwich complex with Ba^{2+} cations, the mutual arrangements of 2-styrylbenzothiazole molecules **9** are favourable for the occurring of the reaction of the photocycloaddition. Upon irradiation with blue light, **9** undergoes stereoselective [2+2]-photocycloaddition (PCA) to afford isomeric cyclobutane derivatives "*E*+*E*" (78%) and "*E*+*Z*" (22%) isomers with relatively high combined quantum yield (0.13) (Scheme 11) [32].



Scheme 11

The photochemical investigation of the bis-crown-containing benzobis(thiazole) **10** showed that the irradiation of the compound results in the proceeding of two photochromic processes: *E,Z*-photoisomerization and [2+2]-photocycloaddition (Scheme 12). The last process occurs due to organization of molecules in dimers through the π-stacking interaction of large chromophore systems of molecules. The complex formation of sandwich type between **10** and Ba^{2+} cations increases the effectivity of photocycloaddition reaction what fully suppresses the *E,Z*-photoisomerization around the double C=C bonds. The photochemical behaviour of the complex $\mathbf{10}{\cdot}(Mg^{2+})_2$ is similar to one of the free ligand **10** [33].



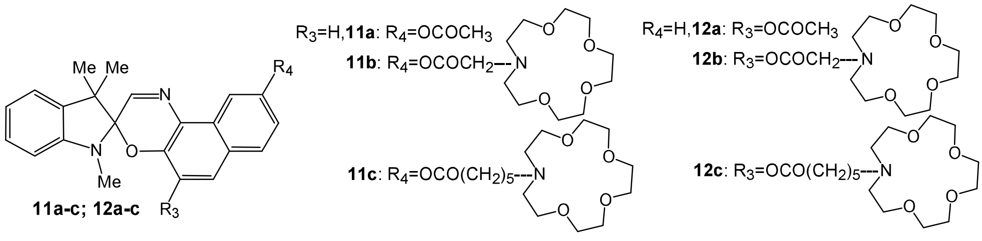
Scheme 12

Thus, the CESD are capable to form supramolecular complexes containing two dye molecules and 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 reaction. The variation of the structure of CESD would make it possible to change the supramolecular spatial structure of the dimer in a desired direction and thus to control the efficiency of interaction and stereochemistry of the final product of PCA.

4. Macrocyclic Systems whose Photochromism is Based on Electrocyclic Reaction

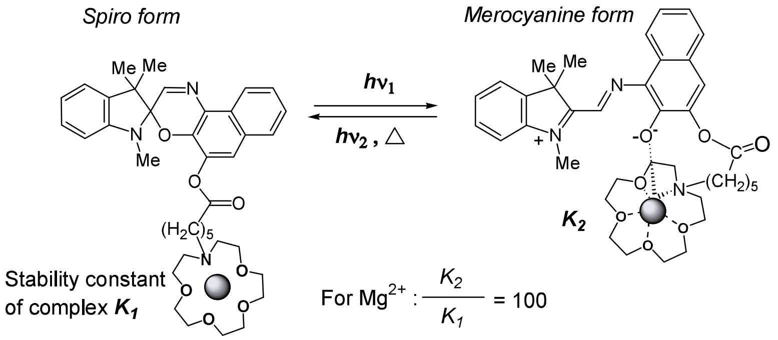
4.1. CROWN-CONTAINING SPIROOXAZINES

The structure and the position of the crown-containing fragments in spiro compound are important factors influencing the stability of the merocyanine form upon complex formation. Thus, investigations into spiroindolinonaphthoxazines bearing an aza-15-crown-5 moiety in 9′-positions (**11a-c**) of naphthalene ring showed insignificant influence of the metal cation presence on the spectral and kinetic characteristics of compounds (Scheme 13) [34]. Otherwise, spironaphthoxazine derivatives with a monoazacrown ether moiety at the 5′-position (**12a-c**) are discovered to be sensitive to the presence of metal cations [35].



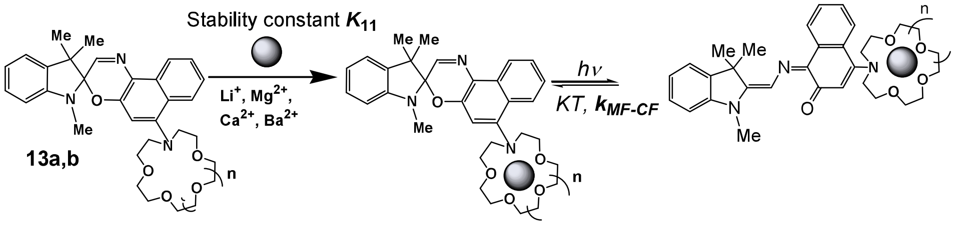
Scheme 13

Binding of alkaline earth metal ions (Mg^{2+}, Ca^{2+} and Ba^{2+}) by the crown moieties in **12a-c** leads to isomerization of the crowned spironaphthoxazines even in the dark. UV-Vis, NMR and Raman spectroscopy suggests that a metal ion complexed by the crown moiety in the merocyanine isomer is subject to intramolecular interaction with the phenoxide anion. In fact, the metal ion is bound more strongly than in the corresponding closed isomer, owing to the additional-binding-site effect. On exposure to visible light, the cation-bound merocyanine form readily reverts to the spiro form, releasing the metal ions to some extent. The alternating irradiation with UV and visible light or alternating switching-on and -off of the visible light causes isomerization of the crowned spironaphthoxazines, which, in turn, provides a tool for controlling their cation-complexing capacity (Scheme 14).



Scheme 14

For the spironaphthoxazines conjugated with aza-15(18)-crown-5(6)-ether moieties at 6'-position of naphthalene fragment (**13a,b**) it was found that the addition of Li^{+} and alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) metal cations to **13a,b** solutions results in a hypsochromic shift of the UV absorption band of the spiro form and a bathochromic shift of the absorption band of the merocyanine form in the visible region [36]. In addition, the equilibrium shifts to the merocyanine form, and the lifetime of the photoinduced merocyanine form increases (Scheme 15). The isomerization of crown-containing compound **13a,b** to the colored merocyanine form was promoted most strongly by the presence of metal ions, which are expected to be the best recognized by the crown ether ring (Scheme 15).



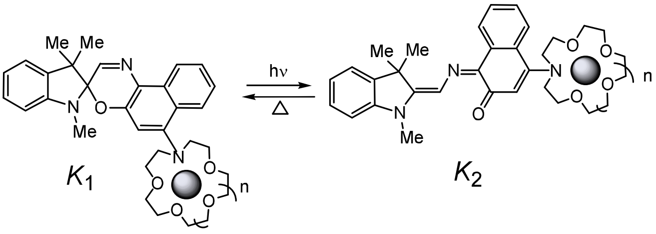
lg K_{11}	Li^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
13a: n=1	3.3	3.2	$\boxed{3.6}$	3.1
13b: n=2		2.2	4.6	$\boxed{5.6}$

$k_{MF\text{-}CF}$ (rate constant of ring-closure reaction)

	Li^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
n=1	7.7	1.2	$\boxed{1.2}$	3.6	5.6
n=2	8.7	0.9	2.2	$\boxed{0.8}$	$\boxed{0.8}$

Scheme 15

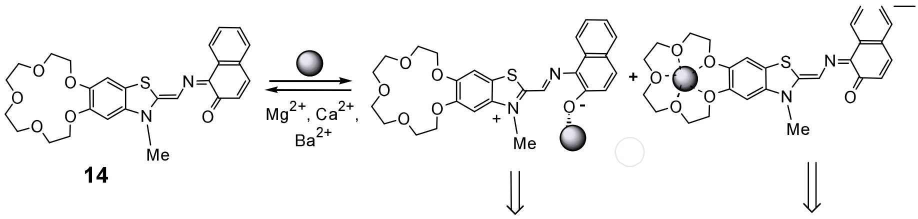
The UV-induced isomerisation of **13a,b** into the merocyanine form causes a decrease of the cation binding ability (Scheme 16).



Ca^{2+}	lgK_1	lgK_2
n = 1	3.6	2.4
n = 2	4.6	2.3

Scheme 16

The method for synthesis of the spirobenzothiazolinonaphthoxazine **14** stable in merocyanine form and containing crown ether fragment in the heterocyclic part was developed [37]. The presence of alkali earth metal cations in the solution of crown ether containing merocyanine dye in MeCN results in coordination of metal cations with two binding centers: crown ether fragment and merocyanine oxygen atom (Scheme 17). These complexes are structurally differ from each other. The complex formation process causes the changes in spectral characteristics and influences on the photochromic behaviour of the prepared compound.



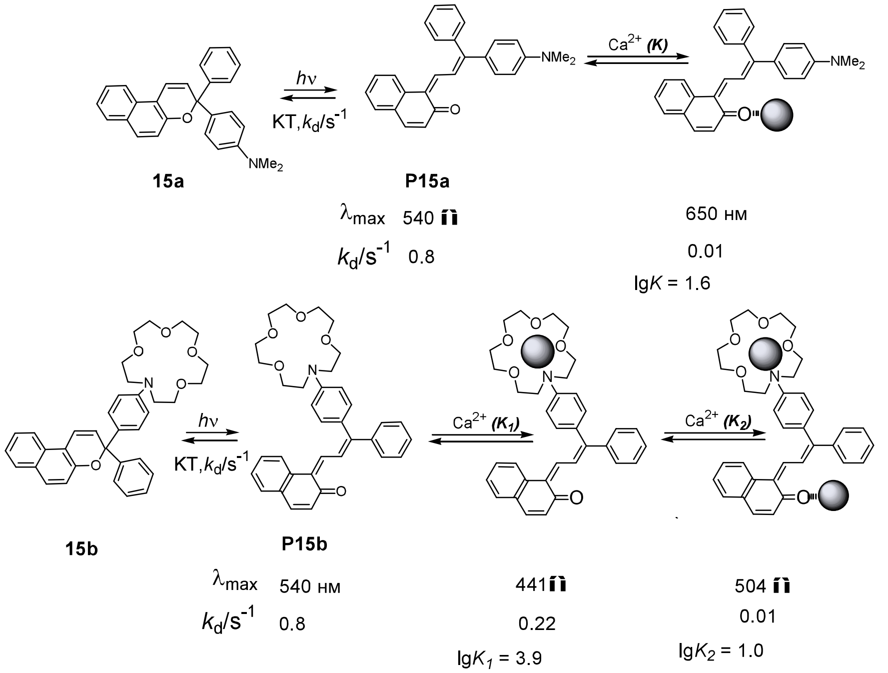
-Large hypsochromic shift of long wavelength absorption band;
-Stabilizing of open form

-Small influence on spectral characteristics;
-Stabilizing of closed form

Scheme 17

4.2. CROWN-CONTAINING BENZOCHROMENES

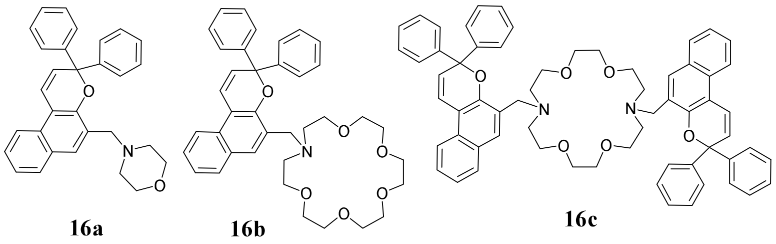
The complex formation and photochromic behaviour of the azacrown-containing chromene **15b** and its crown-free analogue **15a** were studied in detail [38,39]. The addition of $Ca(ClO_4)_2$ to a solution of **15b** led to the shift of the band at 400 nm, indicating the binding of Ca^{2+} by the macrocyclic unit of **15b**. In contrast, the presence of $Ca(ClO_4)_2$ in a solution of **15a** even at a high concentration of 0.1 mol dm^{-3} had no effect on the absorption spectrum of **15a**.



Scheme 18

The photochromic transformation of the closed form of **15b** to merocyanine form (**P15a**) leads to a marked decrease in the ability of **15b** to bind Ca^{2+}. Thus, the stability constant for the merocyanine complex **P15b**•Ca^{2+} is almost one order of magnitude lower than that for the corresponding complex of the closed form. The dimethylamino substituted chromene **15a** unable to bind Ca^{2+} in the dark shows small Ca^{2+}-binding ability upon UV irradiation. The formation of a week 1:1 complex between merocyanine form of **P15a** and Ca^{2+} leads to a large bathochromic effect and to a significant decrease in the rate constant of dark ring-closure reaction of **P15a**, indicating that the metal ion in the 1:1 complex **P15a**•Ca^{2+} coordinates to the oxygen atom of the merocyanine (Scheme 18). The formation of a 1:1 complex between merocyanine form of **P15b** and Ca^{2+} leads to a large hypsochromic effect. For **P15b**, the decrease in the rate constant of dark ring-closure reaction upon 1:1 complexation is less considerable than in the case of **P15a** (Scheme 18). This indicates that the Ca^{2+} ion in this complex coordinates to the crown ether moiety. In addition to the 1:1 complex, the photoinduced merocyanine **P15b** is able to form a very week 1:2 complex **P15b**•$(Ca^{2+})_2$ 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 **P15b**•Ca^{2+} complex (Scheme 18).

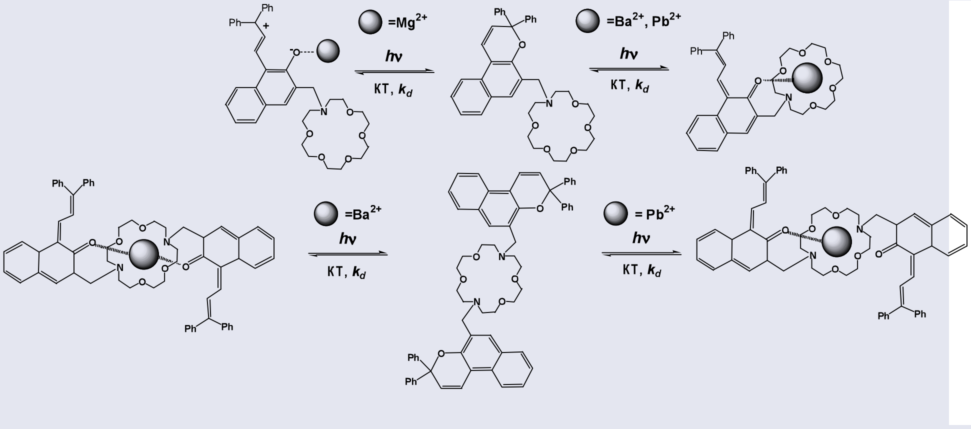
The results of the spectral and kinetic investigations of the benzochromenes **16a-c** and their complexes with Mg^{2+}, Ba^{2+} and Pb^{2+} were presented in [40] (Scheme 19).



Scheme 19

Compounds **16a-c** in MeCN exhibited very similar UV-Vis absorption spectra. The addition of Mg^{2+}, $Ba^{2+}$and Pb^{2+} cations to a solution of **16a-c** led to the small changes in absorption spectra. In contrast, the presence of the metal cations in the solution of photomerocyane form of **16a-c** led to a significant change in the dark lifetime of photomerocyanines and caused strong shifts in their absorption spectra, indicating that these compounds were able to bind metal cations.

The formation of a 1:1 complex between open form of **16a-c** and Mg^{2+} leads to an increase in the rate constant for the dark ring-closure reaction of **16a-c** (Scheme 20, Table 3). The Mg^{2+} ion binds with carbonyl oxygen atom what leads to the increase of the polarity of molecule (Scheme 20). In the polar form the dark ring-closure reaction occurs more easily.



Scheme 20

The formation of a 1:1 complex between open form of **16b,c** and Ba^{2+}, Pb^{2+} leads to a large bathochromic effect and the decrease in the rate constant for dark ring-closure reaction. The effect is explained by the formation of the anion-"capped" complex of metal cation located in crown ether cavity with carbonyl oxygen atom (Scheme 20). Substantial difference in the changes of magnitude of k_d/s^{-1} was obtained for the complexes of mono- and bischromene **16b,c** with Ba^{2+} (Table 3). The difference is due to in the complex of **16c** with Ba^{2+} the carbonyl atoms of both chromene units participate in the formation of anion-"capped" complex, whereas, the anion-"capped" complex between **16b** and Ba^{2+} is formed by formation of one coordination bond (Scheme 20). For the complexes of mono- **16b** and bischromenes **16c** with Pb^{2+} the magnitudes of k_d/s^{-1} are closed to each other, what means the participation of only one chromene unit of **1c** in the formation of anion-“capped” complex with Pb^{2+} (Scheme 20).

TABLE 3. Effect of the Mg^{2+}, $Ba^{2+}$and Pb^{2+} presence on the rate constant k_d / $s^{-1}$of dark ring-closure reaction, relationship ligand:metal cations=1:1

Chromene	k_d / s^{-}			
	---	Mg^{2+}	Ba^{2+}	Pb^{2+}
16a	0.11	0.44	0.18	0.12
16b	0.11	0.49	0.0016	0.00035
16c	0.15	0.19	0.00034	0.00054

Thus, the study of the crown containing systems whose photochromism is based on the electrocyclic transformation demonstrates that the complex formation process can be successfully applied for controlling of its spectral and photochemical properties.

5. Conclusions

The intense research efforts made in photochromic crown ethers convincingly demonstrated that this type of systems represent a novel class of photochromic molecules suited for some possible applications. A substantial influence of complex formation on the spectral characteristics of the molecules and on the kinetics of phototransformation was found. Thus, incorporation of a crown ether moiety, which is able to bind metal ions into the photochromic skeleton, can help to tune the photochromic properties by using complex formation. The development of these photochromic systems is aimed at improving the photostability, increasing the sensitivity and obtaining a broader range of operating wavelengths.

In turn, the conformational transformations of molecules that accompany the photoreaction sharply influence the ability of molecules to bind metal cations. This implies that photocontrolled complex formation is possible in this type of system.

Examples of potential applications utilizing the physical or chemical changes that accompany the observed shift of the absorption maxima include:

- photoswitching extraction of metal cations;
- optoelectronic systems;
- photoswitching transport through membranes;
- optical information storage;
- photochemical switchable enzymatic systems;
- nonlinear optical devices.

The results obtained were extended to novel series of photochromic systems. The important objectives for the future research include: a) synthesis of new compounds; b) more extensive and more detailed investigation of their physico-chemical properties in order to find structure-property correlations; and c) modification of already known systems by incorporating them physically or chemically into liquid crystals or polymers in order to develop new effective materials based on the novel photochromic molecules.

6. Acknowledgements

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