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# Crown Ether–Based Optical Molecular Sensors and Photocontrolled Ionophores

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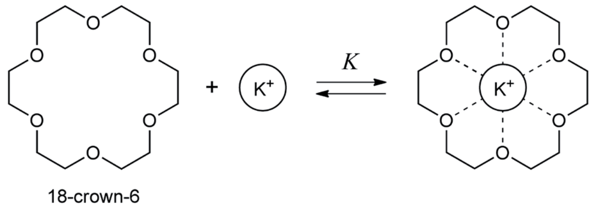
*The main design concepts are reviewed for the polyfunctional crown compounds that are able to operate as optical molecular sensors or photocontrolled ionophores.*

**Keywords:** Crown ethers, optical molecular sensors, fluorescent sensors, photocontrolled ionophores.

## Introduction

The synthesis and complexing properties of crown ethers were first reported by Pedersen in 1967.[1,2] Due to their unique ability to bind selectively alkali metal ions (Scheme 1), crown ethers have found a wide application in chemistry, biochemistry and technology.[3]



**Scheme 1.** Binding of $K^+$ ion by 18-crown-6 ether; $K$ is the complex stability constant (in water lg$K$ = 2.06).

Considerable attention has been focused on the design and physicochemical studies of polyfunctional crown compounds and related supramolecular systems that are capable of operating as optical molecular sensors or photocontrolled ionophores. Crown ether-based optical molecular sensors are expected to be used in compact devices for colorimetric or luminescent analysis of metal ions and some organic cations. The application areas for photocontrolled ionophores include development of new ion-conducting light-sensitive materials, photocontrolled ion transport and ion separation, design of photoswitchable molecular devices and machines.

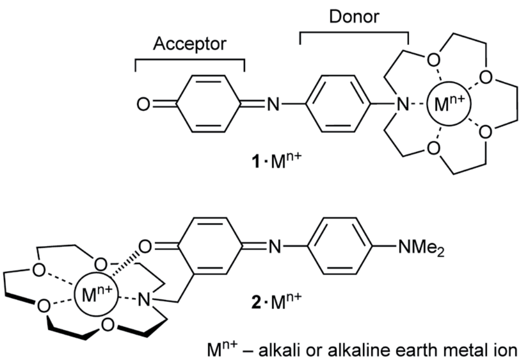
In this paper we briefly review the main design concepts for crown ether-based optical molecular sensors (colorimetric and luminescent indicators) and photocontrolled ionophores.

### *Colorimetric Molecular Sensors (Chromoionophores)*

The general design concept for chromoionophores is as follows. The crown ether fragment is connected to a chromophore so that the metal ion located in the crown cavity can interact with at least one heteroatom of the chromophore. Crown ether-based chromoionophores can be classified into three main groups according to the mechanism of cation-induced changes in the absorption spectrum. The mechanisms of ionochromic effect include (1) charge or electron density redistribution in the chromophore moiety (donor–acceptor chromoionophores), (2) proton elimination (proton chromoionophores) and (3) thermal valence isomerisation.

### *Donor-Acceptor Chromoionophores*

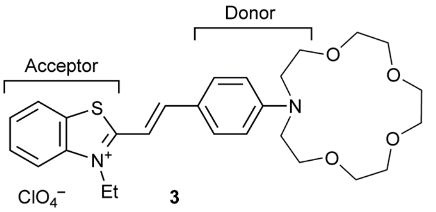
The long-wavelength band in the absorption spectra of organic donor–acceptor dyes is associated with the electronic transition that is accompanied by internal charge transfer between the conjugated electron-donor and electron-acceptor moieties. The chromoionophores derived from these dyes can show either negative or positive ionochromism, depending on the crown ether–chromophore connection scheme. Chromoionophores **1** and **2** derived from the Phenol Blue dye are illustrative examples of different connection schemes.[4]



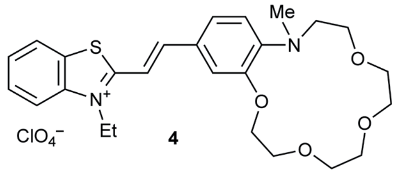
$M^{n+}$ – alkali or alkaline earth metal ion

The azacrown ether moiety of compound **1** reproduces the electron-donor properties of the dimethylamino group of Phenol Blue. Binding of an alkali or alkaline earth metal ion by the azacrown ether induces a hypsochromic shift of the long-wavelength absorption band of **1** ($\Delta\lambda$ = 98 nm with $Ca^{2+}$ in MeCN) because the crowned metal ion coordinates with the amine nitrogen, *i.e.*, the electron-donor fragment of the dye. In compound **2**, the azacrown ether is connected to the electron-acceptor fragment of the chromophore. The geometry of **2** allows direct interaction between the crowned metal ion and the carbonyl oxygen atom, which results in a bathochromic shift of the absorption band ($\Delta\lambda$ = 78 nm with $Ca^{2+}$ in MeCN).

A variety of the donor–acceptor chromoionophores derived from styryl and butadienyl dyes have been studied by Gromov and co-workers.[5-11] Compounds **3** and **4** are representatives of the crown-containing styryl dyes that show negative ionochromism.[6,7]



**3**



**4**

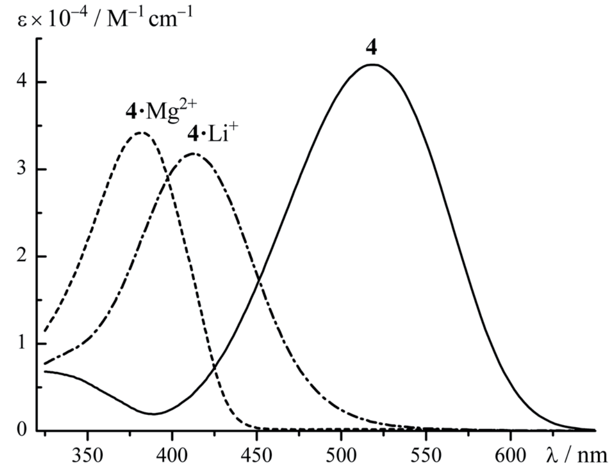
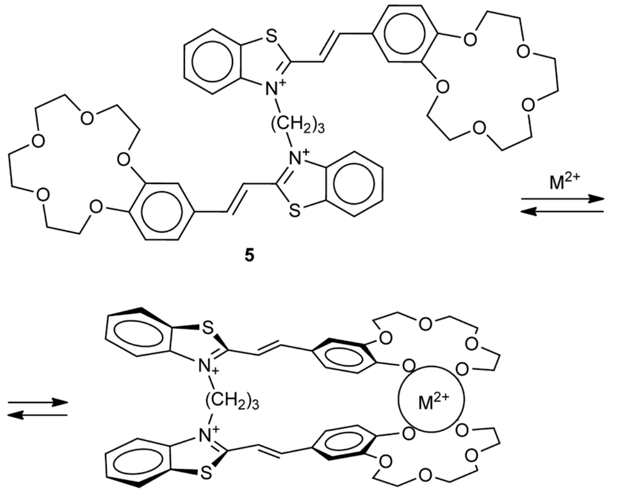


**Figure 1.** Absorption spectra of dye **4** and its 1:1 complexes with $Li^+$ and $Mg^{2+}$ in MeCN.

The *N*-methylazacrown fragment in **4** proved to be better preorganized for binding of metal ions than the *N*-phenylazacrown fragment in **3**. As a result, complexes of **4** with alkali and alkaline earth metal ions are characterized by much higher thermodynamic stability as compared to the corresponding complexes of **3** (for example, the lg*K* values for **4**·$Ca^{2+}$ and **3**·$Ca^{2+}$ in MeCN are about 5.2 and 2.4 respectively). In addition, chromoionophore **4** shows very strong cation-induced hypsochromic shifts in the absorption spectrum even in the case of alkali cations (the $\Delta\lambda$ value with $Li^+$ in MeCN is about 105 nm, see Figure 1).

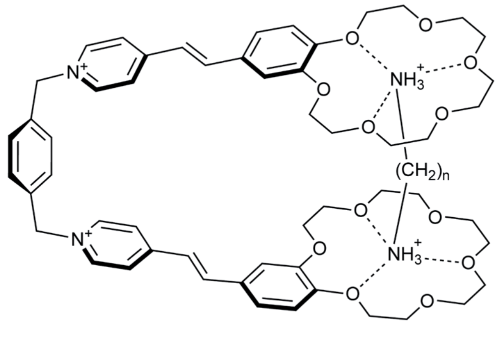
The bisstyryl dye **5** was found to act as ionochromic molecular tweezers.[8] The two 15-crown-5 ether fragments in **5** can selectively capture large alkaline earth cations, such as $Sr^{2+}$ and $Ba^{2+}$, to form intramolecular sandwich-type complexes. The complex formation leads to a strong hypsochromic effect ($\Delta\lambda$ = 52 nm with $Sr^{2+}$ in MeCN) and to the appearance of long-lived excimer luminescence.



**5**

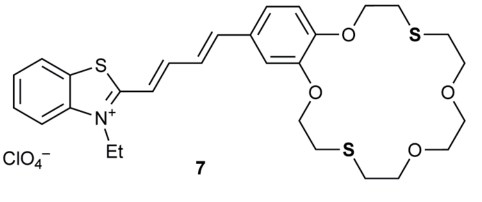
**5**·$M^{2+}$, M = Sr, Ba

The chromogenic bis(18-crown-6) ether **6** binds alkanediammonium dications $NH_3^+(CH_2)_nNH_3^+$ (n = 2–6) to form pseudocyclic 1:1 complexes.[9] The complex formation is accompanied by a pronounced hypsochromic effect ($\Delta\lambda$ = 21–23 nm in MeCN). The complex stability constants for **6** with the diammonium dications are significantly higher than those with the corresponding monocations (the lg*K* values for **6**·$\{NH_3^+(CH_2)_2NH_3^+\}$ and **6**·$\{EtNH_3^+\}$ in MeCN are 5.53 and 3.81 respectively).



Pseudocyclic complex **6**·$\{NH_3^+(CH_2)_nNH_3^+\}$

It is known that the replacement of one or several oxygen atoms in crown ethers by sulphur atoms dramatically changes the ion-binding selectivity. For example, the chromogenic dithia-18-crown-6 ether **7**[10] derived from a butadienyl dye exhibits a very low affinity for alkali and alkaline earth cations in comparison with its 18-crown-6 ether analogue,[11] but it forms very stable complexes with $Hg^{2+}$ and $Ag^+$ both in organic solvents and in water.



**7**

The ionochromic and complexing properties of dye **7** in $H_2O$/MeCN mixtures with different contents of $H_2O$ ($P_W$) were studied by spectroscopic methods and differential pulse polarography. Figure 2 shows the plots of lg$K$ *vs.* $P_W$ for the 1:1 complexes of **7** with $Ag^+$, $Hg^{2+}$ and $Pb^{2+}$. On changing from MeCN to the mixtures with high $P_W$ values, the $Ag^+$/$Pb^{2+}$ selectivity is inverted. This inversion is attributable to the fact that $Ag^+$ ions are preferably solvated by MeCN whereas $Pb^{2+}$ ions are preferably hydrated.

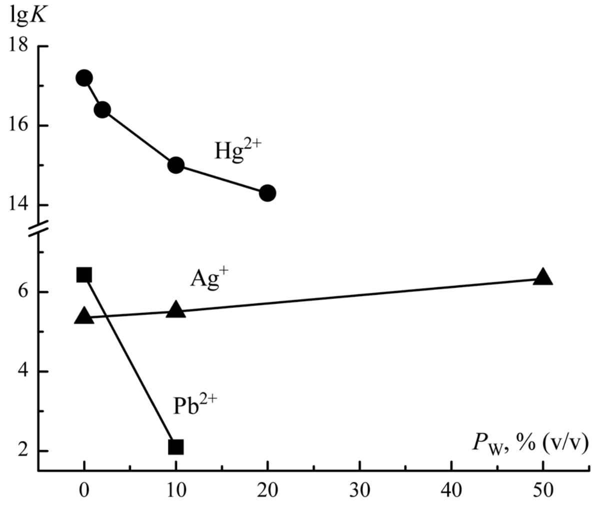
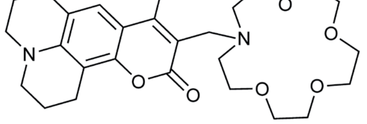
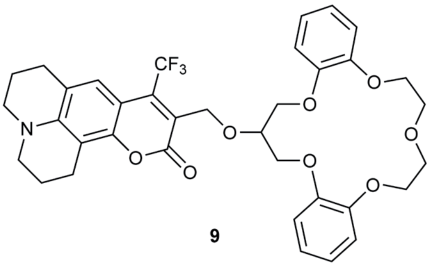


**Figure 2.** Plots of lg$K$ *vs.* water content in $H_2O$/MeCN mixtures ($P_W$) for the 1:1 complexes of dye **7** with $Ag^+$, $Hg^{2+}$ and $Pb^{2+}$.

Crown-containing coumarins **8**[12] and **9**[13] are representatives of the chromoionophores that show positive ionochromism. Chromoionophore **9** in comparison with **8** demonstrates stronger cation-induced bathochromic changes in the absorption spectrum. It is supposed that compound **9** having a longer bridge between the chromophore and the crown ether can adopt a conformation that provides stronger interaction between the crowned cation and the carbonyl oxygen of the coumarin moiety.

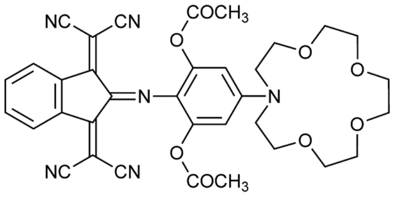


**8**



**9**

Chromoionophore **10**[14] containing a very strong electron acceptor, *viz.,* 1,3-bis(dicyanomethylidene)indane fragment, is of interest for the fact that it can function as a colorimetric sensor for metal ions in the near-IR spectral region.

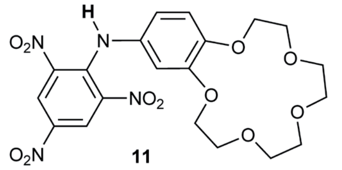


**10**

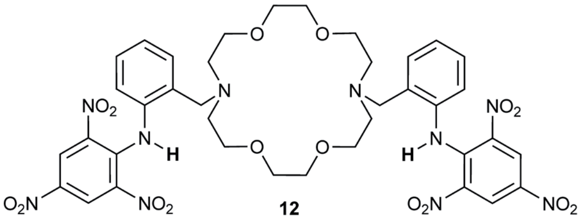
## *Proton Chromoionophores*

Proton chromoionophores are mainly used in extraction photometry. They demonstrate positive ionochromism related to the conversion of the chromophore moiety to the anionic form upon proton elimination. The anionic form is stabilized due to interaction of the crowned metal ion with one or several heteroatoms of the chromophore. Apparently, the optimal structures are those that allow the direct coordination of the crowned metal ion with the chromophore anionic group. The charge of the cation extracted from water to the organic phase is counterbalanced by the charge of the chromophore anionic form. Thus, in order to extract divalent cations, the chromoionophore must have two protons capable of elimination.

Two types of dyes, *viz.*, aniline and phenol derivatives, are mainly used to construct proton chromoionophores. Compounds **11**[15] and **12**[16] are typical examples of proton and diproton chromoionophores based on aniline derivatives.



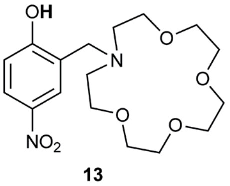
**11**



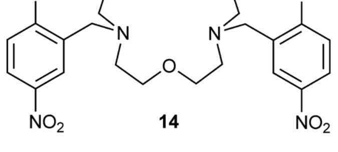
**12**

Compound **11** preferably extracts $K^+$ into chloroform from water solutions of Li, Na and K salts. Diproton chromoionophore **12** extracts only $Ba^{2+}$ from solutions of Mg, Ca, Sr and Ba salts.

Compounds **13**[17] and **14**[18] are representatives of proton and diproton chromoionophores based phenol derivatives.

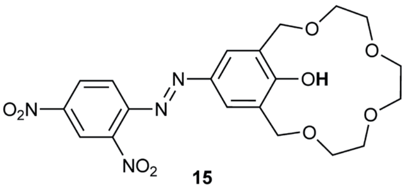


**13**



**14**

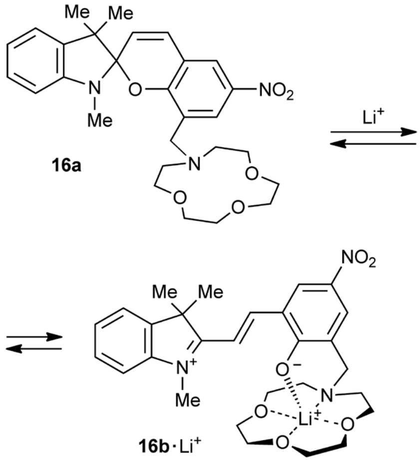
In azobenzene derivative **15**,[19] the phenolic OH group is a part of the macrocyclic moiety. Such compounds can be used for colorimetric analysis of metal cations in organic media.



**15**

## *Chromoionophores Functioning on the Basis of Valence Isomerisations*

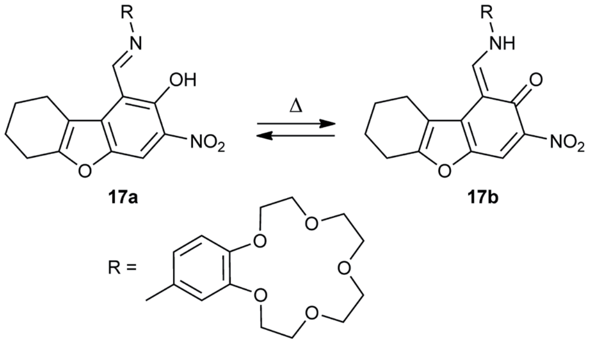
Spiropyrans are well known to undergo photochemically and thermally induced ring-opening reaction leading to coloured valence isomer (merocyanine dye). In most cases, the thermal equilibrium spiropyran–merocyanine is shifted toward the colourless closed form. The crown-containing spiropyran **16a** in the presence of Li$^+$ is partially converted into the coloured valence isomer **16b** because the latter is stabilised due to intramolecular coordination of the phenoxide anion with the crowned Li$^+$ ion.[20]



**16a**

**16b·Li$^+$**

The crown-containing imine **17a** in polar solvents, such as MeCN, exists partly as the quinonoid tautomer **17b**. This tautomer is responsible for the long-wavelength band in the absorption spectrum.[21]



**17a**

**17b**

In the presence of Li$^+$, Mg$^{2+}$ or Ca$^{2+}$, the tautomeric equilibrium is shifted toward the benzenoid form **17a**, which results in the intensity decrease of the long-wavelength absorption.

## *Luminescent Molecular Sensors*

The luminescent molecular sensors that show a significant luminescence enhancement upon cation binding are the most promising from the practical standpoint. They are usually designed by combining a crown ether receptor with a 'triggered' luminophore, *i.e.*, with that molecule the luminescence of which is quenched due to an intramolecular excited-state reaction leading to a non-emissive state. In the properly designed systems, cation binding to the crown ether moiety can trigger off the luminescence by inhibiting the process responsible for its quenching.

The mechanisms of luminescence quenching that have been used in the design of crown ether-based luminescent sensors include photoinduced electron transfer (PET), photoinduced internal charge transfer (PICT) and exciplex or excimer formation. The luminescent sensors operating on the basis of PET and PICT processes are schematically represented in Figure 3.

In the luminophore-spacer-crown structures, the luminescence is quenched owing to the electron transfer between the excited luminophore and the crown ether moiety. Cation binding modulates the redox potential of crown ether moiety, which leads to a decrease in the electron transfer rate and, as a result, to an increase in the luminescence yield.

The design of luminescent PICT sensors is similar to that of donor–acceptor chromoionophores. The A and B type PICT systems differ from each other in the degree of electronic coupling between the donor and acceptor units; in the A type structures, the coupling is relatively weak by steric reasons.

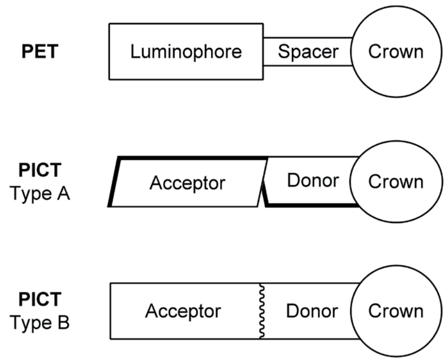
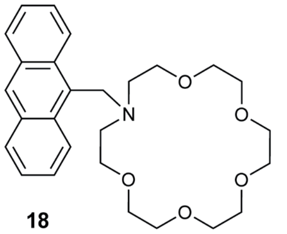


**Figure 3.** Schematic representation of the luminescent molecular sensors operating on the basis of photoinduced electron transfer (PET) and photoinduced internal charge transfer (PICT).

The luminescence quenching in electronically conjugated donor-acceptor systems is commonly interpreted in terms of twisted intramolecular charge-transfer (TICT) state.[22] It is supposed that these systems in the excited state undergo conformational changes *via* single-bond rotation leading to a non-emissive or weakly emissive TICT excited state with a high charge-transfer character. In the case of PICT luminosensors, cation binding to the crown moiety prevents the population of TICT state and thereby induces luminescence enhancement. The population of TICT state in the pre-twisted donor–acceptor systems (type A, Figure 3) is supposed to occur faster than in the coplanar systems (type B, Figure 3). For this reason, the A type design of PICT luminosensors is considered to be more appropriate for synthesis of ‘off-on’ switches.

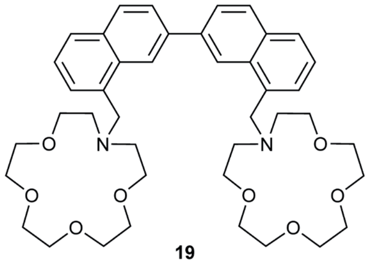
## *PET Luminosensors*

Azacrown anthracene **18**[23] was the first example of crown ether-based luminescent PET sensors. In methanol, the luminescence of **18** is quenched owing to intramolecular PET from the amine nitrogen to the locally excited state of anthracene core. Upon binding of $K^+$, the luminescence quantum yield of **18** increases from 0.003 to 0.14.



**18**

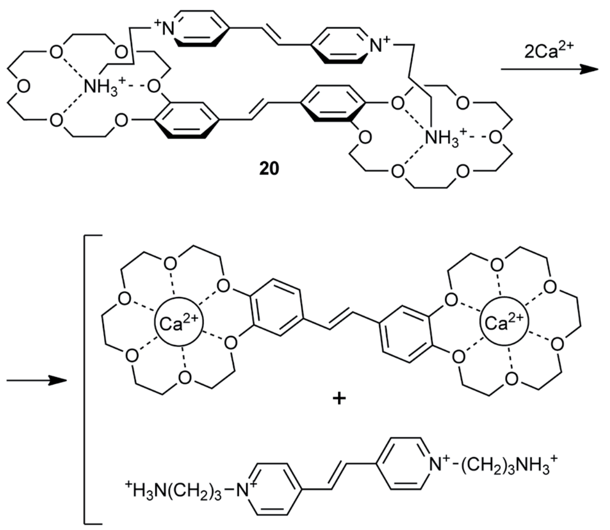
The luminescence of bis(azacrown)binaphthyl **19**[24] is also quenched through intramolecular PET. This compound binds selectively $Ba^{2+}$ ions in MeCN/MeOH mixtures to form intramolecular sandwich-type complexes; the complex formation is accompanied by significant luminescence enhancement.



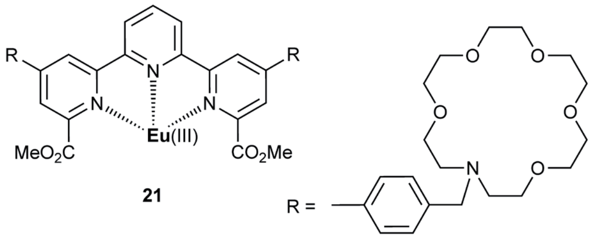
**19**

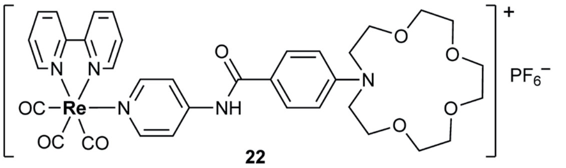
Very original luminescent PET sensors were designed on the basis of bis(18-crown-6) stilbene and bisammonium derivatives of viologen analogues.[25-28] In solution, these compounds are capable of self-assembling into supramolecular ground-state charge-transfer complexes that shows very high thermodynamic stability. For example, the lg*K* value for complex **20** in MeCN was estimated to be 9.08.[26] This complex does not to exhibit any luminescence due to ultrafast PET from the stilbene fragment to the acceptor component.[27] It was found that $Ca^{2+}$ or $Ba^{2+}$ ions are able to displace the acceptor component in complex **20**, which leads to the appearance of the intense luminescence from the metal complexed biscrown stilbene.[28]

PET luminosensors with cation-triggered long-lived emission can be constructed on the basis of metalorganic luminophores. The $Eu^{III}$ complex **21**[29] in methanol is characterized by weak delayed metal-centred emission. On addition of a potassium salt, the delayed luminescence of **21** is enhanced by a factor of 18.



This enhancement is due to the fact that binding of $K^+$ ions to the azacrown fragments of **21** inhibits PET from the amine nitrogen atoms to the luminophore.



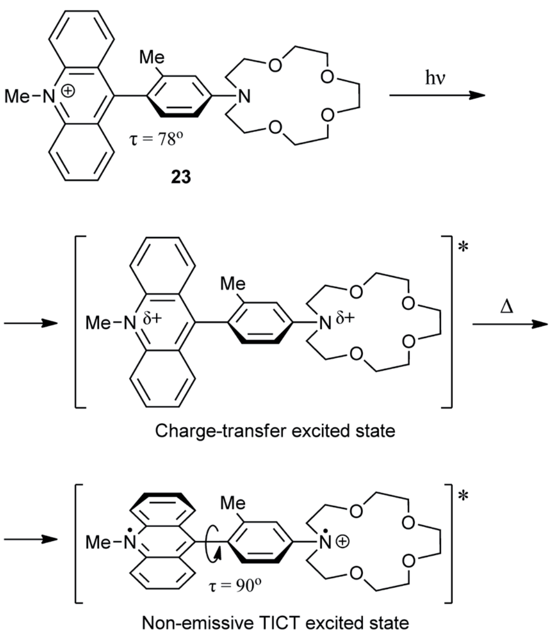


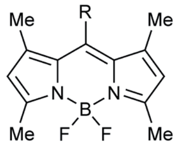
The metal-to-ligand charge-transfer (MLCT) excited state of $Re^I$ complex **22**[30] in MeCN is quenched *via* PET from the azacrown nitrogen atom to the Re atom. The MLCT luminescence is enhanced when the azacrown moiety of **22** binds $Ca^{2+}$.

## *PICT Luminosensors (Type A)*

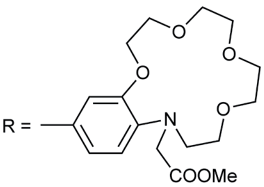
The acridinium derivative **23**[31] containing *N*-phenyl-aza-15-crown-5 ether exhibits a medium-intensity charge-transfer absorption band ($\lambda_{max}$ = 572 nm, $\varepsilon$ = 4200 $M^{-1}\cdot cm^{-1}$, MeCN) despite a large torsion angle between the acridinium acceptor and the aryl group ($\tau$ = 78°). This compound is non-luminescent due to the ultrafast population of a non-emissive TICT excited state. Upon complexation of **23** with $Ag^+$, the acridinium luminescence is switched on. The emission quantum yield for complex **23**·$Ag^+$ in $CH_2Cl_2$ is 0.072.

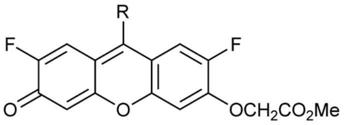
Among other luminoionophores designed similarly to **23**, noteworthy are compounds **24** and **25** containing a benzoannelated azacrown system. They are able to bind alkali metal ions not only in organic but also in aqueous media.[32]





**24**



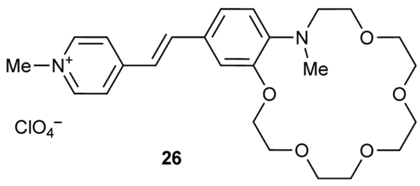


**25**

Compound **25** was reported to perform well as a luminescent indicator for sodium ions in cyto.

### *PICT Luminosensors (Type B)*

The azacrown-containing styryl dye **26** is designed as a donor–acceptor chromoionophore.[7,33] However, it can also operate efficiently as a luminescent sensor for alkaline earth metal ions in non-aqueous solutions.[7]



**26**

In MeCN dye **26** is very weakly luminescent. The complexation of **26** with alkaline earth cations produces a significant luminescence enhancement, the larger the metal ion being the higher the enhancement factor (see Figure 4). In the case of $Ba^{2+}$, this factor is about 60.

For styryl dyes, there exist several possible routes of nonradiative decay of the excited state. These include rotation around the central C=C bond, resulting in *trans-cis* isomerisation, or rotation around one or two single bonds in the C–C=C–C fragment, leading to a non-emissive or weakly emissive TICT state, which returns to the ground state without geometric isomerisation.[22] Dye **26** was found to be photochemically inactive, *i.e.*, neither *trans-cis* photoisomerisation nor other photochemical reactions can be responsible for the low luminescence yield. This fact suggests that the luminescence of **26** is quenched due to fast population of a non-emissive TICT state. The presence of alkaline earth cation in the azacrown cavity of **26** hinders the formation of TICT state and thereby results in significant luminescence enhancement.

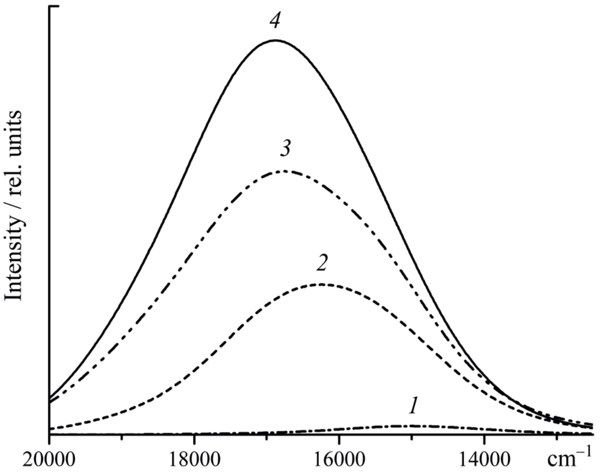
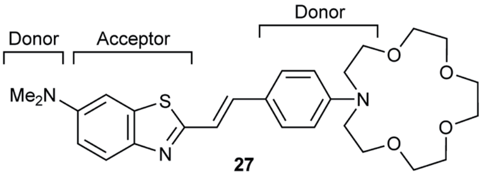


**Figure 4.** Corrected luminescence spectra of dye **26** (*1*) and complexes **26**$\cdot Ca^{2+}$ (*2*), **26**$\cdot Sr^{2+}$ (*3*) и **26**$\cdot Ba^{2+}$ (*4*) in MeCN; the spectra are normalized so that the integral intensities are directly proportional to the luminescence quantum yields; the quantum yields are 0.0013 (**26**), 0.029 (**26**$\cdot Ca^{2+}$), 0.056 (**26**$\cdot Sr^{2+}$) and 0.078 (**26**$\cdot Ba^{2+}$).

Azacrown compound **27** has a conjugated donor–acceptor–donor system. This intrinsic luminoionophore also exhibits cation-induced ‘switching on’ of the luminescence.[34] Compound **27** was designed by rational tuning of the donor–acceptor substitution pattern using a reaction model comprising three excited states, including a highly polar TICT state.



**27**

The luminescence quantum yield of **27** in MeCN is 0.027. Binding of an alkali or alkaline earth metal ion to the azacrown moiety of **27** induces a luminescence enhancement. In the case of $Ca^{2+}$, the enhancement factor is about 30.

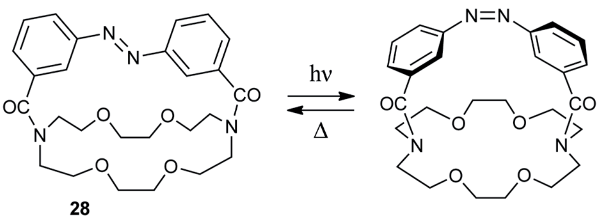
## Photocontrolled Ionophores

The key route to photocontrolled ionophores is covalent bonding of a crown ether receptor to photochromic compound that is able to undergo substantial structural changes upon photoirradiation. Rational design can result in a photochrome–crown system in which the photochromic reaction has a substantial influence on the complexing properties of the crown ether moiety. It is important that the photoinduced structural changes arising in the system be either thermally or photochemically reversible. Various types of photochromes have been tested for use as photoswitches of the ionophoric function. These include azobenzenes, styryl dyes, diarylethylenes, bisanthracenes, spiro compounds, chromene derivatives, triphenylmethane dyes. In this review, the photocontrolled ionophores are classified according to the type of photochromic reaction.

### *Geometric trans-cis Photoisomerisations*

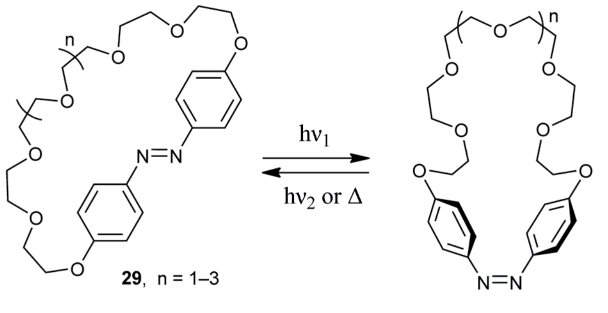
Shinkai and co-workers suggested several design concepts for photoresponsive crown compounds. To control the cation-binding function they used *trans-cis* photoisomerism of azobenzenes.

<u>Photocontrol of the shape of polyether cycle</u>. The azobenzene-capped diazacrown ether **28** undergoes photoinduced reversible interconversion between the *trans* and *cis* azo linkages, resulting in substantial changes in its cation-binding behaviour.[35] It is reported that the *trans*-isomer of **28** binds $Li^+$ and $Na^+$, whereas the *cis*-form prefers the larger $K^+$ and $Rb^+$. This fact is rationalized in terms of photoinduced expansion of the azacrown cycle.



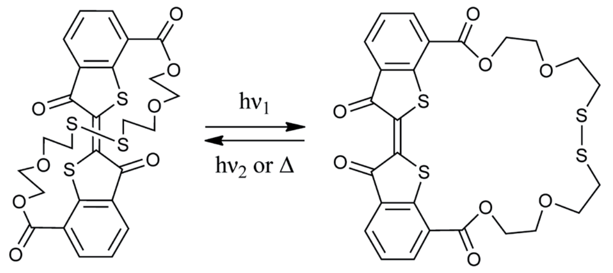
**28**

Azobenzenophane-type crown ethers **29** are the first examples for photocontrolled crown ethers which exhibit ‘all-or-nothing’ changes in cation-binding ability.[36] Solvent extraction experiments showed that compounds **29** in the *trans*-form totally lack affinity toward metal ions, whereas the *cis*-isomers are able to extract considerable amounts of alkali metal ions. This result is attributed to the fact that the polyoxyethylene chains in the *trans*-isomers are linearly extended, whereas those in the *cis*-isomers form the crown-like loops.



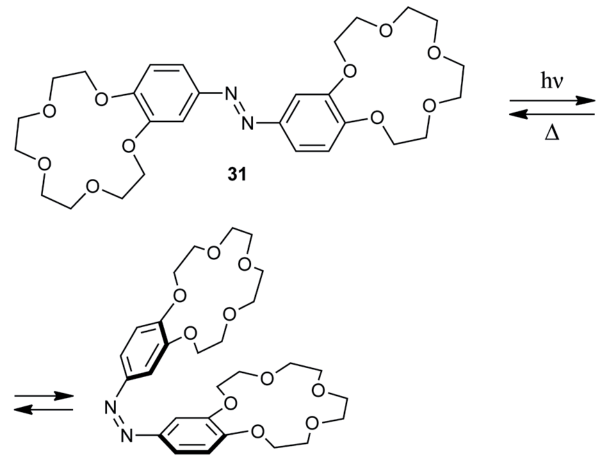
**29**, n = 1–3

Thioindigo derivative **30** is one more example of photoinduced modification of the shape of macrocycle.[37] This compound shows reversible *trans-cis* photoisomerism around the central C=C bond. It is reported that the *trans*-isomer of **30** lacks affinity toward metal ions because it can not form a crown cavity. As a result of *trans-cis* photoisomerisation, thioindigo **30** acquires the ability to bind alkali cations.

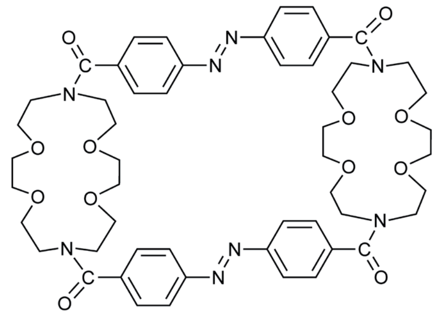


**30**

<u>Photocontrol of the distance between two cation-binding sites</u>. The ion selectivity of bis(15-crown-5) azobenzene **31** changes upon photoinduced *trans-cis* interconversion: the *trans*-isomer binds preferably $Na^+$, whereas the *cis*-isomer shows high selectivity towards $K^+$.[38] It is supposed that the two crown fragments in the *cis*-isomer can cooperatively capture the relatively large $K^+$ to form a sandwich-type complex.

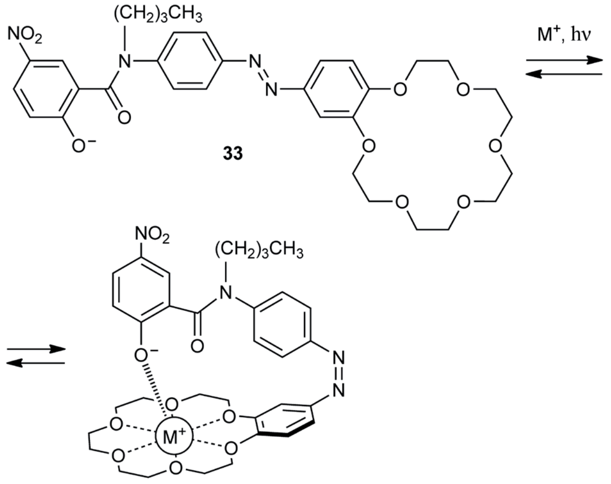


In the cylindrical ionophore **32** the distance between the two diazacrown rings is readily convertible by photoinduced *trans-cis* isomerism of the azobenzene pillars.[39] It is reported that the ability of **32** to bind dications $NH_3^+(CH_2)_nNH_3^+$ ($n$ = 4, 6, 10, 12) changes significantly upon *trans*-to-*cis* conversion. The binding ability decreases when $n$ = 10 or 12 and increases for the shorter dications with $n$ = 4 and 6, which is explained by a decrease in the distance between the diazacrown moieties.

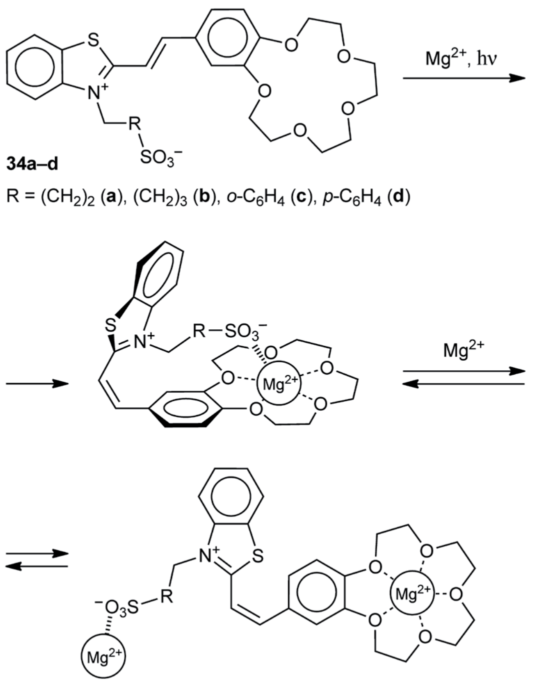


**32**

In the crown-containing azobenzene **33**, the phenoxide anion plays the role of second cation-binding site.[40] In solvent extraction experiments, the extractability of **33** for alkali metal ions was enhanced by ultraviolet irradiation. To interpret this result, the authors assumed that the phenoxide anion in the photogenerated *cis*-**33** coordinates with the crowned metal cation. However, no direct evidence for this coordination was presented.



Direct spectroscopic evidence for the photoinduced formation of 'anion-capped' complexes was obtained with the crown-containing styryl dyes **34a–d** bearing a tethered sulfonate group (Scheme 2).[41-43] These dyes, both free and complexed with $Mg^{2+}$, readily undergo *trans-cis* photoisomerisation upon irradiation with blue light. Ultraviolet irradiation induces the back reaction, *i.e.*, *cis-trans* photoisomerisation. Figure 5 shows the absorption spectra of complexes (*trans*-**34a**)·$Mg^{2+}$, (*cis*-**34a**)·$Mg^{2+}$ and (*cis*-**34a**)·$(Mg^{2+})_2$ in MeCN. The *trans*-to-*cis* conversion of the styryl chromophore in complex **34a**·$Mg^{2+}$ is accompanied by unusually strong hypsochromic effect, which is related to the pseudocyclic structure of complex (*cis*-**34a**)·$Mg^{2+}$ (Scheme 2).



**Scheme 2.** Synthesis of complexes (*cis*-**34a**)·$Mg^{2+}$ and (*cis*-**34a**)·$(Mg^{2+})_2$.

The dye in this complex has a twisted conformation with disrupted π-conjugation between the donor benzocrown moiety and the acceptor benzothiazole residue, which results in disappearance of the long-wavelength charge-transfer absorption band. When a large amount of $Mg(ClO_4)_2$ is added to a solution of (*cis*-**34a**)·$Mg^{2+}$, the intramolecular coordination of the sulfonate anion to the crowned $Mg^{2+}$ is disrupted because the *cis*-isomer binds a second $Mg^{2+}$ ion to form an 1:2 complex, *i.e.*, (*cis*-**34a**)·$(Mg^{2+})_2$ (Scheme 2). The chromophore moiety in (*cis*-**34a**)·$(Mg^{2+})_2$ adopts a less twisted conformation, which leads to the recovery of charge-transfer absorption (Figure 5).

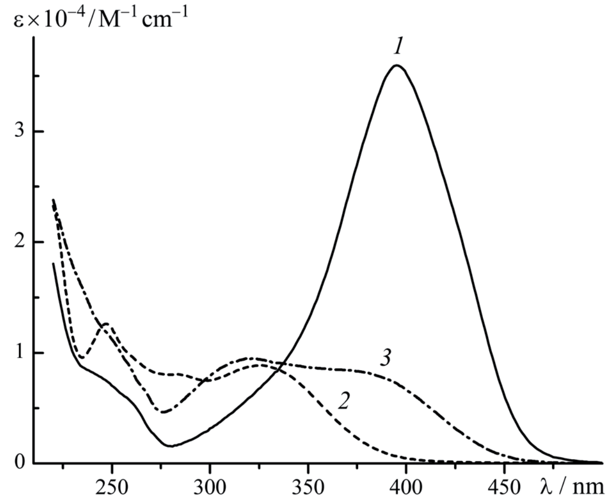
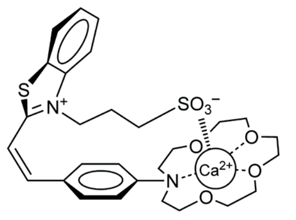


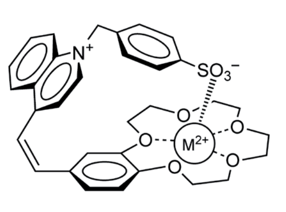
**Figure 5.** Absorption spectra of complexes (*trans*-**34a**)·$Mg^{2+}$ (*1*), (*cis*-**34a**)·$Mg^{2+}$ (*2*) and (*cis*-**34a**)·$(Mg^{2+})_2$ (*3*) in MeCN, as measured at a concentration of $2\times10^{-5}$ M.

As expected, the pseudocyclic complexes (*cis*-**34a–d**)·$Mg^{2+}$ are characterized by higher stability constants when compared to (*trans*-**34a–d**)·$Mg^{2+}$. For the **34b**/$Mg^{2+}$ and **34d**/$Mg^{2+}$ systems, the ratio of the stability constants $K_{cis}/K_{trans}$ is about 500.[44]

Convincing evidence for the photocontrolled formation of anion-'capped' complexes was also obtained with the related crown-containing dyes **35** and **36**.[45,46]



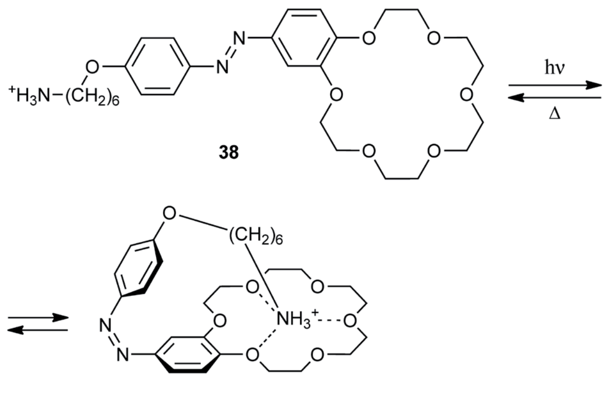
**35**·$Ca^{2+}$



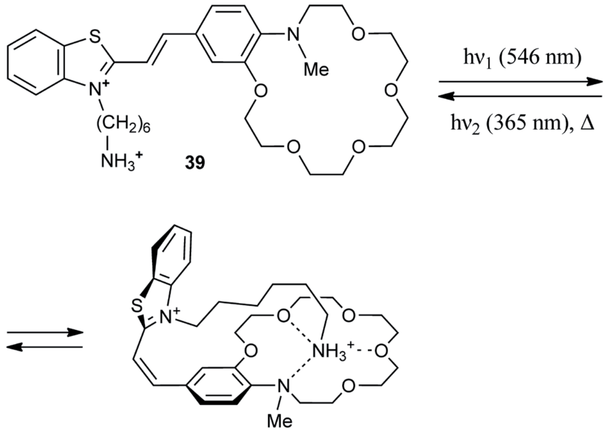
**36**·$M^{2+}$, M = Mg, Ca

Photocontrol of competitive intramolecular binding. Another approach to the photocontrol of cation-binding function was demonstrated in relation to the crown-containing azobenzene **38** bearing a tethered ammonium cation.[47]

The photoresponsive ionophoric properties of **38** were evaluated through solvent extraction of alkali metal ions. The extractability of **38** for $K^+$ was found to decrease significantly upon ultraviolet irradiation. This means that the photogenerated *cis*-**38** has much lower affinity to alkali metal ions than the initial *trans*-isomer. This result was rationalized in terms of competitive intramolecular binding of the ammonium group by the crown ether ring.



The azacrown-containing styryl dye **39** bearing a long ammoniohexyl tail undergoes *trans-cis* photoisomerization in MeCN upon irradiation with green light.[48] The back thermal reaction proceeds slowly at room temperature. The *trans*-to-*cis* conversion is accompanied by a huge hypsochromic effect (see Figure 6). This effect is a direct evidence for intramolecular binding of the ammonium group to the azacrown ether moiety in *cis*-**39**.



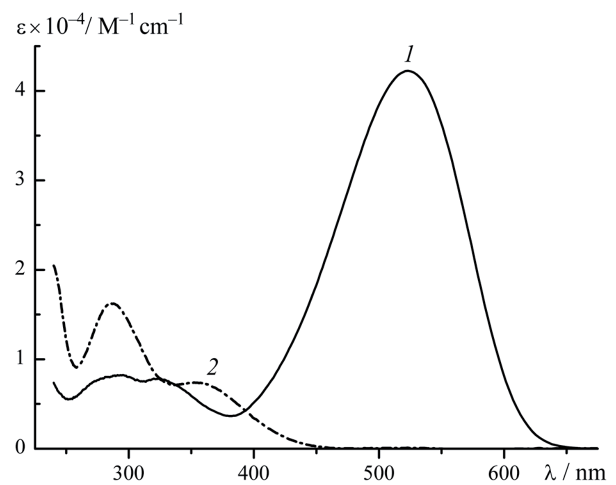
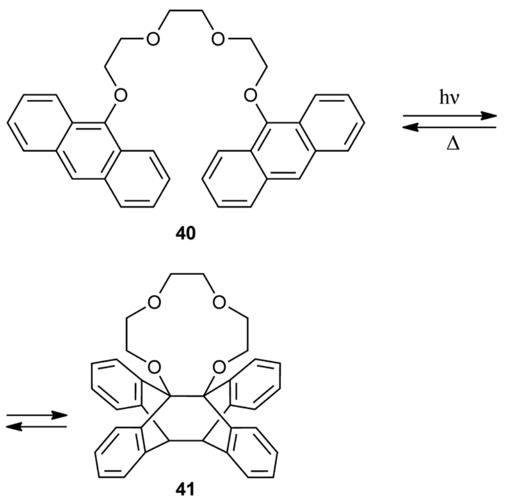


**Figure 6.** Absorption spectra of two isomeric forms of dye **39** in MeCN: *1* – *trans*-isomer, *2* – *cis*-isomer.

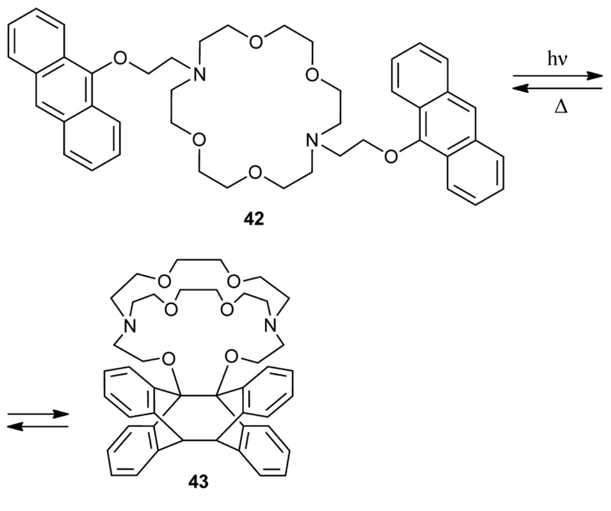
It was found that both geometric isomers of **39** are able to form 1:1 complexes with $Ba^{2+}$. The lg*K* values for complexes (*trans*-**39**)·$Ba^{2+}$ and (*cis*-**39**)·$Ba^{2+}$ in MeCN, as estimated by a spectrophotometric method, are 7.85 and 5.24 respectively.[49] It is evident that the large difference in the thermodynamic stability between these complexes ($K_{trans}/K_{cis} \approx 400$) is due to the intramolecular competitive binding in *cis*-**39**.

### *Photodimerization of Anthracene*

The photodimerization of anthracene is one of the oldest known photochemical reactions. Bisanthracene **40** was the first example of photocontrolled polyether system.[50] This compound undergoes intramolecular photodimerization in benzene to afford crown ether **41**. The back thermal reaction proceeds at room temperature. In the presence of $Li(ClO_4)_2$ the thermal stability of **41** increases dramatically.



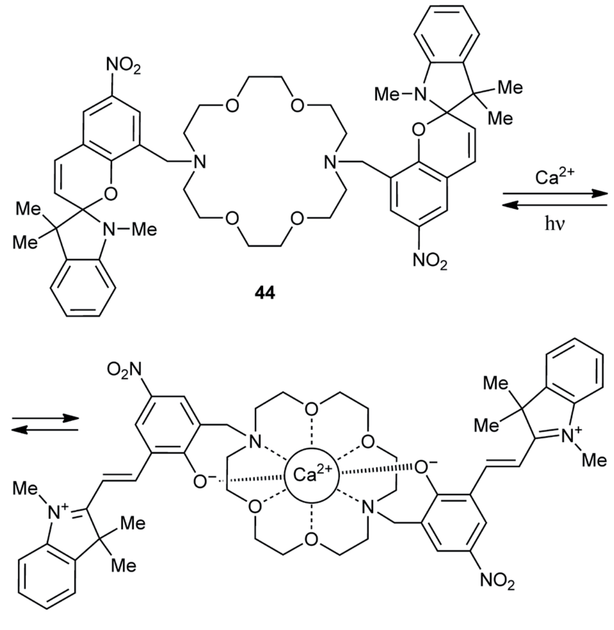
Diazacrown compound **42** bearing two anthracene cores is reported to undergo a reversible intramolecular photodimerization to yield cryptand **43**.[51] Both the photodimerization quantum yield and the efficiency of the back thermal reaction are strongly affected by the presence of metal ions. This is the first example of a molecular system capable of reversible transformation from crown ether to cryptand structure.



### *Photoinduced Ring-Opening Reactions of Spiro Compounds and Chromenes*

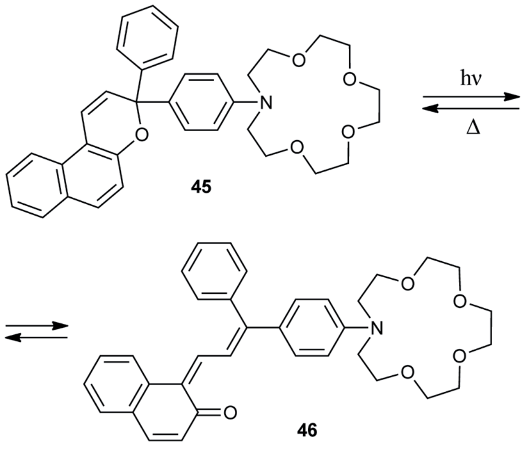
Metal ion-induced ring-opening reaction of spiro compounds has been considered above in connection with colorimetric sensors (compound **16**). The open merocyanine form of **16** is stabilised owing to intramolecular coordination of the crowned metal ion with the phenoxide anion formed upon cleavage of the pyran ring. The relative content of the open form in such systems can be controlled by photoirradiation.

Diaza-18-crown-6 ether **44**[52] has two spirobenzopyran moieties. Binding of $Ca^{2+}$ to the diazacrown moiety of **44** was found to shift the spiropyran–merocyanine equilibrium towards the merocyanine form.



**44**

This form is stabilized owing to intermolecular interaction of the crowned cation with two phenoxide anions. Irradiation of this system with visible light induces the back ring-closure reaction. It was supposed that the back reaction would lead to a decrease in the cation-binding ability of this system. Photoinduced switching of ionic conductivity was realised in composite films containing compound **44** and a calcium salt.



**45**

**46**

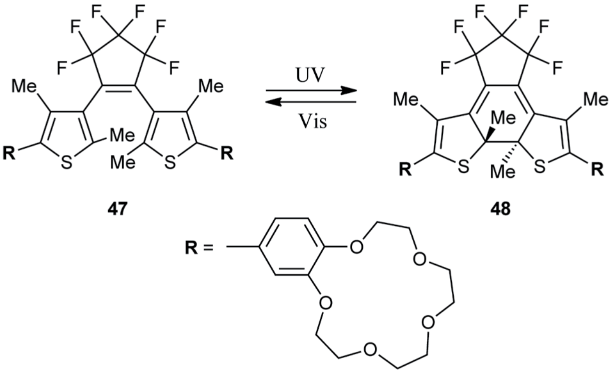
In comparison with spiro compounds, photochromic chromenes are characterized by increased fatigue resistance. Azacrown compound **45** is an example of the photocontrolled ionophores based on chromene derivatives.

Colourless benzochromene **45** undergoes a ring-opening reaction upon ultraviolet irradiation to give coloured isomer **46**.[53,54] The structure of **46** is typical of donor–acceptor chromoionophores. The back thermal reaction occurs with a characteristic time of 1.8 sec. (at 20 °C). In MeCN, isomers **45** and **46** both are able to form 1:1 complexes with $Ca^{2+}$, in which the metal ion is bound by the azacrown moiety. The ring-opening reaction leads to a decrease in the complex stability constant ($\lg K = 4.9$ and 4.1 for **45** and **46** respectively). This decrease is attributable to the electron-withdrawal effect of the naphthalenone fragment of **46** on the phenylazacrown moiety.

### *Photocyclisation of Diarylethylenes*

It is well known that *cis*-isomers of diarylethylenes can undergo intramolecular photocyclisation. As a rule, this photochromic reaction has poor reversibility due to low chemical stability of the photocyclisation products. However, there are specifically designed *cis*-dihetarylethylenes that do not suffer from this drawback.[55]

The photochromic dithienylethylene **47**[56] has two benzo-15-crown-5 ether moieties. It undergoes photocyclisation upon ultraviolet irradiation. The resulting coloured isomer **48** is thermally stable. On exposure to visible light, it is converted to the initial open form.

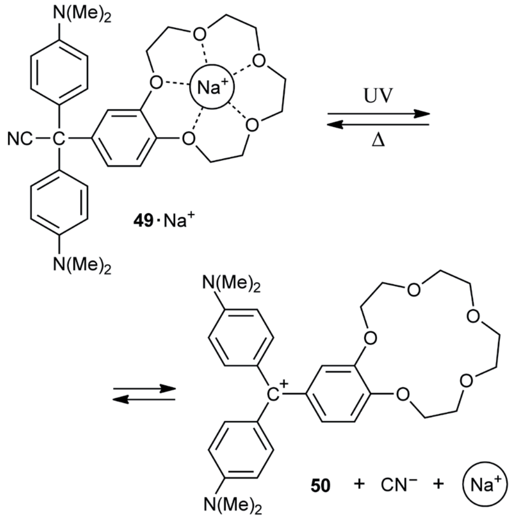


**47** **48**

In solvent extraction experiments, the extractability of biscrown ether **47** for $K^+$ and $Rb^+$ decreased dramatically upon ultraviolet irradiation and then was fully recovered by exposure to visible light. The conclusion was made that the two crown ether moieties of **47** can cooperatively capture large metal ions, such as $K^+$ or $Rb^+$, to form a sandwich-type complex. The conformational rigidity of cyclic isomer **48** disallows the formation of intramolecular sandwich-type complexes.

### *Photodissociation*

The photochromism of triphenylmethane dyes is caused by photodissociation reaction. For instance, Malachite Green leuconitrile in solution ionizes to a triphenylmethyl cation and cyanide anion upon ultraviolet irradiation. This reaction is thermally reversible. The crown ether derivative of Malachite Green leuconitrile, **49**, was synthesised for use in photoresponsive ion-conducting materials.[57]



It is reported that photoinduced ionization of **49** in aqueous methanol decreases the ability of the crown ether moiety to bind $Na^+$ by reason of intramolecular electrostatic repulsion between the resulting organic cation **50** and the crowned metal ion.

## Conclusions

Various approaches to the design of crown ether-based optical molecular sensors and photocontrolled ionophores have been studied. Currently, targeted synthesis of colorimetric indicators that function in a specified spectral range, from near ultraviolet to near infrared, is practicable. Rational design of optical sensors with cation-triggered luminescence is now possible on the basis of both PET and PICT processes. An advantage of the luminescent PICT sensors is the fact that they can also operate as colorimetric indicators. Considerable progress has been attained in the design of photocontrolled ionophores. Various types of photochromic compounds have been tested for use as photoswitches of the ionophoric function. Multifunctional systems on the basis of styryl dyes and spiro compounds have been developed as they can operate both as photocontrolled inophores and as optical molecular sensors.

An applied problem of crown ether-based systems is the low thermodynamic stability of their complexes with alkaline earth metal cations in aqueous media. A possible solution is targeted introduction of additional groups into the crown ether moiety. The aspects related to immobilisation of optical molecular sensors and photocontrolled ionophores on various materials remain little studied. Therefore, investigations dealing with immobilisation of photoresponsive crown compounds in polymeric materials are of considerable interest.[58-60] Currently, development works on luminescent sensors on the basis of quantum dots modified by crown compounds are in progress.[61] The design of nanostructured systems incorporating macrocyclic compounds is a new trend in the research into optical chemosensors and photoswitchable devices.

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## References

1. Pedersen C.J. *J. Am. Chem. Soc.* **1967**, *89*, 2495-2496.
2. Pedersen C.J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.
3. Gokel G.W., Leevy W.M., Weber M.E. *Chem. Rev.* **2004**, *104*, 2723-2750.
4. Löhr H.-G., Vögtle F. *Acc. Chem. Res.* **1985**, *18*, 65-72.
5. Gromov S.P., Alfimov M.V. *Russ. Chem. Bull., Int. Ed.* **1997**, *46*, 611-636.
6. Ushakov E.N., Gromov S.P., Fedorova O.A., Alfimov M.V. *Russ. Chem. Bull., Int. Ed.* **1997**, *46*, 463-471.
7. Russ. P. 2398800, **2010**, Byull. Izobret. (25).
8. Ushakov E.N., Gromov S.P., Fedorova O.A., Pershina Y.V., Alfimov M.V., Barigelletti F., Flamigni L., Balzani V. *J. Phys. Chem. A* **1999**, *103*, 11188-11193.
9. Vedernikov A.I., Ushakov E.N., Lobova N.A., Kiselev A.A., Alfimov M.V., Gromov S.P. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 666-672.
10. Vedernikov A.I., Ushakov E.N., Kuz'mina L.G., Churakov A.V., Strelenko Y.A., Wörner M., Braun A.M., Howard J.A.K., Alfimov M.V., Gromov S.P. *J. Phys. Org. Chem.* **2010**, *23*, 195-206.
11. Gromov S.P., Vedernikov A.I., Ushakov E.N., Kuz'mina L.G., Feofanov A.V., Avakyan V.G., Churakov A.V., Alaverdyan Y.S., Malysheva E.V., Alfimov M.V., Howard J.A.K., Eliasson B., Edlund U.G. *Helv. Chim. Acta* **2002**, *85*, 60-81.
12. Bourson J., Borrel M.-N., Valeur B. *Anal. Chim. Acta* **1992**, *257*, 189-193.
13. Leray I., Habib-Jiwan J.-L., Branger C., Soumillion J.-Ph., Valeur B. *J. Photochem. Photobiol. A: Chem.* **2000**, *135*, 163-169.
14. Citterio D., Sasaki S., Suzuki K. *Chem. Lett.* **2001**, 552-553.
15. Nakamura H., Takagi M., Ueno K. *Talanta* **1979**, *26*, 921-927.
16. Katayama Y., Fukuda R., Iwasaki T., Nita K., Takagi M. *Anal. Chim. Acta* **1988**, *204*, 113-125.
17. Katayama Y., Nita K., Ueda M., Nakamura H., Takagi M., Ueno K. *Anal. Chim. Acta*, 1985, 173, 193-209.
18. Hayashita T., Takagi M. In: *Comprehensive Supramolecular Chemistry. Vol. 1. Molecular Recognition: Receptors for Cationic Guests* (Gokel G.W., Ed.) Oxford: Pergamon **1996**, Ch. 17, p. 635-669.
19. Nakashima K., Nakatsuji S., Akiyama S., Kaneda T., Misumi S. *Chem. Lett.* **1982**, 1781-1782.
20. Kimura K., Yamashita T., Yokoyama M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 613-619.
21. Minkin V.I., Gribanova T.N., Dubonosov A.D., Bren V.A., Minyaev R.M., Shepelenko E.N., Tsukanov A.V. *Ross. Khim. Zh.* **2004**, *48*, 30-37 (in Russ.).
22. Grabowski Z.R., Rotkiewicz K., Rettig W. *Chem. Rev.* **2003**, *103*, 3899-40311.
23. de Silva A.P., de Silva S.A. *J. Chem. Soc., Chem. Commun.* **1986**, 1709-1710.
24. Kondo S., Kinjo T., Yano Y. *Tetrahedron Lett.* **2005**, *46*, 3183-3186.
25. Gromov S.P., Ushakov E.N., Vedernikov A.I., Lobova N.A., Alfimov M.V., Strelenko Y.A., Whitesell J.K., Fox M.A. *Org. Lett.* **1999**, *1*, 1697-1699.
26. Ushakov E.N., Gromov S.P., Vedernikov A.I., Malysheva E.V., Botsmanova A.A., Alfimov M.V., Eliasson B., Edlund U.G., Whitesell J.K., Fox M.A. *J. Phys. Chem. A* **2002**, *106*, 2020-2023.
27. Ushakov E.N., Nadtochenko V.A., Gromov S.P., Vedernikov A.I., Lobova N.A., Alfimov M.V., Gostev F.E., Petrukhin A.N., Sarkisov O.M. *Chem. Phys.* **2004**, *298*, 251-261.
28. Gromov S.P., Vedernikov A.I., Ushakov E.N., Lobova N.A., Botsmanova A.A., Basok S.S., Kuz'mina L.G., Churakov A.V.,

Strelenko Y.A., Alfimov M.V., Ivanov E.I., Howard J.A.K., Johnels D., Edlund U.G. *New J. Chem.* **2005**, *29*, 881-894.

29. de Silva A.P., Gunaratne H.Q.N., Rice T.E., Stewart S. *Chem. Commun.* **1997**, 1891-1892.
30. MacQueen D.B., Schanze K.S. *J. Am. Chem. Soc.* **1991**, *113*, 6108-6110.
31. Jonker S.A., Van Dijk S.I., Goubitz K., Reiss C.A., Schuddeboom W., Verhoeven J.W. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 273-282.
32. Martin V.V., Rothe A., Gee K.R. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1851-1855.
33. Freidzon A.Y., Bagatur'yants A.A., Ushakov E.N., Gromov S.P., Alfimov M.V. *Int. J. Quantum Chem.* published online: 8 sep **2010**, DOI: 10.1002/qua.22778.
34. Rurack K., Rettig W., Resch-Genger U. *Chem. Commun.* **2000**, 407-408.
35. Shinkai S., Nakaji T., Nishida Y., Ogawa T., Manabe O. *J. Am. Chem. Soc.* **1980**, *102*, 5860-5865.
36. Shinkai S., Minami T., Kusano Y., Manabe O. *J. Am. Chem. Soc.* **1983**, *105*, 1851-1856.
37. Fatahur Rahman S.M., Fukunishi K. *J. Chem. Soc., Chem. Commun.* **1994**, 917-918.
38. Shinkai S., Ogawa T., Kusano Y., Manabe O. *Chem. Lett.* **1980**, 283-286.
39. Shinkai S., Honda Y., Kusano Y., Manabe O. *J. Chem. Soc., Chem. Commun.* **1982**, 848-850.
40. Shinkai S., Minami T., Kusano Y., Manabe O. *J. Am. Chem. Soc.* **1982**, *104*, 1967-1972.
41. Gromov S.P., Fedorova O.A., Ushakov E.N., Stanislavskii O.B., Lednev I.K., Alfimov M.V. *Dokl. Akad. Nauk SSSR* **1991**, *317*, 1134-1139 (in Russ.).
42. Gromov S.P., Fedorova O.A., Ushakov E.N., Stanislavskii O.B., Alfimov M.V. *Dokl. Akad. Nauk SSSR* **1991**, *321*, 104-107 (in Russ.).
43. Gromov S.P., Fedorova O.A., Ushakov E.N., Baskin I.I., Lindeman A.V., Malysheva E.V., Balashova T.A., Arsen'ev A.S., Alfimov M.V. *Russ. Chem. Bull., Int. Ed.* **1998**, *47*, 97-106.
44. Ushakov E.N., Gromov S.P., Buevich A.V., Baskin I.I., Fedorova O.A., Vedernikov A.I., Alfimov M.V., Eliasson B., Edlund U. *J. Chem. Soc., Perkin Trans. 2* **1999**, 601-607.
45. Gromov S.P., Ushakov E.N., Fedorova O.A., Soldatenkova V.A., Alfimov M.V. *Russ. Chem. Bull., Int. Ed.* **1998**, *46*, 1143-1148.
46. Gromov S.P., Ushakov E.N., Fedorova O.A., Baskin I.I., Buevich A.V., Andryukhina E.N., Alfimov M.V., Johnels D., Edlund U.G., Whitesell J.K., Fox M.A. *J. Org. Chem.* **2003**, *68*, 6115-6125.
47. Shinkai S., Ishihara M., Ueda K., Manabe O. *J. Chem. Soc., Chem. Commun.* **1984**, 727-729.
48. Vedernikov A.I., Kondratuk D.V., Lobova N.A., Valova T.M., Barachevsky V.A., Alfimov M.V., Gromov S.P. *Mendeleev Commun.* **2007**, 264-267.
49. Ushakov E.N., Kondratuk D.V., Gromov S.P., unpublished.
50. Desvergne J.-P., Bouas-Laurent H. *J. Chem. Soc., Chem. Commun.* **1978**, 403-404.
51. Tucker J.H.R., Bouas-Laurent H., Marsau P., Riley S.W., Desvergne J.-P. *Chem. Commun.* **1997**, 1165-1166.
52. Kimura K., Teranishi T., Yokoyama M., Yajima S., Miyake S., Sakamoto H, Tanaka M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 199-204.
53. Ushakov E.N., Nazarov V.B., Fedorova O.A., Gromov S.P., Chebun'kova A.V., Alfimov M.V., Barigelletti F. *J. Phys. Org. Chem.* **2003**, *16*, 306-309.
54. Fedorova O.A., Maurel F., Ushakov E.N., Nazarov V.B., Gromov S.P., Chebunkova A.V., Feofanov A.V., Alaverdian I.S., Alfimov M.V., Barigelletti F. *New J. Chem.* **2003**, *27*, 1720-1730.
55. Hanazawa M., Sumiya R., Horikawa Y., Irie M. *J. Chem. Soc., Chem. Commun.* **1992**, 206-207.
56. Takeshita M., Irie M. *J. Org. Chem.* **1998**, *63*, 6643-6649.
57. Kimura K., Kaneshige M., Yokoyama M. *Chem. Mater.* **1996**, *7*, 945-950.
58. Kimura K., Sakamoto H., Nakamura M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 225-245.
59. Kimura K., Sakamoto H., Uda R. M. *Macromolecules* **2004**, *37*, 1871-1876.
60. Nath S., Maitra U. *Org. Lett.* **2006**, *8*, 3239-3242.
61. Chen C.-Y., Cheng C.-T., Lai C.-W., Wu P.-W., Wu K.-C., Chou P.-T., Chou Y.-H., Chiu H.-T. *Chem. Commun.* **2006**, 263-265.

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