

Photoswitchable molecular receptors

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Abstract

The review describes photoswitchable molecular receptors based on crown-ether systems. The important feature of the systems is reversible change in the capacity of a photochromic host molecule for association with guests upon irradiation. From the other side, the exploration of the complex formation process in crown-ether systems leads to a novel approach to the modification of photochromic behavior. The results obtained show that the introduction of crown-ether moieties into dye molecules affords compounds that can change their spectral and photochromic properties upon complex formation. The researchers believe that the novel photochromic systems can now be regarded as being promising for traditional applications (photochromic ophthalmic lenses or camera filters, reversible holographic systems and cosmetics) and molecular electronics, biomimetic chemistry, and optical information storage.

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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 the most important group of the photochromic system is that based on pericyclic reactions [2,3]; it is used in practice (photochromic lenses) and has potential industrial applications [4].

The incorporation of an ionophore into a photochromic system affords a substance that optically responds to the presence of cations in solution. 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]. Photochromic crown ethers constitute a new class of artificial receptors in which the recognition of metal cations induces a conformational change in the receptor framework accompanied by signaling (coloration). Examples of potential applications utilizing the physical or chemical changes that accompany the observed shift of the absorption maxima include [6]:

- photoswitching extraction of metal cations;
- optoelectronic systems;

- photoswitching transport through membranes;
- optical information storage;
- photochemical switchable enzymatic systems;
- nonlinear optical devices.

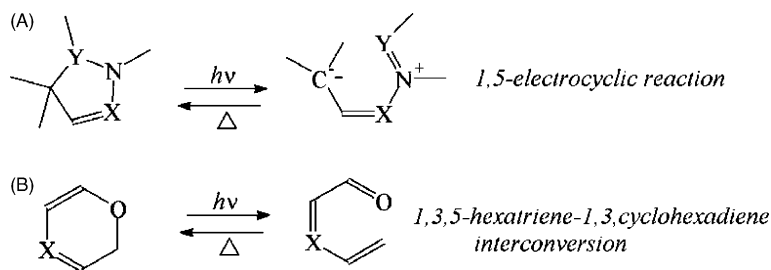
This review surveys studies devoted to the molecular receptors based on photochromic crown ethers. The development of these photochromic systems is aimed at improving the photostability, increasing the sensitivity and obtaining a broader range of operating wavelengths. Incorporation of a crown-ether moiety, which is able to bind metal ions into the chromophore skeleton, can help to tune the photochromic properties by using complex formation.

2. Electrocyclic reactions

Of different classes of pericyclic reactions, electrocyclic reactions have proved to be especially suitable as a basis for photochromic systems [6]. Of numerous possible electrocyclization reactions, only two reactions shown in Scheme 1 have been applied by now in photochromic crown ethers.

It was not until quite recently that the first type of reaction A has been successfully used in effective photochromic systems dihydroindolizines (DHI) [2]. The $4n + 2$ systems whose photochromism results from the electrocyclic 1,3,5-hexatriene-1,3-cyclohexadiene interconversion (reaction B) comprise spirobenzopyrans, spironaphthoxazines, chromenes, fulgides, and diarylethylenes [6].

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Scheme 1.

2.1. Dihydroindolizines

The photochromism of DHI was discovered only in 1979 [7]. New molecules based on a pentaatomic, six-electron $(4n + 2)\pi$ system can undergo ring opening to give a zwitterionic species or neutral heteropentadienes (Scheme 1, reaction A).

The photochemical transformation of the colorless form to betaines can be induced only photochemically; however, the back reaction can be brought about thermally or photochemically. 1,5-Electrocyclization can be controlled by varying the substituents in the molecule. A new approach to fine tuning of physical properties of DHI includes the use of complex formation in crown ether-containing DHI [8–11]. Data on DHI linked to podand, crown-ether or calixarene anchor groups can be found in the literature (Scheme 2).

After addition of metal cations, DHI **1** shows the following specific properties of the excited state:

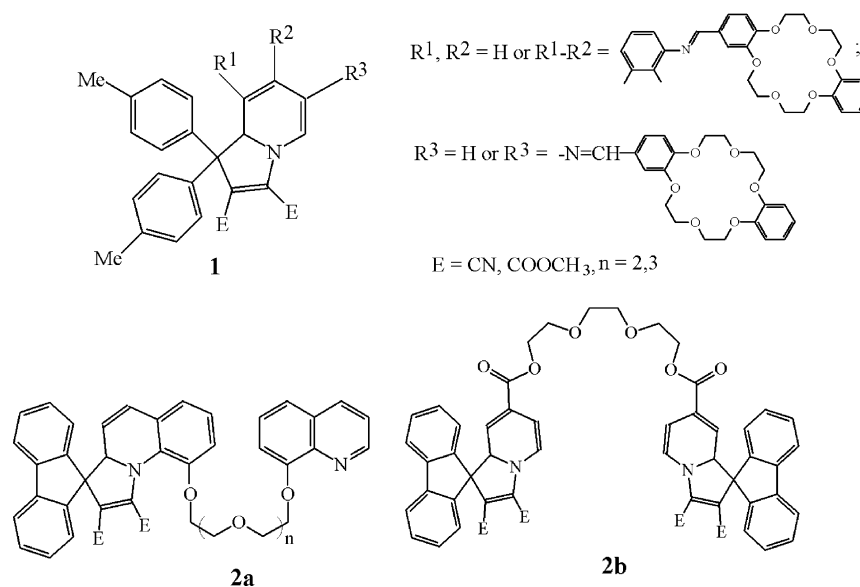
- Bathochromic shift (up to 40 nm for Ba^{2+}) in the UV spectra of both the colorless and betaine isomers.
- An increase of the fluorescence intensity.
- Changes in the rate of ring opening reaction; in particular, alkali metal cations decelerate and alkaline earth

metal cations accelerate the photoinduced reaction. The effect depends on the selectivity of the cation binding.

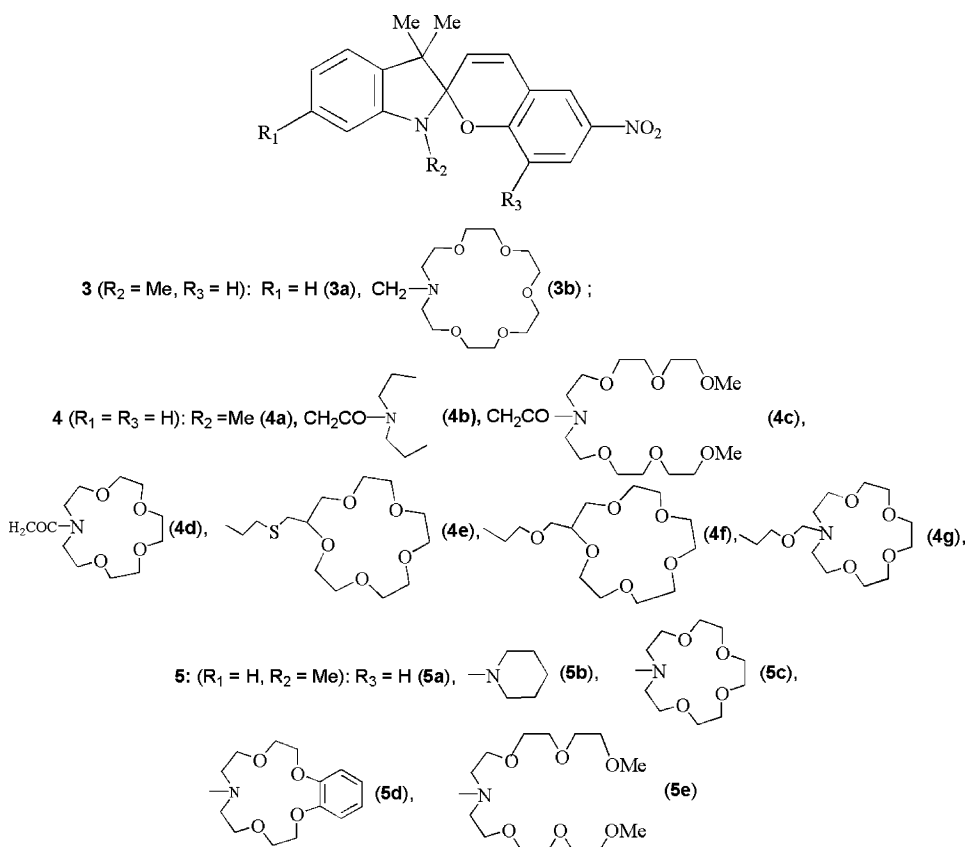
In the case of DHI **2a**, **2b**, coordination to alkaline earth metal cations was found to be weak; thus, it has only a slight influence on the spectral and photochromic properties. This may be due to the high flexibility of the podand chain in DHI **2a**, **2b**, which prevents the formation of a sufficiently stable complex with metal cations.

2.2. Spirobenzopyrans

An electrocyclic $(4n + 2)$ reaction has been found for spiroopyrans. UV irradiation of the colorless spiro compounds leads to the cleavage of the C–O bond to give open-chain compounds which strongly absorb in the visible region (Scheme 1, reaction B, X = CH) [6]. The crowned spirobenzopyrans can modulate the cation-complexing capacity of the crown-ether moiety due to photoisomerization, namely, interconversion of electrically neutral spiroopyran and a zwitterionic merocyanine form (MF). In turn, complexation with cations can substantially change the spectral and photochromic characteristics of the molecules.



Scheme 2.



Scheme 3.

Spirobenzopyran derivatives containing monoazacrown ether and 15-crown-5 ether moieties and their acyclic analogues, either at the 6'-position of the indoline cycle (**3a**, **3b**), or at the N atom (**4a–4g**), or at the 8-position of the benzopyrane ring (**5a–5e**) have been synthesized (Scheme 3) [12–14].

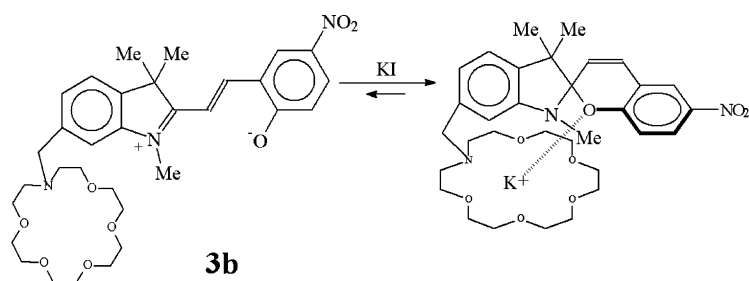
In the study of compounds **3a**, **3b** and **4a–4g**, the following results were obtained [12]. The absorption spectra of spiropyrans **3a** and **4a** containing no crown ether were not at all affected by alkali metal iodides. The isomerization of crown-containing compound **3b** to the colored MF was suppressed most strongly by the presence of K^+ , which is expected to be the best recognized by the crown-ether ring (Scheme 4).

The design of the crowned spirobenzopyrans **4b–4g** was based on the fact that the strong interaction between the

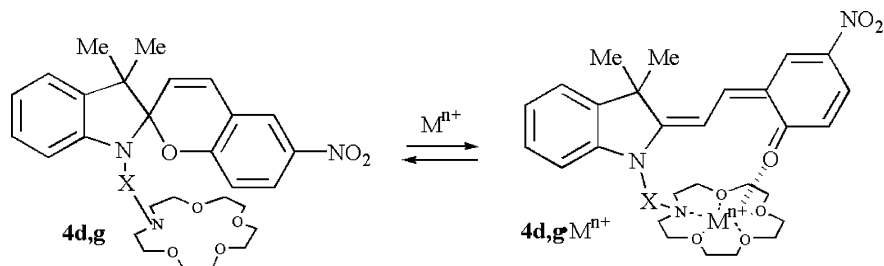
complexed cations and the phenoxide anion of the MF could favor the spiro-to-merocyanine isomerization. The colored complex formed by spiropyrans **4d**, **4g** and alkali metal cations is shown in Scheme 5 [12,13].

The influence of alkali metal cations on the coloration was found to be governed by several factors: (1) the size of the crown ring; (2) the position of the recognition; (3) the electric properties of both the complexed cation and the merocyanine dipole; (4) the length of the alkyl chains linking the spiro-pyran moiety and the crown-ether moiety. For spiropyrans containing azacrown fragments **4d**, **4g**, selective coloration was found in compounds bearing a short linkage (CH_2CO) and aza-15-crown-5 ether (**4d**, $n = 1$) in the case of Li^+ and for aza-18-crown-6 (**4d**, $n = 2$) in the case of Na^+ .

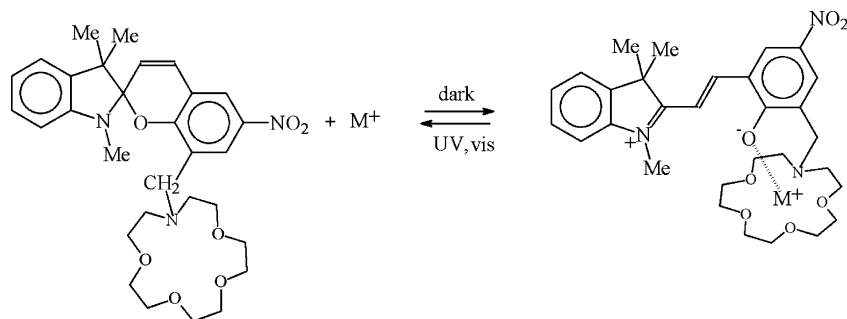
Spirobenzopyran derivatives having a monoazacrown moiety such as 12-crown-4, 15-crown-5 and 18-crown-6 or



Scheme 4.



Scheme 5.



Scheme 6.

their acyclic analogue at the 8-position (**5a–5e**) have been studied in detail [14,15]. Binding of alkali metal ions (Li^+ , Na^+ , and K^+) by the crown moieties leads to isomerization of the crowned spiropyrans even in the dark. The data of ^7Li and ^{23}Na NMR spectroscopy suggest that an alkali metal ion, especially Li^+ , complexed by the crown moiety in the merocyanine isomer is subject to intramolecular interaction with the phenoxide anion and hence it is bound more strongly than that in the corresponding spiropyrans isomer, owing to the additional-binding-site effect. On exposure to visible light, the cation-bound MF readily reverts to the spiropyrans 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 spiropyrans even in the presence of alkali metal ions, which in turn provides a tool for controlling their cation-complexing capacity (Scheme 6).

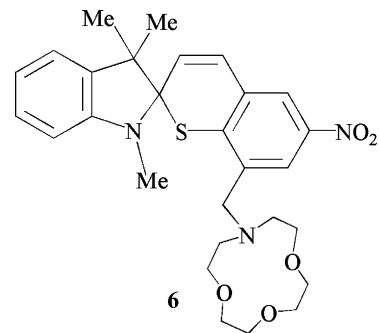
The isomerization behavior of crown-containing spiropyrans **6** (Scheme 7) is very different from that of its corresponding spiropyrans **5b**, the pyran ring of which can be opened readily by Li^+ complexation even without UV light irradiation. Thermal decoloration of the **6** solution in the presence and absence of Li^+ was followed by turning off UV light, the half life time of the merocyanine isomer increases from 5 s to 2 min in the presence of Li^+ [16,17].

The photochromic behavior of benzocrown ether-linked spiropyrans **7b** and its analogue **7a**, which has no crown ring, was studied in a dichloromethane solution and in a poly(vinyl chloride) membrane (Scheme 8) [18].

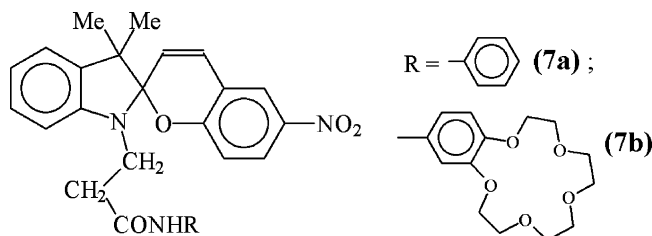
A dichloromethane solution containing compound **7b** extracts alkali metal picrates from water; the binding capacity varies in the sequence $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$. The liq-

uid extraction of alkali metal picrates by **7b** decreases by up to 3–6% after exposure to UV light; compound **7a** does not bind these cations either before or after irradiation with light. Both spiropyrans **7a**, **7b** show normal photochromism in membranes. In the case of **7b**, the magnitude of the photoinduced change depends on the sort and concentration of the alkali metal cation.

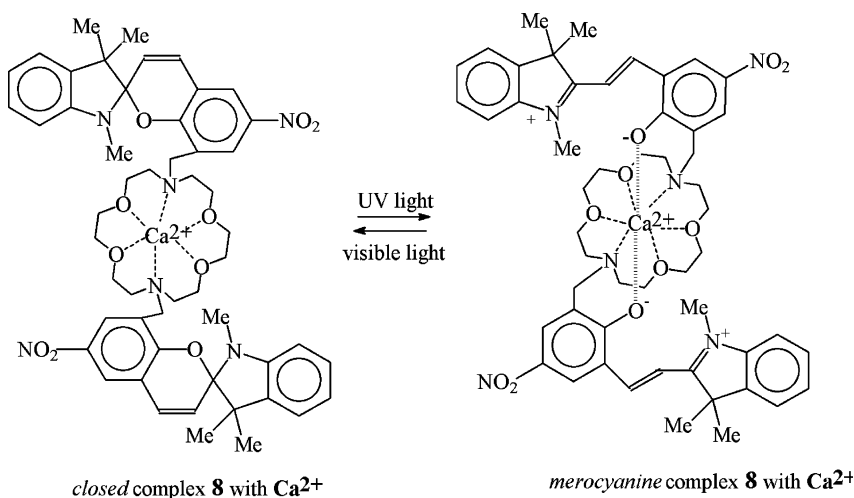
Crowned bis(spiropyrans) **8** was investigated in solution and compared with the corresponding derivative



Scheme 7.



Scheme 8.



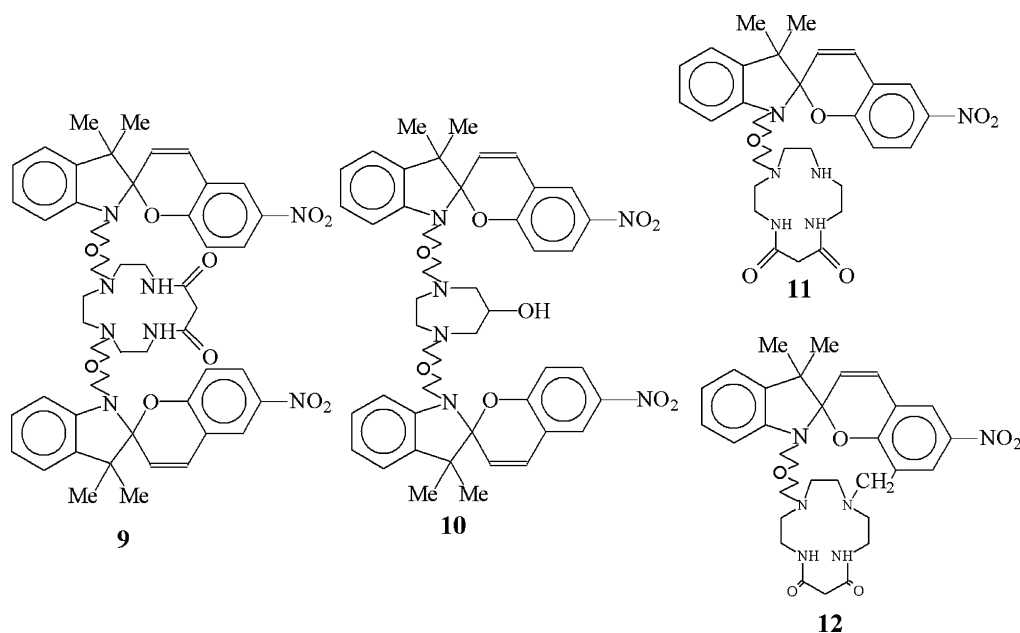
Scheme 9.

incorporating only one spirobenzopyran unit [19–21]. Complexing of multicharged metal ions, especially Ca^{2+} and La^{3+} , by crowned bis(spirobenzopyran) facilitates isomerization of the spirobenzopyran moiety to the corresponding MF due to the effective intramolecular interaction between the crown-complexed cation and the two phenoxide anions in the cation complexes of the MF (Scheme 9). The isomerization of **8** to the corresponding MF induced by complexation with a cation has been studied by spectrophotometry, NMR spectroscopy, and molecular orbital calculations. The results indicate that, upon complexation with Li^+ , one of the two spirobenzopyran units in compound **8** isomerizes to the MF. The complexation of divalent and trivalent metal cations by **8** forces two spirobenzopyran units to isomerize due to the intermolecular interaction between the multicharged

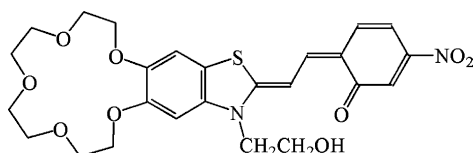
cation and the two phenoxide anions. Significant photoinduced switching of ionic conductivity was implemented in composite films containing compound **8** and calcium salts.

Bis(spiropyran)s containing an azacrown fragment (**9**, **10**) and their monomeric analogues (**11**, **12**) showed the recognition of transition metal cations (Cu^{2+} , Co^{2+} , Ni^{2+}) accompanied by isomerization to the corresponding merocyanine isomers (Scheme 10) [22]. Compounds **9–12** exhibit a high selectivity with respect to Co^{2+} and compound **12**, with respect to Cu^{2+} .

Spirobenzothiazolinopyran **13**, which contains a crowned benzothiazolium fragment, has been prepared [23]. It is stable as the open form (λ_{max} 488–579 nm in various solvents). Compound **13** exhibits a reversed type of photochromism.



Scheme 10.

**13**

Scheme 11.

No experiments on the effect of introducing metal cations into the crown-ether moiety have been reported (Scheme 11).

2.3. Spirooxazines

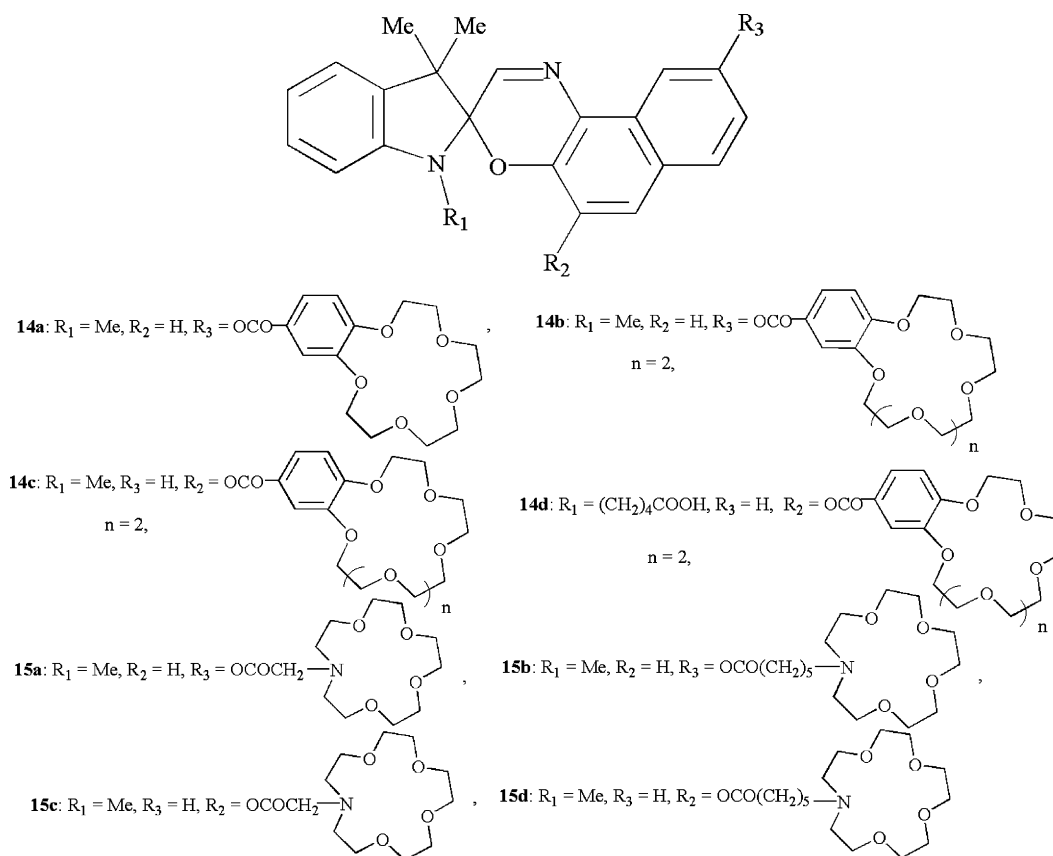
Photochromic spirooxazine compounds are molecules containing 2H-[1,4]oxazine in which the number 2 carbon of the oxazine ring is involved in a spiro linkage. Photochromism of spirooxazines implies the heterolytic or homolytic cleavage and reformation of the carbon–oxygen single bond of the oxazine ring (Scheme 1, reaction B, X = N).

Methods for the synthesis of new spironaphthoxazines containing benzo-15(18)-crown-5(6) (**14a–d**) and aza-15-crown-5 (**15a–15d**) moieties in two different positions (5' and 9') have been developed (Scheme 12) [24–27].

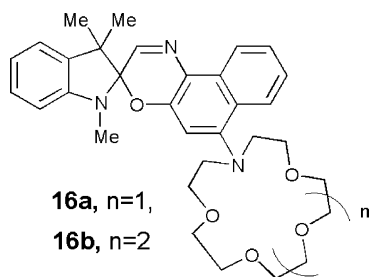
The structure and the position of the crown-containing fragments in spiro compound are important factors influencing the stability of the MF. Thus, investigations into spiroindolinonaphthoxazines bearing a benzo-15(18)-crown-5(6) moiety in different positions (**14a–14d**) showed that the rigid structure of the spacer prevents the formation of an additional coordination bond between the oxygen atom of the MF of the dye and the metal cation in the crown-ether cavity, which results in substantial stabilization of the MF [24,25].

The investigation of the series of compounds **15a–15d** showed that the introduction of a flexible spacer into position 5' of a spiro compound shows the significant influence of complex formation on the kinetics of decoloration of the MF of the spiro compound. A comparative study of the spectral properties of crown-ether-containing and crown-ether-free compounds indicated that complexation follows two competing routes, involving both free metal cations and those linked to the crown fragment [26,27].

Spironaphthoxazines conjugated with aza-15(18)-crown-5(6)-ether moieties at 6'-position of naphthalene fragment (**16a, 16b**) were synthesized and studied for the first time (Scheme 13) [28,29]. The addition of Li⁺ and alkaline earth (Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) metal cations to **16a, 16b** solutions results in a hypsochromic shift of the UV absorption band of the spiro form and a bathochromic shift of the



Scheme 12.



Scheme 13.

absorption band of the MF in the visible region. In addition, the equilibrium shifts to the MF, and the lifetime of the photoinduced MF increases. The UV-induced isomerization of **16a**, **16b** into the MF causes a decrease of the cation binding ability.

The method for synthesis of the spirobenzothiazolinonaphthoxazine **17** stable in MF and containing crown-ether fragment was developed [30]. It was found that the addition of alkaline earth metal cations into the solution of crown ether-containing merocyanine dye in MeCN results in coordination of metal cation with two binding centers: crown-ether fragment and merocyanine oxygen atom (Scheme 14). These complexes are substantial structurally

differ from each other. The complex formation process causes the changes in UV spectra and influences on the photochromic behavior of the prepared compound.

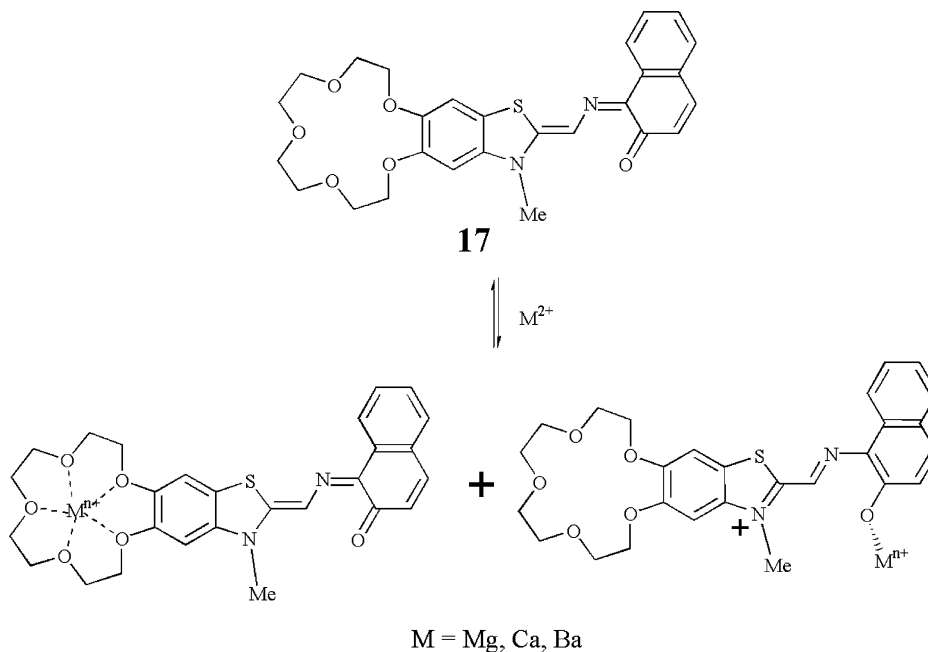
2.4. Benzo and naphthopyrans (chromenes)

The general structure of benzo and naphthopyrans in which R_1 and R_2 are not joined to form a spiro heterocyclic group, is shown in Scheme 15 [31].

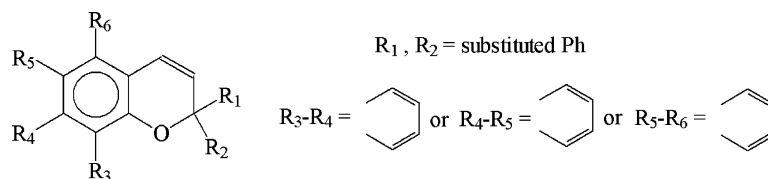
The photochromism of benzo and naphthopyrans is believed to involve rupture of the oxygen–carbon bond of the pyran ring ($4n + 2$ electrocyclic reaction), as shown in Scheme 16 [32].

A reasonable level of room-temperature photochromism requires that the pyran is substituted at the 2-position with conjugate substituents such as phenyl. The color of the open forms can be varied over a broad range of the visible spectrum by introducing substituents into the naphthyl moiety or into the aromatic groups present in the 2-position of the pyran ring [33].

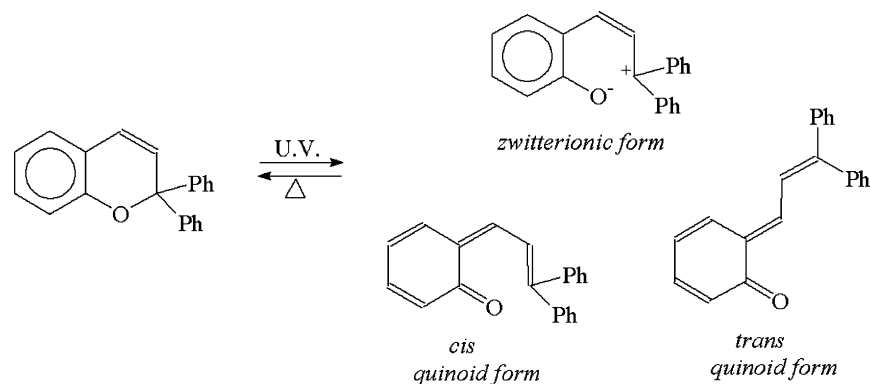
As regards crown-ether-containing compounds of this series, a report devoted to the photoreversible binding of Pb^{2+} by a crowned photochromic naphthopyran **18** has been published [34]. It was reported that binding of Pb^{2+} to a



Scheme 14.



Scheme 15.

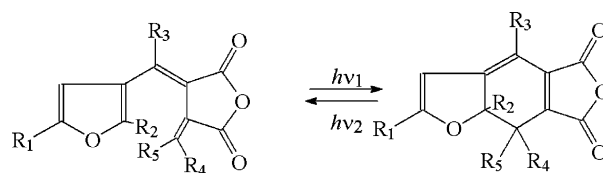
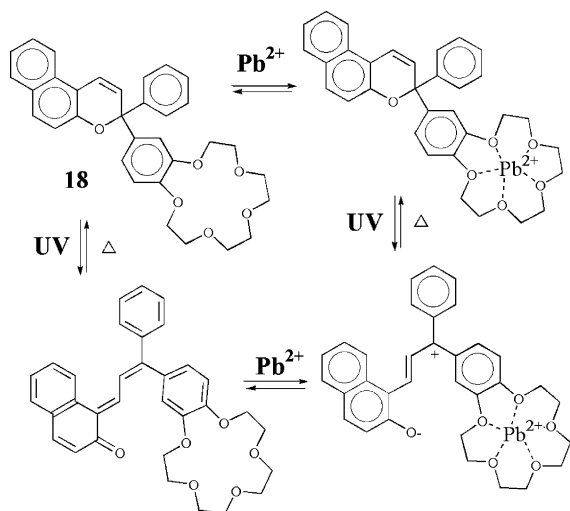


benzo-15-crown-5 ether occurs in the dark and is followed by liberation of Pb^{2+} from the crown ether on exposure to the UV light. This reversible phenomenon may be due to the pronounced geometry change which accompanies cleavage of the carbon–oxygen ring during absorption of UV light, and/or to the change in the affinity to Pb^{2+} caused by the fact that the electron density of the crown-ether oxygen participates in the stabilization of the newly formed carbocation charge (Scheme 17).

2.5. Fulgides

The fulgides belong to a class of photochromic compounds for which the thermal reversal or decoloration of the colored species is forbidden [35]. Therefore, the transformation is largely driven photochemically, as illustrated in Scheme 18. In this class of compounds, the photochromic transformation includes 1,5-hydrogen shift following a photochemical valence isomerization.

The cyclic crowned fulgenates, corresponding to 14-crown-4 (**19a**), 17-crown-5 (**19b**), and 20-crown-6 (**19c**) were synthesized and the association constants with Li^+ ,



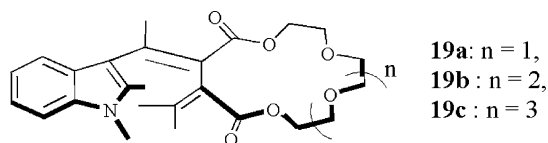
Na^+ , K^+ , were determined for colorless and colored isomers [36]. The following features are worth noting: (1) the association constant with Na^+ is the greatest for **19b**, and that with K^+ is the greatest for **19c**. The association of the open form is stronger than that of the cyclic form. The complexes exhibit no photocoloration (Scheme 19).

The indolylfulgide **20a** containing a benzo-18-crown-6 moiety has been synthesized; its photochromic properties are being studied (Scheme 20) [37].

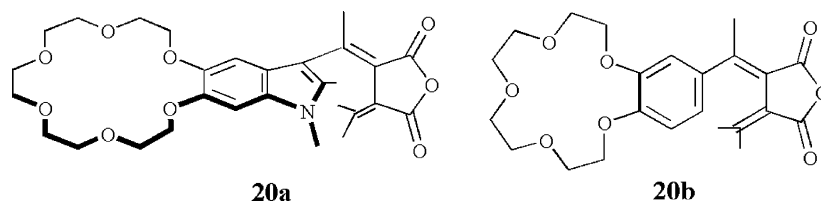
It has been found [37] for novel benzo-15-crown-5-modified fulgide **20b** that the absorption spectra of the initial and colored forms shift hypsochromically by up to 50 nm upon complex formation with alkali and alkaline earth metal cations. The decoloration rate evidently decreases upon selective cation binding.

2.6. Diarylethenes with heterocyclic groups

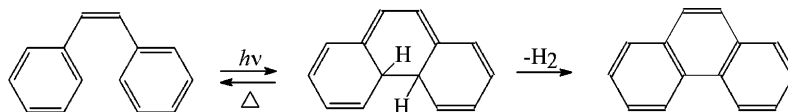
Stilbene is well known to undergo a *trans*–*cis* photoisomerization upon irradiation with UV light [38,39]. In addition to this isomerization, stilbene shows a photocyclization reaction to produce dihydrophenanthrene. Although in the presence of air, the dihydrophenanthrene irreversibly converts to phenanthrene upon hydrogen abstraction with oxygen, it returns thermally to the initial stilbene in the absence of oxygen (Scheme 21).



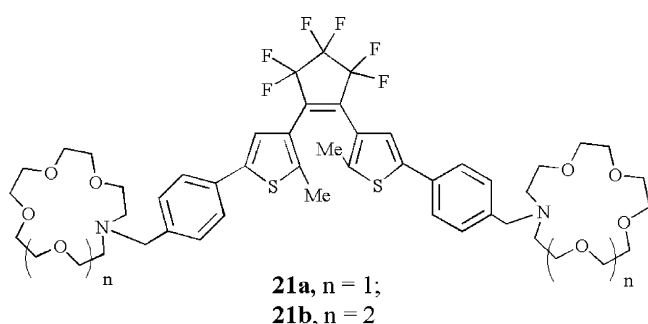
19a: $n = 1$,
19b: $n = 2$,
19c: $n = 3$



Scheme 20.



Scheme 21.



Scheme 22.

The synthesis and behavior of novel bis(azacrown ether)-containing diarylethenes **21a**, **21b** were described in [40] (Scheme 22). The experiments on the extraction of metal picrates demonstrated selectivity of **21a** toward Na^+ and **21b** toward K^+ and Rb^+ . The open form exhibits higher capacity for cation binding (by 5–10%) than the cyclic form. The conformational flexibility of the system in the open form permits the crown ethers to act in concert in the binding of a metal cation (biscrown effect).

The quantum yield of the photocyclization of 1,2-bis-(2,4-dimethyl-3-thienyl)perfluorocyclopentene having two benzo-15-crown-5 ethers **22** was decreased by the addition of K^+ and Rb^+ perchlorates [41,42]. The phenomenon was explained by the formation of photochemically inert complex having a parallel conformation upon the intramolecular interaction of the two crown moieties with the metal ions (Scheme 23).

3. Cycloaddition reactions

3.1. [4 + 4] photocycloaddition reactions

Cycloaddition is yet another important class of pericyclic reactions, which provides a basis for photochromic molecules. Examples are provided by [4 + 4] cycloaddition of dianthracene derivatives. Photodimerization of an-

thracene can also be employed as a photochemical switch for photosensitive crown ethers. Photoirradiation of **23** in the presence of Li^+ gives the photocycloisomer (Scheme 24) [43]. The compound is fairly stable with Li^+ but readily reverts to the open form when the metal cation has been removed from the ring.

Yamashita et al. [44] have synthesized compound **24** in which intermolecular photodimerization of anthracene is completely suppressed. The cyclic form of the compound showed excellent Na^+ selectivity (Scheme 25).

In compound **25**, two anthracenes are linked by two polyether chains (Scheme 26) [45–48]. Intramolecular photodimerization proceeds rapidly in the presence of Na^+ as the template metal cation.

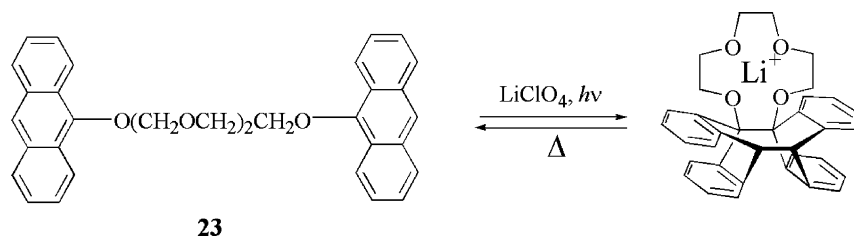
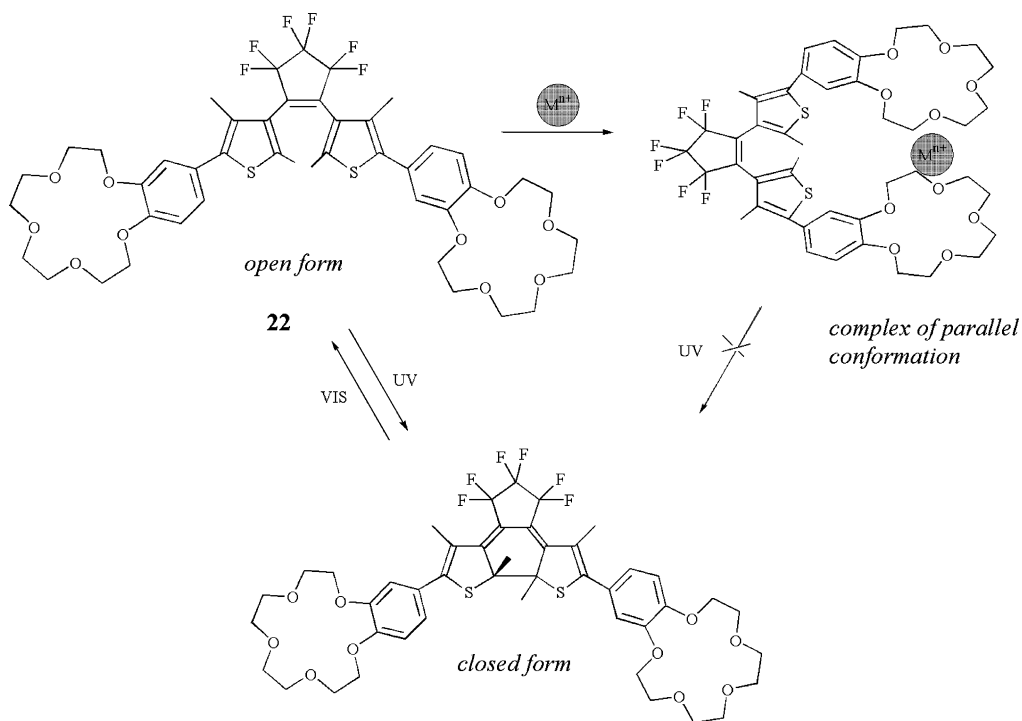
Photochemical dimerization of naphthalene end-labeled poly(ethylene glycol) oligomers in methanol in the presence of alkali metal and lanthanide cations (**26a–26f**) has been investigated [49]. Photoirradiation of the compounds resulted in a cubane-like dimer, the quantum yield of photodimerization being affected by alkali metal cations (Scheme 27). The process also shows dependence on the chain length (Table 1). All the results indicate that the polyether chain of the compounds is involved in the complex formation with the cations. Thus, the orientation of the terminal chromophores makes the dimerization reaction dependent on the cation size and the polyether length.

The reversibility of photodimerization is excellent, but the synthesis of anthracene- or naphthalene-containing crown ethers is fairly difficult and, therefore, these compounds are of limited utility.

Table 1
The relative quantum yield of photodimerization of **26** in methanol in the presence of alkali metal chlorides^a

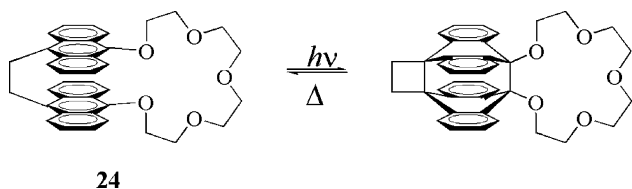
| <i>n</i> | Relative quantum yield | | | | |
|-------------------|------------------------|---------------|---------------|--------------|---------------|
| | Metal-free | Li^+ | Na^+ | K^+ | Cs^+ |
| 4 (26a) | 0.34 | 1.00 | 1.31 | 1.16 | 1.12 |
| 10 (26f) | 1.45 | 1.00 | 1.03 | 1.28 | 1.37 |

^a [Ligand] = $2.70 \times 10^{-5} \text{ mol dm}^{-3}$; [metalchloride] = $1.14 \times 10^{-4} \text{ mol dm}^{-3}$.

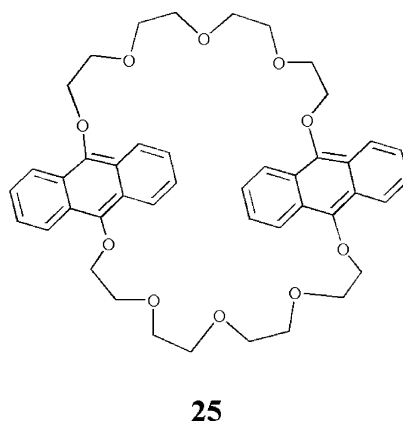


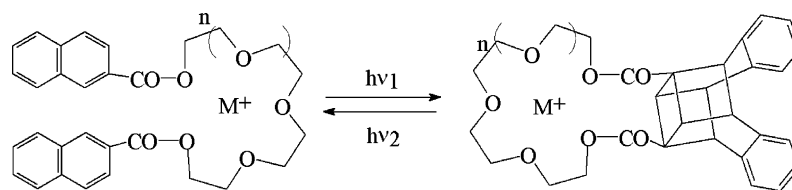
3.2. [2 + 2] photocycloaddition reactions

Photocycloaddition can be used to prepare a new kind of crown ether containing face-to-face oriented aromatic systems, which might modify their properties. The examples of this type of crown ether are few in number [50,51]. A new crown compounds **27a**, **27b** fused in a cyclophane skeleton was prepared by intramolecular [2 + 2] photocycloaddition (Scheme 28) [52–54]. The photophysical investigation of the cycloaddition revealed that it is an efficient reaction with a high quantum yield. The addition of an alkali metal ion increases the yield of the cycloadduct due to the template effect.



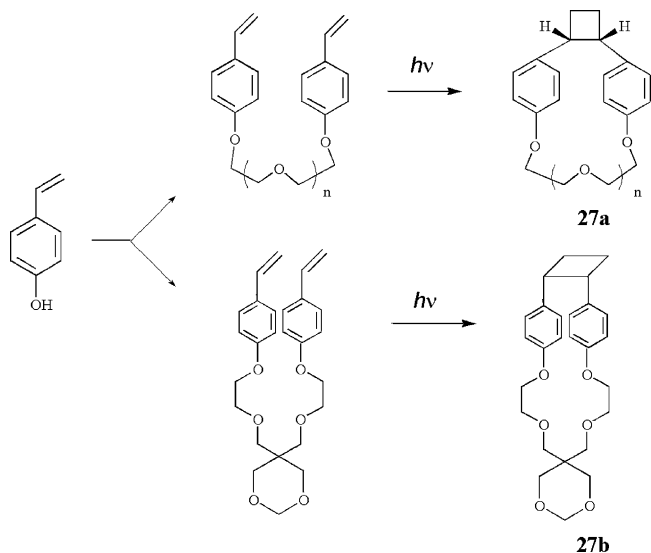
Cyclobutanecrown ethers formed by intramolecular [2+2] photocycloaddition have received considerable attention in view of the purpose in question [55–58]. However, the above-mentioned reaction was found to be irreversible.





26a-f: a, n = 4; b, n = 5; c, n = 6; d, n = 7; e, n = 8; f, n = 10

Scheme 27.



Scheme 28.

The possibility of photoreversible cleavage of the cyclobutane-crown ethers has been reported [59–62]. Irradiation of a solution of the crown ethers **28a–28c** in acetonitrile with light (300 nm) gave intramolecular [2 + 2] photocycloadducts in an excellent yield (above 90%) (Scheme 29). Subsequently, cyclobutanes were transformed into the initial compound upon irradiation with 220 nm UV light. The yield of the reversible reaction was much lower (up to 30%) because of side reactions.

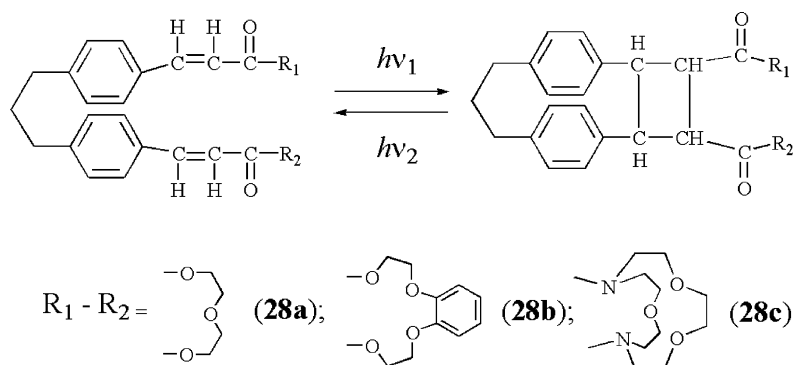
The stereochemistry of the major product of concerted [2 + 2]-photocycloaddition (PCA) of alkenes, which in-

volves the lowest singlet excited state of one of the two reacting molecules, is determined by taking into account the orbital symmetry and orbital overlap [63]. In solution, these intermolecular transformations are characterized by low quantum yields, since the reactants undergo a bimolecular reaction, while the excited state is rapidly deactivated, due to the occurrence of competing processes, first of all, *trans-cis*-photoisomerization. The intermolecular PCA reactions normally have low regio- and stereoselectivities because the reacting molecules can have different mutual arrangements.

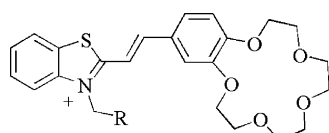
A promising tool for controlling the regio- and stereoselectivity of PCA as well as the efficiency may be provided by assembling alkenes into a supramolecular structure with pre-organization of reactants such that that the spatial arrangement of molecules would be favorable for the formation of only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

This idea was realized using crown-ether styryl dyes (CESD) **29a–29f** (Scheme 30) [64].

The compounds **29c–29f** having betaine structures form supramolecular dimers with a crossed arrangement of molecules (*anti*-head-to-tail) in the presence of Mg^{2+} ions, due to the intramolecular interaction between the sulfo group of one of the molecules and a Mg^{2+} ion located in the crown-ether cavity of the other molecule [65]. It was shown that photoirradiation of solutions of dimer **29c** results in stereospecific PCA giving only 1 of the 11 possible derivatives of cyclobutane **31c**, which is expected in conformity with the concerted superficial (s,s) addition of the reactants (Scheme 31) [66–69]. It is noteworthy that neither *trans*-**29a–29f** without alkaline earth metal cations



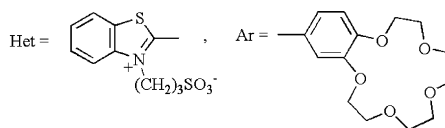
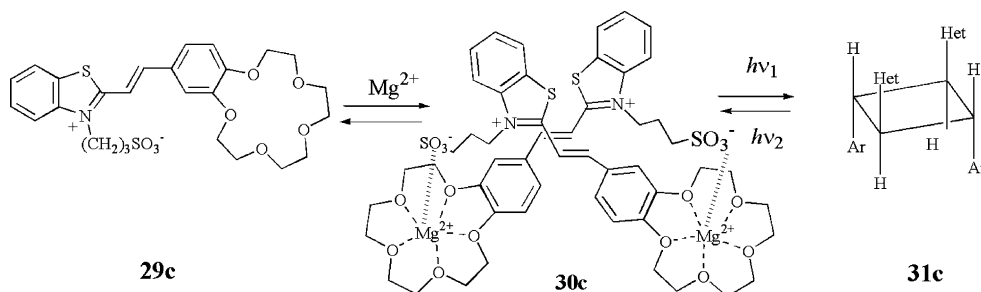
Scheme 29.

**trans-29a-f**

a R = Me (anion ClO_4^-), **b** R = $(\text{CH}_2)_2\text{SO}_3^-$, **c** R = $(\text{CH}_2)_3\text{SO}_3^-$, **d** R = $(\text{CH}_2)_4\text{SO}_3^-$,

e R = *o*- $\text{C}_6\text{H}_4\text{SO}_3^-$, **f** R = *p*- $\text{C}_6\text{H}_4\text{SO}_3^-$

Scheme 30.



Scheme 31.

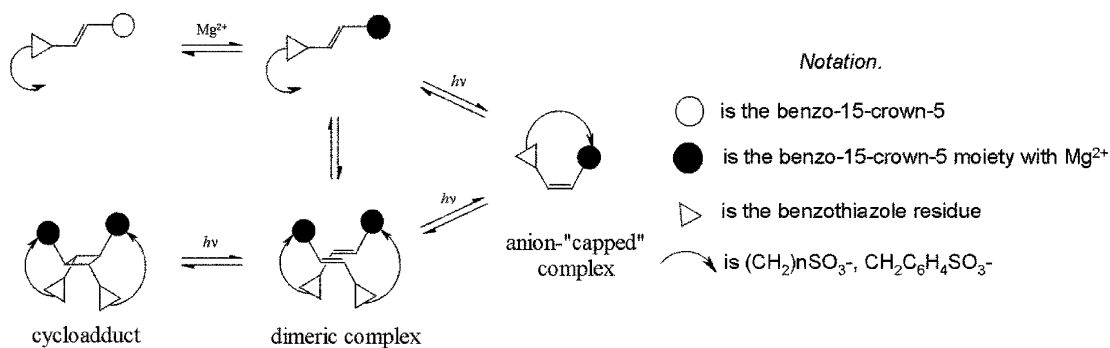
nor complexes of *trans*-**29a**, **29b** with Mg^{2+} , Ca^{2+} , Ba^{2+} undergo PCA even in saturated solutions. Transition from spacers with flexible polymethine chains to *N*-substituents in which the sulfo group is rigidly arranged in space, makes it possible to influence the efficiency of these photochemical reactions and also change the route of transformation of CESD.

The CESD **29c–29f** are able to form anion-“capped” complexes (Schemes 32, 33) 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. How-

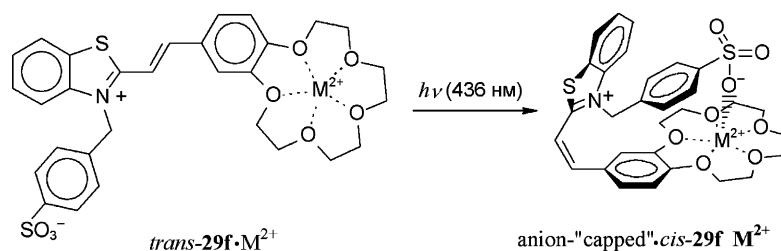
ever, the data obtained confirmed the previous conclusion that the *Z*-isomer of **29b** is unable to form an anion-“capped” complex.

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 with conformationally rigid spacers. The ratio of the stability constants of the anion-“capped” complexes (*Z*-**29f**)· Mg^{2+} and (*Z*-**29e**)· Mg^{2+} is about 500.

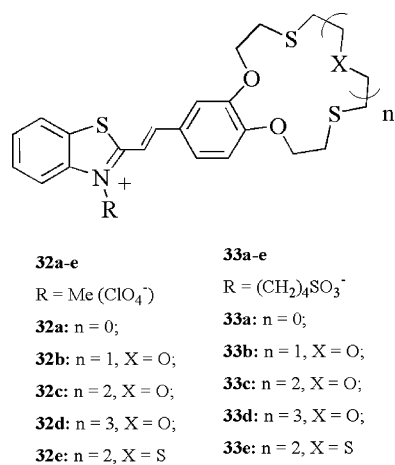
It can be suggested that the variation of the structure of CESD would make it possible to change the supramolecular



Scheme 32.

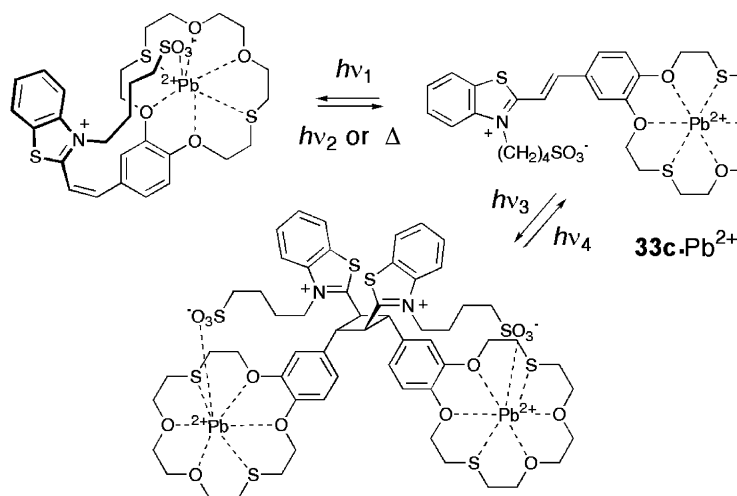


Scheme 33.



Scheme 34.

spatial structure of the dimer in a desired direction and thus control the efficiency of interaction and stereochemistry of the final product of PCA [70]. Thus, styryl dye with sulfobenzyl spacers **29e**, **29f** could demonstrate ability to control way of conversion of multiphotochromic dyes by means of fine changes in molecule structure ("fine tuning" of molecule). It is very promising in the development of new photoswitched molecular devices. Upon irradiation with UV light reversible [2 + 2]-photocycloaddition reaction takes place only in case of styryl dye with *ortho*-sulfobenzyl substituent (**29e**).



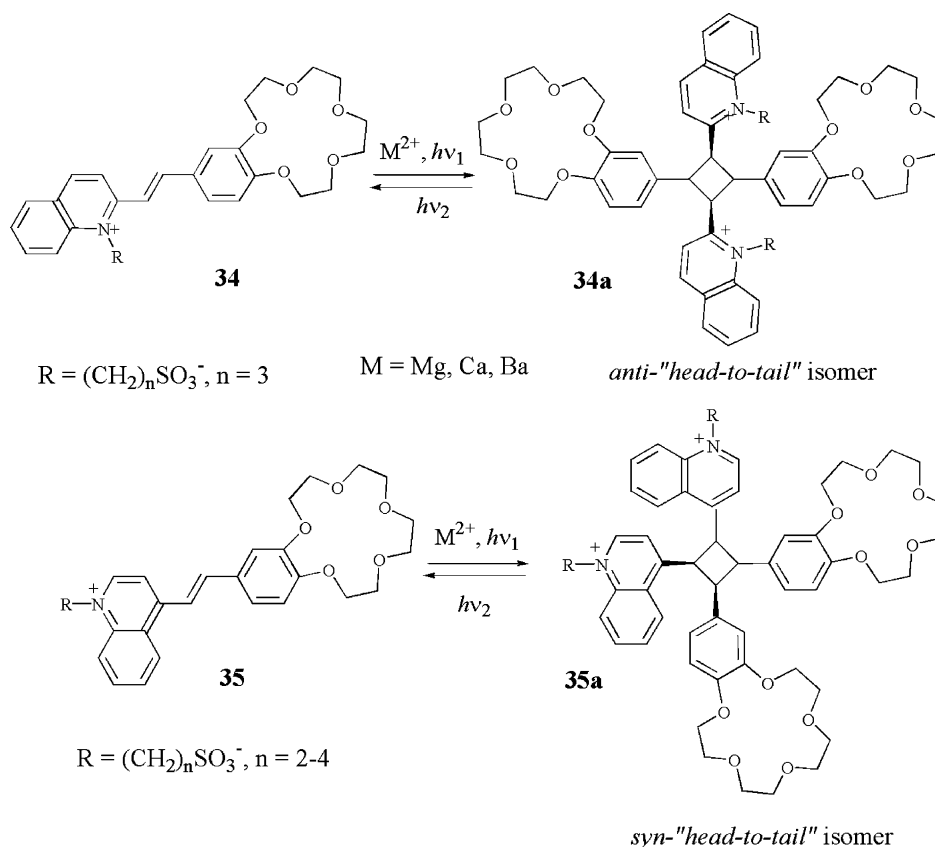
Scheme 35.

Syntheses of two series of new styryl dyes (CESDs **32a–32e**, **33a–33e**) incorporating thiacycrown-ether moieties are described (Scheme 34) [71,72]. ¹H NMR and UV-Vis measurements show that these compounds exhibit a strong preference for formation of complexes with heavy metal ions. Polarographic measurements allow conversion of relative complex formation stability constants, determined spectrophotometrically, into absolute values.

The photochromic properties of the CESDs are based on reversible *trans–cis* isomerization and [2 + 2]-photocycloaddition (Scheme 35).

The single [2 + 2]-photocycloadduct obtained by irradiating thiacycrown-containing dye **33a–33f** in the presence of either Pb²⁺ or Hg²⁺ was assigned the cyclobutane structure. The quantum yield of photodimer formation is substantially more efficient in the presence of Pb²⁺ than in the presence of Hg²⁺. 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 Pb²⁺/SO₃⁻ than Hg²⁺/SO₃⁻ coordination bonds.

Isomeric chromogenic 15-crown-5-ethers of the quinoline series **34** and **35** were shown to undergo PCA in acetonitrile to give cyclobutane derivatives **34a** and **35a** only in the presence of Mg(ClO₄)₂ and Ca(ClO₄)₂ [73]. The modification



Scheme 36.

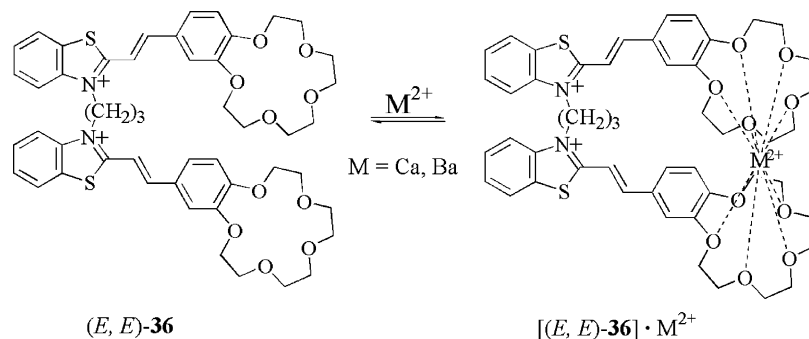
of the heterocyclic residue from 2-methylquinoline to 4-methylquinoline appears to change in principle the PCA route (Scheme 36). The overall quantum yield in the PCA of **34** was 0.0007. In the case of the PCA of **35**, the high quantum yield (0.15) was found, which indicates that the degree of dimerization 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 favorable for PCA.

The structure of the spacer has a significant effect on the efficiency of photocycloaddition reaction of **35a** [74]. The PCA quantum yield is of 0.20, 0.14, and 0.072 for dyes ($n = 2, 3$ and 4), respectively (irradiation at 436 nm).

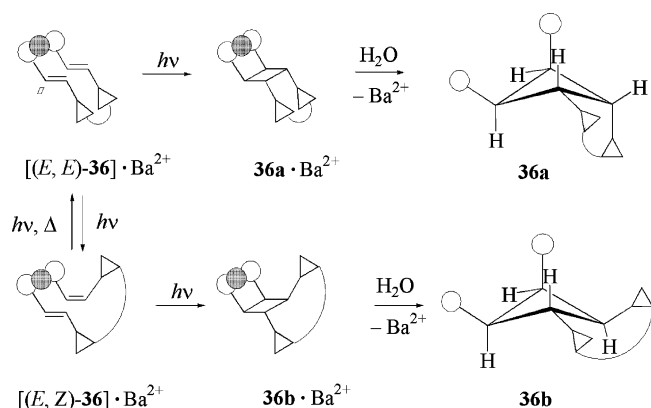
The reaction is photochemically reversible. Upon irradiation of the cycloadducts with 313 nm light, the initial dyes are formed with a quantum yield ranging from 0.02 to 0.01.

Bis-crown-containing styryl dye (*E,E*)-**36** having the structure and properties of molecular pincers has been synthesized. In acetonitrile solution, dye (*E,E*)-**36** is able to form intramolecular sandwich complexes with Ca^{2+} and Ba^{2+} cations (Scheme 37) [75,76].

The spontaneous assembly of bisCESD **36** 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



Scheme 37.



Notation. ○ is the benzo-15-crown-5-ether moiety; ● is Ba²⁺;
 ◁ is the benzothiazole residue; ◡ is (CH₂)₃

Scheme 38.

controlling the efficiency and stereoselectivity of intramolecular PCA with the formation of cyclobutanes. Indeed, in the case of the Ba²⁺ complexes of bisCESD **36**, prolonged photolysis of a photostationary mixture of the geometric isomers led to complete consumption of the dye.

The analysis of 2D COSY and NOESY NMR spectra of the PCA products showed the presence of two isomeric crown-containing cyclobutane derivatives **36a** and **36b** (Scheme 38) in 17:83 ratio.

A molecular-mechanics procedure for the computer simulation of PCA of CESD complexes with metal cations has been proposed [77–79]. This procedure allows prediction of the stereochemistry of the cyclobutane derivatives expected in conformity with the calculated predominant conformation of the dimeric supramolecular complexes.

4. Conclusion

The intense research efforts made by several groups of investigators interested in photochromic crown ethers convincingly demonstrated that photochromic crown ethers 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 kinetics of phototransformation can be expected. 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. The results obtained were extended to novel series of photochromic systems. The important objectives for the future research include:

- synthesis of new compounds;

- more extensive and more detailed investigation of their physico-chemical properties in order to find structure–property correlations;
- 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.

Acknowledgements

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References

- [1] G.H. Brown (Ed.), *Photochromism*, Wiley, New York, 1971.
- [2] H. Durr, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 413.
- [3] H. Durr, H. Bouas-Laurent (Eds.), *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990.
- [4] C.B. McArdle (Ed.), *Applied Photochromic Polymer Systems*, Blackie, New York, 1992.
- [5] Y. Inoue, G.W. Gokel (Eds.), *Cation Binding by Macrocycles, Complexation of Cationic Species by Crown Ethers*, Marcel Dekker, New York, 1990.
- [6] J.C. Crano, R. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Plenum Press, New York, 1999.
- [7] H. Durr, G. Hauck, *Deutsche Offenlegungs Schrift Patent* 29 06 193.6 (1979).
- [8] H. Durr, A. Thome, C. Kranz, S. Bossman, *J. Phys. Org. Chem.* 5 (1992) 111.
- [9] H. Durr, C. Kranz, *Mol. Cryst. Liq. Cryst.* 246 (1994) 135.
- [10] H. Durr, *Chimia* 48 (1994) 514.
- [11] H. Durr, C. Kranz, H. Kilburg, *Mol. Cryst. Liq. Cryst.* 298 (1997) 89.
- [12] M. Inouye, M. Ueno, K. Tsuchiya, N. Nakayama, T. Konishi, T. Kitao, *J. Org. Chem.* 57 (1992) 5377.
- [13] Inouye, M. Ueno, T. Kitao, *J. Org. Chem.* 57 (1992) 1639.
- [14] K. Kimura, T. Yamashita, M. Yokoyama, *J. Chem. Soc., Perkin Trans. 2* (1992) 613.
- [15] S.-H. Lui, Ch.-T. Wu, in: *Proceedings of the Third International Symposium on Organic Photochromism*, Fukuoka, Japan, 1999, p. 92.
- [16] M. Tanaka, K. Kamada, K. Kimura, *Mol. Cryst. Liq. Cryst.* 334 (2000) 319.
- [17] M. Tanaka, K. Kamada, H. Ando, T. Kitagaki, Ya. Shibuyani, K. Kimura, *J. Org. Chem.* 65 (2000) 4342.
- [18] H. Sasaki, A. Ueno, J.-I. Anzai, T. Osa, *Bull. Chem. Soc. Jpn.* 59 (1986) 1953.
- [19] K. Kimura, T. Teranishi, M. Yokoyama, S. Yajima, S. Miyake, H. Sakamoto, M. Tanaka, *J. Chem. Soc., Perkin Trans. 2* (1999) 199.
- [20] T. Teranishi, M. Yokoyama, H. Sakamoto, K. Kimura, *Mol. Cryst. Liq. Cryst.* 334 (2000) 274.
- [21] M. Nakamura, T. Fujioka, H. Sakamoto, K. Kimura, *New J. Chem.* 26 (2002) 554.
- [22] S.-H. Lui, Ch.-T. Wu, in: *Proceedings of the Third International Symposium on Organic Photochromism*, Fukuoka, Japan, 1999, p. 93.
- [23] D.-X. Wu, P.-F. Xia, H.-M. Zhao, *Youji Huaxue* 12 (1992) 76.
- [24] M. Bibout, P. Lareginie, L. Noussi, A. Samat, R. Guglielmetti, *Mol. Cryst. Liq. Cryst.* 246 (1994) 177.
- [25] V.B. Nazarov, V.A. Soldatenkova, M.V. Alfimov, P. Lareginie, A. Samat, R. Guglielmetti, *Russ. Chem. Bull.* 45 (1996) 2220.
- [26] O.A. Fedorova, S.P. Gromov, Yu.V. Strokach, Yu.V. Pershina, S.A. Sergeev, V.A. Barachevsky, G. Pepe, A. Samat, R. Guglielmetti, *Russ. Chem. Bull.* 48 (1999) 1950.

- [27] O.A. Fedorova, S.P. Gromov, Yu.V. Strokach, Yu.V. Pershina, S.A. Sergeev, V.A. Barachevsky, G. Pepe, A. Samat, R. Guglielmetti, *J. Chem. Soc., Perkin Trans. 2* (1999) 1950.
- [28] O.A. Fedorova, Y.P. Strokach, S.P. Gromov, A.V. Koshkin, T.M. Valova, M.V. Alfimov, A.V. Feofanov, I.S. Alaverdian, V.A. Lokshin, A. Samat, R. Guglielmetti, R.B. Girling, J. Moore, R.E. Hester, *New J. Chem.* 26 (2002) 1137.
- [29] O.A. Fedorova, S.P. Gromov, A.V. Koshkin, Y.P. Strokach, V.A. Barachevsky, A.V. Lokshin, A. Samat, R. Guglielmetti, M.V. Alfimov, *Russ. Chem. Bull.* 51 (2002) 58.
- [30] A.V. Koshkin, O.A. Fedorova, S.P. Gromov, V.G. Avakyan, M.V. Alfimov, V. Nazarov, N.A. Brichkin, T.G. Vershinina, T.M. Nikolaeva, L.A. Chernyak, *Russ. Chem. Bull.* 51 (2002) 1441.
- [31] J.C. Crano, T. Flood, D. Knowles, A. Kumar, B. Van Gemert, *Pure Appl. Chem.* 68 (1996) 1395.
- [32] Y. Hirshberg, E. Fisher, *J. Am. Chem. Soc.* 88 (1966) 5931.
- [33] B. Van Gemert, M. Bergomi, D. Knowles, *Mol. Cryst. Liq. Cryst.* 246 (1994) 67.
- [34] M.T. Stauffer, D.B. Knowles, C. Brennan, L. Funderburk, F-T. Lin, S.G. Weber, *J. Chem. Soc., Chem. Commun.* (1997) 287.
- [35] A. Santiago, R.S. Beker, *J. Am. Chem. Soc.* 90 (1968) 3654.
- [36] Ya. Yokoyama, M. Kubo, Ya. Yokoama, T. Ohmori, T. Okuyama, S. Uchida, *Mol. Cryst. Liq. Cryst.* 344 (2000) 265.
- [37] Z. Guo, G. Wang, Yi. Tang, X. Song, *Liebigs Ann./Recueil.* (1997) 941.
- [38] J. Saltiel, J.L. Charlton, in: P. de Mayo (Ed.), *Rearrangement in Ground and Excited States* Academic Press, New York, vol. 3, 1980, p. 25.
- [39] K. Uchida, S. Nakamura, M. Irie, *Res. Chem. Intermed.* 21 (1995) 861.
- [40] S.H. Kawai, *Tetrahedron Lett.* 39 (1998) 4445.
- [41] M. Takeshita, C.F. Soong, M. Irie, *Tetrahedron Lett.* 39 (1998) 7717.
- [42] M. Takeshita, M. Irie, *J. Org. Chem.* 63 (1998) 6643.
- [43] H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, *Pure Appl. Chem.* 52 (1980) 2633.
- [44] I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, T. Otsuba, *Tetrahedron Lett.* 21 (1980) 541.
- [45] H. Bouas-Laurent, A. Castellan, M. Daney, J.-P. Desvergne, G. Guinand, P. Marsua, M.-H. Riffaund, *J. Am. Chem. Soc.* 108 (1986) 315.
- [46] H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* 30 (2001) 248.
- [47] J.-P. Desvergne, E. Perez-Inestrosa, H. Bouas-Laurent, G. Jonusauskas, J. Oberle, C. Rullier, in: B. Valeur, J.-C. Brochon (Eds.), *New Trends in Fluorescence Spectroscopy, Application in Chemical and Life Sciences*, Springer/Verlag, Berlin/Heidelberg, 2001, Chapter 8.
- [48] J.-P. Desvergne, H. Bouas-Laurent, E. Perez-Inestrosa, P. Marsua, M. Contrait, *Coord. Chem. Rev.* 185–186 (1999) 357.
- [49] Ch.-H. Tung, L.-Zh. Wu, *J. Chem. Soc., Faraday Trans.* 92 (1996) 1381.
- [50] R.C. Helgenson, T.L. Tarnovski, J.M. Timko, D.J. Cram, *J. Am. Chem. Soc.* 99 (1977) 6411.
- [51] N. Kawashima, T. Kawashima, T. Otubo, S. Misumi, *Tetrahedron Lett.* 19 (1978) 5025.
- [52] S. Inokuma, T. Yamamoto, J. Nishimura, *Tetrahedron Lett.* 31 (1990) 97.
- [53] S. Ionokuma, T. Yasuda, S. Araki, S. Sakai, J. Nishimura, *Bull. Chem. Soc.* 67 (1994) 1462.
- [54] S. Ionokuma, K. Kimura, T. Funaki, J. Nishimura, *J. Incl. Phenom. Macrocycl. Chem.* 39 (2001) 35.
- [55] A.J. Ors, R. Srinivasan, *J. Am. Chem. Soc.* 100 (1978) 315.
- [56] M. Shirai, A. Ueda, M. Tanabe, *Macromol. Chem.* 186 (1985) 493.
- [57] M. Shirai, J. Orikata, M. Tanaka, *Macromol. Chem. Rapid Commun.* 4 (1983) 65.
- [58] K. Hiratana, S. Aiba, *Bull. Chem. Soc. Jpn.* 57 (1984) 2657.
- [59] S. Akabori, Y. Habata, M. Nakasawa, Y. Yamada, Y. Shindo, T. Sugimura, S. Sato, *Bull. Chem. Soc. Jpn.* 60 (1987) 3453.
- [60] S. Akabori, T. Kumagai, Y. Habata, S. Sato, *Bull. Chem. Soc. Jpn.* 61 (1988) 2459.
- [61] S. Akabori, T. Kumagai, Y. Habata, S. Sato, *J. Chem. Soc., Chem. Commun.* (1988) 661.
- [62] S. Akabori, T. Kumagai, Y. Habata, S. Sato, *J. Chem. Soc., Perkin Trans. 1* (1989) 1497.
- [63] M. Nogradi, *Stereochemistry*, Akademiai Kiado, Budapest, 1981, Chapter 6.
- [64] S.P. Gromov, M.V. Alfimov, *Russ. Chem. Bull.* 46 (1997) 611.
- [65] A.V. Barzykin, M.A. Fox, E.N. Ushakov, O.B. Stanislavsky, S.P. Gromov, O.A. Fedorova, M.V. Alfimov, *J. Am. Chem. Soc.* 114 (1992) 6381.
- [66] S.P. Gromov, O.A. Fedorova, M.V. Alfimov, *Mol. Cryst. Liq. Cryst.* 246 (1994) 183.
- [67] M.V. Alfimov, S.P. Gromov, O.B. Stanislavskii, E.N. Ushakov, O.A. Fedorova, *Russ. Chem. Bull.* 42 (1993) 1385.
- [68] S.P. Gromov, O.A. Fedorova, E.N. Ushakov, I.I. Baskin, A.V. Lindeman, E.V. Malysheva, T.A. Balashova, A.S. Arsen'ev, M.V. Alfimov, *Russ. Chem. Bull.* 47 (1998) 97.
- [69] S.P. Gromov, O.A. Fedorova, E.N. Ushakov, A.V. Buevich, I.I. Baskin, Yu.V. Pershina, B. Eliasson, U. Edlund, M.V. Alfimov, *J. Chem. Soc., Perkin Trans. 2* (1999) 1323.
- [70] S.P. Gromov, E.N. Ushakov, O.A. Fedorova, A.V. Buevich, M.V. Alfimov, *Russ. Chem. Bull.* 45 (1996) 654.
- [71] O. Fedorova, Y. Fedorov, A. Vedernikov, O. Yescheulova, S. Gromov, M. Alfimov, L. Kuz'mina, A. Churakov, J. Howard, S. Zaitsev, T. Sergeeva, D. Möbius, *New J. Chem.* 26 (2002) 543.
- [72] O. Fedorova, Y. Fedorov, A. Vedernikov, S. Gromov, O. Yescheulova, M. Alfimov, M. Woerner, S. Bossmann, A. Braun, J. Saltiel, *J. Phys. Chem.* 106 (2002) 6213.
- [73] E.N. Ushakov, S.P. Gromov, A.V. Buevich, I.I. Baskin, O.A. Fedorova, A.I. Vedernikov, M.V. Alfimov, B. Eliasson, U. Edlund, *J. Chem. Soc., Perkin Trans. 2* (1999) 601.
- [74] E.N. Andrioukhina, O.A. Fedorova, E.N. Ushakov, A.V. Buevich, M.V. Alfimov, B. Eliasson, U.G. Edlund, J.K. Whitesell, M.A. Fox, S.P. Gromov, in: *Proceedings of the XXV International Symposium on Macrocyclic Chemistry, MACROCYCLES 2000*, Scotland, UK, July 2–7, 2000, p. 63.
- [75] E.N. Ushakov, S.P. Gromov, O.A. Fedorova, Yu.V. Pershina, M.V. Alfimov, F. Barigelletti, L. Flamigni, V. Balzani, *J. Phys. Chem. A* 103 (1999) 1188.
- [76] S.P. Gromov, O.A. Fedorova, E.N. Ushakov, A.V. Buevich, M.V. Alfimov, *Russ. Chem. Bull.* 44 (1995) 2131.
- [77] I.I. Baskin, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, *Dokl. Akad. Nauk* 335 (1994) 313.
- [78] A.Ya. Freidzon, I.I. Baskin, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, *Russ. Chem. Bull.* 47 (1998) 2117.
- [79] I.I. Baskin, A.Ya. Freidzon, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, *Internet J. Chem.* 1 (1998) 19. <http://www.ijc.com/articles/1998v1/19/>.