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# Design principles for optical molecular sensors and photocontrolled receptors based on crown ethers

E N Ushakov, M V Alfimov, S P Gromov

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**Abstract. Design principles are discussed for the polyfunctional crown compounds that are able to act as optical molecular sensors or photocontrolled receptors with respect to metal and ammonium cations. The bibliography includes 237 references.**

## I. Introduction

Macrocyclic compounds are abundant in nature. They are responsible for a series of chemical processes taking place in the living matter such as photosynthesis, transport of atmospheric oxygen to the cells, membrane transport of ions and enzymatic transformations. An important feature of these processes is the selectivity of 'host – guest' interactions. This is why Pedersen's [1–3] synthesis of macrocyclic polyethers (crown ethers) capable of selective binding of alkali metal cations aroused enormous interest and triggered vigorous development of macrocyclic chemistry. The subsequent advances in the synthesis of macrocyclic compounds [4,5] and studies of complexation in 'host – guest' systems laid the foundation of a new interdisciplinary field of research called supramolecular chemistry.[6]

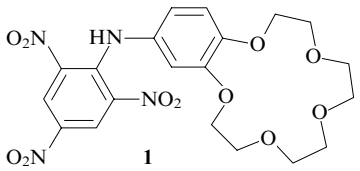
The selective complexation behaviour made crown ethers unique in a number of fields such as chemical synthesis, analytical chemistry, medicine and simulation of biological systems.[7–9] Currently, considerable attention is paid to the design and physicochemical studies of polyfunctional macrocyclic compounds and supramolecular systems based on them that can act as chemosensors, molecular switches, controllable molecular devices and machines. In particular, of considerable interest are chromogenic and luminogenic crown compounds capable of changing their photophysical properties upon selective binding of a substrate.[10–13] They are expected to be used in compact devices for colorimetric or luminescence determination of metal cations and some organic cations. The optical methods for detection of cations by molecular sensors have essential advantages (high sensitivity, fast response, low cost, remote control option) over the analytical methods employed now for determination of cations using ion selective electrodes and atomic absorption spectrometry.

Topical studies are devoted to the properties of crown compounds that undergo, on exposure to light, reversible structural changes affecting the selectivity and efficiency of substrate binding.[14–18] The possible application areas of these compounds include photocontrolled ion transport, ion extraction and separation, the design of ion-conducting light sensitive materials for solar energy conversion and new information technologies and design of photoswitchable molecular devices for nanoelectronics.[19–21]

This review describes the principles of design of polyfunctional crown compounds capable of operating as optical molecular sensors or photocontrollable receptors with respect to metal and ammonium cations.

## II. Colorimetric sensors

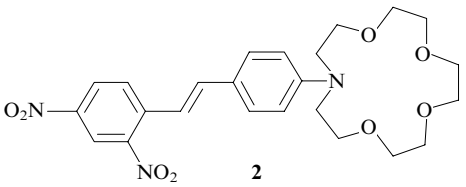
Chromogenic crown compounds (chromoionophores) synthesised by Takagi [22] (compound **1**) and Vögtle [23] (compound **2**) became the first synthetic reagents for colorimetric determination of alkali metal cations.




**1**

**E N Ushakov** Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-496) 515 54 20, tel. (7-496) 524 43 46, e-mail: eushakov@icp.ac.ru
**M V Alfimov, S P Gromov** Photochemistry Centre, Russian Academy of Sciences, ul. Novatorov 7a, 119421 Moscow, Russian Federation. Fax (7-495) 936 12 55, tel. (7-495) 936 77 53, e-mail: alfimov@photonics.ru (M V Alfimov), tel. (7-495) 935 01 16, e-mail: gromov@photonics.ru (S P Gromov)

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**2**

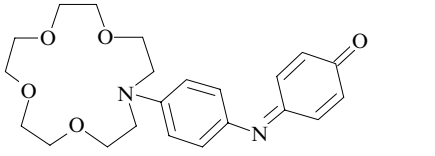
Although compounds **1** and **2** differ in structure, the concept of their design is the same. In both cases, the crown ether fragment is connected to a chromophore in such a way that the metal cation located in the crown ether cavity can interact with one or several chromophore heteroatoms. Most colorimetric molecular sensors based on macrocycles are designed within the bounds of this concept.

The interaction of the cation with chromophore heteroatoms is a necessary but not a sufficient condition for the appearance of strong ionochromic effect. Its magnitude is largely determined by the structure of the chromophore fragment. In terms of the mechanism of colour changes, crown compounds with most clear-cut ionochromic properties can be divided into three main groups. One comprises systems based on donor–acceptor chromophores with strong electronic conjugation between the donor and acceptor fragments. This group includes chromoionophores synthesised by Vögtle and co-workers from azobenzene, stilbene and the dye Phenol Blue.[23–27] One more group comprises systems in which the formation of the cation–macrocycle complex promotes proton elimination in the chromophore moiety. The Takagi chromoionophores are members of this group. Finally, the third group is formed by systems in which colour change upon complexation is caused by thermal isomerisation and rearrangement reactions.

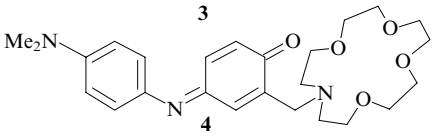
## 1. Donor–acceptor chromoionophores

The long-wavelength band in the UV/Vis absorption spectrum of organic donor-acceptor chromophores with strong electronic conjugation between the donor and the acceptor fragments corresponds, most often, to the intramolecular (internal) charge transfer electronic transition (ICT transition). The energy of this transition depends on the electronic structure of the conjugated fragments of the chromophore and on the solvent nature. In the case of a crown compound with the donor–acceptor chromophore, the ICT transition energy would change considerably upon electronic interaction between the metal cation located in the macrocycle cavity and the electron-donor or electron-acceptor fragment of the chromophore. The interaction of the cation with the donor fragment of the chromophore induces hypsochromic changes in the absorption spectrum, while the interaction of the cation with the acceptor fragment of the chromophore induces a bathochromic effect.

Molecules **3** (Refs 24, 25) and **4** (Refs 25, 26) are typical examples of donor–acceptor chromoionophores possessing negative and positive ionochromism, respectively.



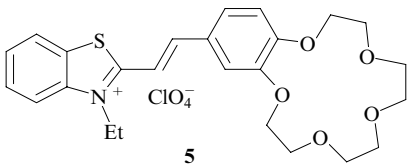
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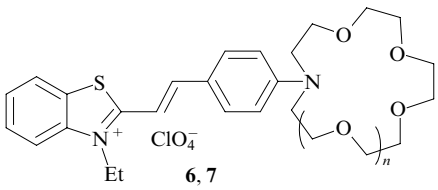
**4**

In both compounds, the dye Phenol Blue was used as the chromophore. In molecule **3**, the azacrown ether fragment reproduces the function of the $Me_2N$ group of the dye; thus, the cation interacts with the electron-donor fragment of the dye. In molecule **4**, the azacrown ether moiety is connected to the dye in such a way that the metal cation that resides in the macrocycle cavity can interact with the carbonyl oxygen atom, *i.e.*, the acceptor fragment of the dye. Acetonitrile solutions of compounds **3** and **4** show an intense long-wavelength absorption band (LAB) with a peak at 580–590 nm. After the addition of alkali or alkaline earth metal salts, the LAB of chromoionophore **3** shifts hypsochromically (by 98 nm with $Ca^{2+}$) and the LAB of chromoionophore **4** conversely shifts bathochromically (by 78 nm with $Ca^{2+}$).[27]

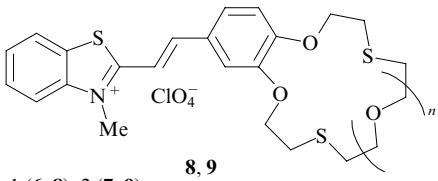
A broad range of donor–acceptor chromoionophores, *i.e.*, crown-containing styryl,[28–41] butadienyl[42–49] and bis-styryl[50–53] dyes, have been prepared by a group of Russian researchers. In each series of dyes, various structural parameters were varied such as the macrocycle size, the nature of macrocycle heteroatoms, the nature of the heterocyclic fragment of the chromophore. Crown styryl dyes **5**–**9** show negative ionochromism.



**5**



**6**, **7**



**8**, **9**

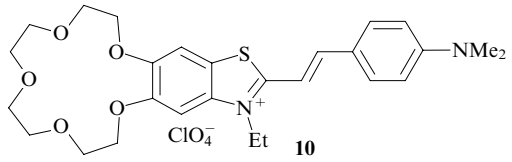
$n$ = 1 (**6**, **8**), 2 (**7**, **9**).

Of a series of alkali and alkaline earth metal cations dye **5** binds selectively $Mg^{2+}$ cations in acetonitrile;[50] the complexation with $Mg^{2+}$ is accompanied by the highest hypsochromic shift of the LAB (38 nm). Chromoionophore **6** shows a more pronounced hypsochromic shift of the LAB upon the complexation with the $Mg^{2+}$ cation (132 nm)[54] than dye **5** owing to more pronounced electron-donor properties of the azacrown ether moiety compared with the crown ether moiety. However, complexes containing dye **6** have a relatively low thermodynamic stability.[37, 54] The main reason is apparently the planar structure of the junction section of the azacrown ether and benzene moieties in compound **6**,[55] which requires considerable conformational changes on complexation. The problem of relatively low stability of chromoionophores like **6** can be solved by using the benzoazacrown ether moiety instead of the *N*-phenylazacrown ether moiety (dyes with the benzoazacrown ether moiety are more pre-organised for complexation).[56, 57]

A distinctive feature of chromoionophores **8** and **9** is high selectivity with respect to $Hg^{2+}$ ions.[39] However, the hypsochromic shifts for complexes of **8** and **9** with the $Hg^{2+}$ cation ($\sim$17 nm) are much smaller than for complexes of **5** with alkaline earth metal cations. This is due to the preferred

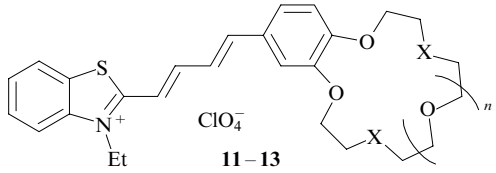
coordination of the $Hg^{2+}$ cation to the sulfur atoms of the dithiacrown ether fragment.

Unlike compounds **5**–**9**, styryl dye **10** (Ref. 36) in which the macrocycle is linked to an electron-acceptor fragment of the chromophore shows positive ionochromism (the bathochromic shift of the LAB for the $Mg^{2+}$ complex of dye **10** in acetonitrile reaches 14 nm).




**10**

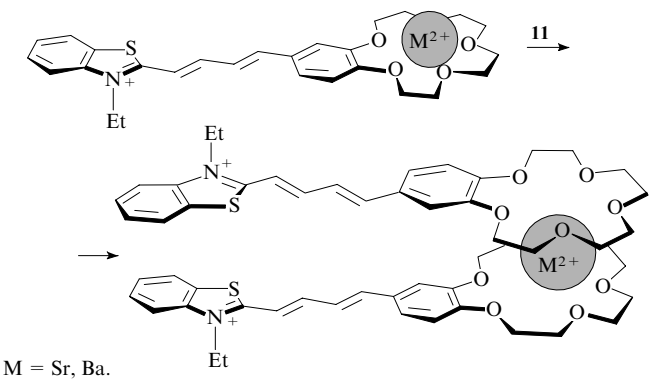
Butadienyl dye **11** (Ref. 44) forms thermodynamically more stable complexes with alkaline earth metal cations than its styryl analogue **5**, because elongation of the polymethine chain in the chromophore mitigates the electron-withdrawing effect of the heterocyclic residue on the benzocrown ether moiety.




**11**–**13**

**11**: X = O, $n$ = 1; **12**: X = S, $n$ = 1; **13**: X = S, $n$ = 2.

The magnitude of the hypsochromic effect for 1 : 1 complexes almost does not change on going from dye **5** to **11**. A distinctive feature of butadienyl dye **11** is the abnormally high tendency to form 2 : 1 sandwich complexes with $Sr^{2+}$ and $Ba^{2+}$ ions. The sandwich complexes are stabilised by stacking interactions between two butadienyl chromophores.[44]




M = Sr, Ba.

Figure 1 shows the dependence of $\Delta\lambda/Z$ ($\Delta\lambda$ is the hypsochromic shift of the LAB, $Z$ is the metal cation charge) on the effective radius of the metal cation ($r_M$) for 1 : 1 complexes of dye **11** with alkali and alkaline earth metal cations in acetonitrile.[54] In the range of $r_M$ values close to the radius of the 15-crown-5 ether cavity ($r_C$ = 0.85–0.92 Å),[58] the $\Delta\lambda/Z$ dependence *vs.* $r_M$ is rather smooth and has a maximum at $r_M \approx r_C$, *i.e.*, the hypsochromic shift of LAB is proportional to the metal cation charge provided that the effective radius of the cation corresponds to the radius of the crown ether cavity.

This trend is not universal. For example, it is inapplicable to some donor–acceptor chromoionophores based on *N*-phenylazacrown ethers.[59] For interpretation of specific iono-

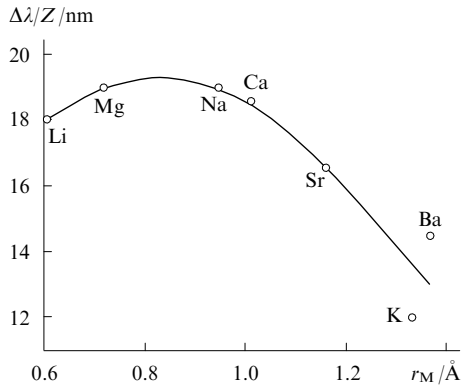
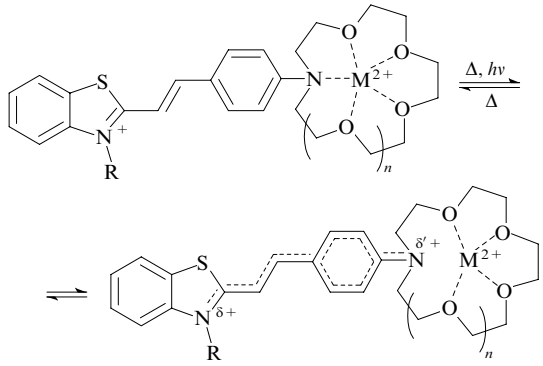



**Figure 1.** Dependence of $\Delta\lambda/Z$ on $r_M$ for the 1 : 1 complexes of dye **11** with alkali and alkaline earth metal cations in acetonitrile.[54]

chromic and ionofluorochromic properties of derivatives of *N*-phenylazacrown ethers **6** and **7**, it was hypothesised that complexes of these compounds with alkaline earth metal cations can exist in two forms, one lacking the coordination bond between the metal cation and the macrocycle nitrogen atom.[37, 54] The two hypothetical forms of the complex occur in dynamic equilibrium. In most cases, in the ground state, the equilibrium is shifted to the left, except for complexes of **7** with small-size cations ($Mg^{2+}$ and $Ca^{2+}$). Upon the electronic excitation of the chromophore, the equilibrium is shifted to the right. The loss of one coordination bond may be counterbalanced by the decrease in the conformational energy of the complex or by introduction of the solvent molecule into the first coordination sphere of the metal cation.[60]




For chromoionophores **12** and **13**, the effect of water content ($P_W$ /vol.%) in the water–acetonitrile mixture on the cation-induced hypsochromic shift and the complexation selectivity was studied.[48, 54] Dyes **12** and **13** demonstrate negative solvatochromism; therefore, the ionochromic effect decreases with an increase in $P_W$. Figure 2 shows the dependences of the logarithm of the stability constant of the complex (log$K$) on $P_W$ for complexes of dye **13** with $Ag^+$, $Hg^{2+}$ and $Pb^{2+}$ cations. It can be seen that on going from anhydrous acetonitrile to mixtures with higher water content, the $Ag^+/Pb^{2+}$ selectivity is inverted. The contrasting patterns of log$K$ *vs.* $P_W$ dependences for $Ag^+$ and $Pb^{2+}$ and for $Ag^+$ and $Hg^{2+}$ are attributable to the fact that $Ag^+$ ions are preferably solvated by acetonitrile and $Pb^{2+}$ and $Hg^{2+}$ ions are preferably hydrated.

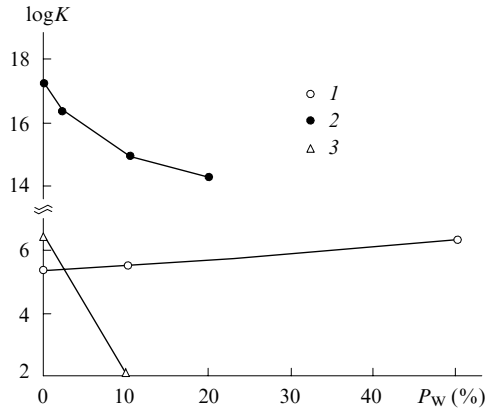
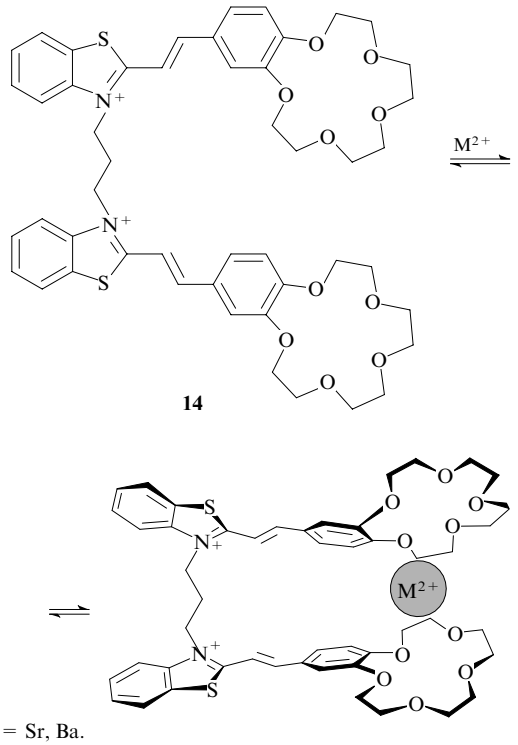



**Figure 2.** Dependences of log$K$ on $P_W$ for the complexes of chromogenic dithiacrown ether **13** with $Ag^+$ (curve *1*), $Hg^{2+}$ (*2*) and $Pb^{2+}$ (*3*) (see Ref. 54).

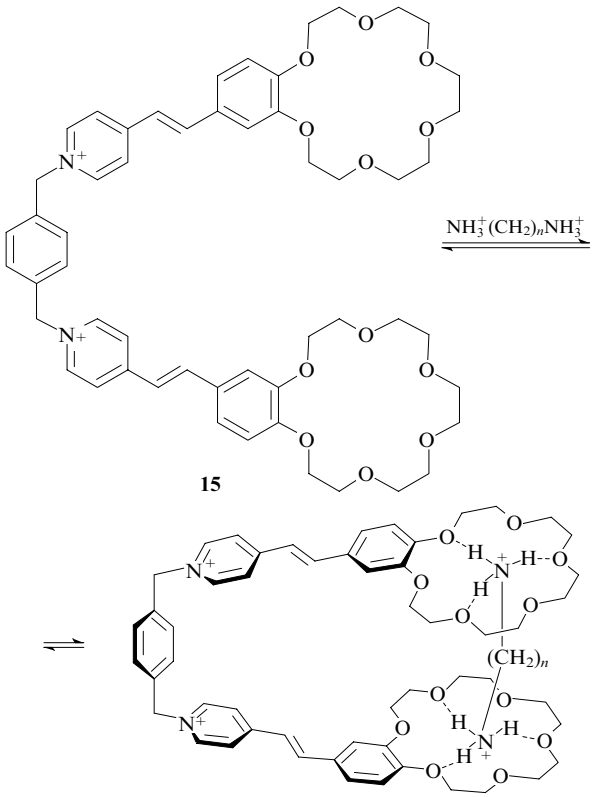
The bis-styryl dye **14** (Ref. 50) is designed as ionochromic molecular tweezer. It can selectively capture alkaline earth metal cations with large diameters ($Sr^{2+}$ and $Ba^{2+}$) owing to cooperative action of two 15-crown-5 ether moieties. Complexes of **14** with $Sr^{2+}$ and $Ba^{2+}$ ions are constructed as intramolecular sandwiches. They show a significant hypsochromic effect and exciton splitting of the LAB and long-lived excimer fluorescence.[50]




**14**

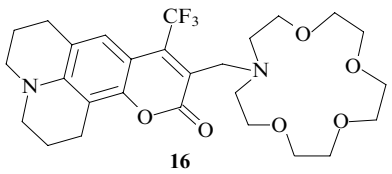
M = Sr, Ba.

The chromogenic bis(18-crown-6) ether **15** (Ref. 52) exhibits its high selectivity with respect to dications $NH_3^+(CH_2)_nNH_3^+$ ($n = 2-6$) in a mixture with $EtNH_3^+$-type ions. The 1 : 1 complexes of compound **15** with $NH_3^+(CH_2)_nNH_3^+$ have a pseudocyclic structure and show a pronounced hypsochromic shift of the LAB (21–23 nm in acetonitrile).

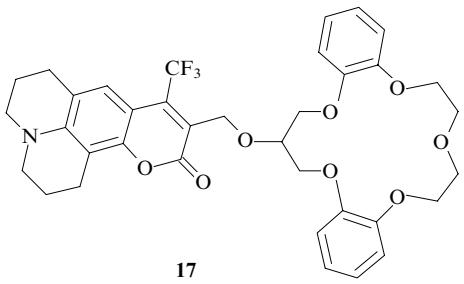



**15**

Other examples of donor-acceptor chromoionophores based on crown ethers are crown-containing derivatives of 1,2-disubstituted ethylenes,[61–68] polymethine dyes,[69] azo dyes [70,71] and coumarins.[72–76] Coumarin-type dyes **16** (Ref. 72) and **17** (Ref. 76) are typical examples of chromoionophores with positive ionochromism.



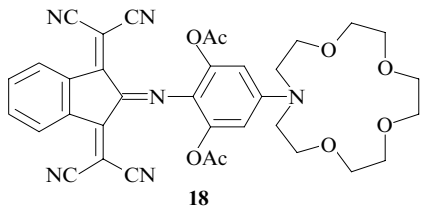

**16**




**17**

Dye **17** demonstrates stronger cation-induced bathochromic changes in the absorption spectrum than dye **16**.[76] The researchers [76] believe that compound **17** containing a longer bridge between the chromophore and the crown ether can assume a conformation that ensures a stronger interaction between the cation located in the crown ether moiety and the oxygen atom of the chromophore carbonyl group.

Donor-acceptor chromoionophore **18** (Ref. 77) incorporates a very strong electron acceptor, namely, 1,3-bis(dicyanomethylidene)indane fragment. This compound is of interest for the fact that it can function as a colorimetric sensor for metal cations in the near-IR region of the spectrum.



**18**

Analysis of published data on the complexation of alkali and alkaline earth metal cations with donor–acceptor chromoionophores based on crown ethers shows that the magnitude of the ionochromic effect ($\Delta\lambda$) is dictated by the following factors:

(i) the metal cation charge (in the case of cations of equal diameters, $\Delta\lambda$ increases with an increase in charge);

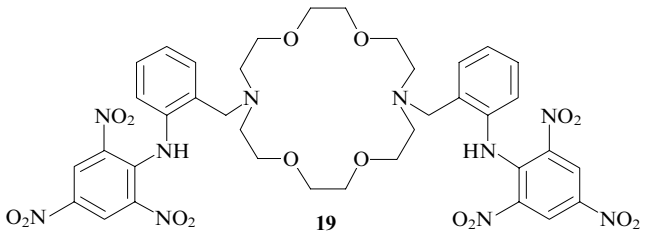
(ii) geometric matching between the metal cation and the crown ether cavity (for cations of equal charges, the better the matching the greater $\Delta\lambda$);

(iii) the nature of the solvent (donor-acceptor chromoionophores show pronounced solvatochromism; therefore, the value of $\Delta\lambda$ depends on the solvent polarity).

## 2. Proton chromoionophores

Proton chromoionophores are mainly used in extraction photometry. They demonstrate positive ionochromism related to the transition of the chromophore fragment to the anionic form upon proton elimination. For stabilisation of the anionic form of the chromophore, the metal cation located in the macrocyclic cavity must be able to interact with the chromophore heteroatoms. Apparently, the optimal structures are those that allow the formation of direct coordination bond between the metal cation and the anionic group of the chromophore. The specific feature of proton chromoionophores used in the extraction photometry is that the charge of the cation extracted from water to the organic phase should be counterbalanced by the charge of the chromophore anionic form. For example, extraction of doubly charged cations to the organic phase requires that chromoionophore possessed two protons capable of elimination.

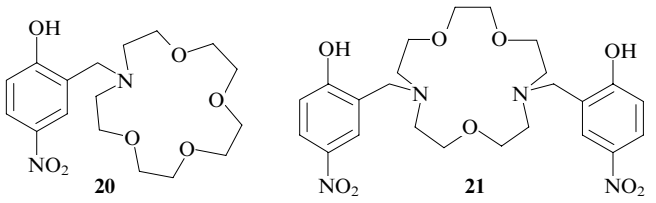
Actually, the crown ether-based proton chromoionophores known to date can be classified into two groups. One comprises aniline derivatives,[22,78–83] and the other phenol derivatives.[83–91] Compounds **1** (Refs 22 and 78) and **19** (Ref. 82) are typical examples of proton chromoionophores based on aniline derivatives.



**19**

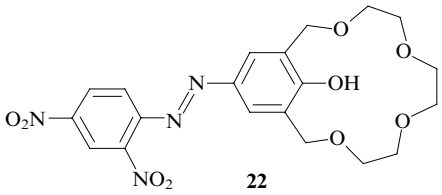
Chromoionophore **1** is used to extract $K^+$ ions into chloroform from an aqueous solution of Li, Na and K salts, while diproton chromoionophore **19** is used to extract $Ba^{2+}$ ions from aqueous solutions of Mg, Ca, Sr and Ba salts.

As examples of proton and diproton chromoionophores based on phenol derivatives, consider compounds **20** (Ref. 85) and **21** (Ref. 92), respectively.



**20** **21**

In some proton chromoionophores, the phenolic OH group is actually a part of the macrocyclic moiety.[93–95] Azobenzene derivative **22** is a typical example of such chromoionophores.[94]



**22**

This type of compounds can be used for colorimetric analysis of metal cations in organic media.

More information on the proton and diproton chromoionophores based on crown ethers and other macrocyclic ligands can be found in a review.[10] The authors of the review identify the most important factors affecting the ion selectivity and extraction ability of chromoionophores, which should be taken into account in the design of chromogenic crown compounds for extraction photometry. These include:

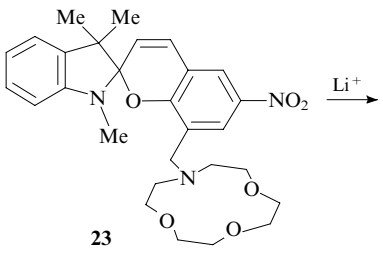
(i) structure of the macrocycle, as dehydration of the metal cation depends on the size of the crown ether fragment and the nature of heteroatoms it contains;

(ii) steric factors determining the mutual orientation of and the distance between the macrocycle and the proton group of the chromophore;

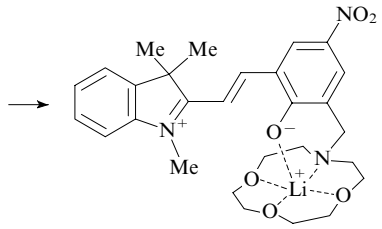
(iii) basicity of the anion form of the chromophore and the Lewis acidity of the metal cation, as these factors determine the extraction ability and the magnitude of the ionochromic effect.

## 3. Systems functioning on the basis of thermal isomerisations and rearrangements

It is known that photolysis of almost colourless spiropyrans is accompanied by cleavage of the carbon–oxygen bond in the pyran ring giving rise to a merocyanine dye.[96] The valence isomerisation of spiropyrans can also be thermally induced; however, the thermal equilibrium spiropyran–merocyanine is most often shifted toward the colourless ring form. Crown spiropyrans and spironaphthoxazines that can be partially converted into the coloured open form upon complexation with alkali or alkaline earth metal cations have been synthesised.[97–106] The design principle for these systems can be illustrated using azacrown spirobenzopyran **23** as an example.[100,101]

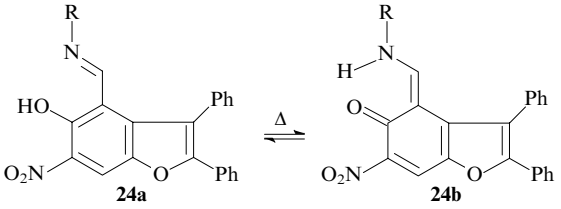


**23**

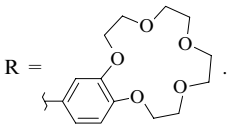


Thermal isomerisation of compound **23** is selectively promoted by $Li^+$ ions, which is due to stabilisation of the merocyanine isomer by intramolecular interaction of the lithium cation located in the azacrown ether cavity with the phenoxide ion. The existence of this interaction was proved by $^7Li$ NMR spectroscopy.[101]

Recently, synthesis of a number of crown-containing imines of *o*-hydroxyaldehydes of benzo[*b*]furan and benzo[*h*]-coumarin series has been reported.[107–109] Some of the described compounds (for example, imine **24a**) can function as chromoionophores. The principle of their action is based on shifting of the tautomeric equilibrium upon complexation.



**24a** **24b**

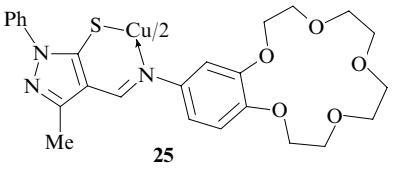


In polar solvents, compound **24a** exists partly as the quinonoid tautomer **24b**. On complex formation between the crown ether moiety of compound **24** and alkaline earth metal cation, the tautomeric equilibrium shifts to the benzenoid form **24a**, resulting in a considerable decrease in the LAB intensity.

### 4. Other chromoionophore systems

Some known chromogenic metal complex systems based on crown tetrapyrrole derivatives are able to function as $K^+$-selective colorimetric sensors.[110,111] The interaction of $K^+$ ions with 15-crown-5 ether moieties of such metal complexes gives rise to aggregates with specific spectral properties.

Recently, chelates formed by crown-containing Schiff bases with transition metal cations have been reported;[109,112] chromogenic crown compound **25** is an example.



**25**

It was found that light-green acetonitrile solutions of compounds **25** turn crimson upon the addition of a barium salt.[109] The addition of other alkaline earth metals does not induce any noticeable colour changes. Presumably, the selectivity of compound **25** with respect to $Ba^{2+}$ ions is related to the formation of a sandwich complex involving two crown ether moieties. A drawback of this system is relatively low molar extinction coefficients in the visible region.

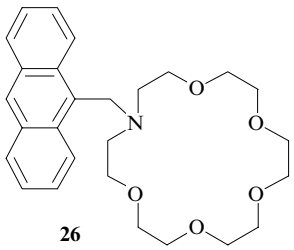
## III. Luminescent sensors

The first puplications on the synthesis of luminogenic crown compounds[113–116] appeared almost at the same time as publications on chromogenic crown compounds. However, they did not give clear recommendations concerning the design of effective luminescent molecular sensors (LMS) based on crown compounds. The first examples of rational design of these LMS date back to the mid-1980s.[117,118]

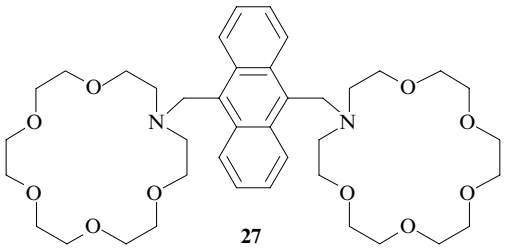
The LMS that show strong luminescence only within a complex, *i.e.*, after selective binding of a substrate, but luminesce weakly if at all without a substrate are considered most promising from practical standpoint. Owing to high sensitivity of the luminescence analysis, these systems can be used to determine very small amounts of the analyte.

The general concept of the design of LMS that are triggered upon selective binding of a substrate is based on luminescence self-quenching caused by intramolecular processes such as photoinduced electron or proton transfer, exciplex or excimer formation, transition of the excited molecule into a twisted intramolecular (internal) charge transfer state (TICT state). From this it follows that the macrocyclic and luminophore fragments in the 'triggered' LMS should be connected in such a way that the substrate located in the macrocycle cavity be able to suppress the process responsible for luminescence quenching.

As examples of luminescent sensors based on crown compounds designed according to this concept, consider azacrown anthracenes **26** (Ref. 118) and **27**.[119]



**26**



**27**

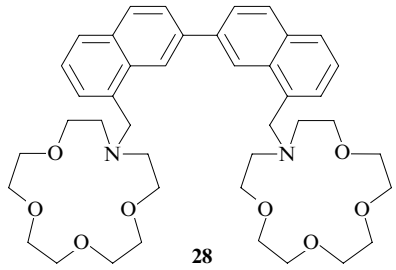
These compounds dissolved in methanol (**26**) or in a methanol–chloroform mixture (1 : 1) (**27**) show very low yields of luminescence as a result of intramolecular electron transfer from the nitrogen atom of the macrocyclic moiety to the locally excited anthracene fragment. On complexation of azacrown ether **26** with $K^+$ cation, the quantum yield of fluorescence increases 47-fold.[118] The reason for fluorescence enhancement is the fact that the metal cation, having entered the azacrown ether cavity, blocks the nitrogen lone pair and thus prevents the electron transfer to the excited anthracene core.

Considerable fluorescence enhancement for bis(azacrown) anthracene **27** can be attained if the substrate blocks the lone pairs on both nitrogen atoms. This condition is met in the case of dications (*e.g.*, alkanediammonium dications), which form

pseudocyclic complexes with compound **27**. When bis-ether **27** reacts with butane-1,4-diammonium, the quantum yield of fluorescence increases by almost two orders of magnitude.[119]

For the analogue of **26** containing a benzo-15-crown-5 ether moiety,[120] photoinduced electron transfer is inefficient due to the relatively low electron-donating ability of the benzocrown ether moiety; therefore, the complexation of this compound with alkali metal cations has only little influence on the quantum yield of fluorescence. However, when an electron-withdrawing CN group is introduced into the anthracene core, the benzocrown anthracene acquires the properties of a triggered LMS.[120]

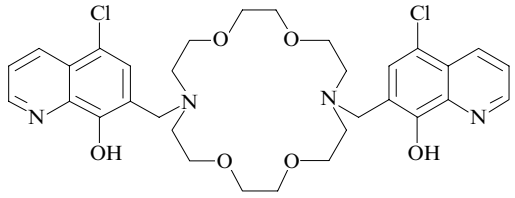
The luminescence of bis(azacrown) binaphthyl **28** (Ref. 121) is also quenched through intramolecular photoinduced electron transfer.



**28**

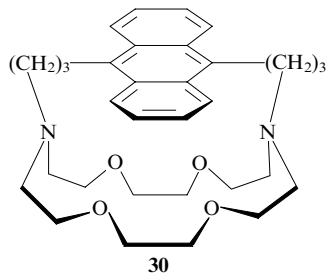
This compound binds selectively $Ba^{2+}$ cations in acetonitrile–methanol mixtures owing to the formation of an intramolecular sandwich complex. The complexation is accompanied by enhancement of the binaphthyl luminescence.

The quenching of luminescence in diazacrown ether derivative **29** [122] containing two luminophoric 5-chloro-8-hydroxyquinoline fragments is due to two photoinduced intramolecular reactions, proton transfer and electron transfer.[123] In water–methanol mixtures, diazacrown ether **29** binds selectively $Mg^{2+}$ ions, the complexation being accompanied by a considerable increase in the quantum yield of luminescence.[122]



**29**

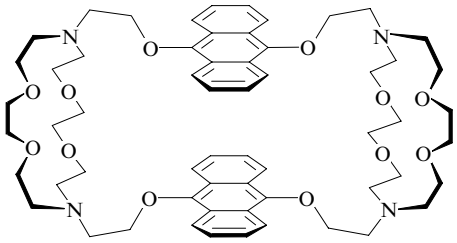
Anthracenocryptand **30** (Refs 117, 124) dissolved in methanol shows a weak fluorescence of the anthracene core existing in the locally excited state and longer-wavelength luminescence, which was attributed to the exciplex formed upon the interaction of the aromatic fragment with the macrocycle nitrogen atoms.



**30**

The complexation of compound **30** with $K^+$ cation quenches the exciplex luminescence but enhances the fluorescence of the anthracene core in the locally excited state; as a result, the overall luminescence yield substantially increases.

The 'cylindrical' receptor **31** (Refs 125–127) exhibits a two-band luminescence spectrum; the long-wavelength band was attributed to an intramolecular excimer formed upon interaction of two anthracene fragments.



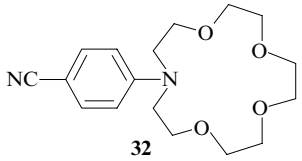
**31**

This compound operates as an LMS with respect to some organic dications. When the complex is formed, the dication is arranged between two anthracene cores and thus prevents the excimer formation. As a result, the excimer luminescence is quenched and the monomer luminescence is enhanced.

All of the above LMS have a common feature, namely, they all contain a spacer between the macrocyclic and luminogenic fragments. In other words, there is no electronic conjugation between the luminogen and macrocycle heteroatoms in these systems. Lots of such LMS are known to date, in particular, crown derivatives of anthracene,[128–134] pyrene [135,136] and other luminogens.[137–143]

Another group of LMS includes luminogenic crown compounds containing a conjugated donor–acceptor electronic system. In these compounds, one of the macrocycle heteroatoms is a part of the luminophore moiety.[144–151] The luminescence properties of such conjugated donor–acceptor systems cannot always be unambiguously interpreted. *p*-Dimethylaminobenzonitrile (DMABN), which exhibits a luminescence spectrum with two bands in polar solvents, can serve as an example.[152] Best known is the hypothesis [153] according to which in the charge transfer excited state, DMABN undergoes conformational changes related to the rotation of the dimethylamino group, resulting in a twisted state with a higher degree of charge separation (TICT state). The short-wavelength band in the luminescence spectrum is assigned to the initial excited state of DMABN, while the long-wavelength band corresponds to the TICT state.

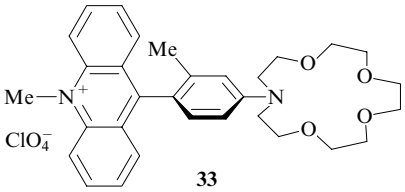
Like DMABN, the nitrile derivative of *N*-phenylazacrown ether **32** (Ref. 144) shows two-band fluorescence. Upon complexation of compound **32** with the $Ca^{2+}$ cations in acetonitrile, the intensity of the long-wavelength fluorescence band decreases, as the cation prevents the formation of a polar TICT state. The intensity of short-wavelength fluorescence increases simultaneously. However, the change in the overall yield of luminescence is insignificant for this system.



**32**

In azacrown compound **33**,[145] the planes of the acridine core and the benzene ring are arranged, for steric reasons, at a substantial angle, *i.e.*, the electronic conjugation between the

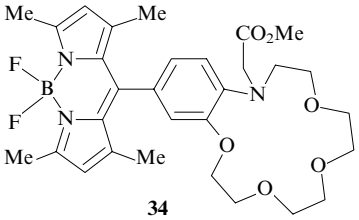
donor and acceptor fragments of the chromophore is considerably violated.



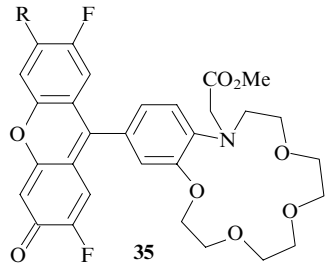
**33**

In a neutral medium, compound **33** virtually does not luminesce, which is attributable to the fast transition of excited molecules into the non-radiative TICT state. Complexation with $Ag^+$ ions enhances the fluorescence from the locally excited state of the acridine core.

Later, other luminoionophores designed similarly to compound **33** have also been described.[146–150] Among these, noteworthy are benzoazacrown ethers **34** and **35** (R = $OCH_2OAc$), which can operate as triggered LMS for metal cations not only in organic but also in aqueous media.[150]



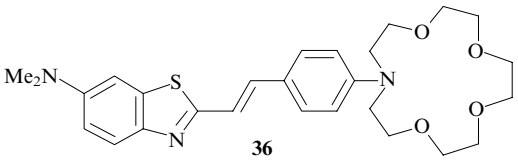
**34**



**35**

The possibility of using compound **35** as a selective fluorescent sensor for intracell sodium ions has been demonstrated.[150]

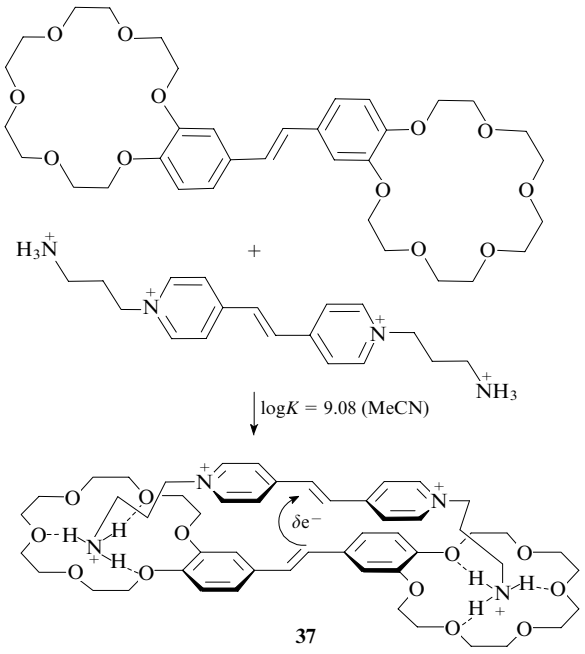
The chromophore fragment of azacrown compound **36** (Ref. 151) is a conjugated donor–acceptor–donor system.



**36**

The quantum yield of luminescence of compound **36** in acetonitrile is 0.027. After the addition of a calcium salt, it increases 30-fold and the luminescence band shifts bathochromically by 32 nm. Among the triggered LMS described previously, so high factors of cation-induced enhancement of luminescence were found only for those compounds where the conjugation between the chromophore and the macrocyclic fragment is either missing (as in **26**) or is fairly weak (as in **33**). In this respect, system **36** is unique. The luminescence properties of this system were interpreted using a reaction model comprising three electronically excited states.[151]

An original approach to the design of highly efficient triggered LMS was demonstrated by synthesising supramolecular charge transfer complexes (CTC) between bis(18-crown-6)stilbene and bis-ammonium derivatives of π-acceptor heterocyclic compounds.[154–157] The supramolecular CTC of type **37**, unlike the usual organic CTC, have very high thermodynamic stability. Complex **37** does not luminesce and does not undergo photochemical transformations due to ultrafast deactivation of the electronically excited state by back electron transfer reaction.[158]




**37**

Figure 3 presents the results of investigations of the luminescence properties of CTC **37** in acetonitrile in the presence of alkaline earth metal salts.[156] A dilute solution of CTC **37** ($2 \times 10^{-6}$ mol litre$^{-1}$) shows very weak luminescence caused by the small portion of donor and acceptor molecules existing in the unbound state. The optical properties of the solution virtually do not change upon the addition of $Mg(ClO_4)_2$ in a fourfold excess with respect to the CTC. Meanwhile, the addition of small amounts of $Ca(ClO_4)_2$ or $Ba(ClO_4)_2$ results in pronounced luminescence enhancement caused by replace-

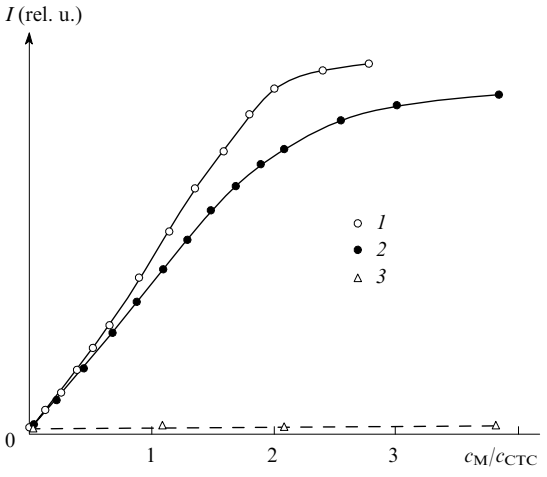
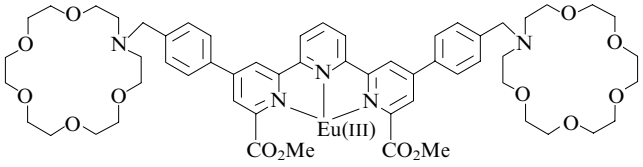



**Figure 3.** Fluorescence intensity of an acetonitrile solution of CTC **37** ($c_{CTC} = 2 \times 10^{-6}$ mol litre$^{-1}$) *vs.* relative concentration of the metal salt added (observed at 375 nm).[156]
Salt: (*1*) $Ba(ClO_4)_2$, (*2*) $Ca(ClO_4)_2$, (*3*) $Mg(ClO_4)_2$.

ment of the acceptor in the supramolecular CTC by metal ions. The complexes formed by bis(18-crown-6)stilbene with $Ca^{2+}$ and $Ba^{2+}$ cations show high fluorescence quantum yield ($\geqslant 0.3$).

In recent years, considerable progress in the design of triggered LMS based on crown ethers containing an organometallic luminophore has been attained. As organometallic components, complexes of nitrogen-containing ligands with rare earth [159–161] or transition [162–167] metals were used.

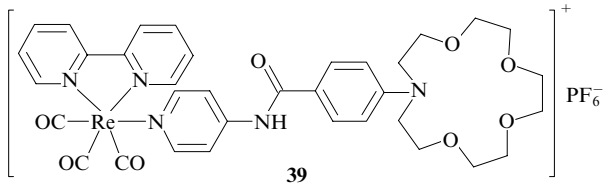
It is known that the electronic excitation of rare earth metal complexes with nitrogen-containing ligands may give rise to long-lived luminescence of the metal cation in the locally excited state. In system **38**,[159] the Eu(III) luminescence is quenched due to electron transfer from the nitrogen atom of the azacrown ether moiety to the europium ion. The addition of a potassium salt into a methanolic solution of system **38** results in a more than an order of magnitude increase in the Eu(III) luminescence quantum yield.




**38**

Recently, diaza-15-crown-5 and diaza-18-crown-6 ether derivatives containing a cyclene Tb(III) complex as the luminophore have been reported.[160, 161] Aqueous solutions of these systems at physiological pH values are characterised by very low yields of Tb(III) luminescence. The factors responsible for luminescence quenching are not exactly known. Presumably, as in the case of system **38**, photoinduced electron transfer is the main factor. On the addition of sodium or potassium salt to such systems, Tb(III) luminescence is appreciably enhanced.

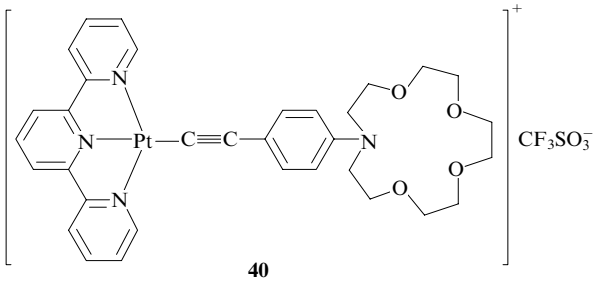
An important photophysical characteristics of complexes of di- and polypyridyl ligands with Ru(II), Os(II), Re(I) or Pt(II) is the metal-to-ligand charge transfer electron transition (MLCT transition). The triplet MLCT excited state in these systems is usually luminescing. However, azacrown-containing rhenium complex **39** (Ref. 162) has a very low luminescence quantum yield, as electron transfer from the crown ether nitrogen to the electron-deficient rhenium atom takes place in the MLCT excited state.




**39**

This reaction affords a non-radiative ligand – ligand charge transfer excited state (LLCT state). When the $Ca^{2+}$ ion is complexed with the azacrown ether moiety of compound **39**, electron transfer becomes inefficient; therefore, the quantum yield of luminescence of a system in the MLCT state considerably increases.

For azacrown-containing platinum complex **40**,[166] direct electron transition to the non-radiative LLCT state is possible (similar complexes have also been described [164, 165]). In acetonitrile, the LLCT absorption band of system **40** is shifted bathochromicically with respect to the MLCT absorption band. The excitation of **40** to the MLCT state does not induce luminescence because the system undergoes fast internal conversion to the lower-energy nonradiative LLCT state. Upon the interaction of $Mg^{2+}$ or $Ca^{2+}$ ions with the azacrown ether moiety of complex **40**, the energy of LLCT transition considerably increases and becomes higher than the MLCT transition energy. As a result, luminescence from the MLCT state is enhanced.




**40**

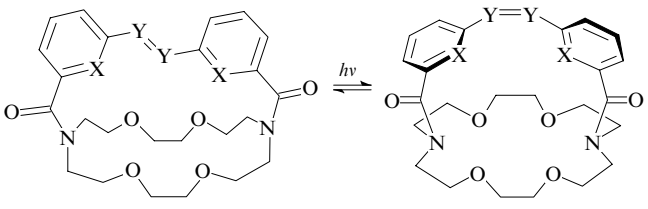
Additional information on LMS based on crown ethers and other ligands can be found in reviews.[11, 168–170]

## IV. Photocontrolled receptors

The key route to photocontrolled receptors is covalent binding of a photochrome able to undergo substantial changes on exposure to light to a macrocycle that can accommodate selectively metal cations or other species. The molecular system should be designed in such a way that structural changes arising in the photochromic fragment have an appreciable influence on the receptor properties of the macrocycle. In addition, the photochromic reaction should be either thermally or photochemically reversible. In this review, the photocontrolled crown compounds are classified according to the type of photochromic reaction.

### 1. Geometric *trans – cis* photoisomerisation

A variety of photocontrolled crown compounds based on photochromes that undergo geometric *trans – cis* photoisomerisation are described in the literature. These include diazacrown ethers in which nitrogen atoms are connected by a photochromic fragment: azobenzene (compound **41**),[171, 172] 2,2′-azopyridine (**42**)[173] or stilbene (**43**).[174] It was found by extraction that the ability of diazacrown ethers **41** – **43** to bind alkali metal cations changes upon *trans – cis* photoisomerisation of the photochromic fragment. In the case of compound **41**, the photogenerated *cis*-isomer binds more efficiently large-size cations ($K^+$, $Rb^+$) and, conversely, binds more poorly small cations ($Li^+$, $Na^+$) as compared with the initial *trans*-isomer.



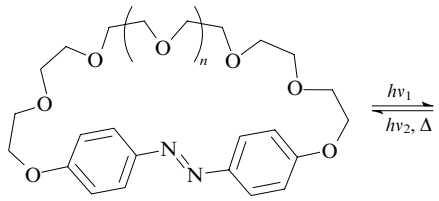

**41** – **43**

**41**: X = CH, Y = N; **42**: X = Y = N; **43**: X = Y = CH.

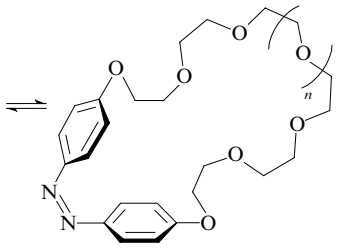
It is supposed that *trans – cis* isomerisation of the azobenzene fragment in compound **41** results in an extension of the diazacrown ether cavity. The reverse *cis – trans* isomerisation of compounds **41** and **42** is thermally induced. For stilbene

derivative **43**, no data on the reversibility of *trans*–*cis* photoisomerisation are available. It is noteworthy that *cis*-isomers of stilbenes can undergo oxidative photocyclisation to give phenanthrene derivatives, *i.e.*, in the case of stilbene-containing crown ethers, reversibility of *trans*–*cis* photoisomerisation may be a problem.

Azobenzene derivatives **44**–**46** [175, 176] in which positions 4 and 4′ are connected by a polyether chain comprising 7 to 9 oxygen atoms readily undergo photochemically and thermally reversible *trans*–*cis* photoisomerisation.




**44**–**46** (*trans*)

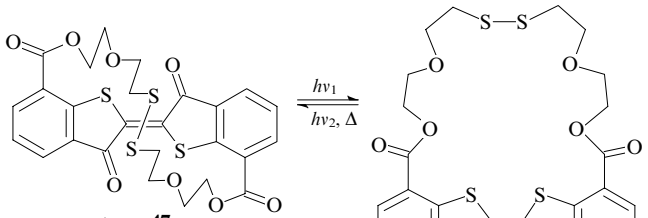


(*cis*)

$n$ = 1 (**44**), 2 (**45**), 3 (**46**).

It was found that *trans*-isomers **44**–**46** are unable to extract alkali metal cations from water into organic phase, whereas photogenerated *cis*-isomers **44**–**46** efficiently extract them. The extraction selectivity depends on the length of the polyether chain: *cis*-**44** shows selectivity towards $Na^+$, *cis*-**45**, towards $K^+$ and *cis*-**46**, towards $Rb^+$. The results were attributed to the fact that the polyether chain in the *trans*-isomer is stretched along the azobenzene fragment, while in the *cis*-isomer it has the shape of a crown ether ring.

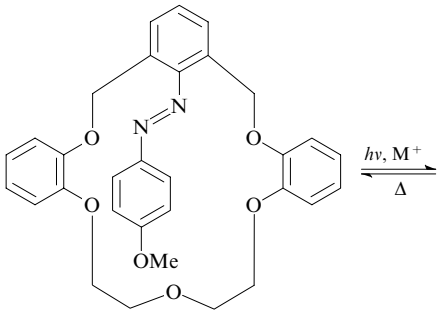
A similar idea can be followed in the design of thioindigo derivative **47**.[177] On exposure to visible light, this compound undergoes *trans*–*cis* photoisomerisation around the central C=C bond. The reaction is reversible both photochemically and thermally.



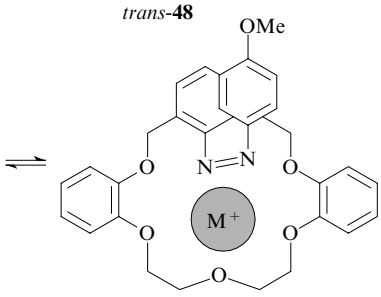

*trans*-**47** *cis*-**47**

As a result of *trans*–*cis* photoisomerisation, thioindigo **47** acquires the ability to extract alkali metal cations and $Ca^{2+}$ from water to the organic phase (the selectivity varies in the sequence $Cs^+ > K^+ > Na^+ > Ca^{2+} > Li^+$).

Yet another method of photoinduced modification of the macrocycle cavity was demonstrated for crown compound **48** as an example.[178] Under usual conditions, the azobenzene fragment of molecule **48** is located near the macrocycle cavity, which creates some steric hindrance to complex formation between the metal cation and the macrocycle.

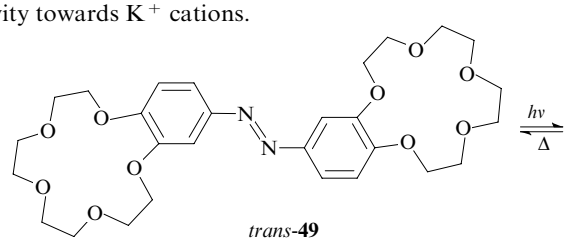



*trans*-**48**

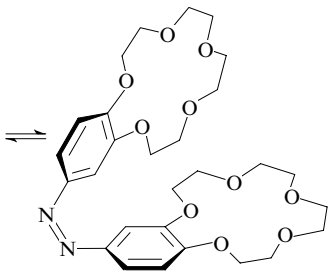



In *o*-dichlorobenzene–methanol mixture (5 : 1), *trans*-isomer **48** is virtually unable to bind $Na^+$ cations, whereas the photogenerated *cis*-isomer forms a complex with this cation having a large stability constant ($\log K = 4.81$).[178] It was assumed [178] that *trans*–*cis* photoisomerisation of the azobenzene fragment partly removes the steric hindrance to complex formation. In addition, it was suggested that in the complex *cis*-**48** · $Na^+$, the sodium cation coordinates one nitrogen atom of the photochromic group.

As a result of *trans*–*cis* photoisomerisation of biscrown azobenzene **49**,[179–181] two macrocyclic fragments approach each other to such an extent that they can cooperatively bind ions with large diameters. Isomerisation changes the ion selectivity of this ditopic receptor: the *trans*-form binds preferably the $Na^+$ cations, while the *cis*-form shows high selectivity towards $K^+$ cations.



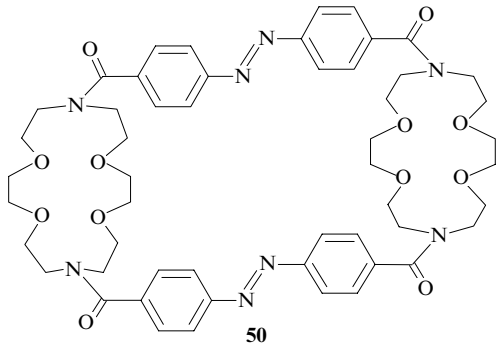

*trans*-**49**



*cis*-**49**

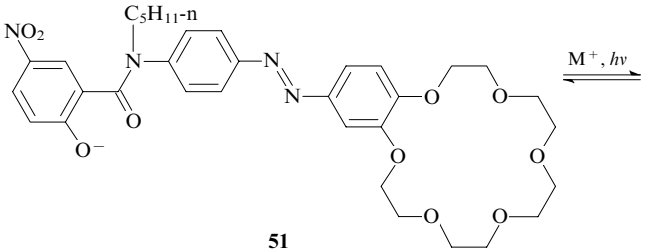
Compound **50** containing two diazacrown ether fragments is able to extract dications $NH_3^+(CH_2)_nNH_3^+$ ($n$ = 4, 6, 8, 10, 12) from water into organic phase.[182, 183] The extraction efficiency increases with an increase in the length of the polymethylene chain in the dication. Upon *trans*–*cis* photoisomerisation of azobenzene spacers, the distance between the two

diazacrown ether moieties decreases and, hence, the selectivity of the ditopic receptor **50** moves toward smaller dications.

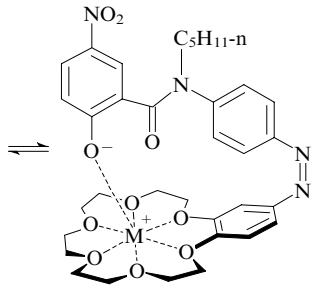


**50**

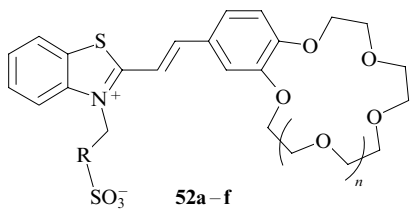
The idea of controlling the receptor properties of photochromes by photoinduced change in the mutual arrangement of two ionophoric groups has been developed in studies dealing with anion-'capped' complexes of crown ethers. It was found [184] that the efficiency of extraction of alkali metal cations with azobenzene derivative **51** containing a crown ether fragment and the phenoxide ion markedly increases after *trans*–*cis* isomerisation of this compound induced by UV radiation. The authors assumed [184] that the phenoxide ion in compound *cis*-**51** forms an intramolecular coordination bond with the metal cation located in the crown ether cavity.



**51**



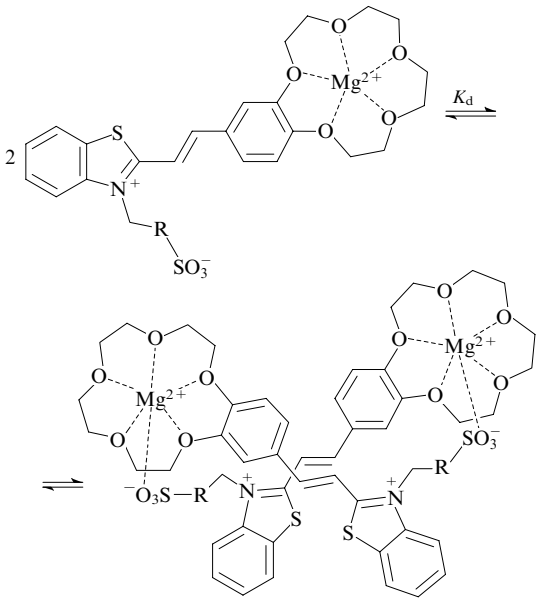
Direct experimental evidence for the photoinduced formation of anion-'capped' complexes was obtained in a comprehensive study of crown styryl dyes with the betaine structure.[185–198] The photocontrolled complexation of benzothiazole dyes **52a**–**d** with $Mg^{2+}$ cations in acetonitrile has been studied at a quantitative level.[185–192]



**52a**–**f**

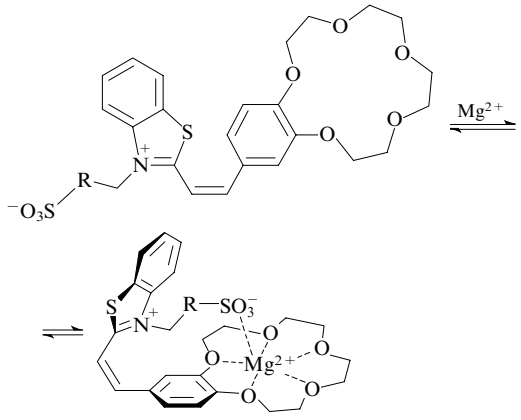
R = $(CH_2)_2$ (**a**, **e**), $(CH_2)_3$ (**b**, **f**), *o*-$C_6H_4$ (**c**), *p*-$C_6H_4$ (**d**);
*n* = 1 (**a**–**d**), 2 (**e**, **f**).

It was found [188, 192] that 1 : 1 complexes of *trans*-**52a**–**d** with $Mg^{2+}$ tend to undergo self-organisation to form pseudocyclic dimeric structures. The equilibrium constant for the dimerisation of the complexes ($K_d$) depends substantially on the structure of the betaine fragment in the dye: for the *trans*-**52a**/$Mg^{2+}$ system, the log$K_d$ value is ~5.5, while for *trans*-**52b**/$Mg^{2+}$, log$K_d$ > 6.5.



Dyes *trans*-**52a**–**d**, both free and complexed with $Mg^{2+}$, easily undergo *trans*–*cis* photoisomerisation upon irradiation with blue light. UV irradiation of *cis*-isomers induces the back reaction, *cis*–*trans* photoisomerisation. It is noteworthy that 2 : 2 complexes of *trans*-isomers **52a**–**c** with $Mg^{2+}$ cations undergo, apart from photoisomerisation, stereospecific [2 + 2]-autophotocycloaddition (PCA).[190, 191] The quantum yield of PCA was relatively low. UV irradiation of PCA products (cyclobutane derivatives) induces the back reaction, *retro*-PCA. In the complex of dye *trans*-**52d** with the $Mg^{2+}$ cation, no PCA reaction occurs.[191]

It was shown experimentally [185–192] that 1 : 1 complexes of *cis*-isomers **52a**–**d** with $Mg^{2+}$ exist in the anion-'capped' form, *i.e.*, these complexes have an intramolecular coordination bond between the sulfonate group of the *N*-substituent and the metal cation located in the crown ether cavity.

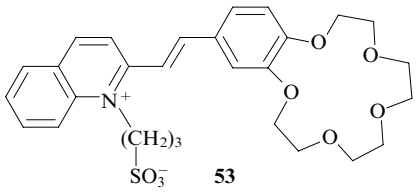


Anion-'capped' complexes formed by *cis*-isomers are thermodynamically more stable than the complexes of *trans*-isomers (Table 1). For the **52b**/$Mg^{2+}$ and **52d**/$Mg^{2+}$ systems, the ratio of the stability constants $K_{cis}/K_{trans}$ is about 500.[192]

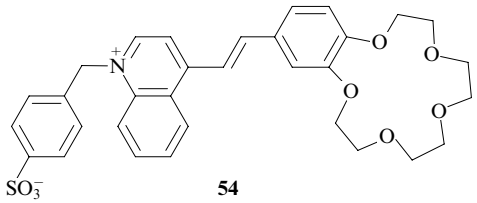
**Table 1**. Stability constants of $Mg^{2+}$ complexes of *trans*- and *cis*-isomers of dyes **52a–d** in acetonitrile.[192]

| Dye | log*K* | | $K_{cis}/K_{trans}$ |
|---|---|---|---|
| | *trans*-isomer | *cis*-isomer | |
| **52a** | 7.1 | 9.4 | 200 |
| **52b** | 7.6 | 10.3 | 500 |
| **52c** | 6.7 | 7.3 | 4 |
| **52d** | 7.3 | 10.0 | 500 |

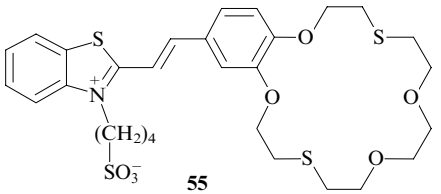
Convincing evidence for the formation of anion-'capped' complexes upon *trans–cis* photoisomerisation of the styryl chromophore was also obtained for **52e**,**f**/$Ca^{2+}$ (Ref. 193), **53**/$Mg^{2+}$ (Ref. 194), **54**/$Mg^{2+}$ (Ref. 195), **55**/$Hg^{2+}$ (Refs 196, 197) and **56**/$Ca^{2+}$ (Ref. 198) systems.



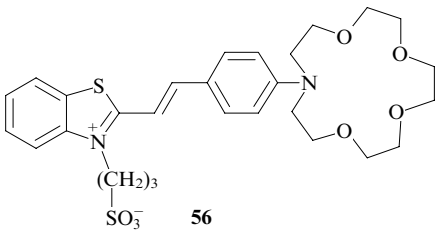
**53**



**54**



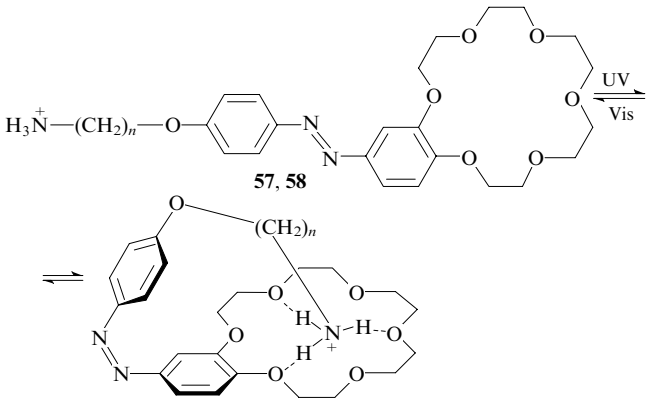
**55**



**56**

Another approach to the photocontrol of receptor properties of macrocycles was demonstrated in relation to azobenzene derivatives **57** and **58**[199,200] containing 18-crown-6 ether and $(CH_2)_nNH_3^+$ fragments. In the usual state, compounds **57** and **58** exist as *trans*-isomers.

UV irradiation induces *trans–cis* photoisomerisation of the azobenzene fragment in compounds **57** and **58** resulting in the formation of intramolecular complexes between the ammonium group and the crown ether moiety. Because of intramolecular coordination, photogenerated *cis*-isomers are much inferior in the ability to bind alkali metal cations than the initial *trans*-isomers.[199] (Later, it has been found[201] that *trans*-azobenzenes **57** and **58** form pseudocyclic dimers through intermolecular complexation of ammonium groups with crown ether moieties.)

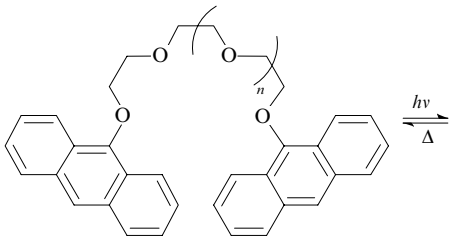


**57**, **58**

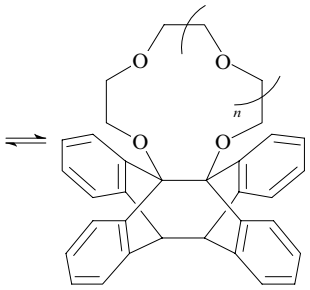
*n* = 6 (**57**), 10 (**58**).

## 2. Photodimerisation of polyether systems containing anthracene fragments

There are several known supramolecular systems based on polyethers containing two anthracene substituents such that the anthracene nuclei are prone to photodimerisation, resulting in appreciable structural change of polyether fragments.[202–207] Compounds **59a–d** are the first examples of such systems.[202,203]



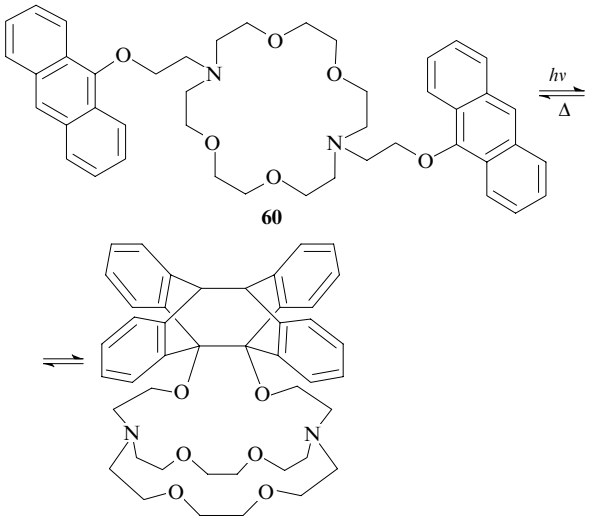
**59a–d**



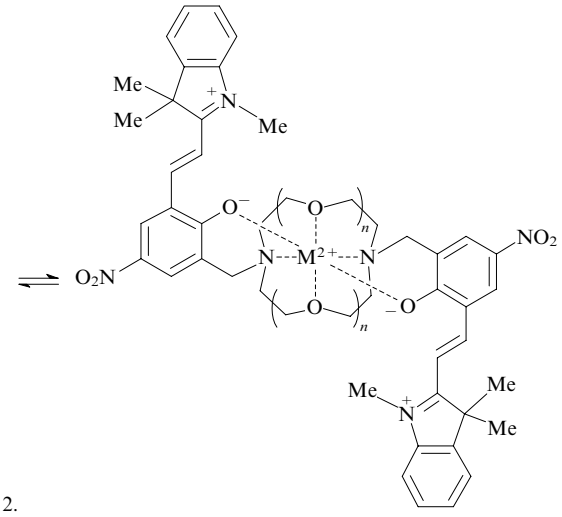
*n* = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**).

Intramolecular photodimerisation of anthracene fragments in compounds **59a–d** affords crown ether derivatives. The back reaction proceeds at room temperature. After the addition of alkali metal salts, the thermal stability of photocycloisomers substantially increases, while the quantum yield of photodimerisation remains the same. Later, other supramolecular systems in which photodimerisation of the anthracene cores resulted in crown ether derivatives have been described.[204–206]

Diazacrown ether **60**[207] containing two anthracene fragments is the first example of a molecular system capable of reversible transformation from crown ether to cryptand structure on exposure to light. Photoirradiation of compound **60** in methanol gave a cycloadduct with the cryptand structure (quantum yield of about 0.10). The dark lifetime of the cryptand is about 50 h at 25 °C. After complexation of compound **60** with $Cs^+$, the quantum yield of photodimerisation decreases 2.5-fold and the dark lifetime of the cycloadduct increases almost 20-fold.



**60**



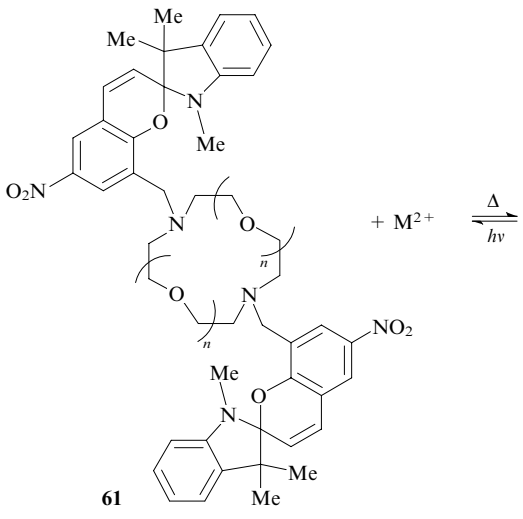
$n$ = 1, 2.

Unfortunately, no stability constants of complexes were reported in the publications cited.[202–207]

## 3. Photoisomerisation of spiro compounds and chromenes

The crown spiro compounds that are partially transformed into a coloured open form (merocyanine isomer) upon complexation with metal cations have already been considered above. The open form is stabilised through coordination of the metal cation located in the crown ether cavity to the phenoxide ion formed upon cleavage of the pyran ring. The relative concentration of the open form in such systems can be controlled by photoirradiation. The anion-'capped' complex of the merocyanine isomer is expected to be thermodynamically more stable than the complex of the ring form, *i.e.*, at appropriate design, crown spiro compounds can function as photocontrolled receptors. This type of systems are presented rather comprehensively in a review by Alfimov *et al.*;[16] therefore, we will consider only one example.

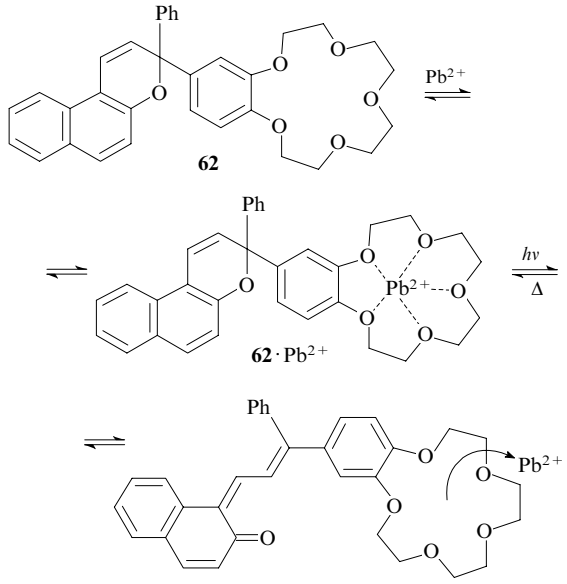
Crown bis(spirobenzopyrans) **61** (see Refs 208, 209) form rather stable complexes with $Na^+$, $Ca^{2+}$ and $Sr^{2+}$ cations in methanolic solutions. The spiropyran–merocyanine thermal equilibrium is shifted in these complexes towards the merocyanine isomer. On exposure to visible light, photoinduced closure of the pyran ring takes place. According to data from mass spectrometry, the stability constant of the complex decreases appreciably upon this reaction. The smaller the diameter and the larger the charge of the metal cation the more pronounced



**61**

the observed effect. Data on photocontrolled selective transport of $Li^+$ ions through a liquid membrane containing compound **61** ($n$ = 1) have recently been reported.[210]

A number of photochromic crown compounds based on benzochromenes are documented.[211–217] On exposure to UV radiation, benzochromenes, like spiropyrans, undergo valence photoisomerisation with pyran ring cleavage giving rise to a coloured open isomer.[218] In particular, the effect of UV radiation on the complexation of crown benzochromene **62** with $Pb^{2+}$ ions in acetonitrile has been studied by the electrochemical method.[211] As a result, it was concluded that crown compound **62** forms in the dark a relatively stable complex with the $Pb^{2+}$ ion, which dissociates under UV irradiation with elimination of a metal cation. No quantitative data on the thermodynamicc stability of complexes of the valence isomers were reported in the publication cited.[211]



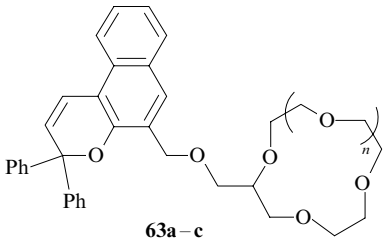
**62**

**62** · $Pb^{2+}$

The synthesis of a series of azacrown benzochromenes and their photochromic transformations in the presence of alkali and alkaline earth metal cations have been reported.[212,213] However, nothing was said about the stability constants of the complexes formed by valence isomers.

The stability constants of the complexes formed by crown benzochromenes **63a–c** with alkali metal cations in acetonitrile were determined.[214] Benzochromene **63a** containing

12-crown-4 ether moiety was found to form 2 : 1 sandwich complexes with $Na^+$ cations. After photoinduced cleavage of the pyran ring, the equilibrium shifts towards 1 : 1 complex (the stability constant for the complex of the open form was not reported).



**63a–c**

$n$ = 1 (**a**), 2 (**b**), 3 (**c**).

The photocontrolled complexation of alkaline earth metal cations with azacrown benzochromene **64a** in acetonitrile has been studied at a quantitative level.[215–217] The results obtained in these studies[215–217] have later been analysed and generalised.[54] It was found that on exposure to UV radiation, colourless benzochromene **64a** is isomerised to give coloured open isomer **64b** ($\lambda_{max}$ = 543 nm, dark lifetime 1.8 s at 20 °C).

Scheme 1 shows the complexation of $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ ions with isomers **64a** and **64b**. A distinctive feature of the 1 : 1 complex of photoisomer **64b** with $Mg^{2+}$ is the fact that it exists as two forms. In one of these ($\lambda_{max}$ = 430 nm), the $Mg^{2+}$ ion is linked to the azacrown ether moiety, while in the other ($\lambda_{max}$ = 692 nm), which is present in a minor amount, the metal ion is linked to the carbonyl group. The formation of complexes with different composition and structure involving photoisomer **64b** results in retardation of the dark closure of the pyran ring. Complexes of the initial benzochromene **64a** have higher thermodynamic stability than analogous complexes of photoisomer **64b**. The ratio of the stability constants for the complexes of isomers **64a** and **64b** with alkaline earth metal cations varies in the series $Mg^{2+}$ (12.9) > $Ca^{2+}$ (7.2) > $Sr^{2+}$ (5.9) > $Ba^{2+}$ (4.0).

Using the microsecond flash photolysis technique, dissociation of cation–macrocycle complexes taking place after the photoinduced cleavage of the pyran ring in **64a** was monitored[217] and the rate constants for dissociation and formation of 1 : 1 complexes with isomer **64b** were determined (Table 2). It was concluded[54] that the rate of formation of cation–macrocycle complexes with compound **64b** is limited by the rate of elimination of the acetonitrile molecule from the first coordination sphere of the metal cation.

**Table 2**. Stability constants ($K$) and rate constants for formation ($k_1$) and dissociation ($k_{-1}$) of the complexes of photoisomer **64b** with alkaline earth metal cations in acetonitrile at 20 °C.[217]

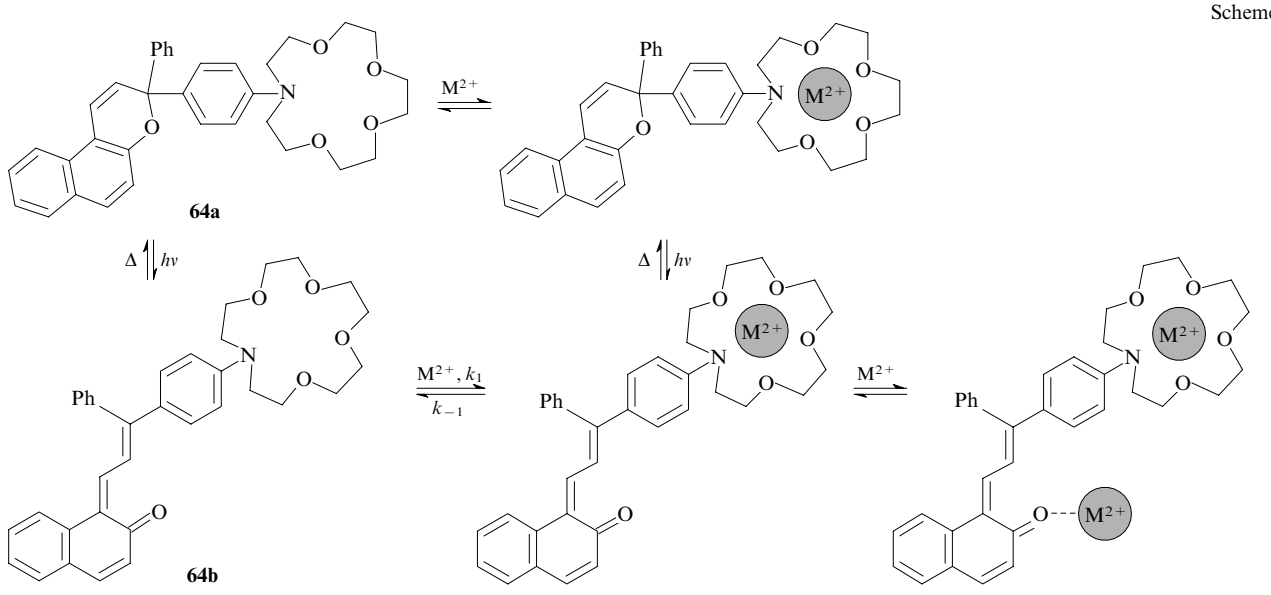
| Cation | log$K$ | $k_1$ /litre mol$^{-1}$ s$^{-1}$ | $k_{-1}$ /s$^{-1}$ | log($k_1/k_{-1}$) |
|---|---|---|---|---|
| $Mg^{2+}$ | 3.07 | $\sim 5 \times 10^4$ | $\sim 40$ | – |
| $Ca^{2+}$ | 4.12 | $3.46 \times 10^7$ | $2.49 \times 10^3$ | 4.14 |
| $Sr^{2+}$ | 3.25 | $3.17 \times 10^7$ | $1.54 \times 10^4$ | 3.31 |
| $Ba^{2+}$ | 3.26 | $6.50 \times 10^7$ | $3.42 \times 10^4$ | 3.28 |

## 4. Photocyclisation of diarylethylenes

It is well known that *cis*-isomers of stilbene and many other diarylethylenes undergo intramolecular photocyclisation. As a rule, this photochromic reaction has poor reversibility due to low chemical stability of the photocyclisation products. In particular, the photocycloisomer of stilbene, 4*a*,4*b*-dihydrophenanthrene, is easily dehydrogenated to phenanthrene in the presence of air oxygen or other oxidants. However, a number of specially synthesised photochromic *cis*-dihetarylethylenes do not suffer from this drawback. For example, some derivatives of *cis*-dithienylethylenes[219] withstand more than $10^4$ cycles of photochromic transformations. Coloured photocycloisomer formed upon UV irradiation of nearly colourless *cis*-dithienylethylenes has a very high thermal stability. On irradiation with visible light ($\lambda$ > 500 nm), the ring isomer is converted rather easily into the initial *cis*-dithienylethylene. A number of photochromic crown compounds containing a dithienylethylene fragment were described in the literature.[220–223]

Takeshita and Irie[220, 221] synthesised dithienylethylene (**65**) and bis(benzothienyl)ethylene (**66**) containing benzocrown ether fragments and studied the extraction efficiency of these compounds with respect to alkali metal picrates prior to irradiation and in the photostationary state during UV irradiation.[221] It was found that UV irradiation of compounds **65**

Scheme 1

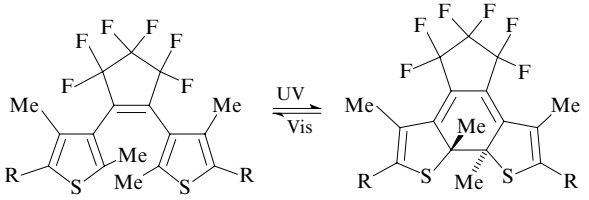


**64a**

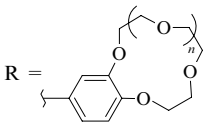
**64b**

M = Ca, Sr, Ba.

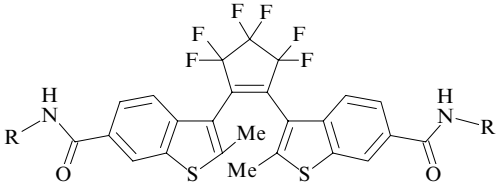
and **66** results in a substantial decrease in their extraction efficiency with respect to metal cations the diameter of which exceeds the diameter of the crown ether cavity in these compounds. On irradiation of photocycloisomers of these compounds with visible light, the efficiency of the extraction is completely retained.



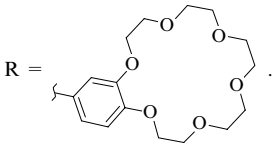
**65**



($n = 1-3$).

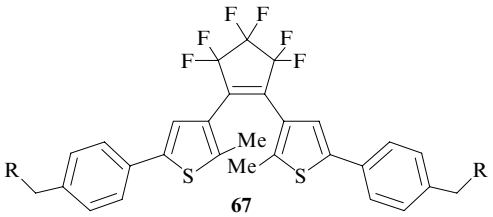


**66**

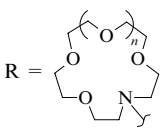


Takeshita and Irie[221] believe that crown ether moieties in molecules **65** and **66** are capable of cooperative binding of relatively large metal cations as sandwich complexes, but after photocyclisation of the dithienylethylene fragment the cooperative binding becomes impossible for steric reasons.

The synthesis and study of properties of dithienylethylenes **67** containing two azacrown ether fragments have been described.[222] According to the extraction data for alkali metal picrates, compound **67** at $n = 1$ binds selectively the $Na^+$ ions and at $n = 2$, $K^+$ and $Rb^+$ ions. After UV irradiation, the extraction efficiency of compounds **67** decreases by 5% – 10%. The decrease in the extraction efficiency may be attributed to the conformational rigidity of the ring isomer formed upon irradiation resulting in hampered formation of intramolecular sandwich type complexes.

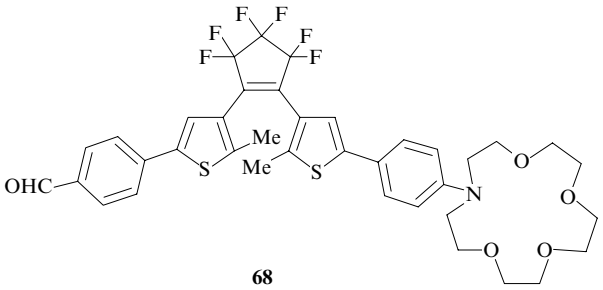


**67**



($n = 1, 2$).

The results of studies of the photochemical and receptor properties of the dithienylethylene derivative **68** containing azacrown ether fragment have been reported.[223]

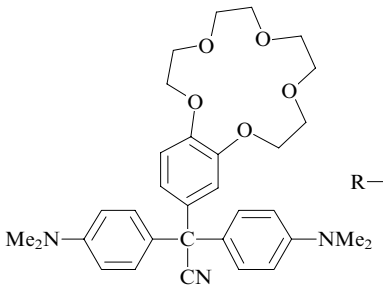


**68**

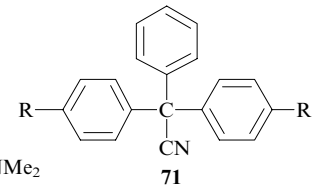
According to spectrophotometric measurements, photocyclisation of compound **68** results in a decrease in the thermodynamic stability of the complexes of this compound with $Ca^{2+}$, $Na^+$, and $Ag^+$ cations. The stability constant of the complex formed by the ring isomer of compound **68** with $Ca^{2+}$ in acetonitrile is smaller by almost four orders of magnitude with respect to the stability constant of the complex in the open form ($\log K = 5.4$ and 1.7 for the open and ring forms, respectively). It was assumed[223] that this is due to the decrease in the electron density on the nitrogen atom upon cyclisation of the dithienylethylene fragment.

## 5. Photodissociation

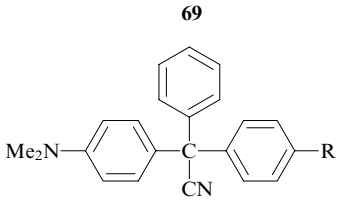
The photochromism of crown derivatives of triphenylmethane dyes **69** – **72** (see Refs 224 — 227) is caused by photodissociation reaction resulting in elimination of the $CN^-$ anion.



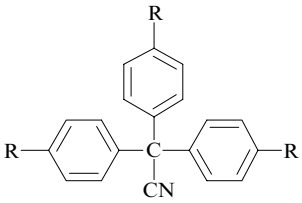
**69**



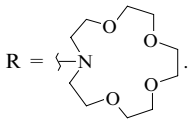
**71**

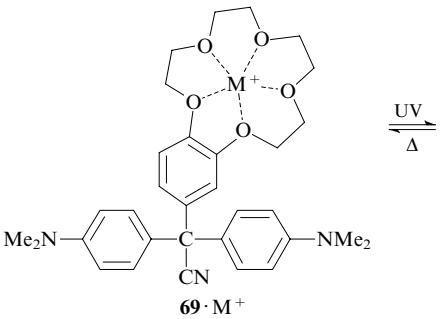


**70**

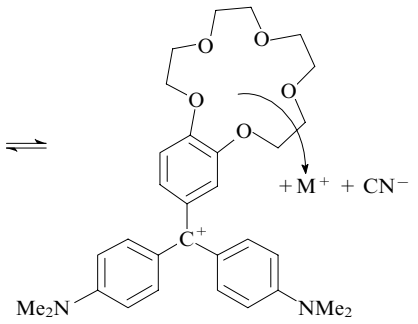


**72**





**69** · $M^+$



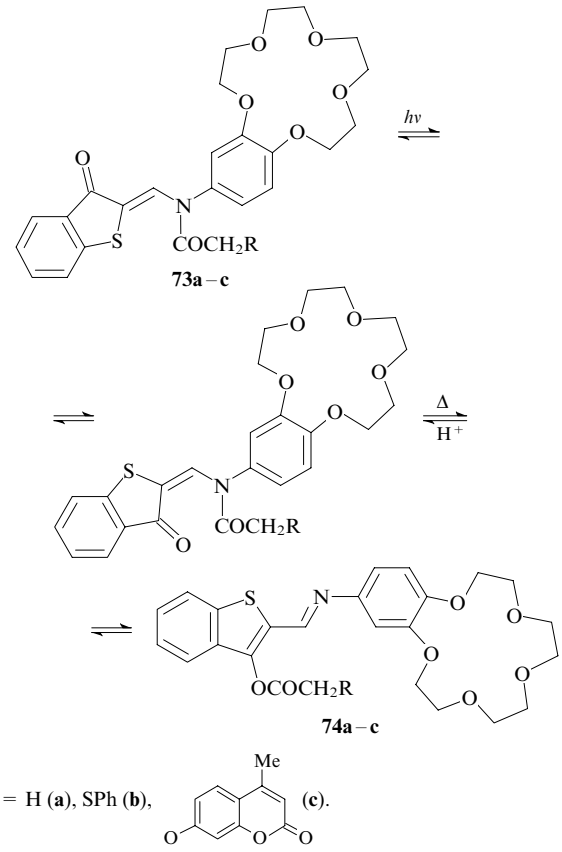

The back reaction, *i.e.*, recombination of the triphenylmethyl cation and the $CN^-$ anion, occurs on heating. According to potentiometric data, the thermodynamic stability of the complexes of crown compound **69** with $Na^+$ ions in aqueous methanol substantially decreases after photoinduced elimination of $CN^-$ upon UV irradiation.[224, 225]

Extraction experiments with alkali metal cations showed[227] that crown compound **70** selectively binds $Na^+$ cations, compound **71**, $K^+$ cations, and compound **72**, $Cs^+$ cations. The selectivity of compound **71** with respect to $K^+$ is due to the fact that two macrocyclic fragments of the dye can bind the $K^+$ ion as a sandwich complex. Similarly, the selectivity of compound **72** with respect to $Cs^+$ is attributable to the fact that three macrocyclic fragment of this compound are able to capture cooperatively the large $Cs^+$ ion. It was shown by mass spectrometry and NMR spectroscopy[227] that, after the photoinduced elimination of the $CN^-$ group, crown compounds **70**–**72** lose almost completely their ability to bind alkali metal cations, which is caused by electrostatic repulsion between the metal cation and the triphenylmethyl cation.

### 6. Other photochromic crown compounds

A recent study[228] describes the synthesis of a polyfunctional compound having two crown ether fragments and two photochromic 1-aryloxy-9,10-anthraquinone fragments. Both anthraquinone chromophores were found to readily undergo photoinduced arylotropic rearrangement. The reaction is fully photochemically reversible. The complexation in this system has not been studied as yet.

The photochromism of crown compounds **73a**–**c** (Refs 229, 230) is due to the acylotropic rearrangement. On exposure to blue light, compound **73a**–**c** easily undergo geometric photoisomerisation followed by fast thermal transfer of the acyl group. The quantum yields of the reaction resulting in *O*-acyl isomers **74a**–**c** lie in the range of 0.35–0.48 (in acetonitrile). At room temperature, *O*-acyl isomers are thermally stable. The back transfer of the acyl group is catalysed by acids. The addition of alkali or alkaline earth metal salts to solutions of *N*-acyl isomers does not induce significant changes in the absorption spectra of these compounds. However, the complexation of *O*-acyl isomers with alkaline earth metal cations induces a hypsochromic shift of the absorption band, which is most pronounced for compound **74c**. Presumably,[230] in the complexes formed by compound **74c**, a coordination bond connects the metal cation located in the crown ether cavity and the substituent R. Analogous photochromic compounds containing a 18-crown-6 ether fragment have recently been prepared.[231] The publication[231] presents the stability constants of the complexes formed by photogenerated *O*-acyl isomers with the $Ca^{2+}$ and $Ba^{2+}$ cations in acetonitrile. However, no such data are available for complexes of the initial *N*-acyl isomers; therefore, the possibility of using systems of this type as photocontrolled receptors is still an open question.




R = H (**a**), SPh (**b**),  (**c**).

## V. Conclusion

In this review we discussed the principles of design of polyfunctional crown compounds and supramolecular systems based on them, which can function as optical molecular sensors or photocontrolled receptors with respect to metal and ammonium cations. Similar principles can underlie the design of photochromic systems involving other macrocyclic compounds.

As regards the design of colorimetric sensors, the concept of donor-acceptor chromoionophores is best developed. Currently, targeted synthesis of colorimetric indicators that function in a specified spectral range (from near UV to near IR) is practicable. The prediction of the ionic selectivity of such systems may pose some difficulties, because it depends on not only the structure of the receptor fragment but also on the chromophore structure.

In the field of design of luminescent sensors, most promising are the 'triggered' LMS the luminescence of which is switched on upon substrate binding due to the suppression of intramolecular processes responsible for luminescence quenching. The most pronounced luminescence enhancement effects are attained for systems with photoinduced electron transfer or for conjugated systems with internal charge transfer on electronic excitation. An advantage of the latter is the fact that they operate simultaneously as both luminescent and colorimetric sensors. However, luminescence self-quenching mechanisms in such systems are not always obvious, which complicates their targeted synthesis.

Considerable progress has been attained in the design of photocontrolled receptors based on crown ethers. A number of methods for photoinduced change of the receptor properties of

photochromic crown compounds such as modification of the crown ether cavity, the change in the mutual spatial arrangement of two ionophoric groups, the formation of the cationic form of the crown compound upon photodissociation have ben proposed. Several types of photochromic reactions have been proposed to control the receptor function. It should be noted, however, that most of investigations in this field were performed at a qualitative level. As a rule, the results obtained are suitable only for evaluation of whether the given crown compound can in principle operate as a photoswitchable receptor. Moreover, conclusions are often based on only indirect data, *i.e.*, drawn without measurement of the key quantitative characteristics such as quantum yields of the reversible photochromic reactions or the stability constants of complexes formed by the initial and photogenerated forms. This complicates to a certain extent the targeted design of photochromic crown compounds with specified properties. Hence, of special value are the results obtained in comprehensive quantitative studies of photochromic crown compounds based on styryl dyes and benzochromenes.

An applied problem that concerns most of the systems discussed in this review is the low thermodynamic stability of crown ether complexes with alkaline earth metal cations in the aqueous medium. 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 receptors on various materials remain little studied. Therefore, investigations dealing with immobilisation of photochromic crown compounds in polymeric materials are of considerable interest.[19, 38, 49, 232–235] Currently, studies on the possibility of the design of luminescent sensors based on quantum dots modified by crown compounds are in progress.[236, 237] The design of nanostructured systems incorporating macrocyclic compounds may become a new trend in the research into optical chemosensors and photoswitchable devices.

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