

# Photoinduced recoordination of metal cations in complexes with chromogenic crown ethers

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**Abstract.** A fast photochemical process, namely, photoinduced recoordination of a metal cation in the cavity of a chromogenic crown compound is considered. The photoinduced recoordination of cations is an efficient intramolecular adiabatic relaxation process resulting in the decrease in the excited-state energies of metal complexes, which in some cases may precede the complete release of the cation to the solution. The principles of molecular design of optical sensors based on crown ethers and the photoinduced recoordination and cation photoejection mechanisms are discussed. The attention is focused on the effect of photoinduced recoordination on the spectral luminescence properties of the complexes of crown-containing dyes, on the effect of complexation on the intramolecular charge transfer and cation recoordination in nonexcited complexes and on theoretical methods for investigation of these processes. The bibliography includes 74 references.

## I. Introduction

The discovery of crown ethers<sup>1,2</sup> gave an impetus to rapid progress in coordination and supramolecular chemistry of

macrocyclic compounds. Owing to the ability to selective formation of stable complexes with many inorganic and organic ions, crown ethers became indispensable in such areas as chemical synthesis, analytical chemistry, medicine and simulation of biological systems.<sup>3</sup> Of particular interest are chromogenic and lumogenic crown compounds that can abruptly change their photophysical properties upon binding to substrates and serve efficient molecular optical sensors sensitive to trace amounts of the substances to be determined.<sup>4–8</sup> Studies on the crown compounds characterized by photoinduced reversible structural rearrangements affecting the selectivity and efficiency of substrate binding are also topical.<sup>7–10</sup>

The most interesting avenue of research is the design of photoswitchable molecular devices<sup>11,12</sup> based on reversible photoinduced processes, *viz.*, geometric and valence photoisomerization, photocyclization, photodissociation, *etc.* An example is provided by photoinduced reversible cleavage of the coordination bond between one or more heteroatoms of the macrocycle and the metal cation in the crown ether complexes with metals. The broken bonds are recovered on going from the excited to the ground state. At present, the commonly accepted name of this process is ‘photoinduced recoordination’. The most efficient studies in this field are carried out by researchers from France (B Valeur, R Lapouyade), Germany (W Rettig, K Rurack), United Kingdom (J N Moore) as well as by domestic researchers (M V Alfimov, S P Gromov, B M Uzhinov).

This review is based on analysis of the studies mainly carried out during the last fifteen years. We will consider the principles of molecular design of optical sensors based on crown ethers (Section II), the mechanisms of photoinduced recoordination and photoejection of cations (Section III), the effect of complexation on intramolecular charge transfer (Section IV), the effect of adiabatic photoinduced recoordination on the spectral luminescence properties of complexes

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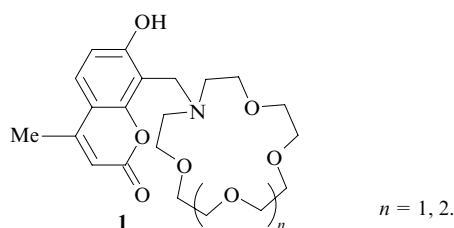
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of crown-containing dyes (Section V), ejection of cations from photochromic compounds, not related to structural rearrangements in the ionophoric fragment (Section VI), as well as recoordination of cations in complexes in the ground state (Section VII) and theoretical research on this process (Section VIII).

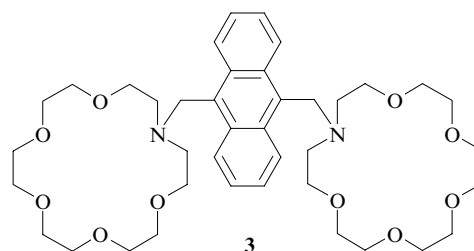
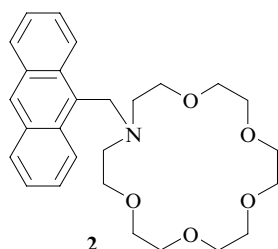
## II. Principles of molecular design of optical sensors based on crown ethers

Absorption spectroscopy is successfully used to study complexation of crown ethers containing aromatic nuclei since the discovery of these compounds in 1967.<sup>2</sup> Studies on target design of chromogenic crown ethers whose molecules contain a polyether macrocycle chemically bound in some way to a fragment of a dye that can efficiently absorb light in a wide spectral region began ten years after the discovery of crown ethers. Such crown-containing dyes can abruptly change their spectral properties upon complexation and serve as specific agents for photometric and colourimetric determination of alkali metal and alkali-earth metal cations.<sup>4,7,8</sup> Since the luminescence methods of analysis offer some advantages over the absorption techniques, the design of crown-containing fluoroionophores began almost simultaneously with the design of chromoionophores. The use of crown-containing 4-methylumbelliferon (**1**) for selective extraction of  $\text{Li}^+$  and  $\text{K}^+$  cations was demonstrated in 1982.<sup>13</sup>



Complexation of compound **1** with metal cations involves deprotonation of the hydroxyl group and the formation of an additional coordination bond between the metal cation present in the crown ether cavity and the anionic fragment just formed. This causes significant shifts of maxima in the fluorescence excitation spectra (from 326 to 380 nm for  $\text{Li}^+$ ).

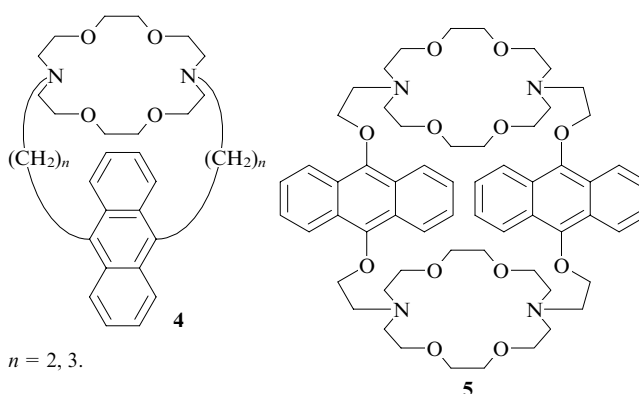
Another approach to the design of fluoroionophores involves the introduction of a macrocyclic substituent into a known fluorophore. The substituent is chosen to provide, in the lack of complexation, with efficient intramolecular quenching of ionophore fluorescence by the mechanism of formation of intramolecular excimers, exciplexes or as a result of intramolecular electron transfer. In turn, complexation should inhibit photoinduced intramolecular quenching and lead to emission of fluorescence. This approach was



first practically implemented using azacrown-substituted anthracenes **2** and **3**.<sup>14,15</sup>

Compounds **2** and **3** dissolved in a methanol/chloroform mixture are characterized by very low quantum yields of fluorescence due to intramolecular transfer of an electron from the lone electron pair of the nitrogen atom of the macrocycle to the excited anthracene nucleus, which results in quenching of fluorescence. Complexation of compound **2** with  $\text{K}^+$  involves binding of the electron pair of the nitrogen atom. As a result, electron transfer is suppressed while the quantum yield of fluorescence increases by a factor of nearly 50. Emission of fluorescence of compound **3** requires that the lone electron pairs of two nitrogen atoms be blocked simultaneously; this can be attained by binding to polymethylenediammonium ions.

Fluorescence of crown-substituted anthracenocryptands **4** and **5** is quenched by the mechanism of formation of intramolecular exciplexes or excimers.<sup>16,17</sup> These compounds are characterized by very weak dual fluorescence from both the local excited state and the intramolecular exciplex (compound **4**) or excimer (compound **5**). Complexation of compound **4** with  $\text{K}^+$  cation or that of compound **5** with  $\text{H}_3\text{N}^+(\text{CH}_2)_7\text{N}^+\text{H}_3$  cation is followed by disappearance of the long-wavelength fluorescence band assigned to the emission of the exciplex or excimer and by bright fluorescence in the region of emission of the anthracene nucleus. This approach to the design of fluoroionophores, which is based on intramolecular quenching of fluorescence in free fluoroionophore, was more recently used in the synthesis of various crown-containing reactants.<sup>5,18-24</sup>



In molecules **2** and **3**, the heteroatom of the macrocycle is not a part of the conjugation chain of the chromophore fragment, being separated from it by a methylene bridge. Therefore, although complexation is followed by a considerable increase in the quantum yield of fluorescence, this increase has almost no effect on positions of spectral bands and on the spectral patterns.

Some luminescence methods of analysis require that complexation be followed by a gradual shift of the fluorescence band or by changes in the relative band intensities

in the case of dual fluorescence with nearly equal band intensities rather than simple quenching or emission of fluorescence at a specified wavelength. In these cases, the concentration of analyte can be monitored based on two wavelengths. Not only proton-containing compounds similar to compound **1**, whose complexation shifts the acid–base equilibrium and produces anions with significantly different spectral properties, but also compounds with one or more heteroatoms of the macrocycle involved in electronic conjugation with the chromophore fragment of the molecule, can be used in these cases. It is known that the introduction of nitrogen- or oxygen-containing auxochromic groups (*e.g.*, amino or methoxy groups) into the dye molecule leads to an increase in the molecular absorption coefficient of the dye and to a bathochromic shift of its electronic spectra. The oxygen or nitrogen atoms in the crown ether macrocycle should not significantly influence their mesomeric electron-donor properties. Meanwhile, complexation with metal cations may strongly affect the hybridizations of these atoms, so eventually they may be excluded from the conjugation chain; this should be accompanied by large antiauxochromic effect and a blue shift of the bands in the electronic spectra. Also, processes leading to formation of the twisted intramolecular charge transfer (TICT) state and accompanied by dual fluorescence may occur in excited molecules containing electron-donor groups.<sup>25,26</sup> One can expect that the cation in the crown ether cavity will block the formation of the TICT state. This will lead to weaker emission in the long-wavelength band. At the same time, the intensity of emission in the short-wavelength band should increase because one deactivation channel of the local excited state is suppressed.

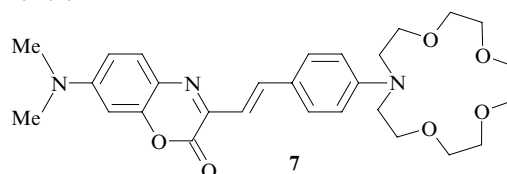
In connection with the aforesaid, in the late 1980s researchers focused their attention on crown-containing fluoroionophores with  $n,\pi$ -conjugation between one (or more) heteroatoms of the macrocycle and the chromophore fragment of the molecule (so-called intrinsic fluorophores).

Earlier studies on the design of chelate-forming fluoroionophores based on ethylenediaminetetraacetic acid revealed unusual changes in the fluorescence spectra of some compounds upon complexation.<sup>27,28</sup> Namely, the shifts of their maxima were abnormally small compared to those of the absorption maxima. The lack of shifts in the fluorescence spectra presents no difficulties to the use of fluoroionophores for dual-wavelength analysis because these wavelengths can be chosen using the fluorescence excitation spectra, which show the necessary spectral shift, instead of the fluorescence spectra. However, the presence of systems with abnormally small shift in the fluorescence spectra in addition to the systems for which the magnitude of this shift is comparable with the corresponding shift in the absorption spectra significantly complicated the design of optical sensors containing  $n,\pi$ -conjugated fragments. Such systems have been a subject of particular studies.

The abnormally small shifts of fluorescence spectra on complexation of chromogenic crown ethers with alkali metal and alkali-earth metal cations were first reported for systems including the monoaza-15-crown-5-ether mero-

cyanine dye **6** based on dicyanomethylidenstyrylpyrane (DCM).<sup>29</sup>

As these metal salts were added to solutions of compound **6** in acetonitrile, the orange-red solutions turned yellow, but the positions of the fluorescence spectra remained almost unchanged. For instance, the hypsochromic shift of the absorption maximum upon 100% complexation with  $\text{Ca}^{2+}$  cation was  $\sim 3600\text{ cm}^{-1}$ , whereas the shift of the fluorescence maximum was ten times smaller. The normalized fluorescence spectra of the complex and the free dye showed very similar patterns. Such an unusual change in the fluorescence spectra of compound **6** with an increase in the salt concentration contrasted with the changes in the spectra of the previously studied crown-containing benzoxazinone **7**.<sup>30</sup>

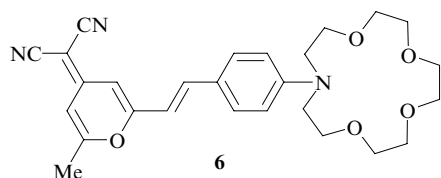


whose absorption and fluorescence spectra exhibited large shifts ( $870$  and  $1800\text{ cm}^{-1}$ , respectively, for the complex with  $\text{Ca}^{2+}$  cation). The lack of the effect of complexation on the lifetimes of the excited molecules of the complexes of compound **6** with alkali metal and alkali-earth metal cations was also unusual. Despite the fact that in some cases, complexation of compound **6** led to a very high degree of quenching of fluorescence, the lifetimes of excited molecules showed almost no changes and corresponded to the excited-state lifetime of a laser dye DCM containing the dimethylamino group ( $\sim 2\text{ ns}$ ). At the same time, complexation of compound **7** led to an increase in the quantum yield of fluorescence and a parallel increase in the lifetimes at constant rate of radiative deactivation.

These spectral features of the systems involving compound **6** were explained by the formation of a relaxed intramolecular charge transfer (RICT) state and by fluorescence from this state. The metal cation in the macrocycle cavity has almost no effect on the deactivation rate of the RICT state, but affects the rate of conversion of the local excited (LE) state to the RICT state. Contrary to this, in the case of compound **7** the intramolecular charge transfer (ICT) state is non-fluorescent and emission occurs exclusively from the LE state. The cation precludes the formation of the ICT state, which leads to an increase in the excited-state lifetime of compound **7** and to more efficient fluorescence. In the case of complexation of compound **7** with alkali-earth metal cations characterized by the highest charge density, the fluorescence spectra of the complexes and the prototype containing no amino groups are very similar. This suggests an almost complete exclusion of the nitrogen atom of the macrocycle from the conjugation chain upon complexation with these cations.

### III. Kinetic parameters of multistep photoejection of metal cation determined by transient absorption spectroscopy

In the studies reported in the early 1990s, researchers paid attention to the fact that the positive polarization of the chromophoric heteroatoms of the macrocycle, occurring as a result of light absorption in the long-wavelength charge-transfer band or as a result of photoinduced formation of



the ICT state, should lead to Coulomb repulsion between these heteroatoms and the metal cation present in the cavity of the excited molecule of the complex. Owing to Coulomb repulsion and weakening of the coordination bond caused by the decrease in the electron density on the heteroatoms of the macrocycle, the metal cation should be displaced from its equilibrium position. The mechanism of this phenomenon was mainly studied by picosecond transient difference absorption spectroscopy. Their research groups mentioned above (see Introduction) interpreted this phenomenon in different manner and gave different explanations for the mechanism responsible for the small shift of the fluorescence spectra upon complexation. Valeur and co-workers<sup>31</sup> used the term 'photoejection' and assumed that most excited molecules of complexes undergo photodissociation with ejection of the cation to the solution within a few picoseconds. It was assumed that the process can be efficient for photo-controlled fast release of cations. In other systems used to this end the photoejection is achieved by changing the cavity size or the geometry of the ionophoric fragment. Owing to fast dark reversibility of photoejection, a cyclic release of the cation is possible; this can be used for automated signal accumulation.

In studies of complexation of crown-containing stilbenes, Lapouyade and co-workers<sup>32,33</sup> first introduced the idea of multistage 'decoordination', which takes times of the order of a few picoseconds or a few tens of picoseconds and involves a successive formation of contact pairs cation–fluorophore (L\*M; L is a ligand, M is a metal) and solvent-separated pairs<sup>32,33</sup> (L\*/S/M; S is a solvent). The emission of fluorescence from the samples with abnormally small shift of fluorescence spectra upon complexation was ascribed to the solvent-separated pairs where cleavage of the coordination bond is followed by occupation of the free position by the solvent molecule or by the counterion.

The notion 'adiabatic photoinduced recoordination' was introduced by Russian researchers who studied fluorescence and complexation of crown-containing styryl dyes.<sup>34,35</sup> It is believed that this term best characterizes the character of the changes in the coordination of the cation in the excited state of the complex. It was assumed that, as the complex goes to the excited state, one coordination bond between the macrocycle and the metal cation is cleaved, the cation is displaced from its equilibrium position and moves away from the chromophore fragment of the molecule. The cation holds in the macrocycle cavity by the remaining coordination bonds but its effect on the molecule becomes much weaker. Abnormally small shifts of the fluorescence maxima of crown-containing styryl dyes were observed at low temperatures in viscous and glassy alcohol solutions.<sup>34,35</sup> In such media, translational diffusion of particles is hindered. Based on this fact, the authors suggested that the relaxation process associated with the change in the coordination of the cation is intramolecular and that the release of the cation from the macrocycle is not a necessary condition for explanation for the observed relaxation process.

The formation of a cation-controlled RICT state was proposed in a study of relaxation in complexes of crown-containing dye **6**.<sup>29</sup> Since then, numerous attempts to detect the photoejection of cations to the solution were made. This could be a breakthrough in the design of systems with photo-controlled cation binding.

Direct experimental proofs of photoejection of Li<sup>+</sup> and Ca<sup>2+</sup> ions from the cavity of crown-containing merocyanine **6** within nearly 5 and 20 ps, respectively, were

reported.<sup>31</sup> The conclusion of photoejection of the cations was based on the consideration of the difference picosecond absorption spectra in which the optical density difference ( $\Delta D$ ) between the excited sample and the non-excited reference solution was recorded at some time delay. The difference spectra recorded in the optical region (450–690 nm) exhibited a transient absorption band at 530 nm with a positive  $\Delta D$  value and a stimulated emission band at 600 nm with a negative  $\Delta D$  value. The difference spectra of free crown-containing DCM exhibited two bands, whereas the spectra of the complexes with Li<sup>+</sup> and Ca<sup>2+</sup> recorded at time delays of about 2 and 15 ps, respectively, exhibited three bands. The band at 600 nm with the negative  $\Delta D$  value was assigned to stimulated emission from the ICT state; it was observed in the same region as the steady-state fluorescence band. The band at 535 nm with positive  $\Delta D$  value was assigned to absorption of the ICT state; it was observed for both free dye and the product formed after photoejection of the cation. The band at 470 nm with positive  $\Delta D$  value was assigned to absorption of those excited molecules in the complex in which no photoejection occurred. The difference spectrum of the calcium complex recorded at a delay time of 1.5 ps exhibited only the band at 470 nm and no band at 535 nm. This suggested that the time interval of 1.5 ps was too short to allow the necessary amount of the photoejection product to accumulate.

The transient absorption bands in the spectra of the complexes of compound **6** with Li<sup>+</sup> and Ca<sup>2+</sup> cations recorded at time delays of 2 and 15 ps, respectively, exhibited clearly seen isosbestic points, which were stable for some time after the time intervals listed. Taking into account this fact, a chemical equilibrium between the bound and free forms of compound **6** was suggested;<sup>31</sup> it was also found that both complexes are characterized by nearly equal  $\Delta pK$  values ( $K$  is the stability constant) on going to the excited state ( $\Delta pK = -2.1$ ).

A shift of the short-wavelength boundary of the transient absorption band from 450 to 370 nm (Ref. 36) made it possible to observe a complex temporal evolution of this band even for the free form of DCM. Three maxima near 410, 470 and 530 nm were observed in the transient absorption region a few tens of picoseconds after excitation. The first two maxima continued to grow with time, whereas the third maximum changed only slightly. A region of constant optical density with an isosbestic point at 482 nm was also observed; this was interpreted as quantitative conversion of the LE state to the RICT state. The photoejection times of the Li<sup>+</sup> and Ca<sup>2+</sup> ions were estimated at 3 and 30 ps, respectively.

The cation photoejection mechanism was specified by introducing two intermediate stages preceding the cation release to the solution.<sup>37</sup> In the first stage, the LE state of the complex is transformed to the so-called loose complex within about 700 fs. The loose complex has a weaker metal–nitrogen bond and is similar in structure and spectral properties to the LE state of the free ligand. In the second stage, the loose complex is transformed to a charge-transfer complex characterized by complete cleavage of the metal–nitrogen coordination bond and a complete charge transfer giving the nitrogen atom bearing a formal positive charge. Thus it was shown that the previously determined photodecomposition times of the lithium and calcium complexes with dye **6** (3 and 30 ps, respectively) characterize the formation of the charge-transfer complex rather than photoejection of the cations. Thorough fluorescence lifetime

measurements by the phase-modulation technique revealed a biexponential fluorescence decay kinetics. The component with a lifetime of 2 ns was attributed to emission of the charge-transfer complex while the short-lived component with a lifetime of 400 ps was considered as corresponding to the loose complex.

An attempt was made to experimentally prove the possibility for photoejection of cations to solution to occur within the excited-state lifetime (2 ns). Since the transient absorption spectra revealed no noticeable changes after a 30-ps time delay, it was concluded that this time can be much shorter than the time necessary for diffusion separation of the cations. Assuming that the rate constant for diffusion-controlled reaction is  $10^{10}$  litre mol<sup>-1</sup> s<sup>-1</sup>, it was suggested<sup>37</sup> that at sufficiently low concentration of calcium cations ( $\sim 10^{-3}$  mol litre<sup>-1</sup>), the characteristic time of cation rebinding in the dark should be 100 ns, which will allow one to detect excess free ligand in solution from the positive deviation of the optical density of the spectra at a time delay of about 20 ns (tenfold excited-state lifetime). However, no reliable indications of photoejection of cations were obtained.

The dipole moment of the DCM molecule in the ICT state is 26 D and the degree of charge transfer is about 70% for the LE state and 100% for the ICT state.

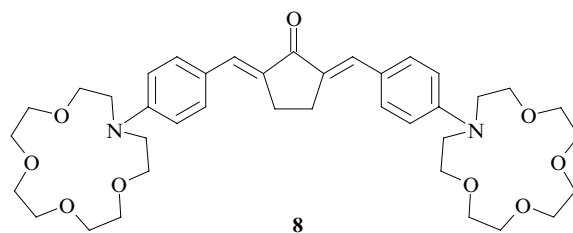
Studies on the possibility of cation release from the macrocycle cavity of compound **6** were continued<sup>38</sup> taking a system containing a Sr<sup>2+</sup> cation as an example. The mechanism of photoejection of the cation was augmented with a new intermediate stage, *viz.*, the formation of an ultra-loose complex from the charge-transfer complex in about 400 ps. The authors of Ref. 38 also observed a thermal process of cation rebinding in the ground state after nearly 110 ns. It was found that only 5%–10% of molecules of the ultra-loose complex undergo dissociation with release of the cation. This illustrated a complete closed cycle of photoejection of the cation. The conclusion of formation of the ultra-loose complex was drawn taking account of the continuous long-wavelength shift of the stimulated emission band at subnanosecond time delays.

The conclusion of the possibility for the cation to release from the macrocycle was based on the positive  $\Delta D$  value in the region 480 nm; this was observed in the spectra recorded at time delays of 10 ns and even a few hundreds of nanoseconds, which much exceeds the excited-state lifetime ( $\sim 2$  ns). Excess absorption was ascribed to an abrupt change in the concentration of the free ligand as a result of photoejection of the cation, while the absorption decay time (110 ns) was attributed to recomplexation in the ground state. In this experiment, the concentration of the alkali-earth metal salt was 100 times higher than in the previous study.<sup>37</sup> For the previously proposed diffusion-limited rate of cation binding in the dark at strontium salt concentrations of the order of 0.1 mol litre<sup>-1</sup>, the recomplexation should take about 1 ns. However, an analysis of published data carried out by the authors of Ref. 38 showed that complexation of the metal cations with crown ethers is not a diffusion-limited process and proceeds much slower (by two or three orders of magnitude). For instance, the rate constants for association of 15-crown-5-ether with Sr<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> cations in water are  $6.5 \times 10^7$ ,  $2.6 \times 10^8$  and  $4.3 \times 10^8$  litre mol<sup>-1</sup> s<sup>-1</sup>, respectively. The rate constant for Ba<sup>2+</sup> binding to a benzothiazolium-based, azacrown-containing styryl dye also has a close value of  $7 \times 10^7$  litre mol<sup>-1</sup> s<sup>-1</sup>. These values agree with the reverse reaction

time (about 100 ns at a Sr<sup>2+</sup> concentration of 0.1 mol litre<sup>-1</sup>).

A study of the possibility of photoinduced elimination of Ca<sup>2+</sup> cation from the complex with dye **6** using a setup with a 100-fs resolution allowed one to refine the kinetic parameters of multistep photoinduced recoordination and photoejection of the cation from the macrocycle cavity.<sup>39</sup> Earlier, it was assumed that the primary photodissociation of the metal–nitrogen bond resulting in a loose complex takes a time equal or shorter than the excitation pulse duration of the previously used setup (500–700 fs; see Refs 31, 36–38). According to the new data, the primary photodissociation of this bond takes 130 fs. In addition, a three-exponent kinetics of the evolution of the transient absorption band with the characteristic times of 1, 8 and 77 ps was established and a red shift of the stimulated emission band with a characteristic time of 56 ps was observed. It is believed that this temporal evolution of the transient absorption band and the stimulated emission band indicates the formation of a continuum of complexes with different distances between the metal cation and the chromophore system during the first few tens of picoseconds instead of the only charge-transfer state formed after 30 ps, as was proposed earlier. As previously,<sup>38</sup> a shift of the stimulated emission band with a characteristic time 670 ps was observed in the subnanosecond range of time delays. In contrast to Ref. 38 where a similar process was attributed to the formation of an ‘ultra-loose’ complex, this process was attributed<sup>39</sup> to the photoejection of the cation from the macrocycle and the shift of the stimulated emission band in time was treated as a proof of displacement of the cation from the excited ligand molecule after photoejection.

A study<sup>40</sup> of the possibility of photoejection of cations from complexes of crown-containing bis(phenylmethylidene)cyclopentanone (**8**) revealed an ultrafast (nearly 17 ps) release of the cation from the macrocycle cavity, as was assumed in the early stage of the studies of DCM.<sup>31, 37</sup>



Complexation of compound **8** with Ca<sup>2+</sup> cations in acetonitrile involves a successive formation of complexes ML<sub>2</sub>, ML and M<sub>2</sub>L. The absorption spectra of the complexes ML<sub>2</sub> and ML are only slightly blue-shifted relative to the absorption spectra of the free ligand, whereas the shift of the absorption maxima of the complexes M<sub>2</sub>L is large (5100 cm<sup>-1</sup>). At the same time, at salt concentration corresponding to almost quantitative conversion of the dye **8** to M<sub>2</sub>L, the fluorescence spectra show a paradoxical red shift (640 cm<sup>-1</sup>).

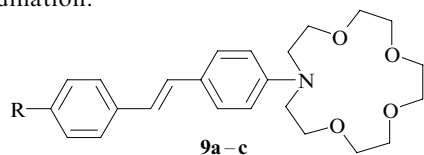
It is believed<sup>40</sup> that the bathochromic shift of the fluorescence spectra cannot be explained by simultaneous cleavage of two metal–nitrogen bonds and the formation of certain ‘loose-bound’ states structurally similar to the free ligand. In the excited state, the complex M<sub>2</sub>L undergoes a fast photoejection of one cation, and emission of fluorescence occurs from the 1:1 complex. This is confirmed by the fact that the parameters of M<sub>2</sub>L fluorescence are close to

those of the model compound 2,5-[4-(diethylaminophenyl)-phenyl]methylidencyclopentanone containing only one amino group. In addition, the excited-state lifetimes of compounds **8** and  $M_2L$  (0.8 and 1.1 ns, respectively) are inverted with respect to the fluorescence quantum yields (0.14 and 0.057, respectively), *i.e.*, the quantum yield of fluorescence of  $M_2L$  is lower than that of fluorescence of compound **8**. This was also considered as evidence for the fact that the excited complex contains only one cation. The possibility of fluorescence emission from the ultra-loose complex  $M_2L$  with one cation bound and one cation free but residing in the macrocycle cavity was also rejected based on the transient absorption spectra recorded at long time delays corresponding to the expected recombination of the ultra-loose complexes  $M_2L$  in the ground electronic state. However, no indications of such a recombination were obtained.

Thus, the scheme of photoejection of the cation is as follows.<sup>40</sup> The first stage involves a fast cleavage of the cation–nitrogen bond within about 2.5 ps. This is indicated by the changes in the transient absorption spectra recorded within 6 ps after excitation. The absorption band at 428 nm significantly weakens, whereas the band at 514 nm becomes much stronger. The second stage involves photoejection of the cation from the macrocycle with a characteristic time of about 17 ps and diffusion of the cation to the solution. This is indicated by the evolution of the spectra in the stimulated emission band, recorded at time delays from 6 to 50 ps. The third stage involves deactivation of the 1:1 complex to the ground electronic state and simultaneous accumulation of the triplet state with the characteristic times of 1.9 and 3.6 ns, respectively. The formation of triplet species is indicated by an increase in absorption in the region 640–850 nm, as observed in the spectra recorded at time delays of 50–1500 ps.

Unlike the studies by Valeur and co-workers,<sup>31, 36–39</sup> investigations by Lapouyade and co-workers<sup>32, 33</sup> were initially focused on ‘decoordination’ of the cation in the excited state of complexes rather than its photoejection from the macrocycle. For fluoroionophores with the excited-state lifetimes of the order of a few nanoseconds, a complete photoejection of cations within such a short time seemed to be unlikely because this requires significant changes in the macrocycle geometry and a complete solvation of the cation.

A study<sup>32</sup> of complexation of calcium cations with crown-containing stilbenes **9a–c** showed that the fluorescence spectra of the complexes with compounds **9a** and **9b** are only slightly blue-shifted owing to photoinduced recoordination.



R = CN (a), H (b), Ph (c).

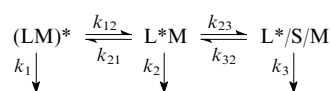
It is believed that emission of fluorescence of these complexes occurs from the solvent-separated pairs cation–fluorophore  $L^*/S/M$ . Unlike this, the calcium complex of compound **9c** in acetonitrile fluoresces from both the solvent-separated pairs and the local excited state  $(LM)^*$ ,

which leads to dual fluorescence. The long-wavelength shoulder in the fluorescence spectrum is shifted relative to the free ligand emission band by  $620\text{ cm}^{-1}$  only, whereas the short-wavelength shoulder is shifted by  $5400\text{ cm}^{-1}$ , which is comparable with or even more than the shift of the absorption maximum ( $3200\text{ cm}^{-1}$ ). The ratio of the fluorescence intensities of the undissociated and solvent-separated pairs increases as the solvent polarity decreases, *viz.*, whereas in acetonitrile the emission of fluorescence of the calcium complex of compound **9c** occurs almost solely from the  $L^*/S/M$  state, in dichloromethane it occurs from the local excited state. Since the short-wavelength emission band resembles the fluorescence spectra of the protonated form of compound **9c** and the prototype containing no electron-donor amino groups, the authors of Ref. 32 concluded that the short-wavelength band corresponds to emission from the local excited state which is formed immediately from the Franck–Condon state by the vibrational relaxation mechanism. The free dye **9c** in the excited electronic state exists in two forms, *viz.*, the LE and the TICT states. Rotation of the dialkylaniline group relative to the arylethylene group was proved by comparing the properties of the ICT state with those of a prototype having such a rotation in the ground state owing to the bridging bonds. The dipole moment of the TICT state of molecule **9c** determined by solvatochromy is 15.8 D.

A picosecond absorption spectroscopy study showed that the formation of the TICT state from the LE state of free compound **9c** takes a characteristic time of 7 ps. This was indicated by the blue shift of the transient absorption band in a wide spectral region (510–750 nm) and by the red shift of the stimulated emission band (440–465 nm).

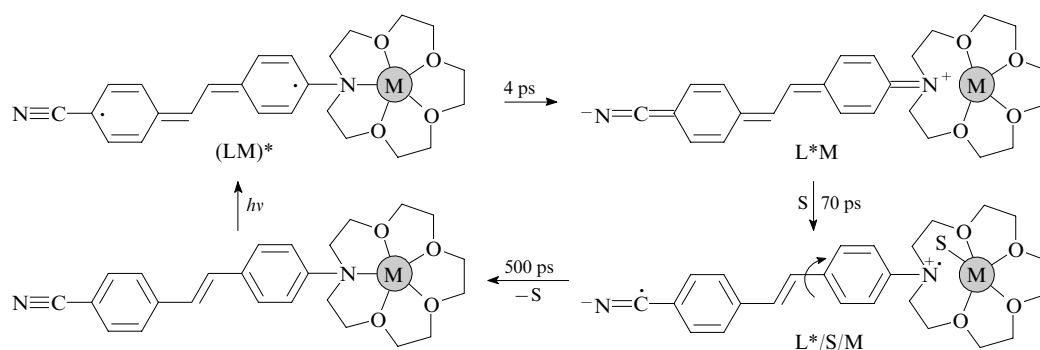
The authors of a study<sup>32</sup> on the dynamics of photo-induced recoordination of calcium cation in the excited complex with compound **9c** proposed a two-step mechanism of cation recoordination (Scheme 1).

Scheme 1



Initially, absorption of light by the calcium complex with compound **9c** leads to formation of the local excited state  $(LM)^*$ . This state manifests itself as a peak at 370 nm in the stimulated emission band, which agrees with position of the maximum of steady-state fluorescence of this state (387 nm). This peak appears immediately after excitation and soon disappears. The first stage involves the formation of a contact pair cation–fluorophore  $L^*M$  from the  $(LM)^*$  state (this takes about 8 ps) and establishment of an equilibrium with the rate constants for the forward and reverse reactions equal to  $k_{12} = 1.3 \times 10^{11}$ ,  $k_{21} = 6.6 \times 10^{10}\text{ s}^{-1}$ , respectively. The contact pair  $L^*M$  thus formed corresponds to the loose complex according to Valeur. The next 50 ps are spent for establishment of an equilibrium between the contact pair  $L^*M$  and the solvent-separated pair  $L^*/S/M$  with the rate constants for the forward and reverse reactions equal to  $k_{23} = 2 \times 10^{10}$ ,  $k_{32} = 6.9 \times 10^9\text{ s}^{-1}$ , respectively. The two-step character of recoordination leading to successive formation of  $L^*M$  and  $L^*/S/M$  is indicated by the fact that the shift of the transient absorption band with time is described by two exponents with the characteristic times of 8 and 50 ps and nearly equal

Scheme 2



contributions. The complexity of the fast recoordination processes has no effect on the kinetics of fluorescence emission, which decays by a monoexponential law with the rate constant  $k_1 = k_2 = k_3 = 2 \times 10^9 \text{ s}^{-1}$ .

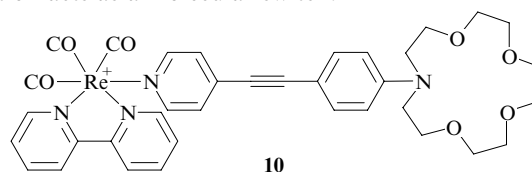
The absorption spectroscopic characteristics of transient species involved in the photoinduced recoordination were determined<sup>33</sup> using 4-(*N*-monoaza-15-crown-5)-4'-cyanostilbene (**9a**) in which charge transfer is more pronounced than in 4-(*N*-monoaza-15-crown-5)-4'-phenylstilbene (**9c**).

Transformation of the LE state of free ligand **9a** to the TICT state occurs with the characteristic times of 1 ps in acetonitrile and 4 ps in butyronitrile. When the fluoroionophore is completely involved in the calcium complex, electronic excitation successively leads to formation of the local excited state (LM)\*, the contact pair cation–fluorophore (L\*M) in about 4 ps in acetonitrile and 3 ps in butyronitrile and the solvent-separated pair L\*/S/M in about 70 ps in acetonitrile and 25 ps in butyronitrile (Scheme 2). Unlike the previously considered system with compound **9c**, the description of this system does not require the introduction of excited-state equilibria. Deactivation of L\*/S/M to the ground state takes nearly 500 ps. The  $S_1 \rightarrow S_N$  spectrum of the contact pair L\*M is similar to that of the LE state of the free dye. Based on this fact, it was concluded that cleavage of the cation–nitrogen bond is driven by the recovery of the initial degree of charge transfer, which occurs in the free dye on excitation. Maxima in the  $S_1 \rightarrow S_N$  absorption spectra of the L\*M and L\*/S/M states are blue-shifted relative to the maximum in the spectrum of the (LM)\* state by 860 and 1400  $\text{cm}^{-1}$ , respectively. This indicates a further increase in the degree of charge transfer in the solvent-separated pair L\*/S/M. Attempts to detect the release of the cation from the macrocycle cavity have failed because the transient absorption bands and the stimulated emission bands remained unchanged after nearly 300-ps time delays.

The photoejection of the cation was reliably detected in studies of crown-containing complexes (bpy)Re<sup>I</sup>(CO)<sub>3</sub>L (bpy is bipyridine) whose long-lived excited states have lifetimes of the order of tens and hundreds of nanoseconds. It was found that photoejection in such systems takes the times comparable with the lifetimes of these states.

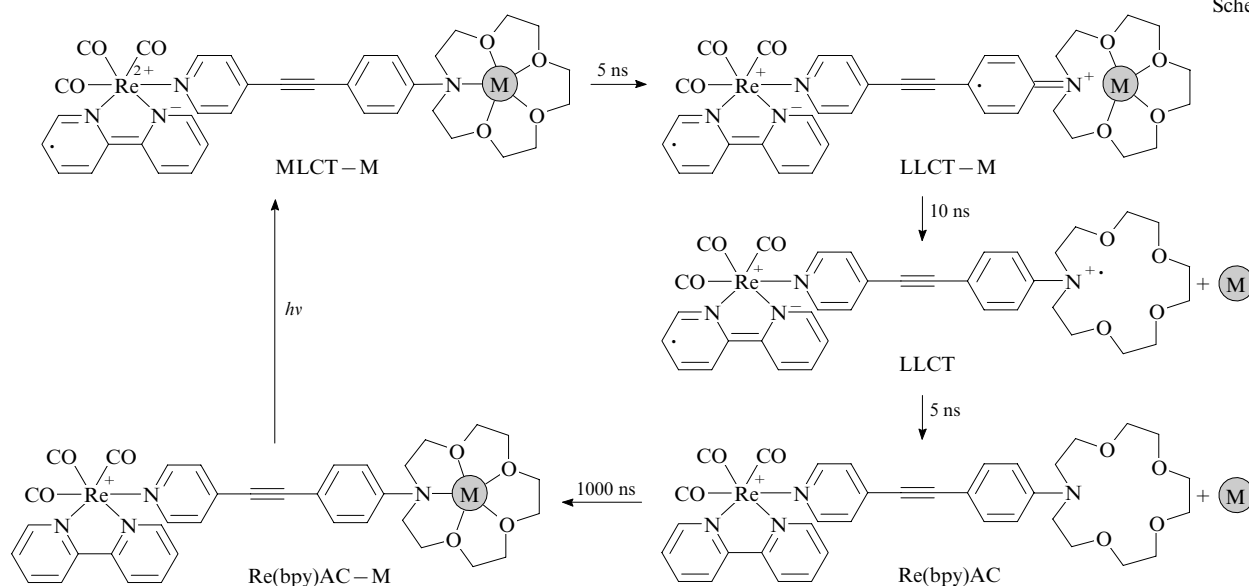
A study<sup>41</sup> of photoejection and thermally induced rebinding of Ba<sup>2+</sup> cation on the nanosecond and microsecond time scales in the reactions involving azacrown-substituted phenylpyridylacetylene involved in the coordination bond with Re<sup>I</sup> along with bipyridine and carbon monoxide (compound **10**) showed that the rhenium complex

in which the crown ether moiety is coordinated to the Ba<sup>2+</sup> cation acts as a molecular switch.



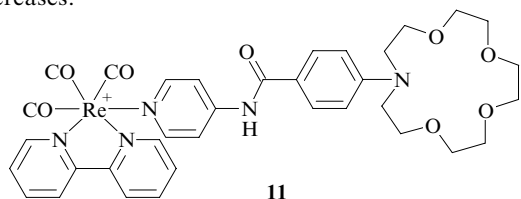
When exposed to light, the Ba<sup>2+</sup> cation is released within about 10 ns and then can be thermally rebound from solution in 1  $\mu\text{s}$ . The H-analogue of compound **10** containing no donor nitrogen atom is characterized by moderate absorption in the region 350 nm [molar extinction coefficient ( $\epsilon$ ) is 3500 litre mol<sup>-1</sup> cm<sup>-1</sup>], which leads to the formation of a metal–ligand charge transfer (MLCT) state; in this case, charge transfer occurs from the rhenium ion to bipyridine. This state is characterized by bright emission at 570 nm and a lifetime of about 260 ns. In turn, the absorption spectrum of compound **10** exhibits an intense band in the region 405 nm, which is due to the formation of the intraligand charge transfer (ILCT) state; here, ILCT occurs in the azacrownphenylpyridylacetylene moiety. Excitation in the region 355 nm causes weak fluorescence of compound **10** with a much shorter excited-state lifetime ( $\sim 5$  ns). This is due to the fact that the MLCT state is quenched owing to fast electron transfer from the nitrogen atom of the macrocycle to the Re<sup>II</sup> ion with the formation of a non-fluorescent ligand–ligand charge transfer (LLCT) state. Complexation of compound **10** with Ba<sup>2+</sup> cation causes the absorption maximum of the ILCT band to shift from 405 to 352 nm. The barium complex with compound **10** excited to the 355-nm band is characterized by very weak emission with a fluorescence decay time of nearly 5 ns. The transient absorption spectra do not change after a 20-ns time delay and exhibit bands at 340–360 nm with a negative  $\Delta D$  value and at 410 nm with a positive  $\Delta D$  value. The kinetics of spectral changes at 410 nm is biexponential with the characteristic times of 10 and 110 ns. The long-lived component of this kinetics depends strongly on the concentration of the Ba<sup>2+</sup> cations in solution, *viz.*, it increases from 110 to 1800 ns as the barium salt concentration increases from 0.1 to  $1.8 \times 10^{-3}$  mol litre<sup>-1</sup>. The bimolecular constant of thermally induced binding of Ba<sup>2+</sup> cation by compound **10** in the ground state determined from the concentration dependence of the long-lived component is  $9.3 \times 10^7$  litre mol<sup>-1</sup> s<sup>-1</sup>, being comparable with the rate constant for association of Sr<sup>2+</sup> cation with DCM ( $10^8$  litre mol<sup>-1</sup> s<sup>-1</sup>).<sup>38</sup>

Scheme 3



Scheme 3 presents a complete cycle of photoejection and thermal binding of the cation. Excitation of the barium complex with compound **10** to the 355-nm band leads to formation of the MLCT state in which an electron is transferred from the  $\text{Re}^{\text{I}}$  ion to bipyridine. Subsequent transfer of one more electron leads to the appearance of a formal positive charge on the nitrogen atom of the macrocycle, to the reduction of  $\text{Re}^{\text{II}}$  to  $\text{Re}^{\text{I}}$  and to the formation, within about 5 ns, of a non-fluorescent LLCT state in which the cation undergoes photoejection to the solution within 10 ns, as indicated by the similarity between the transient absorption spectrum recorded at 20-ns time delay and by the difference between the steady-state absorption spectra of compound **10** and its complex with  $\text{Ba}^{2+}$ . Since photoejection of cation violates the thermodynamic equilibrium between compound **10** and its complex, the last step after deactivation of the LLCT state to the ground state involves rebinding of cations with a bimolecular constant of  $9.3 \times 10^7 \text{ litre mol}^{-1} \text{ s}^{-1}$ , which takes from 100 to 1000 ns depending on the concentration of the barium salt in the solution.

The rate of photorelease of the alkali metal and alkali-earth metal cations from the complexes of these metals with compound **11** decreases as the charge density on the cation increases.<sup>42</sup>



The photorelease of cations from the LLCT state of the complexes on the nanosecond time scale, the  $\text{Li}^+$  and  $\text{Na}^+$  cations being released faster than the  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations; however,  $\text{Mg}^{2+}$  undergoes no photorelease. As compound **11** returns to the ground electronic state, the thermodynamic equilibrium is established in a few microseconds.

The absorption spectrum of compound **11** in acetonitrile exhibits an intense band at 344 nm, which was attributed to the ILCT state. This band masks a weaker band at 350 nm

corresponding to the MLCT state. However, owing to the formation of 1:1 complexes with alkali metal and alkali-earth metal cations, the former band undergoes a hypsochromic shift by 1000 to 4000–5000  $\text{cm}^{-1}$  depending on the charge density on the cation. Therefore, excitation of the complexes at 355 nm leads to the MLCT state characterized by emission at 600 nm irrespective of the nature of the cation. With no cation, the MLCT state of compound **11** is efficiently quenched due to the formation of the non-fluorescent LLCT state in nearly 500 ps. Complexation of compound **11** with metal cations precludes this process; therefore, the lifetime of the MLCT state considerably increases on complexation, being equal to 12, 10, 140, 56 and 47 ns for the complexes of compound **11** with the  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations, respectively, and 140 ns for the protonated form of compound **11**. The lifetimes of the MLCT states of the H-analogue of compound **11** and the complex with  $\text{Mg}^{2+}$  are 140 ns, which indicates a complete suppression of the formation of the LLCT state in these cases.

At time delays shorter than 50 ns, the transient absorption spectra of the complexes of compound **11** with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations resemble those of the protonated form while the spectra of the complexes with the  $\text{Li}^+$  and  $\text{Na}^+$  cations are similar to the spectra of the free form. This suggests, on the time scale considered, the formation of the LLCT state in the complexes with  $\text{Li}^+$  and  $\text{Na}^+$ , whereas for other complexes this state is formed more slowly or lacks at all. As the time delay increases to 50–200 ns, the spectra of the complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  change significantly ( $< 400 \text{ nm}$ ), while the spectra of the complex  $\text{Mg}^{2+}$  and the protonated form show no such changes. This indicates no photoejection of the  $\text{Mg}^{2+}$  cation or proton abstraction.

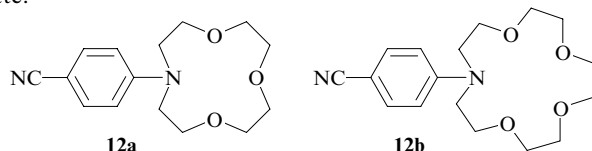
Thus, the mechanism of photoejection of the cation from the excited complexes of compound **11** is analogous to the mechanism involving compound **10** (see above). At the same time, the nature of the metal cation significantly affects the rate of transformations of the transient species. Complexation of compound **11** with metal cations slows down the formation of the LLCT state from a characteristic time of 500 ps for free compound **11** to nearly 10 ns for the complexes with alkali metal cations and 50 ns for the



complexes with alkali-earth metal cations. Photoejection of cations takes about 8, 6, 90 and 40 ns for the complexes of compound **11** with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , respectively. Complexation with  $\text{Mg}^{2+}$  completely inhibits the formation of the LLCT state; therefore, no photorelease of the  $\text{Mg}^{2+}$  cation was observed. The lifetime of the LLCT state of the free ligand is about 20 ns; during this time interval, cations travel distances from 50 to 70 Å, moving away from the macrocycle with a diameter of nearly 2 Å. Thermal process of cation rebinding by an excess dye in the ground state takes from 100 to 10000 ns depending on the salt concentration in the solution and is characterized by the bimolecular rate constants for binding equal to  $1.3 \times 10^8$ ,  $6.9 \times 10^7$ ,  $2.5 \times 10^7$  and  $5 \times 10^7$  litre  $\text{mol}^{-1} \text{s}^{-1}$  for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations, respectively. In contrast to  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , rebinding of the  $\text{Li}^+$  and  $\text{Na}^+$  cations does not occur immediately. The transient absorption spectra recorded at time delays in the range 1–100  $\mu\text{s}$  indicate the existence of intermediates that were called exclusive complexes. Their spectrum resembles the difference between the steady-state spectra of the complexes and the corresponding protonated forms. In such complexes, the cation is far from the equilibrium position in the macrocycle. The characteristic time of transformation of exclusive complexes to endo-complexes is 150  $\mu\text{s}$ , being independent on the concentration of cations in solution.

#### IV. Effect of complexation on intramolecular charge transfer in systems with dual fluorescence

Dual fluorescence of crown-containing phenylstilbene **9c** was considered above. Crown-containing benzonitriles **12a** and **12b** are electronic analogues of dimethylaminobenzonitrile (DMABN). Dual fluorescence of DMABN is due to partial conversion of the locally excited state to the TICT state.<sup>43</sup>



The efficiency of formation of the TICT state of DMABN, **12a** and **12b** in a given solvent is significantly different. For instance, in diethyl ether at room temperature, DMABN mainly fluoresces from the LE state, compound **12a** fluoresces from the LE and TICT states with nearly equal contributions, while compound **12b** mainly fluoresces from the TICT state. This is indicated by the ratio of the quantum yields of fluorescence from the TICT and LE states, which is equal to 0.31 (DMABN), 1.3 (**12a**) and 9.4 (**12b**).

The activation energies of the forward and reverse transitions between the LE and TICT states of benzonitrile **12b** in toluene ( $E_a = 8.9$ ,  $E_d = 23.7$  kJ  $\text{mol}^{-1}$ ) were correlated with the activation energies of the reactions of unsubstituted DMABN ( $E_a = 7.8$ ,  $E_d = 13.7$  kJ  $\text{mol}^{-1}$ ). These values show that owing to higher activation energy of the reverse reaction of compound **12b** the contribution of emission from the TICT state is higher than for the parent compound DMABN while the rate of the reverse reaction is lower (rate constants for the reverse reaction for compounds **12b** and DMABN are  $1.2 \times 10^9$  and  $2.8 \times 10^{10}$   $\text{s}^{-1}$ , respectively).

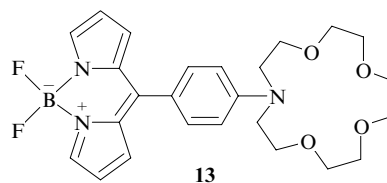
The dipole moments of the molecules DMABN, **12a** and **12b** in the LE and TICT states were determined using

solvatochromy (by analyzing the dependence of the position of bands in the absorption and fluorescence spectra on the solvent polarity) within the framework of the Lippert–Mataga formalism. The solvatochromic effect is much more pronounced for the emission band of the TICT state compared to the LE-state band. This indicates that the dipole moments of the molecules in the TICT state (13–15 D) are larger than those in the LE state (9–11 D) and that the formation of the TICT state is related to charge transfer.

The addition of calcium perchlorate to the solution of compound **12b** in acetonitrile causes the ratio of the quantum yields of fluorescence for the long-wavelength and short-wavelength emission bands to decrease from 46 to 2. In addition, maxima of these spectral bands are blue-shifted. The maximum of the short-wavelength emission band of the complex is shifted by 860  $\text{cm}^{-1}$  relative to the emission maximum of the LE state of compound **12b** while the maximum of the long-wavelength emission band of the complex is shifted by 1300  $\text{cm}^{-1}$  relative to the emission maximum of the TICT state of compound **12b** (*cf.* a 4000  $\text{cm}^{-1}$  blue shift of the absorption maximum upon complexation).

Dual fluorescence of the complex of benzonitrile **12b** with  $\text{Ca}^{2+}$  is due to the emission of the cation–fluorophore contact and solvent-separated pairs. No emission from the locally excited state (LM)\* occurs. An analogous picture is also observed for the complex of benzonitrile **12a** with  $\text{Mg}^{2+}$  cation. This set of the emitting species distinguishes the systems based on crown-containing benzonitriles from the previously studied stilbene **9c** where the short-wavelength emission band was ascribed to emission from the (LM)\* state with unbroken coordination bond metal–ligand. This is a parent state rather than a recoordination product.

Additional information on the subject can be obtained by studying the effect of complexation with alkali metal and alkaline-earth metal cations on the intramolecular charge transfer in crown-containing boron dipyrromethene **13**.<sup>44</sup>



The molecule of compound **13** is nonplanar due to rotation of its aniline fragment by 75° relative to the dipyrromethene unit. In the ground state, the electron-donor and electron-withdrawing fragments of the molecule do not interact with each other owing to the lack of electronic conjugation between them. This relates compound **13** to the previously studied compound **2** and other compounds whose structures were modified by introducing an insulating bridge.

A strong absorption band at 500 nm ( $\epsilon = 88\,000$  litre  $\text{mol}^{-1} \text{cm}^{-1}$ ) in the spectra of compound **13** and its NMe<sub>2</sub>- and H-analogues is due to the local excitation of the boron dipyrromethene fragment rather than charge transfer. An increase in the solvent polarity has almost no effect on the position of the maximum of this spectral band.

Contrary to this, the fluorescence of compound **13** and its NMe<sub>2</sub>-analogue depend strongly on the solvent polarity. If fluorescence of these compounds in hexane occurs solely from the LE state and is characterized by a rather high

quantum yield (0.3), in more polar solvents, quenching of the band of the LE state is accompanied by emission of the second fluorescence band, *viz.*, the band of emission from the ICT state. The total quantum yield of fluorescence of compound **13** decreases by a factor of 65 on going from hexane to diethyl ether and by a factor of 1300 on going to acetonitrile. Position of the band corresponding to emission from the LE state is almost insensitive to the solvent polarity, whereas the band corresponding to emission from the ICT state exhibits a noticeable solvatochromic effect, which indicates a high degree of charge transfer in the ICT state.

The H-analogue is characterized by monoexponential fluorescence decay kinetics and a lifetime of about 3 ns, whereas the fluorescence decay kinetics of compound **13** and its NMe<sub>2</sub>-analogue are at least biexponential with a short-lived ( $\sim 3$ –10 ps) and a long-lived ( $\sim 2$ –3 ns) component attributed to emission from the LE and ICT states, respectively. The short-lived component of fluorescence decay indicates a fast charge separation in the initial LE state with a rate constant of  $1.6 \times 10^{11} \text{ s}^{-1}$  (in dioxane). Charge transfer can be completely blocked by protonation of the nitrogen atom of the macrocycle, which leads to an increase in the quantum yield of fluorescence of compound **13** in acetonitrile from 0.0002 to 0.68.

Similarly to protonation, complexation of compound **13** with alkali metal and alkaline-earth metal cations in acetonitrile also has almost no effect on the position of its absorption and fluorescence spectra, but significantly affects the quantum yield of fluorescence. The fluorescence enhancement factor varies from 90 for Li<sup>+</sup> cation to 2250 for Mg<sup>2+</sup> cation. Except for the complex with Mg<sup>2+</sup>, the fluorescence decay kinetics of other complexes are biexponential. The short-lived component was ascribed to emission of the loose complex which seemingly corresponds to the solvent-separated pair L\*/S/M, while the long-lived component was attributed to the tightly-bound complex corresponding to the (LM)\* state. At the same time, an analysis of the time-resolved spectra reconstructed from the fluorescence decay kinetics and the independence of the relative contributions of the exponents on the detection wavelength indicate the lack of dynamic photoinduced recoordination in the excited state; the biexponential kinetics is due to simultaneous excitation of two conformers in the ground state. Nevertheless, for the complexes of compound **13** with metal cations one can say about the recoordination reaction in the ground electronic state. Upon excitation, the loose equilibrium product of recoordination has a shorter lifetime compared to the tightly-bound complex due to deactivation followed by the formation of the ICT state that does not fluoresce in acetonitrile.

A study<sup>45</sup> of the spectral luminescence and electrochemical properties of azacrown-substituted carbazoles **14**

and **15** and their complexes with Ca<sup>2+</sup> showed that the absorption spectra of compounds **14** and **15** are little sensitive to the solvent polarity.

This is consistent with the small dipole moments of their molecules in the ground state (1 and 2.5 D, respectively, according to CNDO/S calculations). On the contrary, the fluorescence spectra are significantly red-shifted as the solvent polarity increases. This indicates a considerable increase in the dipole moments of molecules **14** and **15** on excitation due to the formation of photoinduced ICT states. The dipole moments of the ICT states of molecules **14** and **15** estimated using the Lippert–Mataga formalism are 9 and 19 D, respectively.

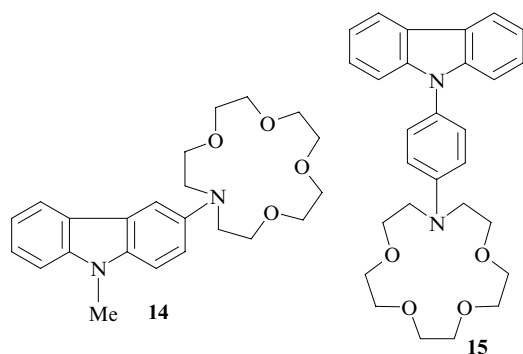
The fluorescence spectra of the complexes of carbazoles **14** and **15** with Ca<sup>2+</sup> in acetonitrile exhibit two emission bands whose maxima are blue-shifted relative to the fluorescence maxima of the free forms by 5200 and 160 cm<sup>-1</sup> for compound **14** and by 6200 and 750 cm<sup>-1</sup> for compound **15** (*cf.* 4100 and 3900 cm<sup>-1</sup>, respectively, for the blue shifts of the absorption spectra of molecules **14** and **15** in the case of protonation with trifluoroacetic acid). The short-wavelength emission band is mirror symmetrical to the absorption band. It was assigned to emission from the locally excited state (LM)\* with unbroken cation–nitrogen bond. The emission band in the long-wavelength spectral region is only slightly shifted relative to the band associated with emission from the ICT state of the free forms and was assigned to emission from the solvent-separated pair L\*/S/M. Usually, the  $\Delta pK$  values for the complexes on going to the excited state cannot be determined by simple fluorimetric titration because attempts to determine the stability constants of the complexes based on the fluorescence spectra lead to the same values of the constants as those obtained by photometric titration. This is due to the relatively short lifetime of singlet excited states of organic molecules; therefore, chemical equilibrium in the excited state is often not established.

At the same time, the lifetimes of radical cations produced in electrochemical reactions can be long enough to establish the chemical equilibrium. Although the radical cations, unlike the singlet excited states, are formed due to intermolecular electron transfer, the electron density on the nitrogen atom of the macrocycle decreases in both cases.

The addition of calcium salt to the solutions of compounds **14** and **15** in acetonitrile causes their first oxidation potentials corresponding to the oxidation of the phenylazacrown ether residue to shift towards higher potentials. The second oxidation potential of compound **14** corresponding to the oxidation of the carbazole unit of the radical cation is also shifted towards higher values. The change in the stability of the complex upon abstraction of an electron estimated from the shift value (0.183 V) was found to be  $\Delta pK = -3.1$ . Contrary to this, the second oxidation potential of compound **15** is independent of the salt concentration in the solution; this fact underlies the conclusion about the release of the cation from the macrocycle in the formation of the radical cation of the complex of compound **15** with Ca<sup>2+</sup>.

The spectral luminescence properties and effects of complexation of many unsymmetrical cyanine dyes, styryl dyes and styryl-containing heterocyclic compounds were studied.<sup>46</sup> The electron-withdrawing fragments of the cyanine and styryl dye molecules bear formal positive charges.

The absorption spectra of cyanine dyes exhibit a narrow band and a shoulder due to partial resolution of the vibrational structure. The fluorescence spectra of such dyes are



mirror symmetrical to the absorption spectra and show a small Stokes shift ( $\sim 500\text{--}900\text{ cm}^{-1}$ ).

Complexation of cyanine dyes is characterized by low stability constants whose logarithms for the 1:1 complexes with  $\text{Ca}^{2+}$  are in the range 0.9–1.4. Moreover, many cyanine dyes studied are not prone to complexation with  $\text{Ca}^{2+}$  cation at all. This can be explained by a high degree of conjugation of the multiple bonds in molecules, which leads to almost complete equalization of the corresponding bond orders and the appearance of a formal positive charge of 0.5e on the nitrogen atom of the macrocycle. This positive polarization of the nitrogen atom precludes the cation–macrocycle binding.

If complexation is possible, it leads to large hypsochromic shifts ( $\sim 2000\text{--}4000\text{ cm}^{-1}$ ). At the same time, the shifts in the fluorescence spectra are much smaller than the shifts in the absorption spectra and lie in the range from about 100 to  $300\text{ cm}^{-1}$ . This is a consequence of photoinduced recoordination in the excited molecules of the metal complexes of crown-containing cyanine dyes.

Compared to cyanine dyes, the styryl dyes are characterized by broad structureless absorption and fluorescence spectra and by more pronounced Stokes shifts. Despite the fact that both cyanine and styryl dye molecules bear a positive charge of 1e, the metal complexes of the styryl dyes are much more stable owing to a lower degree of equalization of the orders of the multiple bonds involved in the interaction between the macrocycle and the electron-deficient heterocyclic residue. The logarithms of the stability constants of the calcium complexes of styryl dyes are in the range from 2.0 to 3.1. Complexation of styryl dyes with  $\text{Ca}^{2+}$  cation in acetonitrile leads to pronounced hypsochromic shifts of the absorption maxima ( $4000\text{--}6200\text{ cm}^{-1}$ ). At the same time, the corresponding blue shift in the fluorescence spectra is small ( $80\text{--}880\text{ cm}^{-1}$ ). As in the case of cyanine dyes, this phenomenon was explained by the photoinduced ‘decoordination’, or ‘recoordination’ in the molecules of the complexes on excitation.

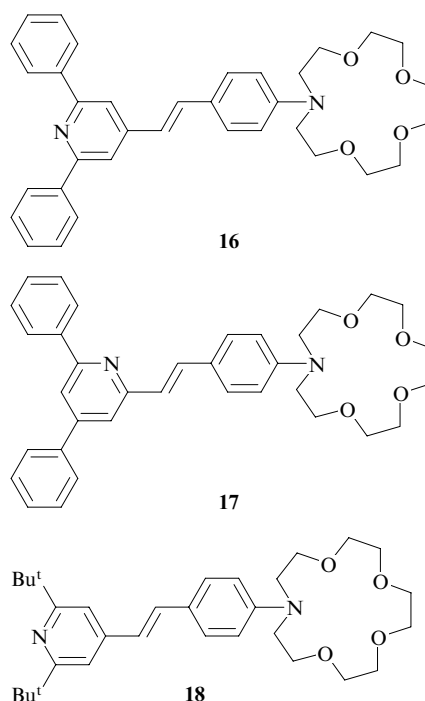
Based on the number of electron-donating groups in the molecule, the styryl-containing heterocyclic compounds studied can be divided into two classes, *viz.*, the structures of the D–A type with one donor group and those of the  $\text{D}^1\text{--A--D}^2$  type with two donor groups. As for benzoxazinone **7** and dimethylidencyclopentanone **8** (see above), the shifts observed in the absorption and fluorescence spectra of the compounds  $\text{D}^1\text{--A--D}^2$  on complexation with one mole of metal are not too large; in some cases, the shift in the fluorescence spectrum can be changed from a blue to a red one. Anomalies observed for this group of ionophores are due to the second electron-donor group which can efficiently compete with the macrocycle, especially when the electron-donating ability of the latter decreases upon complexation with the cation. No recoordination was observed for these compounds.

Contrary to this, styryl-containing heterocyclic compounds of the D–A type are characterized by rather large Stokes shifts ( $\sim 5000\text{--}7000\text{ cm}^{-1}$ ) and absorption in the charge-transfer band. Moreover, despite a decrease in the electron-withdrawing ability of neutral heterocyclic residues compared to the charged analogues, excited molecules of styryl-containing heterocyclic compounds can go to the ICT state in which the degree of charge transfer increases compared to the locally excited state.

At the same time, complexes of styryl-containing heterocyclic compounds are much more stable than the com-

plexes formed by the charged styryl and cyanine dyes. The logarithms of their stability constants are in the range from 4.4 to 4.8. Complexation of styryl-containing heterocyclic compounds with  $\text{Ca}^{2+}$  cation leads to hypsochromic shifts of the absorption maxima by  $2600\text{--}4500\text{ cm}^{-1}$  and fluorescence maxima by  $520\text{--}1600\text{ cm}^{-1}$ . As for the cyanine and styryl ionophores, the complexes of styryl-containing heterocyclic compounds also undergo recoordination in the excited state, which leads to abnormally small shifts of the fluorescence maxima and to abnormally large Stokes shifts ( $\sim 9000\text{--}10\,000\text{ cm}^{-1}$ ).

Complexes of crown-containing styrylpyridines **16–18** exhibit dual fluorescence. A similar phenomenon, where the decrease in the electron-withdrawing ability of the heterocyclic residue led to the appearance of dual fluorescence, was considered above for stilbenes **9a–c**.

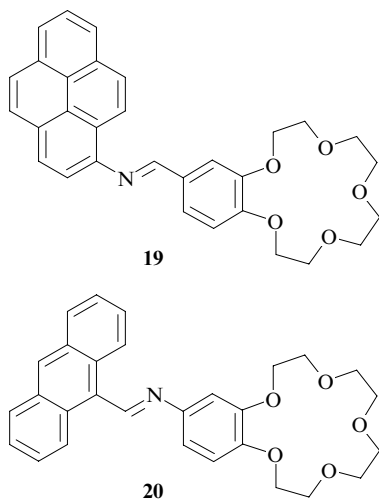


Calcium complexes with compounds **16** and **17** exhibit dual fluorescence. Maxima in the dual fluorescence spectrum are shifted relative to maxima in the fluorescence spectra of the free forms by  $520$  and  $5800\text{ cm}^{-1}$  for free compound **16** and by  $780$  and  $4200\text{ cm}^{-1}$  for free compound **17**. Probably, emission of these complexes in the long-wavelength region can be treated as emission from the solvent-separated pairs  $\text{L}^*/\text{S}/\text{M}$ , while emission in the short-wavelength region can be interpreted as emission from the locally excited states  $(\text{LM})^*$ . At the same time, the fluorescence excitation spectra of the complexes of compounds **16** and **17** depend on the excitation wavelength; therefore, the dynamic character of recoordination of the metal cation still remains a moot question.

Complexation of compound **18** with  $\text{Ca}^{2+}$  causes blue shifts of the absorption and fluorescence maxima (by  $4100$  and  $560\text{ cm}^{-1}$ , respectively). Thus, the behaviour of the spectra of compound **18** in the formation of 1:1 complexes is typical of other fluorophores studied. At the same time, at increased concentrations of metal salt, the absorption and fluorescence spectra of compound **18** are red-shifted by  $920$  and  $5000\text{ cm}^{-1}$ , respectively. This anomaly in the direction of the spectral shifts on complexation is due to the coordi-

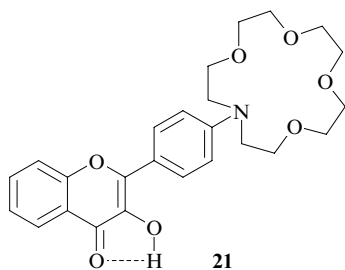
nation of the second  $\text{Ca}^{2+}$  cation to the pyridine nitrogen atom, which leads to abrupt increase in its electron-withdrawing properties and facilitates the formation of the ICT state on excitation. The large shift of the fluorescence spectra was explained by the fact that recoordination of the metal cation in the macrocycle cavity due to weakening of the metal–nitrogen bond on excitation is accompanied by the reverse process, *viz.*, strengthening of the bond between the cation and the nitrogen atom of the pyridine moiety. As a consequence, the formation of the ICT state of the complexes of compound **18** with two moles of metal is facilitated. No 2 : 1 complexes of compounds **16** and **17** were detected.

A study<sup>47</sup> of complexation of crown-containing Schiff bases containing the pyrene (**19**) or anthracene (**20**) nuclei with alkali metal and ammonium cations revealed that complexation leads to significant changes in the pattern of the fluorescence spectrum of compound **19** and to an increase in the quantum yield of fluorescence by a factor of 5 to 15. This suggests suppression of charge transfer from the nitrogen atom of the Schiff base on complexation. The largest increase in the quantum yield of fluorescence is due to complexation with ammonium ion. This was explained by the presence of the hydrogen bond between ammonium ion and the nitrogen atom of the Schiff base.



Contrary to the data for compound **19**, the fluorescence ability of imine **20** increases only slightly on complexation. Among the cations, this effect weakens with an increase in the atomic mass of the metal owing to quenching by the heavy-atom mechanism.

Studies of the spectral luminescence characteristics of crown-containing flavone **21** and its complexes with sodium  $\text{M}_2\text{L}$  revealed<sup>48</sup> a fast photoejection of one cation from the macrocycle cavity in the excited state of the complex.



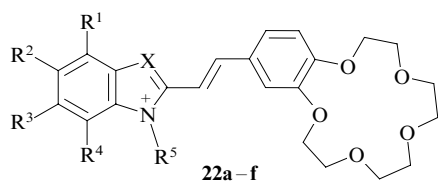
The addition of  $\text{NaClO}_4$  to a solution of flavone **21** in acetonitrile causes a successive formation of the 1 : 1 and 2 : 1 complexes characterized by the stability constants of 72 and  $3.8 \text{ litre mol}^{-1}$ , respectively. The initial blue shift of the absorption spectra is followed by their red shift. Maxima in the absorption spectra of the 1 : 1 and 2 : 1 complexes undergo a blue shift by 2000 and  $1300 \text{ cm}^{-1}$ , respectively. The smaller shift of the absorption spectra of the complex  $\text{M}_2\text{L}$  is explained by coordination of the second  $\text{Na}^+$  to the carbonyl group. This enhances the electron-withdrawing properties of the flavone nucleus and decreases the energy necessary for charge transfer to occur.

The fluorescence spectrum of free compound **21** exhibits two emission bands with maxima at 507 and 575 nm, which were respectively assigned to the charge-transfer (CT) state and the zwitterionic (Z) state formed as a result of intramolecular phototransfer of proton. The addition of sodium salt causes these bands to disappear and a new emission band at 524 nm appears, which was assigned to emission of a 1 : 1 complex formed as a result of photoejection of a cation from the 2 : 1 complex. In the excited molecule of the 1 : 1 complex, the only  $\text{Na}^+$  cation is coordinated to the carbonyl group, which also precludes the formation of the zwitterionic state Z. An analogous photoejection of one cation from the 2 : 1 complexes and anomalous red shifts of the fluorescence spectra were considered above taking compounds **8** and **18** as examples. The ground state of the 1 : 1 complex in which the only cation is coordinated to the macrocycle does not manifest itself in the fluorescence spectra.

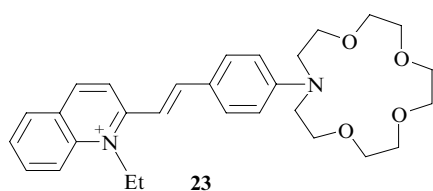
It is believed<sup>48</sup> that the experimental results obtained do not unambiguously indicate a complete release of the cation from the macrocycle. Yet another possible case involves retention of the cation in the macrocycle cavity by oxygen atoms, the inclusion of the cation in certain loose complexes, which almost precludes the photoejection during the excited-state lifetime. At the same time, compound **21** and its  $\text{NMe}_2$ -analogue containing no macrocycle exhibit almost identical luminescence properties and are characterized by nearly equal lifetimes of the CT and Z states and the 1 : 1 complex with the coordination to the carbonyl group. This was interpreted as an argument in favour of complete photoejection of the cation.

## V. Effect of photoinduced recoordination of metal cations on the spectral luminescence properties of complexes with crown-containing dyes

Complexation of crown-containing styryl dyes **22a–f** with  $\text{Na}^+$  in ethanol at 293 K causes noticeable ( $700\text{--}800 \text{ cm}^{-1}$ ) hypsochromic shifts of the absorption maxima, whereas for the azacrown-containing dye **23** this shift is small ( $50 \text{ cm}^{-1}$ ).<sup>34</sup> Owing to low quantum yields of fluorescence of dyes **22a–f** under normal conditions, the fluorescence spectra of free dyes and their complexes with  $\text{Na}^+$  were recorded at 173 K. The shifts of the fluorescence maxima ( $50\text{--}200 \text{ cm}^{-1}$ ) obtained under these conditions were much smaller than the corresponding shifts in the absorption spectra at 293 K. Based on this fact, a conclusion about photoinduced recoordination in the excited molecules of these complexes was made.

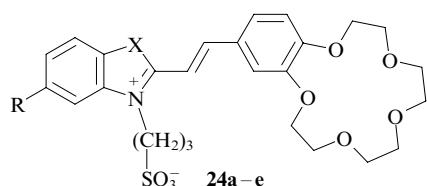


Compound <b>22</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	X
<b>a</b>	H	Me	Me	H	Me	Me <sub>2</sub> C
<b>b</b>	H	H	Ph	H	Et	O
<b>c</b>	H	H	H	H	Et	S
<b>d</b>	H	H	benzo		Et	S
<b>e</b>	H	H	H	H	Et	C <sub>2</sub> H <sub>2</sub>
<b>f</b>	H	H	OMe	H	Et	S



At the same time, a study<sup>35</sup> of the temperature dependence of the position of the maximum in the absorption spectrum of compound **22a** revealed that the decrease in temperature from 293 to 173 K and then to 77 K causes a hypsochromic shift of the spectra of free dye, probably, due to complexation with the solvent molecules. Complexation with Na<sup>+</sup> has little effect on the positions of both fluorescence and absorption spectra. To eliminate this undesired effect, complexation of compound **22a** with Na<sup>+</sup> was studied at an intermediate temperature of 223 K. In this case, the shift of the spectral maximum due to the complexation with Na<sup>+</sup> is 710 cm<sup>-1</sup> for the absorption spectra and 160 cm<sup>-1</sup> for the fluorescence spectra, which confirms the suggested occurrence of photoinduced recoordination in excited molecules of the complexes of styryl dyes.

Complexation of dyes **24a–e** with Mg<sup>2+</sup> cation in acetonitrile<sup>49</sup> leads to noticeable blue shifts of the absorption maxima (2800, 2500, 2300, 1900 and 1600 cm<sup>-1</sup>, respectively); the shifts of the fluorescence maxima may be comparable or smaller than the shifts in the absorption spectra (1400, 1400, 2300, 500 and 200 cm<sup>-1</sup>, respectively). Photoinduced recoordination in the complexes of magnesium with compounds **24d** and **24e** was also reported.

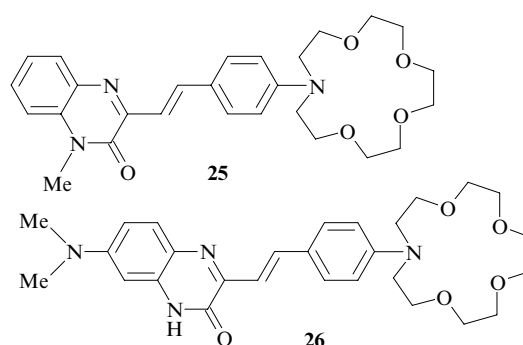


Compound <b>24</b>	X	R
<b>a</b>	O	H
<b>b</b>	S	H
<b>c</b>	CH=CH	H
<b>d</b>	S	Ph
<b>e</b>	S	MeO

A quite unexpected result consists in that the introduction of electron-donor groups at position 5 of the benzo-

thiazolium residue favours photoinduced recoordination of the cation. At the same time, enhancement of the electron-donating ability of the substituent in the series of compounds **24b**, **24d**, **24e** causes a regular decrease in the hypsochromic shifts upon complexation (2500, 1900 and 1600 cm<sup>-1</sup>, respectively), and a decrease in the Stokes shifts of free compounds (4500, 4100 and 4000 cm<sup>-1</sup>, respectively) because charge transfer upon excitation becomes difficult as the electronegativity of the heterocyclic residue decreases. The heterocycle in compound **24c** is characterized by the greatest electron-withdrawing ability, a particularly large Stokes shift (5400 cm<sup>-1</sup>) and by the lack of photoinduced recoordination of the cation, which is also unusual.

Complexation of styrylbenzodiazinone **25** with Mg<sup>2+</sup> and Ca<sup>2+</sup> cations in acetonitrile leads to blue shifts of the absorption maxima by 4100 and 3900 cm<sup>-1</sup>, respectively.<sup>50</sup> The corresponding shift of the fluorescence maxima is much smaller (~500 cm<sup>-1</sup>).



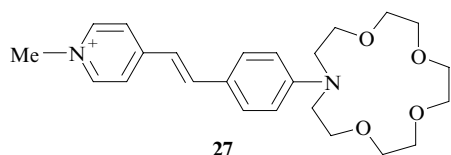
Complexation of compound **26** with Mg<sup>2+</sup> cation has almost no effect on the position of its absorption maximum. Rather, complexation with Ca<sup>2+</sup> cation is accompanied by a noticeable hypsochromic shift (800 cm<sup>-1</sup>). The blue shifts of the fluorescence maxima on complexation of compound **26** (1100 and 700 cm<sup>-1</sup> for Mg<sup>2+</sup> and Ca<sup>2+</sup> cations, respectively) are larger than the corresponding shifts for complexation of compound **25**.

The Stokes shifts of compounds **25**, **26** and their complexes with Ca<sup>2+</sup> cation are respectively 5600, 3900, 8100 and 3500 cm<sup>-1</sup>.

Compound **25** and its complex are characterized by large Stokes shifts. This is an indication of relaxation processes, *viz.*, the formation of the ICT state and photoinduced recoordination of the cation. Contrary to this, compound **26** and its complex with Ca<sup>2+</sup> are characterized by nearly equal Stokes shifts, which suggests no photoinduced recoordination in this complex.

The difference in the behaviour of the dyes **25** and **26** is analogous to the difference in the behaviour of compounds **7** and **6** (see above) and can be explained by the fact that they belong to two different types of dyes containing the donor and acceptor groups, namely, D–A and D<sup>1</sup>–A–D<sup>2</sup>, respectively.

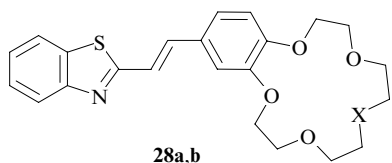
A study<sup>51</sup> of a crown-containing styryl dye **27** bearing a methylpyridinium residue showed that complexation with Li<sup>+</sup> and Na<sup>+</sup> cations in a dichloromethane:acetonitrile mixture (95:5) is accompanied by not too large blue shifts of the absorption maxima (1500 and 500 cm<sup>-1</sup>, respectively) and fluorescence maxima (300 cm<sup>-1</sup>). The Stokes shifts are 3100, 4200 and 3300 cm<sup>-1</sup> for free compound **27** and its complexes with Li<sup>+</sup> and Na<sup>+</sup>, respectively.



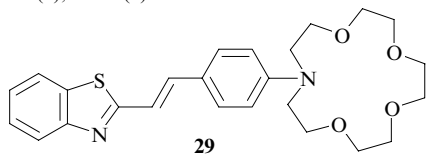
Positions of the fluorescence spectra of compound **27** are almost independent of the solvent polarity, which is believed to be an indication of a low polarity of the excited state responsible for emission.<sup>51</sup> At the same time, the absorption spectra of **27** show clearly seen solvatochromism; maxima in absorption spectra undergo a blue shift as the solvent polarity increases. Therefore, one deals with a considerable increase in the Stokes shift (to  $5500\text{ cm}^{-1}$ ) and a nearly tenfold quenching of fluorescence, which may suggest the formation of the ICT state.

It seems that one cannot say with certainty about photoinduced recoordination in a solvent of low polarity, which was chosen to study the complexation of compound **27**. Probably, photoinduced recoordination occurs in the case of  $\text{Li}^+$  cation, which is characterized by high charge density, and lacks in the case of  $\text{Na}^+$  cation.

Studies of the effect of the nature of the crown ether fragment on the spectral luminescence properties and complex-forming ability of styrylbenzothiazoles **28** and **29** showed<sup>52</sup> that the largest hypsochromic shifts are observed for the complexation of compound **29** ( $3000\text{--}4000\text{ cm}^{-1}$ ) containing the *N*-phenylazacrown ether as ionophoric fragment. The corresponding shifts upon complexation of compounds **28a,b** containing a benzocrown ether fragment are much smaller ( $400\text{--}1000\text{ cm}^{-1}$ ). The reverse is observed for the shifts of the fluorescence maxima. Complexation of cations with compounds **28a,b** causes blue shifts that are comparable or larger than the corresponding shifts in the absorption spectra. Contrary to this, the shifts of the fluorescence maxima on complexation of styrylbenzothiazole **29** are much smaller ( $300\text{--}400\text{ cm}^{-1}$ ) than the corresponding shifts in the absorption spectra. This was explained by photoinduced recoordination in the complexes of styrylbenzothiazole **29** with alkaline-earth metal cations. No photoinduced recoordination was observed for the corresponding complexes of compounds **28a,b**.



X = O (a), NMe (b).



Compounds **28** and **29** can form strong complexes with alkaline-earth metal cations. The stabilities of the 1:1 complexes of compounds **28a,b** ( $\log K = 5.5$ ) are about two orders of magnitude higher than those of the complexes of compound **29** ( $\log K = 3.5$ ). In addition, a characteristic feature of compound **28a** whose crown ether moiety contains no nitrogen atoms is the formation of 2:1 sandwich complexes. Compounds **28b** and **29** form no such complexes. This is due to the destabilizing effect of the 'soft'

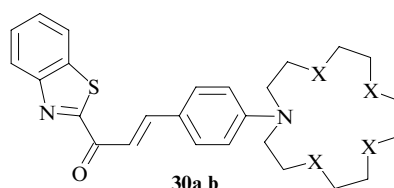
nitrogen atoms in these compounds, because 'hard' alkaline-earth metal cations prefer coordination to 'hard' oxygen atoms.

The effect of rigidity and donor ability of the aniline fragment on the spectral properties of crown-substituted chalcones was studied.<sup>53</sup> The donor groups were the 4-*N*-dimethylamino group (DMA), 4-*N*-tetraoxa-15-crown-5-ether (A15C5), 4-*N*-tetrathia-15-crown-5-ether (AT4-15C5) and 3-julolidine fragment (Jul). It was shown that the yield of the fluorescent ICT state decreases in the order:



due to an increase in the 'hardness' of the substituent. This manifests itself in a decrease in the quantum yield of fluorescence in polar solvents from 0.02 to 0.001 in the series of compounds with the benzothiazolium residue and these electron-donor fragments.

As the solvent polarity increases, the absorption and fluorescence spectra of compounds **30a,b** undergo a red shift, but the fluorescence spectra are shifted to a greater extent and therefore the Stokes shift also increases. This suggests a larger dipole moment of molecules in the excited state compared to that in the ground state. The increase in the dipole moment on excitation estimated using the Lipert–Mataga formalism is about 20 D.



X = O (a), S (b).

Complexation of compound **30a** with alkali metal and alkaline-earth metal cations, as well as with  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  cations leads to hypsochromic shifts of the absorption maxima. In the case of the singly charged alkali metal cations the shifts are much smaller than those observed upon the complexation with the doubly charged cations ( $700\text{--}1400\text{ cm}^{-1}$  vs.  $4700\text{--}7000\text{ cm}^{-1}$ , respectively). Complexation of compound **30a** with  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  cations may involve a chelate-like coordination of the second cation near the carbonyl group.

Being a measure of the complexation effects, the hypsochromic shifts in the fluorescence spectra of compound **30a** are much smaller than in the absorption spectra, *viz.*, about three times smaller for the singly charged metals and five- to tenfold smaller for the doubly charged cations. For instance, complexation of compound **30a** with  $\text{Ca}^{2+}$  cation causes maxima in the absorption and fluorescence spectra to shift by  $6200$  and  $900\text{ cm}^{-1}$ , respectively. As always in related situations, this indicates a photoinduced recoordination of the cation in the excited molecules of the complexes.

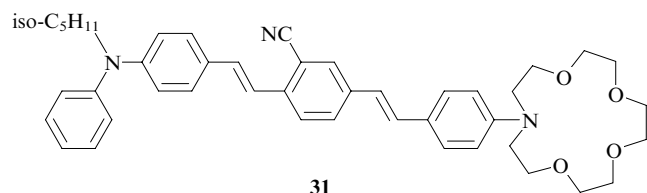
Compound **30b** is characterized by selective formation of tightly bound complexes with  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  cations. However, the addition of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  cations to the solutions of compound **30b** causes no changes in the corresponding absorption spectra. Complexation of compound **30b** with  $\text{Hg}^{2+}$  leads to a nearly sixfold increase in the quantum yield of its fluorescence

despite the fact that binding of this metal usually causes a complete quenching of fluorescence. As in the complex of compound **30a** with  $\text{Ca}^{2+}$ , photoinduced recoordination of the cation occurs in the complex of compound **30b** with  $\text{Hg}^{2+}$ ; the reaction is detected from inconsistency between the magnitudes of the shifts of the absorption and fluorescence maxima upon complexation (7320 and  $1300\text{ cm}^{-1}$ , respectively).

The fluorescence decay kinetics of compounds **30a,b** in acetonitrile obey a monoexponential law and are characterized by the times 71 and 170 ps, respectively. Unlike free compounds **30**, the fluorescence decay kinetics of their complexes are at least biexponential. For instance, compound **30a** is characterized by the short-lived and long-lived components with the characteristic times of 90 and 200 ps, respectively. For the complex of compound **30a** with  $\text{Ca}^{2+}$ , the fast and slow components have the respective characteristic times of 50 and 192 ps. The fluorescence decay kinetics of the complex of compound **30b** with  $\text{Ag}^+$  is biexponential, being three-exponential, with the characteristic times of 90, 568 and 1.1 ns, for the complex of compound **30b** with  $\text{Hg}^{2+}$ .

The instantaneous fluorescence spectra of the species with the lifetimes of 90 and 568 ps, reconstructed from the fluorescence decay kinetics of the complex of compound **30b** with  $\text{Hg}^{2+}$ , exhibit maxima at 580 and 584 nm. Based on the large overlap of these spectra, it was concluded<sup>53</sup> that the short-lived component cannot be attributed to emission from the locally excited state (ML)\*. It was ascribed to emission from the contact pair cation–fluorophore  $\text{L}^*\text{M}$ , assuming that the main source of emission is the solvent-separated pair  $\text{L}^*/\text{S}/\text{M}$ . The three-exponential fluorescence decay of the complex of compound **30b** with  $\text{Hg}^{2+}$  was explained by the equilibrium between two conformers of the complexes in the ground state with similar properties; simultaneous excitation of both of them leads to two different solvent-separated pairs with the lifetimes 568 and 1070 ps. The authors of that study believed that a complete release of the cation is a slow process and is not observed under the experimental conditions.

Complexation of compound **31**, which emits bright fluorescence in acetonitrile (the quantum yield of fluorescence is 0.47), with  $\text{Ca}^{2+}$  causes a moderate hypsochromic shift of the absorption maxima ( $\sim 1000\text{ cm}^{-1}$ ); the fluorescence spectrum is almost not shifted and its intensity is nearly halved.<sup>54</sup> Seemingly, this is an indication of photoinduced recoordination of the cation.

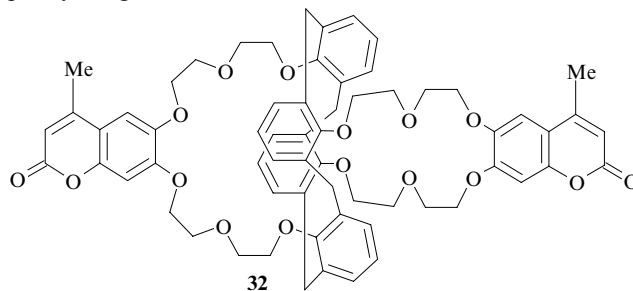


The stability constants of the complexes of compound **31** with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations determined from the fluorescence spectra under one-photon excitation and from changes in the section of two-photon absorption are almost equal. The addition of  $\text{Ca}^{2+}$  to a solution of compound **31** in acetonitrile causes a fivefold decrease in the cross-section of two-photon absorption.

Complexation of calixarene **32** with  $\text{Cs}^+$ ,  $\text{K}^+$  and  $\text{Na}^+$  cations is followed by a minor quenching of fluorescence and a short-wavelength shift of the maximum in the

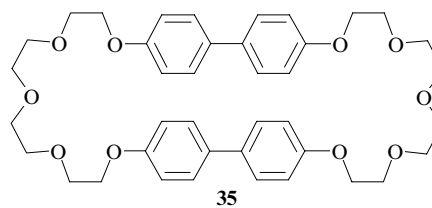
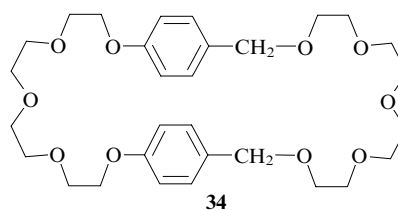
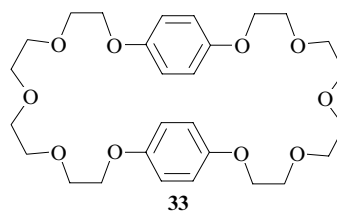
fluorescence spectrum.<sup>18</sup> The selectivity of the reaction of compound **32** with  $\text{Cs}^+$  resulting in the complex ML in ethanol is 16000:1 with respect to  $\text{Na}^+$  and 75:1 with respect to  $\text{K}^+$ .

Calixarene **32** forms both 1:1 and 2:1 complexes with  $\text{Cs}^+$  cations. It is important that the blue shift of the fluorescence maxima of the 1:1 complex ( $170\text{ cm}^{-1}$ ) is much smaller than the halved corresponding shift for the 2:1 complex ( $670\text{ cm}^{-1}$ ). This was explained<sup>18</sup> by photoinduced recoordination of  $\text{Cs}^+$  in the excited molecules of the 1:1 complex. This reaction results in ejection of the  $\text{Cs}^+$  cation from the macrocycle cavity to a 'tunnel' formed by phenyl rings.



The fluorescence decay kinetics of the 1:1 complex is three-exponential due to three possible states of the dioxy-coumarin fragment, *viz.*, the free state, the bound state and the state with the reCOORDINATED cation displaced to the 'tunnel' formed by phenyl rings.

A complexation study of  $\text{Ba}^{2+}$  cation with a family of non-conjugated dichromophoric bis(*p*-phenylene)- and bis(*p*-diphenylene)polyoxamacrocyclic coronands **33–35** in the ground and excited electronic states showed<sup>55</sup> that these macrocyclic coronands can form both 1:1 and 2:1 complexes.



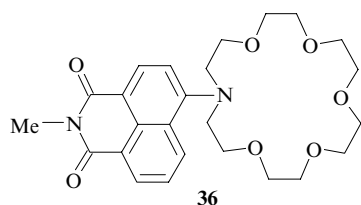
The conclusion about photoinduced recoordination or, probably, photoejection of the cation in the barium complexes of these compounds was based on the fact that the shifts of absorption maxima (600, 400 and  $865\text{ cm}^{-1}$ , respectively) due to complexation are larger than the corre-

sponding shifts of the fluorescence spectra (195, 335 and 250  $\text{cm}^{-1}$ , respectively). The Stokes shift is particularly large for compound **35** and its complex with  $\text{Ba}^{2+}$  (8700 and 9300  $\text{cm}^{-1}$ , respectively). This can be explained by the fact that charge transfer in the excited molecule **35** may be followed by flattening of the diphenyl fragment (angle between the phenyl ring planes decreases from  $42^\circ$  to  $25^\circ$ ) and changes in the macrocycle geometry.

Yet another factor indicating a change in the character of the  $\text{Ba}^{2+}$  cation binding or even the possibility of photoejection of cations from the macrocycle cavity is the formation of only 1:1 complexes ( $\log K = 3.84$  and 2.73, respectively), whereas in the ground electronic state the molecules **33** and **35** successively form the 1:1 ( $\log K = 3.77$  and 2.87) and 2:1 ( $\log K = 2.01$  and 2.24, respectively) complexes. Unlike the coronands **33** and **35**, both 1:1 and 2:1 complexes of compound **34** fluoresce. However, the total stability of the complex  $\text{M}_2\text{L}$  of ionophore **34** in the excited state is lower than in the ground state ( $\log K = 9.11$  and 10.26, respectively).

The fluorescence decay kinetics of coronands **34** and **35** is monoexponential, whereas that of compound **33** is biexponential due to the excimer-type interaction between aromatic nuclei. A model acyclic podand showed a monoexponential kinetics for both the initial ionophore and the barium complex. Contrary to this, the barium complexes of coronands **33–35** exhibit a biexponential fluorescence decay kinetics. This is believed<sup>55</sup> to indicate also a photoinduced recoordination. In all cases, complexation leads to quenching of fluorescence and shortening of excited-state lifetimes.

Changes in the spectra on complexation of crown-containing naphthalimide **36** with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations are presented in Table 1.



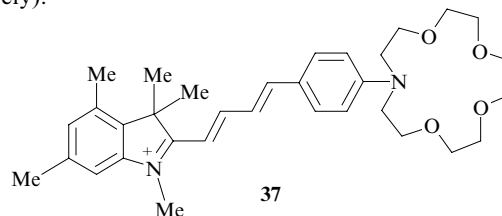
**Table 1.** Changes in spectroscopic characteristics for the complexation of compound **36** with metal cations ( $\text{cm}^{-1}$ ).<sup>56</sup>

Parameter	$\text{Na}^+$	$\text{K}^+$	$\text{Cs}^+$	$\text{Ca}^{2+}$	$\text{Ba}^{2+}$
Shift in absorption spectrum	840	2300	4900	1800	3600
Shift in fluorescence spectrum	770	660	190	1500	1300
Stoke's shift	3600	7800	11000	6500	8500

Based on these data, one can suggest that photoinduced recoordination is most pronounced for the  $\text{K}^+$ ,  $\text{Cs}^+$  and  $\text{Ba}^{2+}$  cations, *i.e.*, large ions whose diameters best match the size of the macrocycle cavity. Mention of the photoinduced recoordination in the complexes of compound **36** with  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  cations was made because in these cases, complexation causes a tenfold and fivefold increase in the quantum yield of fluorescence, respectively, due to production of hindrances to rotation of the crown ether residue necessary to form the TICT state. Based on the criterion treating the emission of fluorescence as an indica-

tion of photoinduced recoordination, the complex of naphthalimide **36** with  $\text{Cs}^+$  was placed among the poorly fluorescent compounds with no photoinduced recoordination.<sup>56</sup> We believe that the abnormally large Stokes shift for this complex (11 000  $\text{cm}^{-1}$ ) explicitly indicates a relaxation process (most probably, photoinduced recoordination).

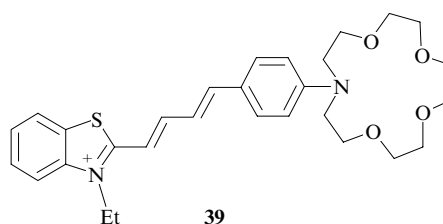
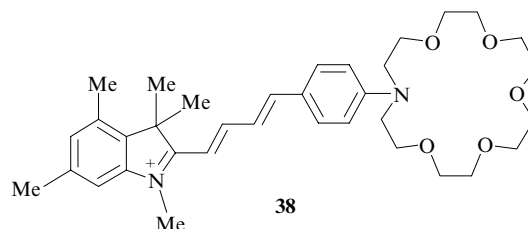
Complexation of butadienyl dye **37** with  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations in acetonitrile causes considerable blue shifts of the absorption maxima (by 2000 and 5100  $\text{cm}^{-1}$ , respectively).<sup>57,58</sup>



The corresponding shifts of the fluorescence maxima are very small (30 and 260  $\text{cm}^{-1}$ , respectively). The Stokes shifts for the free dye **37** and its complexes with  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are respectively 2400, 5000 and 7800  $\text{cm}^{-1}$ . Taking account of the small shifts in the fluorescence spectra and the abnormally large Stokes shifts for the complexes of compound **37** with  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , the authors of those studies suggested the occurrence of photoinduced recoordination in the excited molecules of the complexes.

The stability constants of the 1:1 complexes determined after processing of the absorption and fluorescence spectra agree with each other. Based on this fact, it was concluded that photoinduced recoordination is a fast intramolecular process and that the excited-state lifetime is too short for the cation to be ejected to solution. This is also indicated by a nearly twofold increase in the quantum yield of fluorescence of compound **37** on complexation. The complexation-induced shifts of the maxima in the fluorescence excitation spectra of compound **37** in glassy butyronitrile at 77 K are similar in magnitude to the shifts of the absorption maxima in acetonitrile at room temperature, while the shifts of the emission maxima are small in both acetonitrile and glassy butyronitrile. Diffusion of cations in glassy butyronitrile is impossible, which can also serve as a substantiation of the intramolecular character of photoinduced recoordination.

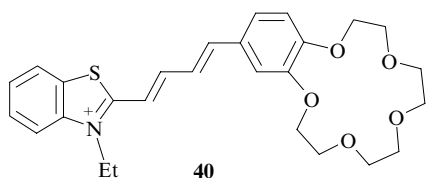
The authors of a study of complexation of butadienyl dyes **37–39** with alkali metal and alkaline-earth metal cations proposed a classification of such complexes based on the correlations between the complexation-induced spectral shifts and the charge density on the metal cation.<sup>59</sup>





There are three types of complexes differing in the extent to which the charge on the cation affects the spectral shifts, *viz.*, the tightly bound, loose and solvent-separated complexes. In the ground state, all three types of complexes can be formed, whereas in the excited state the tightly bound complexes are rapidly transformed to the loose and solvent-separated ones, thus being unobservable. It was proposed to consider photoinduced recoordination as a process leading to changes in the type of the complex upon electronic excitation. It was found that the quantum yield of fluorescence of solvent-separated complexes is nearly twice as high as that of free dyes, whereas in the case of loose complexes one deals with quenching of fluorescence of the initial form of the dye.

A study<sup>60</sup> of the structure and properties of the butadienyl dye **40** and its complexes with alkali metal and alkaline-earth metal cations showed the formation of not only the 1:1 complexes ML ( $M = \text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ), but also sandwich complexes with unusual structure (two dye molecules are arranged one above the other obeying the 'head-to-head' motif).



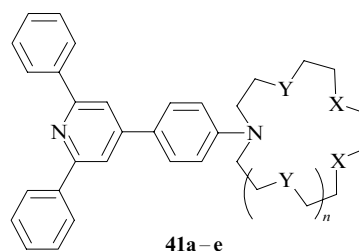
Complexation of compound **40** with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  cations leads to blue shifts of the absorption maxima (1970, 1910, 1690 and  $1470\text{ cm}^{-1}$ , respectively) and fluorescence maxima (1860, 1470, 1260 and  $950\text{ cm}^{-1}$ , respectively). The Stokes shift is nearly  $6000\text{ cm}^{-1}$  for free dye **40** and  $6500\text{ cm}^{-1}$  for its complex with  $\text{Ca}^{2+}$  cation. Owing to similar values of the shifts of the absorption and fluorescence maxima on complexation, as well as the Stokes shifts of the free dye **40** and its complexes, no photoinduced recoordination of cations occurs in excited molecules of the complexes of compound **40** unlike compound **39** despite the indication of a quinonoid structure of molecule **40**, as determined by X-ray diffraction analysis. Thus, replacement of azacrown ether fragment by a crown ether moiety with lower electron-donating ability may inhibit the reaction of photoinduced recoordination of the metal cations, as was observed for, *e.g.*, compounds **28** and **29**.

The structures of azacrown-containing 2,6-diphenylpyridines, **41** include two sites for coordination of metal cations,<sup>61</sup> namely, the pyridine nitrogen atom and the crown ether macrocycle.

Depending on the nature of the metal, four types of cation binding are possible. These are selective binding of (i) pyridine fragment and (ii) crown ether macrocycle, (iii) simultaneous cation binding by both the pyridine fragment and the macrocycle and (iv) no binding to all possible coordination sites. Fluorescence of compounds **41** in solutions in acetonitrile occurs from the highly polar ICT state, which is characterized by high quantum yield of fluorescence equal to 0.5 and a dipole moment of 16 D.

Selective binding of pyridine fragment was observed upon complexation of compound **41a** with  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  cations and compound **41d** with  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  cations. This leads to a bathochromic shift of the absorption maxima (by  $6500\text{ cm}^{-1}$ ) and fluorescence maxima (by

$4000\text{--}6000\text{ cm}^{-1}$ ). The bathochromic shift of the fluorescence maxima is accompanied by a considerable decrease in the quantum yield of fluorescence and in the lifetimes (for compound **41d**, the lifetimes decrease from 1 ns to 31 ps and 5 ps for its complexes with  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$ , respectively). This was explained<sup>61</sup> by transformation of the ICT state with a moderate degree of twisting of molecular fragments to the TICT state with almost complete twisting of these fragments owing to an increase in the electron-withdrawing ability of the pyridine fragment upon cation binding.



Compound <b>41</b>	X	Y	n	Compound <b>41</b>	X	Y	n
<b>a</b>	O	O	0	<b>d</b>	O	S	1
<b>b</b>	O	O	1	<b>e</b>	S	O	1
<b>c</b>	O	O	2				

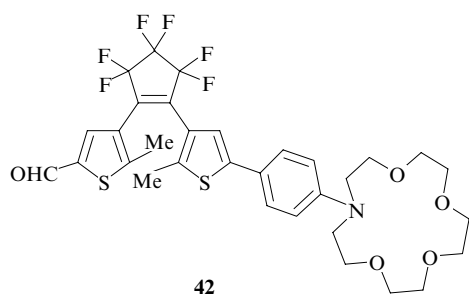
Selective binding of the crown ether macrocycle was observed in the reactions of compounds **41d,e** with  $\text{Hg}^{2+}$ . The binding leads to moderate hypsochromic shifts of the absorption maxima ( $2500\text{ cm}^{-1}$ ) and to smaller shifts of the fluorescence maxima ( $800\text{ cm}^{-1}$ ). The latter was explained by photoinduced recoordination.

The type of the metal cation binding may vary in the presence of 'alien' anions introduced into the system in the form of, *e.g.*, tetrabutylammonium salts. In the presence of anions, solutions change their colour. This can serve a basis for the design of optical sensors for anions.

## VI. Photoejection of metal cations from photochromic crown-containing compounds, not related to structural rearrangements in the ionophoric fragment

Photocontrolled cation binding to crown-containing photochromes due to reversible interconversions of two forms of a photochromic compound can be attained by changing the macrocycle geometry, by photocyclization of polyether chains, by producing steric hindrances to arrangement of the cation in the macrocycle cavity, by forming additional coordination bonds in 'anion-capped' complexes of the merocyanine form of spiropyrans or in complexes of styryl dyes with the sulfo group, *etc.*<sup>7-9</sup> In this Section we will consider crown-containing photochromes in which the photochromic transformation leads to considerable changes in the electron density on the heteroatoms of the macrocycle, included in the chromophore fragment of the molecule, but causes no structural rearrangements in the ionophoric fragment. Examination of such systems provides valuable information on photoinduced recoordination and photoejection of metal cations.

The closed form of photochrome **42** shows a high thermal stability. This allows one to determine how the stability constants of its complexes change upon photocyclization.<sup>62</sup>



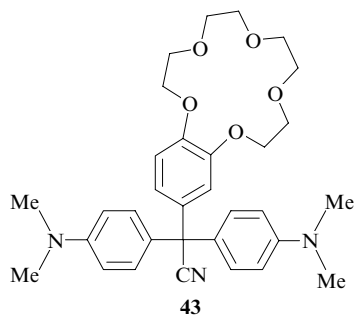
42

It was shown that the stability of a complex of the open form of compound **42** with  $\text{Ca}^{2+}$  is four orders of magnitude higher than that of the corresponding complex of the closed form of the same compound. This suggests the possibility of photoejection of the cation upon photocyclization.

Photochrome **42** based on 1,2-bis(3-thienyl)perfluorocyclopentene in positions 5 and 5' contains a phenyl azo-15-crown-5-ether residue and a formyl group, which exhibit strong electron-donating and electron-withdrawing properties, respectively. These substituents almost do not interact with each other owing to the lack of electronic conjugation between them and to mutual rotation of the thiophene nuclei in the open form. As a consequence, complexes of compound **42** are characterized by high stability constants and absorption in the short-wavelength spectral region. The open form is converted to the closed form upon UV irradiation (mercury lamp, 254 nm) while the reverse reaction occurs upon exposure to visible light. The absorption maximum of the closed form (675 nm) is appreciably red-shifted relative to the absorption maximum of the open form (332 nm). This is due to the elongation of the conjugation chain upon photocyclization and absorption of the closed form in the charge transfer band; the latter increases the shift of the spectral maximum by an additional 100 nm compared to the shift in the spectrum of the analogue containing no formyl group.

The logarithms of the stability constants of the complexes formed by the open form of compound **42** with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ag}^+$  are 2.3, 5.4 and 2.95, respectively (*cf.* 1.6, 1.7 and 1.74, respectively, for the complexes of the closed form with the same cations). On going from the open form to the closed one the stabilities of the complexes of compound **42** with  $\text{Na}^+$  and  $\text{Ag}^+$  change to a much lesser extent than those of the complexes with  $\text{Ca}^{2+}$ . This is due to the fact that the  $\text{Na}^+$  and  $\text{Ag}^+$  cations bear smaller charges and, in addition, the Ag–N (macrocycle) bond is partly covalent.

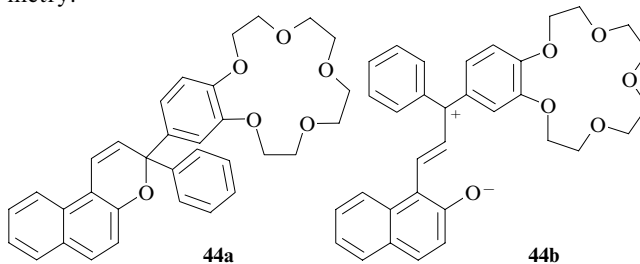
Photoejection of  $\text{Na}^+$  cation from the complex with crown-containing Malachite Green dye **43** was studied by potentiometry using a Na-selective glassy electrode.<sup>63</sup>



43

Colourless solutions of compound **43** rapidly turn green when exposed to UV irradiation. This is due to photochromic ionization of the dye, resulting in triphenylmethyl cation and a cyanide anion. Both neutral and ionized forms of compound **43** can form complexes with metal cations. Complexation of the ionic form of compound **43** with  $\text{Na}^+$  causes a bathochromic shift of the first absorption band by  $420\text{ cm}^{-1}$  and a hypsochromic shift of the second absorption band by  $2800\text{ cm}^{-1}$ . Different directions of the shifts of these bands upon complexation are due to the fact that the electric field of the cation favours charge transfer from dimethylamino groups but precludes charge transfer from oxygen atoms of the crown ether moiety. Exposure of a solution of equimolar amounts of the dye **43** and  $\text{NaClO}_4$  ( $10^{-4}\text{ mol litre}^{-1}$ ) to light causes the potential of the ion-selective electrode to increase by 1 mV. A dark reverse reaction accelerated by heating returns the initial value of the e.m.f. of the solution. These potentiometric studies indicate a release of  $\text{Na}^+$  on irradiation and a thermal process of cation rebinding. In addition, an analysis of the ionic conductivity of composite films containing a complex of compound **43** with  $\text{Na}^+$  showed an increase in the number of carriers in the UV-irradiated samples. The new species are  $\text{Na}^+$  cations released upon photoejection from the complexes.

Photoejection of  $\text{Pb}^{2+}$  cation from its complex with crown-containing chromene on the photoisomerization of chromene from the closed form (compound **44a**) to the open zwitterionic form (compound **44b**) was proved by voltammetry.<sup>64</sup>

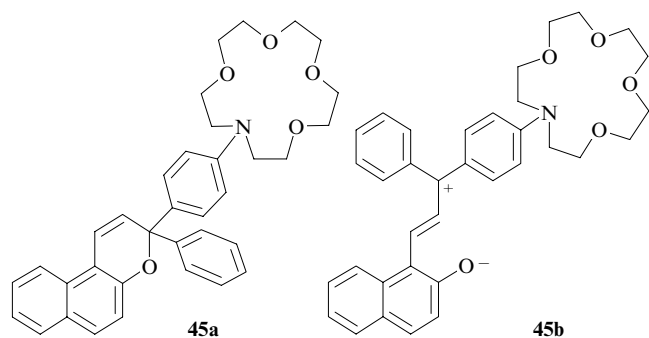


44a

44b

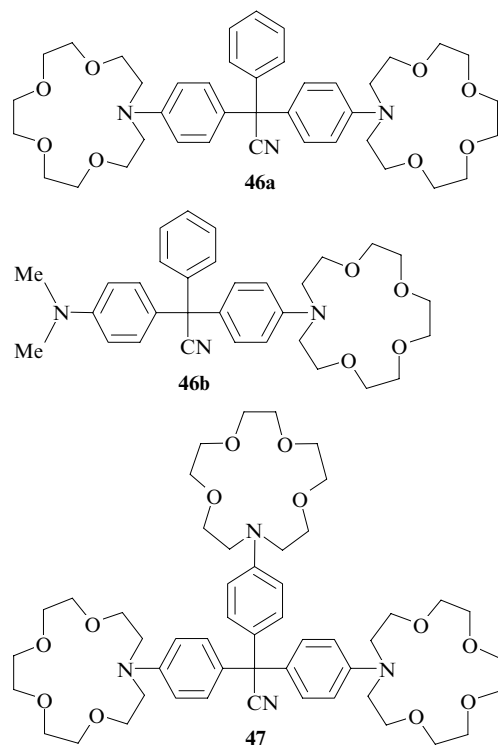
Complexation of the form **44a** with  $\text{Pb}^{2+}$  cation leads to a shift of the reduction potential of the cation from  $-400$  to  $-600\text{ mV vs. AgCl}$  electrode. UV irradiation of the complex of compound **44a** with  $\text{Pb}^{2+}$  at 350 nm causes the appearance of a wave of free  $\text{Pb}^{2+}$  cations in the region  $-420\text{ mV}$  in the voltammogram. This indicates a release of the  $\text{Pb}^{2+}$  cation as the ligand goes from the closed to the open form. In turn, irradiation at 420 nm returns the wave in the region  $-600\text{ mV}$  owing to cation rebinding in the closed form **44a**, which is formed on cyclization of the open form **44b**.

Complexes with alkaline-earth metal cations formed by the ring form of azacrown-containing chromene (compound **45a**), are more stable<sup>7</sup> than the complexes formed by the open form (compound **45b**). The  $\Delta pK$  values of the complexes upon conversion of the form **45a** to **45b** are  $-1.1$  for  $\text{Mg}^{2+}$  and  $-0.9$  for  $\text{Ca}^{2+}$ . Photoejection of metal cations upon pyran ring opening in the molecule of isomer **45a** was proved by microsecond flash photolysis. It was found that the rate constant for dissociation of isomer **45b** with  $\text{Ca}^{2+}$  cation is  $2.49 \times 10^3\text{ s}^{-1}$ , while the rate constant for association of this form with  $\text{Ca}^{2+}$  cation is  $3.46 \times 10^7\text{ litre mol}^{-1}\text{ s}^{-1}$ .



Photochromic ionization of intramolecular sandwich complex of doubly crown-substituted Malachite Green dye **46a** with  $K^+$  cation is followed by complete photoejection of the cation.<sup>65</sup> This was proved by mass spectrometry. In the dark, the mass spectrum exhibits a molecular peak at a mass number of 742 corresponding to a 1:1 complex of compound **46a** with  $K^+$ . The mass spectrum of the UV-irradiated solution exhibited a sharp molecular peak at a mass number of 677 corresponding to free triphenylmethyl ion.

Crown-containing photochromes of the triphenylmethane series, *viz.*, Malachite Green dye **46a,b** and Crystal Blue dye **47**, can selectively bind alkali metal cations and completely photoeject all cations upon exposure to UV irradiation.<sup>66</sup> When considering extraction of cations from the aqueous to organic phase, compound **46a** selectively extracts  $K^+$  cations and to a lesser extent  $Na^+$  cations, compound **46b** selectively extracts  $Na^+$  cations and to a lesser extent  $K^+$  cations, while compound **47** bearing three crown ether substituents selectively extracts  $Cs^+$  cations and to a lesser extent  $K^+$  cations.



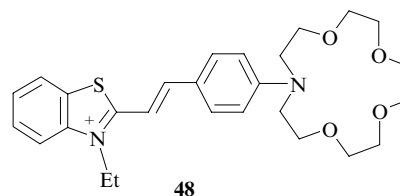
Enhancement of selectivity towards larger cations with an increase in the number of macrocyclic substituents is explained by the formation of complexes with intramolecu-

lar cooperative effect. The intensity distribution of molecular peaks in the mass spectra upon spray ionization of acetonitrile solutions of the complexes with compounds **46a,b** and **47** mainly agrees with the selectivity data obtained in the extraction studies. At the same time, in the case of compound **47** there is a noticeable proportion of peaks corresponding to mixed complexes.

The mass spectra of solutions of photochromes **46a,b**, **47** irradiated in the presence of alkali metal salts exhibit the only molecular peak corresponding to the ionized forms. This indicates a complete photoejection of the cations upon photochromic ionization.

## VII. Reoordination of metal cations in complexes in the ground electronic state

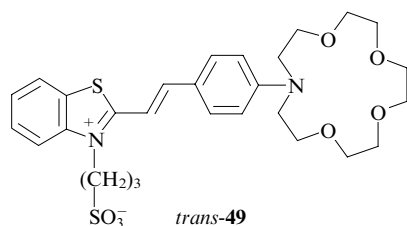
A study<sup>67</sup> of the effect of benzothiazolium residue on the electronic structure and complex-forming ability of phenylaza-15-crown-5 ether fragment showed the introduction of this electron-withdrawing substituent causes an increase in the contribution of the mesomeric quinonoid structure to the electronic structure of the aniline fragment.



As a consequence, the stability constants of the complexes of dye **48** considerably decrease compared to the stability constants of the complexes of its prototype. The model compound phenylaza-15-crown-5 ether forms both 1:1 and 2:1 complexes with  $Ba^{2+}$ , characterized by the stability constants of 20 000 and 220 litre  $mol^{-1}$ , respectively, in acetonitrile. The stability constant of the 1:1 complex of compound **48** with  $Ba^{2+}$  is 250 times smaller (80 litre  $mol^{-1}$ ). The electron density on the nitrogen atom of the macrocycle is crucial to binding a 'soft'  $Ag^+$  cation; therefore, its decrease leads to no binding between this cation and ionophore **48** (binding for the model compound was proved by potentiometry).

Complexation of compound **48** with  $Ba^{2+}$  cation in acetonitrile causes a large (about 4000  $cm^{-1}$ ) bathochromic shift of the absorption maximum. At the same time, even in the case of high concentrations of the metal salt the absorption spectra exhibit a long-wavelength shoulder that cannot be attributed to the residual absorption of free dye. This suggests an equilibrium between complexes with different character of the metal cation binding, *i.e.*, that the reoordination occurs in the ground electronic state owing to a large contribution of the quinonoid structure to the electronic structure of the dye **48**.

In a study of specific features of complexation of a betaine, a crown-containing styryl dye *trans*-**49**, it was established<sup>68</sup> that, unlike the dye **48**, the betaine *trans*-**49** forms not only the 1:1 complexes, but also aggregates comprising four dye molecules and the cation. The effect of cation-induced aggregation was also found for an analogue of *trans*-**49**, which contains a dimethylamino group instead of the azacrown ether fragment. This means that the stability of aggregates is mainly determined by the interaction of the metal cation with betaine sulfo groups.



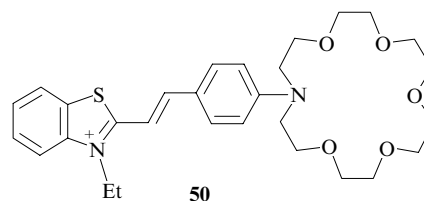
Complexation of dye **48** with  $\text{Ca}^{2+}$  causes hypsochromic shifts of the absorption and fluorescence maxima by 5000 and  $300\text{ cm}^{-1}$ , respectively. The small shift of the fluorescence maximum upon complexation suggests a photoinduced recoordination. As in Ref. 67, the absorption spectra exhibit a long-wavelength shoulder that cannot be treated as a residual absorption of the ligand. The calculated absorption spectrum of the complex at a salt concentration tending to infinity agrees with the experimental spectrum which was measured at high salt concentration and exhibits a long-wavelength shoulder. This shoulder indicates a recoordination reaction in the ground electronic state of the dye.

In contrast to compound **48**, the molecule of dye **49** contains a sulfoalkyl group capable of additionally coordinating metal cations in the formation of 'anion-capped' complexes *cis-49*, which makes them particularly stable.<sup>69</sup> Therefore, compound **49** can serve as chromoionophore with light-controlled cation binding. The *trans-49* isomer behaves as a normal chromoionophore sensitive to metal cations whose concentrations are of the order of  $10^{-2}$  mol litre<sup>-1</sup> and higher, whereas the *cis-49* isomer readily formed on irradiation is a highly sensitive chromophore capable of forming complexes with cations at their concentrations of the order of  $10^{-5}$ – $10^{-4}$  mol litre<sup>-1</sup>. The transition *trans-49* → *cis-49* causes the stability constant of the complex with  $\text{Ba}^{2+}$  to increase by more than three orders of magnitude (from 70 to  $2.7 \times 10^5$  litre mol<sup>-1</sup>).

Complexation of the *trans-49* isomer with  $\text{Ba}^{2+}$  causes a hypsochromic shift of the absorption maxima by about  $3700\text{ cm}^{-1}$ . Since the recoordination reaction occurs in the ground electronic state, the absorption spectrum of the complex of *trans-49* with  $\text{Ba}^{2+}$  exhibits a shoulder, which cannot be treated as residual absorption of free ligand. In contrast to this, complexation of the *cis-49* isomer with  $\text{Ba}^{2+}$  causes no changes in positions of the absorption maxima. The position of the absorption maximum of the complex of the *cis-49* isomer with  $\text{Ba}^{2+}$  almost coincides with the spectral maximum of the free *cis-49* isomer.

Thus, recoordination occurs with particular ease in the 'anion-capped' complexes of the *cis-49* isomer. This is due to an additional stabilizing effect of the cation coordination to the sulfoalkyl group. The complexes of the *cis-49* isomer with  $\text{Ba}^{2+}$  have almost no coordination bond between the cation and the nitrogen atom of the macrocycle in both the excited and ground electronic states.

Attempts to suppress recoordination of  $\text{Ba}^{2+}$  cation in the ground state of the metal complex by immobilizing the dye **50** in the polymeric matrix of a neutral poly(vinylcaprolactam) (PVCa) gel.<sup>70</sup> In a study of the effect of the polymeric matrix on the *trans*–*cis*-photoisomerization, on the complex-forming ability of the crown-containing styryl dye **50** and on the thermal reaction of  $\text{Ba}^{2+}$  recoordination in the complex, it was shown that immobilization of dye **50** in the polymeric matrix has little effect on its absorption spectrum.



The addition of barium perchlorate to the polymer–dye–acetonitrile system causes large swelling of the polymer gel. It was established that the polymer network precludes complexation of dye **50** with  $\text{Ba}^{2+}$  cation due to the interaction between the cation and carbonyl groups of PVCa. High degree of transformation of the immobilized dye to the metal complex can be attained only at high metal salt concentrations such that the molar ratio of  $\text{Ba}^{2+}$  cations and caprolactam units approaches a unity.

The ratio of the intensity of the short-wavelength shoulder to that of the long-wavelength shoulder in the absorption spectrum of the metal complex can serve as a quantitative measure of the extent of thermally induced recoordination of  $\text{Ba}^{2+}$  cation. This ratio is 3.6 for the dye in PVCa gel and 5.1 for the dye in an external gel solution. Thus, immobilization of the dye in gel does not preclude the thermally induced recoordination; rather, it to some extent favours this reaction owing to specific interaction with the carbonyl groups of PVCa.

The dye **50** undergoes a *trans*–*cis*-photoisomerization and a reverse thermal *cis*–*trans*-isomerization both in PVCa gel and in dry PVCa films.

### VIII. Theoretical research on recoordination of metal cations

Reoordination of cations in complexes of chromogenic azacrown ethers with  $\text{Ca}^{2+}$  cation was studied<sup>71</sup> using the density functional approach taking model aryl azacrown ethers containing various electron-withdrawing groups in the aromatic nucleus in *para*-position to the azacrown ether residue as well as a real azacrown-containing styryl dye **48** as examples. Both free aryl azacrown ether molecules and their complexes can adopt two types of conformations:

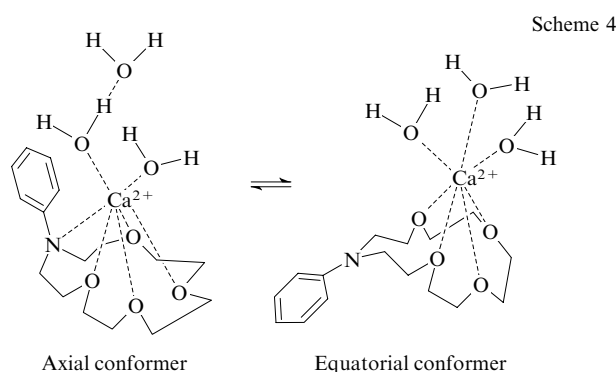
1) axial conformations in which the aromatic ring axis passing through the nitrogen atom of crown ether and the atom in *para*-position to it is normal to the root-mean-square plane of the crown ether (for this plane, the sum of the squared distances to all atoms of the crown ether moiety is minimum);

2) equatorial conformations in which the aromatic ring axis deviates slightly from the root-mean-square plane of the crown ether.

The equatorial conformers are characterized by the metal cation coordination to oxygen atoms of the azacrown ether residue, by the lack of the metal–nitrogen bond and by involvement of the crown ether nitrogen in conjugation with the aromatic ring. In the axial conformers, the metal cation is additionally coordinated to the nitrogen atom of the macrocycle. The electron-withdrawing groups bearing formal positive charges decrease the relative energy of the equatorial conformer and favour cleavage of the metal–nitrogen bond, which leads to recoordination of the metal cation. The experimentally observed photoinduced recoordination in the complexes of azacrown-containing dyes with alkaline-earth metal cations was explained by transitions between the axial and equatorial conformers facilitated by

charge transfer in the excited state of the complex. It was assumed that the long-wavelength shoulder in the absorption spectra originates from recoordination of the metal cation in the crown ether cavity, *i.e.*, by the presence of two forms of the dye in solution, *viz.*, an 'aryl' form in which the cation is bound to four oxygen atoms and the nitrogen atom of the macrocycle, and a 'quinonoid' form with no metal–nitrogen coordination bond. Photoexcitation causes a decrease in the electron density on the nitrogen atom of the macrocycle; therefore, in the excited state of the complexes, the equilibrium will shift towards the formation of the quinonoid structure. The structure with no metal–nitrogen bond makes the major contribution to the fluorescence spectrum. That is why positions of the fluorescence bands of the dye vary only slightly upon complexation.

A study<sup>72</sup> on the effect of local interaction between the metal ion and solvent on the conformations of the calcium complexes of aryl azacrown ethers and azacrown-containing dye **48** showed that the inner coordination sphere of free  $\text{Ca}^{2+}$  cation includes six water molecules or seven acetonitrile molecules. The cation–acetonitrile interaction energy is higher than the cation–water interaction energy up to almost complete filling of the second solvation shell of the cation (eleven water molecules). The inner coordination sphere of the  $\text{Ca}^{2+}$  cation in the macrocycle cavity includes at most three water molecules, whereas the fourth water molecule is displaced to the second coordination sphere. Conformers of the calcium complexes of aryl azacrown ethers and azacrown-containing dye **48** were studied taking account of the local interaction with the solvent (water or acetonitrile). The presence of two to four solvent molecules in the coordination sphere of the cation favours a decrease in the relative energies of the conformers with no metal–nitrogen bond, *i.e.*, facilitates recoordination in the ground state (Scheme 4). If the *para*-position with respect to the nitrogen atom of the crown ether is occupied by an electron-withdrawing group bearing a formal positive charge, the relative energy of the equatorial conformer becomes sufficiently low even without inclusion of solvation effects, which enables recoordination in the ground state.



The nature of the hypsochromic shifts of the absorption maxima of the crown-containing styryl dyes **48** and **50** upon complexation was studied by the time-dependent density functional theory.<sup>73</sup> The nature of these shifts is different for the equatorial and axial complexes. In the former, the nitrogen atom of the macrocycle has a planar configuration and is not coordinated to the metal cation. In this case, the shifts are small and due to electrostatic field of the cation. In the axial complexes, the nitrogen atom of the macrocycle is considerably 'pyramidalized' and excluded from the

electronic conjugation owing to formation of the coordination bond with the metal cation. In this case, the hypsochromic shifts are large and due to the antiauxochromic effect of the metal cation, which correlates with the degree of 'pyramidalization' of the nitrogen atom of the macrocycle.

The geometries and electron density distributions for both types of complexes change insignificantly on going to the excited electronic state. This leads to an increase in the quantum yield of fluorescence of the dyes **48** and **50** because the chromophore fragments in their complexes have equalized bond orders and higher rigidity. At the same time, the energies of excited equatorial complexes are about  $3000\text{ cm}^{-1}$  lower than those of excited axial complexes; this makes photoinduced recoordination energetically favourable.

A characteristic feature of free compounds **48** and **50** (unlike their complexes) consists in fast nonradiative deactivation due to free rotation of the  $\pi$ -system of the molecule about formally single bonds which become true single bonds upon excitation. In contrast to intuitive ideas, the contribution of the mesomeric quinonoid structure to the electronic structures of excited molecules **48** and **50** is no larger than its contribution to the ground state, while nearly vanishes. This is indicated by elongation of the formally single bonds, which can freely rotate upon excitation, and by equalization of the bond lengths in the aromatic nucleus of the aniline fragment. The results of these calculations agree with the results obtained in an experimental study,<sup>74</sup> according to which the formation of the nonfluorescent TICT state is the main channel of deactivation of excited molecules, while the quantum yields of fluorescence and *trans*–*cis*-isomerization are low.

Probably, consideration of only relaxed Franck-Condon states of the dyes **48** and **50** characterized by a low degree of charge transfer and small Stokes shift ( $2100\text{ cm}^{-1}$ ) cannot reveal the complexity of photoinduced recoordination and the role of intramolecular charge transfer. Often, fluorescent samples of chromogenic crown compounds have some other nature related to the formation of highly polar ICT states. These states are responsible for the fluorescence of such related compounds, as **6** and **9**, and are characterized by anomalous Stokes shifts of the order of  $5500$ – $6500\text{ cm}^{-1}$  and more. In this case, the formation of solvent-separated cation–fluorophore pairs with maximum structural rearrangements in the macrocycle is ascribed to the charge-transfer state.

## IX. Conclusion

Photoinduced recoordination of metal cations in the crown ether cavities of chromogenic compounds is a fast relaxation process leading to abnormally large Stokes shifts in the spectra of the complexes and to small shifts of maxima in the fluorescence spectra upon complexation. Transient absorption spectroscopy studies of photoinduced recoordination revealed two main stages of the process (see Scheme 1). The first stage takes from a few hundreds of femtoseconds to a few picoseconds and involves the formation, from the locally excited complexes (LM)\*, of the so-called cation–fluorophore contact pairs  $\text{L}^*\text{M}$  with the same degree of charge transfer as that of the locally excited state of free dye. The second stage takes from a few picoseconds to a few tens of picoseconds and involves the formation of solvent-separated cation–fluorophore pairs

L\*/S/M with the degree of charge transfer equal to that of the ICT or TICT state of free dye. The results obtained for the systems with dual fluorescence which exhibit steady-state emission of a certain pair from the states of excited molecules of the complexes (see above) are complementary to the transient absorption spectroscopy data.

Photoinduced recoordination also occurs in metal complexes of such compounds whose excited states differ from the ICT states (not highly polar in nature). These are the cyanine, styryl and butadienyl dyes, as well as styrylheterocyclic compounds whose free molecules are characterized by normal Stokes shift. The introduction into the heterocyclic residue of electron-donor groups usually suppresses photoinduced recoordination. On the contrary, complexation of the heterocyclic residue with the second metal cation promotes the photoinduced recoordination. Replacement of the azacrown ether fragment by a crown ether moiety also often inhibits photoinduced recoordination.

Photoejection of the cation from the complexes of conventional crown-containing dyes is usually difficult to prove because the main spectral changes occur in the first stage of the photoinduced recoordination reaction. At the same time, photoejection of the cation was established with certainty for the complexes of crown-containing compounds with the transition-metal central ion. The rate of thermal process of cation rebinding is proportional to the salt concentration in solution. Photoejection of cations also efficiently occurs in the complexes of photochromic compounds in the course of their interconversions even if the structure of the ionophoric fragment remains unchanged, but induces an electron density redistribution in it.

According to the results of recent theoretical studies, recoordination of metal cations is possible in both the ground and excited electronic state and should cause the type of the complex to change from the axial to equatorial (*i.e.*, the angle between the chromophore plane and the root-mean-square plane of the macrocycle should change from a nearly right angle to a nearly flat angle). In this case, the metal–heteroatom internuclear distance should considerably increase.

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