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Applied Fluorescence in Chemistry, Biology and Medicine



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Wolfgang Rettig · Bernd Strehmel · Sigurd Schrader ·
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Applied Fluorescence in Chemistry, Biology and Medicine

With 235 Figures and 32 Tables



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Fluorescence Properties of Crown-Containing Molecules

M. V. Alfimov, S. P. Gromov

1 Introduction

Crown compounds may be considered as the most interesting and promising components of photosensitive systems [1–6]. Crown compounds contain several heteroatoms with lone pairs that can participate in formation of coordination bonds with metal cations. The complexing ability of crown compounds depends strongly on their molecular and spatial structures.

For example, photochemical behavior in the absence and presence of metal ions is one of the most intriguing properties of crown-containing dyes [5]. If a crown ether and a dye are connected by a covalent bond in such a way that one or two heteroatoms of the macrocycle are in conjugation with the dye chromophore, the additivity in the manifestation of specific properties of such a crown-ed dye may be violated. Photostructural transformations in the dye moiety can change the efficiency of metal cation binding by the crown-ether moiety, whereas the complexation, in turn, may lead to a change in the spectral and photochemical characteristics of the dye moiety.

Interdependent reactions of this type can occur in supramolecular structures formed by self-assembling crown-containing dyes and metal ions. This phenomenon can be used for the development of new types of photophysical and photochemical molecular devices [7].

Owing to its high sensitivity and selectivity, fluorescent spectroscopy is widely used in various areas of physics, chemistry, biology and medicine. Development of fluorescent techniques both for determination of trace amounts of metals and for identification of metal ions in various complex systems such as, for example, as biological objects is of great interest [8, 9]. Introduction of groups into organic luminophores capable of forming chelate complexes with metal ions was a first step in this direction [9–11]. The purpose was to obtain derivatives whose fluorescence intensity and/or fluorescence wavelength can undergo changes upon formation of metal complexes. The use of fluoroionophores containing an organic luminophore and a crown ether, which exhibit high selectivity and high stability constants, provides new powerful tools for research [12–19].

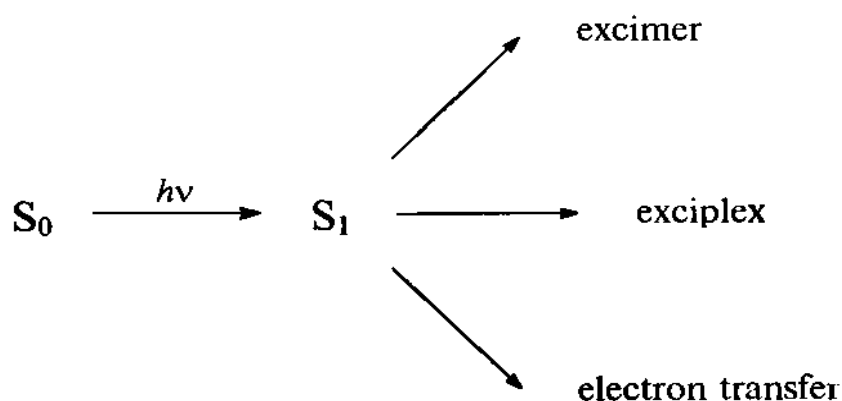
These studies have shown that the values of the fluorescence band shifts on complexation are determined by the following factors [6, 12]:

1. The surface charge density of a metal cation. In a series of cations of identical ionic radius, the spectral shift increases with increasing charge.
2. Geometrical complementarity between a cation and a crown ether cavity. For cations of an identical charge, the better this conformity, the greater the value of the spectral shift.
3. The nature of a solvent. All fluoroionophores under consideration exhibit an appreciable solvatochromism. As a result, the value of the ionochromic effect may in a certain degree depend on the solvent polarity.

In subsequent works, as a basis for the construction of crown-containing fluorophores, systems were chosen in which an effective intramolecular fluorescence quenching can occur by one of the basic mechanisms: via intermediate formation of an excimer, exciplex or by photoinduced electron transfer. An excimer is known to be formed by the interaction of an excited molecule with an unexcited molecule of the same kind, whereas an exciplex is formed by interaction of the excited molecule with an unexcited molecule of a different kind. All of these processes are summarized in Fig. 1.

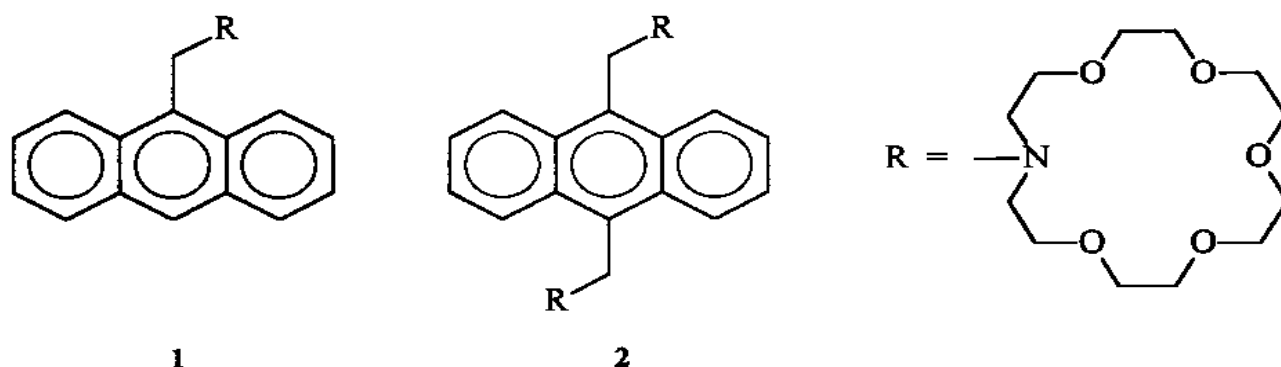
A crown-ether moiety can be linked to a fluorophore in such a way that the formation of a complex with a metal ion would strongly affect the quenching efficiency. Systems in which complexation retards the fluorescence quenching and leads to an enhancement of the fluorescence intensity are of specific interest

Fig. 1. Different pathways of deactivation of electronic excited states (fluorescence quenching) for crown-containing fluoro-ionophores



2 Crown-Containing Arenes

Examples are provided by derivatives of anthracene, **1** and **2**, which exhibit very weak fluorescence in methanolic solutions (for example, $\phi_f = 0.003$ for **1**). In this event, the anthracene fluorescence is efficiently quenched by intramolecular electron transfer from the nitrogen lone pair of the crown-ether moiety to the electronically excited anthracene moiety [20, 21]. Addition of alkali-metal salts to solutions leads to a significant enhancement of the fluorescence quantum yields (by a factor of 47 in the case of potassium ion), while other spectral parameters remain unaffected. The effect of restoring the anthracene fluorescence on incorporating alkali-metal cations into the monoaza-crown ether is



assumed to be connected with stopping the above-mentioned electron transfer by the metal cations.

It is obvious that in the case of compound 2, the fluorescence enhancement can only occur on blocking the lone pairs of the nitrogen atoms of both crown-ether moieties. This was achieved by using dications of polymethylene diammonium, which are capable of forming pseudo-cyclic complexes with 2. As an example, the fluorescence quantum yield of 2 was found to increase by two orders of magnitude in the presence of dications with four methylene units [21].

On replacement of the azacrown-ether fragment in compound 1 by a benzo-15-crown ether moiety, the process of photoinduced electron transfer becomes inefficient [22]. In this case, the complexation with metal cations does not practically influence the fluorescence quantum yield. However, on introduction of an acceptor group CN in the anthracene nucleus, the intramolecular quenching becomes significant and formation of a complex with a metal cation results in an enhancement of the fluorescence quantum yield.

A number of anthracene-containing cryptands were synthesized [23, 24], in which the anthracene nucleus is connected at positions 9 and 10 with the nitrogen atoms of diaza-18-crown-6 ether through identical polymethylene chains. For these compounds, besides weak fluorescence connected with the anthracene nucleus, a greater long-wavelength fluorescence is observed that is caused by formation of an exciplex between the electronically excited anthracene and the nitrogen atoms of the diazacrown-ether moiety. Upon complexation the nitrogen lone pairs are blocked by metal cations and the formation of the exciplex is suppressed. As a consequence, the fluorescence band of the exciplex disappears and the anthracene fluorescence enhances strongly, the overall quantum yield also being sharply increased.

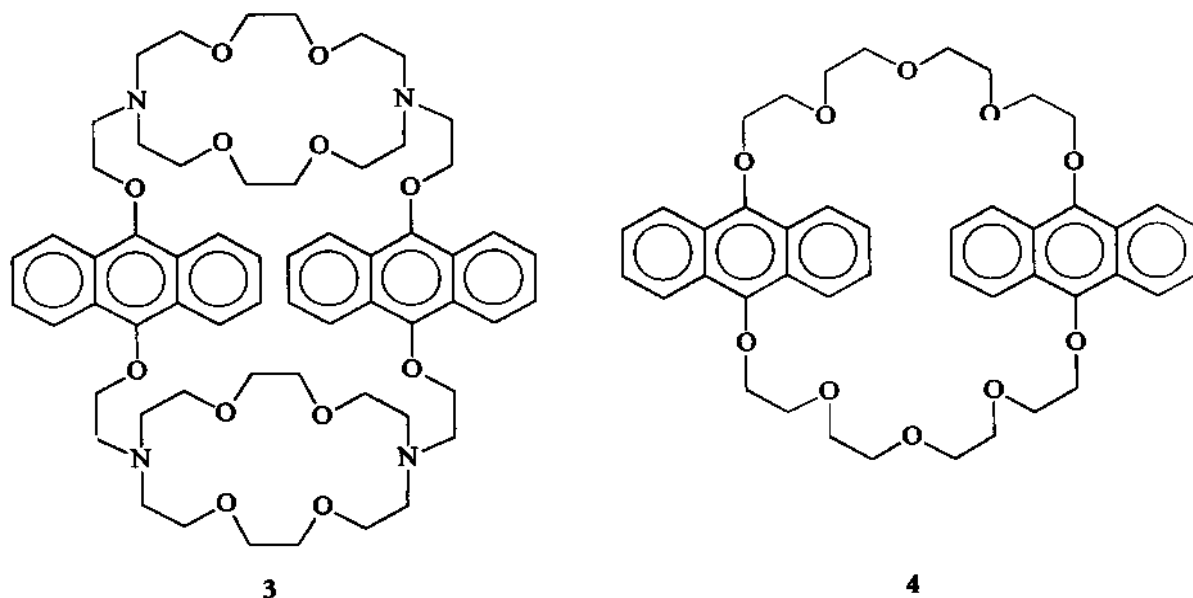
The fluorescence properties of a cylindrical receptor 3 with two sites of binding [25–27] are of interest. Similar to anthracenocryptands, compound 3 displays a dual fluorescence. However, in this case, the authors ascribed the long-wavelength component of the emission spectrum to the intramolecular excimer formed as a result of interaction between two anthracene rings arranged in an appropriate pattern to each other (see Table 1). The exciplex formation between the anthracene ring and the nitrogen atom of the crown-ether moiety appears to be complicated by steric hindrance owing to the rigidity of the molecule. Upon formation of a complex with two Rb^+ ions, the fluorescence caused by excimer formation enhances strongly. This cylindrical receptor is able to recog-

Table 1. Photophysical Characteristics of **3** in the Absence and Presence of MClO_4

	3	Na^+	K^+	Rb^+	Cs^+
Φ_{ft}	0.06	0.22	0.21	0.24	0.21
Φ_{fm}	0.03	0.22	0.13	0.02	0.02
Φ_{fe}	0.03	–	0.08	0.22	0.19
λ_{f}	530	–	570	560	530

Φ_{ft} , Φ_{fm} and Φ_{fe} – quantum yields of overall, monomer, and excimer fluorescence; λ_{f} – excimer fluorescence maximum.

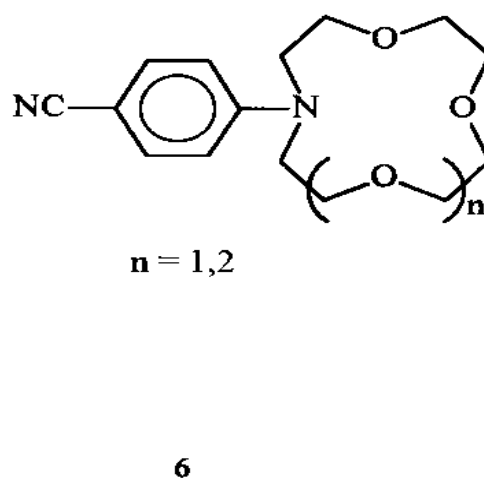
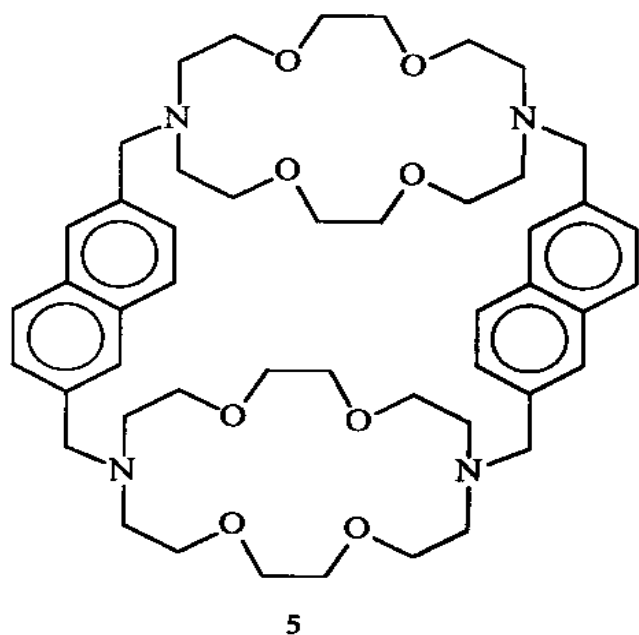
nize linear organic dications. As an example, heptamethylenediammonium dication is located on complexation between two anthracene rings thus hindering the excimer formation. In this compound the intensity of the excimer fluorescence falls sharply on complexation, while the intensity of anthracene fluorescence (monomer fluorescence) grows.



Bisanthraceno-crown ether **4** was also found to display a dual fluorescence consisting of a “monomer” and excimer emission [28]. The compound was found to form a complex of 1:2 stoichiometry with Na^+ , and a positive cooperative effect (when the first complexation facilitates complexation of the second cation) was discovered for the complexation process in methanol and acetonitrile. In acetonitrile, the ability of **4** to complex Na^+ is appreciably higher in the excited state than in the ground state. The effect observed is assumed to be due mainly to a shaping of the cavity that is triggered by intramolecular excimer formation.

A cylindrical receptor **5** with two binding sites was synthesized by using dimethylnaphthalenes [29]. In CH_2Cl_2 solution at room temperature, the disap-

pearance of dimethylnaphthalene fluorescence and the appearance of a broad and weak fluorescence band at 438 nm is characteristic of **5**. This appears to be connected with the intramolecular charge transfer between the nonbonding orbital of the amine moieties and the orbitals of the naphthalene rings. Addition of an acid causes the protonation of the four amine units. As a consequence, the CT fluorescence disappears, whereas the dimethylnaphthalene fluorescence peak at 342 nm reappears and its intensity increases by a factor of about 800. Hence, compound **5** may be considered as a sensitive fluorescence sensor highly responsive to protons.



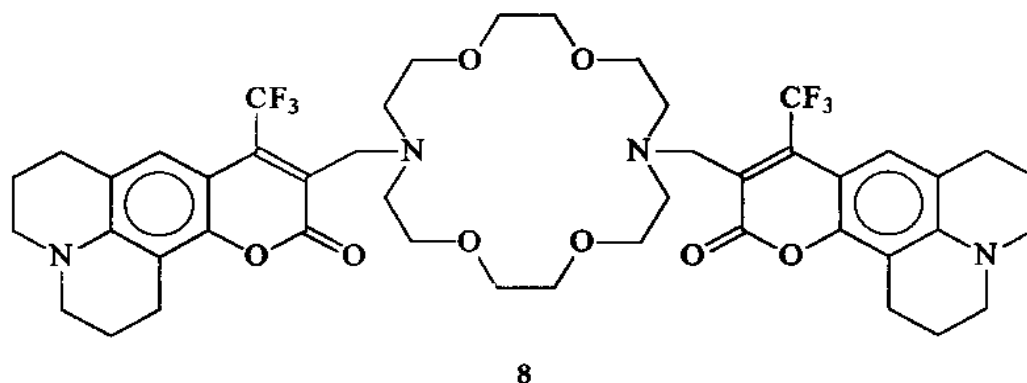
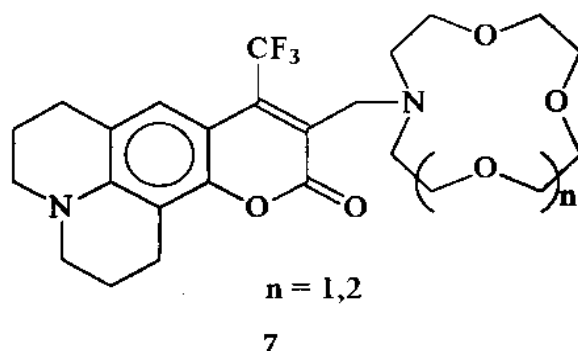
Compounds in which a twisted intramolecular charge transfer (TICT) state is formed on electronic excitation may be considered as perspective fluoroionophores. Simple examples of such systems are crown-containing benzonitriles **6** [30].

These compounds display a dual fluorescence. A short-wavelength component of the emission spectrum of **6** corresponds to the fluorescence from the initial excited state, whereas the long-wavelength component is connected with fluorescence from the TICT state. In the presence of metal cations, the intensity of the long-wavelength fluorescence decreases because a metal cation bound to the crown-ether moiety destabilizes the TICT state. The intensity of the short-wavelength fluorescence increases strongly because one of the main channels of its quenching becomes inefficient upon complexation.

3 Crown-Containing Coumarins

In reported works [31, 32], the properties of fluoroionophores **7** and **8** based on coumarin 153 are considered. On complexation of compounds **7** with alkali,

alkaline-earth and transition metals, the shifts in long-wavelength of the fluorescence band of **7** and an appreciable increase in the fluorescence quantum yields were observed. These effects seem to be connected with increasing the degree of the intramolecular charge transfer in the molecule (increase in conjugation in the chromophore) caused by direct interaction of the metal cation, which is within the cavity of the crown-ether moiety, with the carbonyl group of the coumarin.



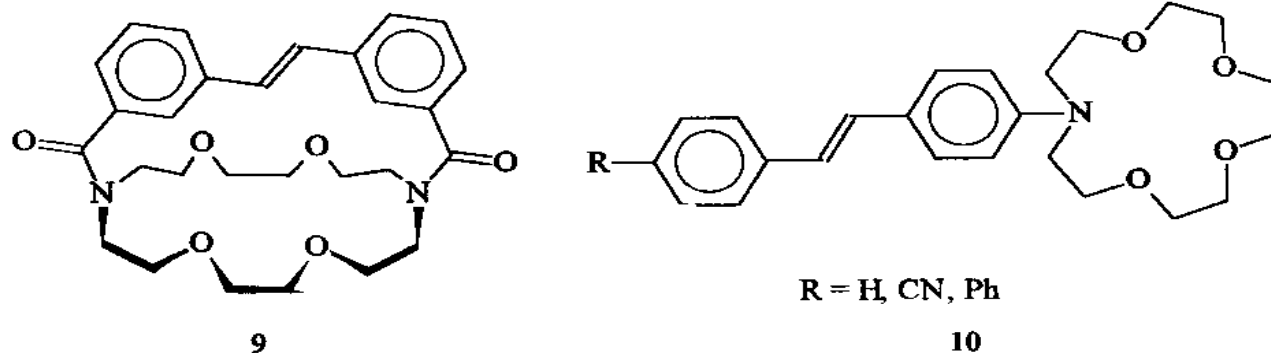
A significant effect of fluorescence self-quenching is characteristic of compound **8**. The mechanism of the self-quenching was not investigated; however, it was assumed that the quenching is connected with intramolecular interaction of two coumarin moieties in the ground state. Such a mechanism is usually used for the description of the concentration quenching of the fluorescence of some laser dyes. The excimer mechanism of self-quenching of **8**, by analogy with the self-quenching of anthracene derivatives, may be an alternative mechanism.

On complexation of **8** with metal cations of small ionic radius, the fluorescence quantum yield changed insignificantly. However, on binding of large cations, such as Ba^{2+} and K^+ , which appear to hinder the interaction of two coumarin rings, the fluorescence intensity is enhanced.

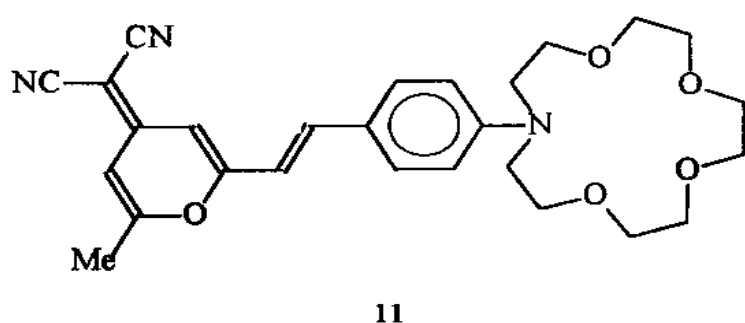
4 Crown-Containing Diarylethylenes

Crown ether **9** with a fluorescent stilbene-cap was the first of the synthesized fluoroionophores of this type [33]. As opposed to the ions of large ionic radius,

such as K^+ , Rb^+ and Cs^+ , complexation of *trans*-9 with Li^+ and Na^+ ions in acetonitrile was found to result in fluorescence quenching. Upon UV irradiation, *cis-trans* isomerization takes place leading to a considerable change in the ability of the compound to extract the alkali metals from water to benzene. It should be noted that UV irradiation which produces photoisomerized *cis*-9 leads to an enhancement of extractability of Li^+ and Na^+ (i. e., to a conformational change in the crown-ether moiety).



Recently, examples of crown-containing derivatives of stilbene 10, which exhibit the twisted intramolecular charge transfer states have been published [34, 35]. An analysis of time evolution of the transient absorption spectra of 10 ($R = Ph$) in the sub-picosecond range after excitation pulse has shown that a bi-exponential decay is observed thus indicating the existence of two fluorescing excited states - the usual Franck-Condon state and a TICT state. Complexation of compounds 10 with Ca^{2+} results in small blue shifts of the fluorescence bands, whereas the fluorescence quantum yields remain unaltered. The effect of metal ions on *trans-cis* photoisomerization of compound 10 was not studied in these works.



5 Crown-Containing Merocyanine Dyes

In a series of works [36-39], the fluorescence of azacrown-containing merocyanine 11, which is an analog of the well-known laser dye DCM, containing the aza-15-crown-ether fragment instead of the dimethylamino group, and its complexes with alkali and alkaline-earth metal cations was studied. The fluo-

Table 2. Photophysical Characteristics of Dye 11 and Its Complexes with Metal Cations

Compound	λ_f (nm)	Φ_f	τ_f (ns)
11	621	0.73	2.20
11 · Li ⁺	606	0.57	1.88
11 · Na ⁺	611	0.65	2.06
11 · Mg ²⁺	610	< 0.05	2.10
11 · Ca ²⁺	608	0.27	1.94
11 · Ba ²⁺	611	0.40	1.99

rescence spectra of the free and complexed compound are alike in shape and only a small hypsochromic shift of 10–20 nm is observed (see Table 2). Complexation was found to induce fluorescence quenching to an extent dependent on the nature of the metal cation. In contrast to the quantum yields, only a slight decrease in the excited-states lifetimes was observed.

It should be noted that compounds having the hydrogen atom instead of the azacrown-ether moiety exhibit a very weak emission band ($\phi_f = 3 \cdot 10^{-4}$) located at a much shorter wavelength ($\lambda_f = 490$ nm) than that of free or complexed compound 11. Hence, the fluorescence emission of 11 may be assumed to result almost solely from an intramolecular charge transfer from the donor moiety (amino group) to the acceptor moiety (dicyanomethylene group). Excitation seems to lead first to a nonemissive “locally” excited (LE) and then to the ICT state having a high fluorescence quantum yield (see Fig. 2).

The absence of marked differences between the lifetimes of 11 and its complexes with metals indicates that the radiative and nonradiative rate constants and the quantum yield of the ICT state are almost unaffected by complexation. However, the overall quantum yield of a given complex depends on the competition between the nonradiative decay from the LE state to the ground state and the intramolecular charge transfer. The competition strongly depends on the ability of the cation to monopolize the lone pair of the crown nitrogen atom, i. e., to decrease the potentiality of charge transfer.

Slight changes in position and shape of the fluorescent spectra of 11 on cation binding as well as in its fluorescence lifetime (whereas the quantum yield is decreased) may be explained by the photoejection of the cation. Direct evidence of photoejection of Li⁺ and Ca²⁺ ions from a crown-ether-linked merocyanine was obtained by picosecond spectroscopy. The appearance of a delayed absorption band (at 530 nm) after subpicosecond excitation appears to be compelling evidence for cation ejection from the excited complexes. It is assum-

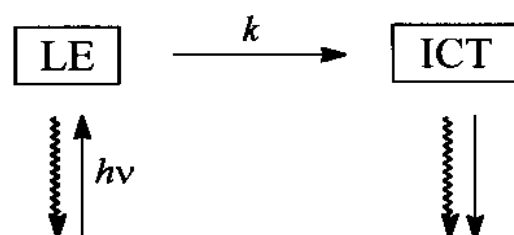
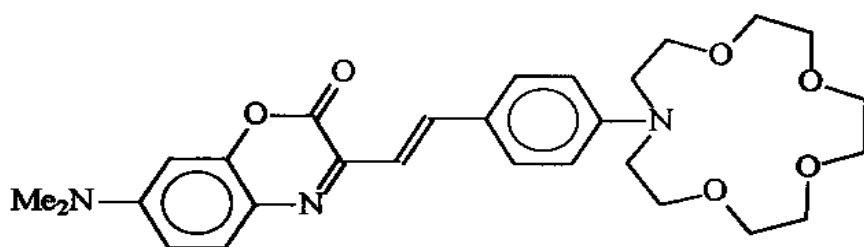
Fig. 2. Kinetic scheme showing emission properties of dye 11

Table 3. Photophysical Characteristics of Dye 12 and Its Complexes with Metal Cations

Compound	λ_f (nm)	Φ_f	$k_{nr} \cdot (10^{-8} \text{ s}^{-1})$
12	642	0.33	3.2
12 · Li ⁺	612	0.44	2.0
12 · Na ⁺	611	0.38	2.5
12 · Mg ²⁺	573	0.48	1.6
12 · Ca ²⁺	574	0.64	1.1
12 · Ba ²⁺	576	0.59	1.3

ed that owing to photoinduced charge transfer from the nitrogen atom of the crown to the dicyanomethylene group, the nitrogen atom of the crown becomes positively polarized, and the resulting repulsion with the complexed cation causes its photoejection. The authors noted that in fact the photophysical data indicate that the coordination bond between the cation and the nitrogen atom of the crown is broken, but some of these cations may still interact with the oxygen atoms of the crown. The fact is that upon photoexcitation an equilibrium is reached on a time scale of a few picosecond, which is much shorter than the time required for cation separation by diffusion.

Unusual properties are exhibited by crown-containing benzoxazinone 12 and its complexes with metal ions [40–43]. Alkaline-earth cations markedly shift the emission wavelength (from 642 nm for the free molecule to 578 nm in the presence of calcium perchlorate) and enhance the fluorescence intensity of 12 (see Table 3). Since the crown can act as a second electron donor (in addition to the dimethylamino group), the observed hypsochromic shift is assumed to be connected with a reduction in the donor character of the crown nitrogen atom, which is involved in the conjugation of the molecule, upon complexation with a metal ion.



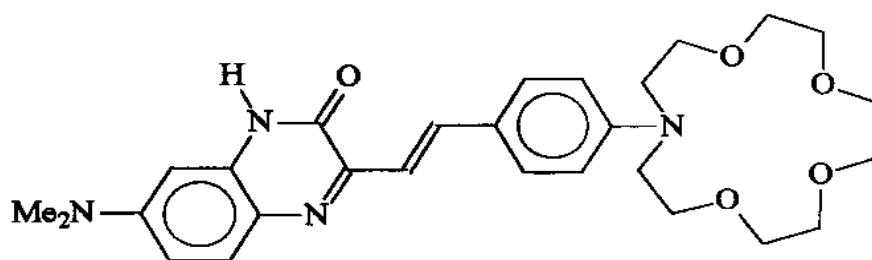
12

It is the opinion of the authors that the differences in the fluorescence intensity of 12 and its derivatives, in which the crown-ether moiety is replaced by a hydrogen atom or an NMe₂ group, are connected with differences in their non-radiative decay rates k_{nr} . A large value of k_{nr} for a dye with the NMe₂ group ($k_{nr} = 4.8 \cdot 10^8 \text{ s}^{-1}$) seems to indicate the relatively free rotation of the group in respect to a crown-ether moiety. The properties of the complexes must be close to the properties of the unsubstituted compound because the nitrogen lone pair takes part in the formation of the bond with a metal ion. In this case, k_{nr} for

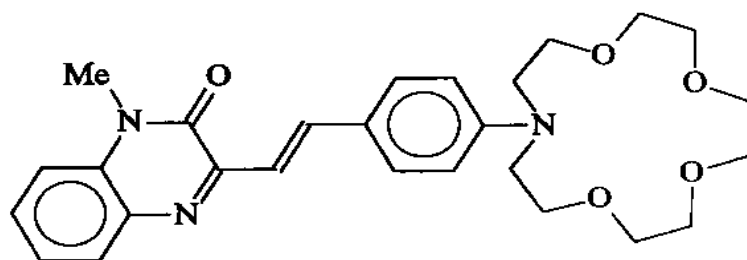
complexes must have a value intermediate between the values characteristic of 12 and its derivative with the hydrogen atom ($k_{nr} = 1.1 \cdot 10^8 \text{ s}^{-1}$). This conclusion has been confirmed experimentally.

At the same time some other properties, for example, strong dependence of the fluorescence spectrum on the solvent polarity, may be explained in the framework of the model of the TICT state.

Crown-containing benzodiazinones 13 and 14 have a similar structure [44–46]. Upon addition of magnesium and calcium perchlorate in acetonitrile solution, a small hypsochromic shift (up to 34 nm) is observed. In the case of dye 14, the fluorescence quantum yield on complexation appreciably increases, while for 13, on the contrary, the yield falls. However, the lifetimes of the excited state condition of 13 and 14 and their complexes with Ca^{2+} are about identical.



13



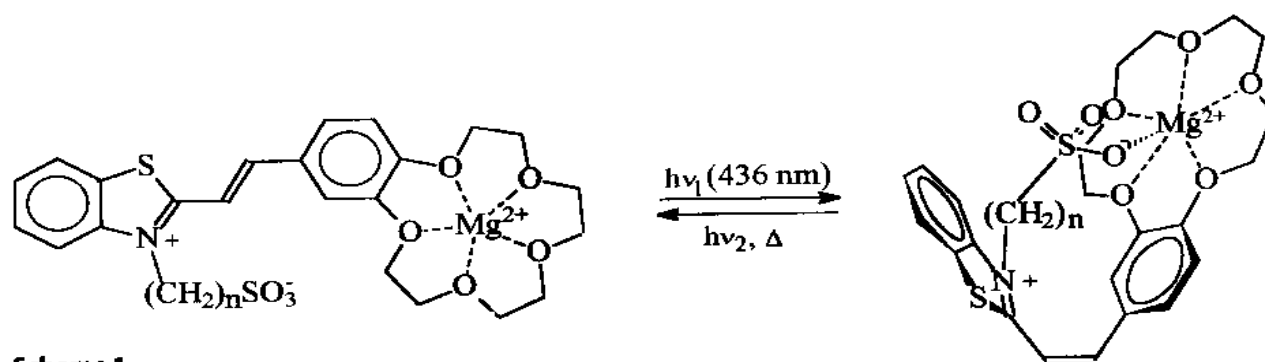
14

On going from 13 to 14, a hypsochromic shift, a large value of the Stokes shift, and a greater nonradiative constant are obtained. This indicates the existence of a TICT state for dye 14. For a correct description of physical properties of these dyes it is necessary to also take into account the rotation isomerism and photoisomerization around the C=C bond.

6

Crown-Containing Styryl and Butadienyl Dyes

The intense absorption bands in the visible region of the spectrum of the *trans*-isomers, the relative high values of the quantum yields of the fluorescence (φ_f) and the *trans-cis* isomerization (φ_{t-c}) allows one to use such compounds for the luminescent information recording [47]. However, thermal instability of non-fluorescent *cis*-isomers is an essential disadvantage: *cis*-isomers cannot be isolated and kept for a long time.



Scheme 1

Earlier, we investigated the interconnected reactions of photoisomerization and complexation of crown-containing styryl dyes (CSD) [48]. Formation of a so-called anion-“capped” complex was observed, in which an additional coordination bond is formed between the SO_3^- group of the N-sulfoalkyl substituent of the heterocyclic ring of the *cis*-form of a styryl dye and a metal cation located in the crown-ether cavity (Scheme 1) [49–51].

This leads to a strong hypsochromic shift of the absorption long-wavelength band and, simultaneously, to a sharp increase in the thermal stability of the *cis*-form of the dye.

Photochemical studies [52] have also shown that such molecules in solutions in the presence of metal cations are capable of self-organizing in the pairs of the “head-to-tail” type, so that the double bonds are located one above the other. It was found that upon irradiation of solutions of such dimeric complexes, a photochemical regio- and stereospecific [2+2]-cycloaddition of the “head-to-tail” type takes place. As a result, a nonfluorescent cyclobutane isomer is formed that is only one of the 11 theoretically possible isomers of cyclobutane (see Fig. 3) [53–55].

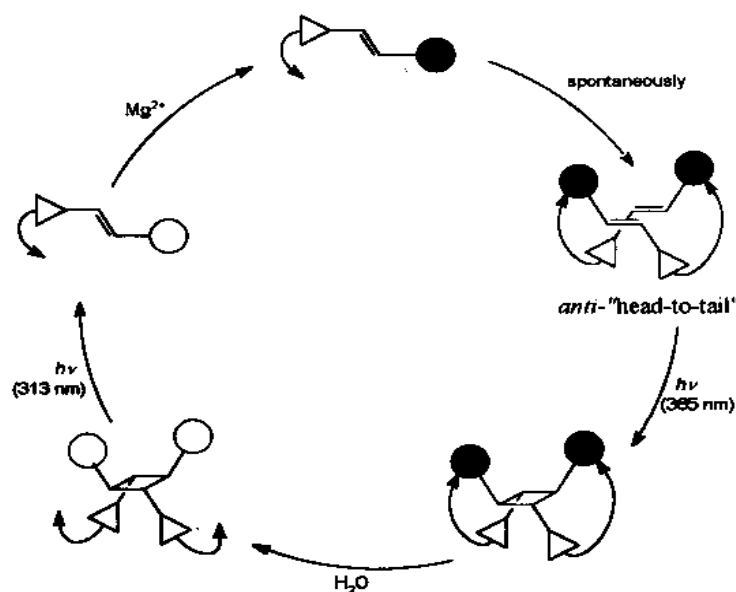


Fig. 3. Transformations of CSD upon complexation and illumination

○ – benzocrown fragment; ● – benzocrown fragment with M^{n+} ; ▷ – heterocyclic residue; ◡ – $(\text{CH}_2)_n\text{SO}_3^-$, $n = 3 - 4$

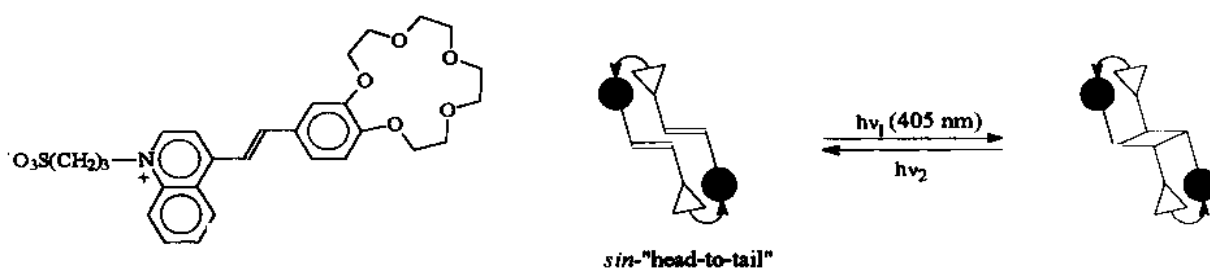


Fig. 4. Dimeric complex and cyclobutane formed by using CSD with a residue of 1,4-disubstituted quinolinium

While dimerization of the *anti*-“head-to-tail” type plays a main role in the case of crown-containing styryl dyes with a benzthiazole residue, this reaction is impossible for 1,4-disubstituted quinoline owing to steric hindrance. Though in the previous example dimerization of the type *syn*-“head-to-tail” is of secondary importance for the same reasons, in the latter case it becomes basic. On irradiation of solutions of such dimeric complexes, a photochemical stereospecific [2+2]-cycloaddition ($\Phi = 0.15$) occurs to also form a nonfluorescent isomer of cyclobutane (see Fig. 4) [56].

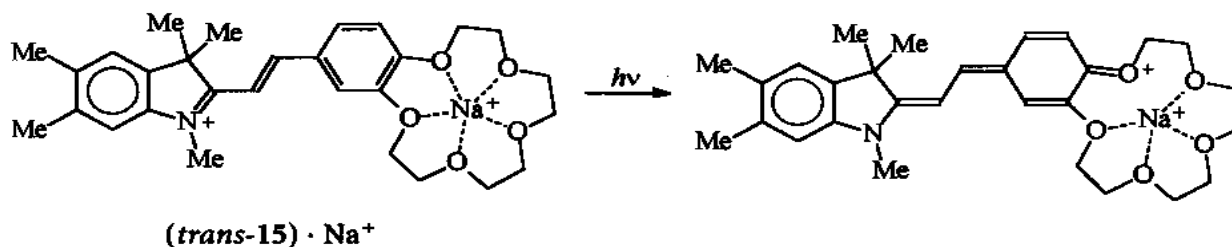
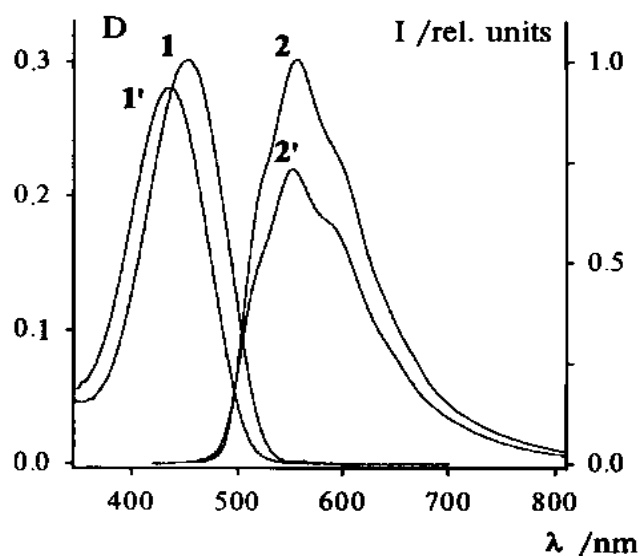
The effects observed permit us to consider the CSD as promising elements on development of fluorescent photoswitching molecular devices.

The *trans*-isomers of CSD are weak fluorescent in MeCN and MeOH at 293 K (fluorescence quantum yield $\varphi_f = 0.002-0.1$) [57, 58], whereas *cis*-isomers of CSD exhibit no fluorescence. The fluorescence intensity of *trans*-isomers of CSD increases significantly on cooling (up to $\varphi_f = 0.6$ at 173 K) in viscous solvents or in a polymeric matrix [57, 59]. An increase in the electron-donating ability of a heterocyclic residue and a crown-ether moiety of CSD results in a red shift of the fluorescence bands and in an increase in φ_f . The enhancement of the fluorescence lifetime from 150 ps in MeOH up to 2.3 ps in glycerol [60–62] is characteristic of CSD. We attribute the observed changes in the fluorescence lifetimes to a barrier *trans-cis* isomerization occurring in the excited singlet state.

As a rule, the addition of salts of alkali and alkaline-earth metals leads to a hypsochromic shift of the fluorescence maxima and to quenching of the fluorescence. The decrease in φ_f cannot be explained by changing the photoisomerization quantum yield, because complexation of CSD is not accompanied by an appreciable change in φ_{t-c} . It is known that the introduction of a methoxy group into the conjugation chain of a chromophore of an organic luminophore usually results in an increase in φ_f [63]. Hence, it could be expected that complexation with a metal ion (when the lone pairs of the oxygen atoms participate in the formation of the coordination bonds and thus are removed from conjugation with the chromophore) will cause an opposite effect, i. e., a decrease in φ_f . We actually observed this in our experiments [57].

In some cases, an unusual behavior of CSD was observed: the position of λ_f changes only slightly after the addition of metal salts [57, 64]. A small shift or even the absence of the shift of the fluorescence spectrum on complexation in comparison with a significant shift of the long-wavelength absorption band, as was found, for example, for *trans*-15 and Na^+ (see Fig. 5), may be explained by

Fig. 5. Absorption spectra (1, 1') at $T = 293$ K and corrected fluorescence spectra (2, 2') at 173 K of *trans*-15 in EtOH. Concentrations of NaClO_4 are 0 (1, 2) and 0.01 mol L^{-1} (1', 2'), respectively



Scheme 2

changing the character of coordination of a metal ion and its position in the macroheterocycle. On transition in the first excited state of *trans*-15, the electronic density on the oxygen atom incorporated in the chromophore and located at the *para*-position with respect to the C=C bond decreases; as a consequence, the coordination bond of the metal ion with this oxygen atom becomes weak (Scheme 2).

This leads to such a change in the equilibrium position of the metal ion in the macroheterocycle that it is bound predominantly to four of the five oxygen atoms of the 15-crown-5 ether. The phenomenon observed can be defined as a photoinduced recoordination of the metal cation.

We observed an interesting example of recoordination in the ground and excited states of *trans*-16 (see Scheme 3) [65]. Analysis of the absorption spectrum shape (see Fig. 6, a) has shown that the long-wavelength shoulder of the band with a maximum at 410 nm cannot be attributed to absorption of the free ligand molecules. This conclusion is confirmed by the fact that the calculated spectrum practically coincides with the experimental one recorded after the addition to a solution of *trans*-16 of a large amount of $\text{Ca}(\text{ClO}_4)_2$ ($C_M = 0.5 \text{ mol L}^{-1}$).

The origin of the low-intensity band can be explained by the existence of a thermodynamic equilibrium between two forms of the complex. In the one form, which corresponds to the long-wavelength band that peaked at 410 nm, the Ca^{2+} ion interacts effectively with the nitrogen atom of the crown-ether moiety. In the other form, the coordination bond with the nitrogen atom is

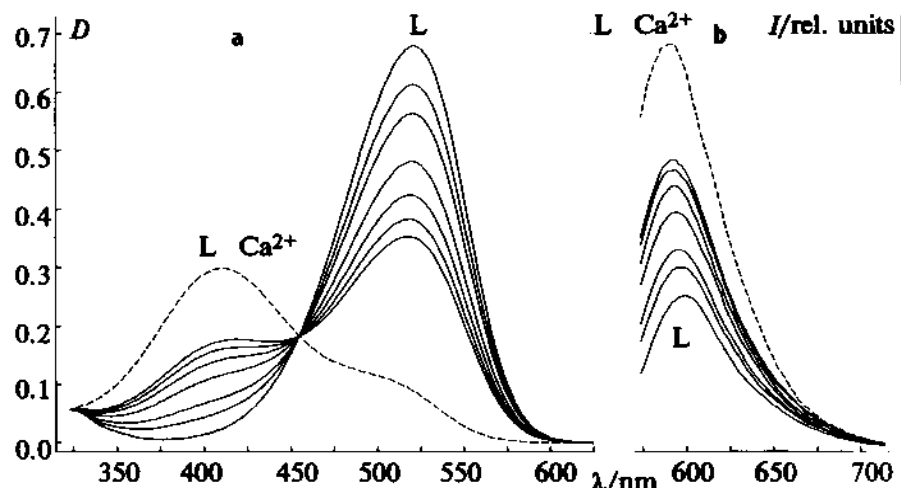
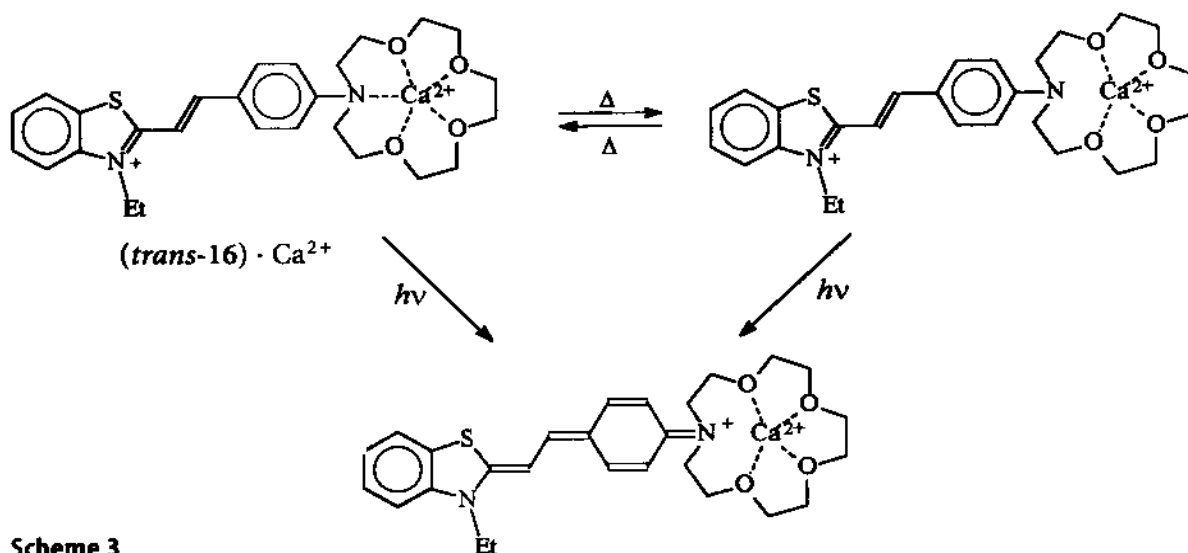
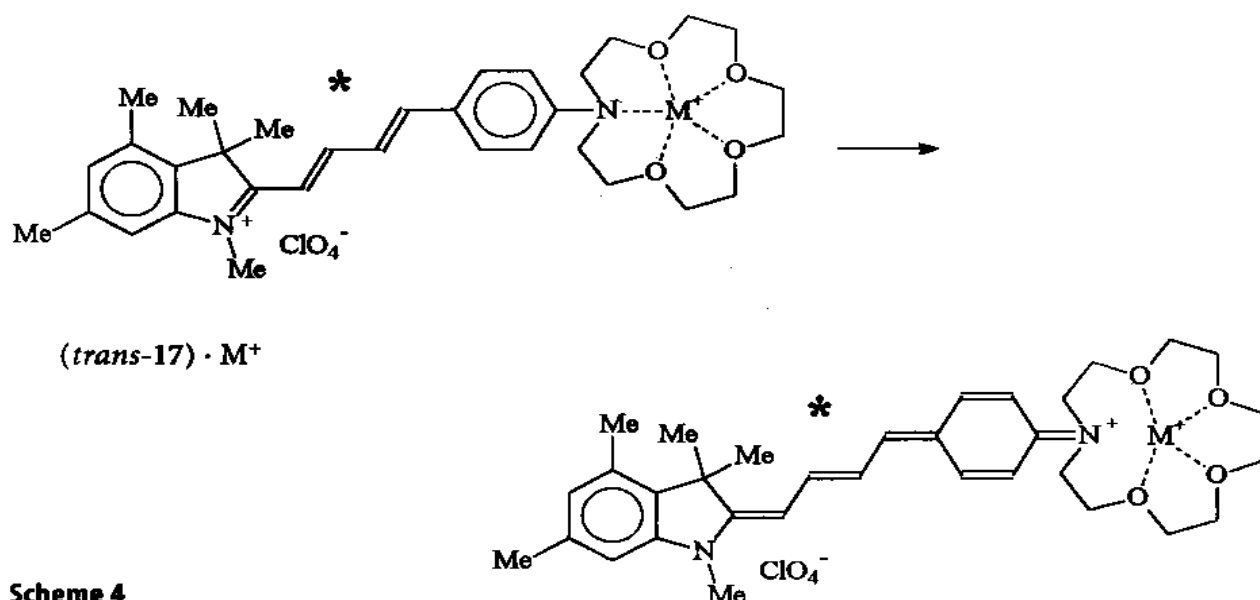


Fig. 6. Dependencies of the absorption **a** and fluorescence **b** spectra of *trans*-16 ($C_L = 1.0 \cdot 10^{-5} \text{ mol L}^{-1}$) in MeCN on the concentration of Ca^{2+} ions ($C_M/C_L = 50, 100, 200, 300, 400, 500$) at a constant concentration of the perchlorate ions $C_A = 0.01 \text{ mol L}^{-1}$. The dashed curve shows the calculated spectra of the complex

weakened, but the interaction with the oxygen atoms is retained. In the latter case, the effect of the cation on the electronic structure of the chromophore is much weaker. In spite of the fact that there are common features in the structure of compounds 10, 11, 16 and even 15 (first of all the presence of the C=C double bond and the crown-ether moiety) and the possibility of proceeding the photoinduced recoordination reaction in their complexes with metal ions, the above example of thermal recoordination reaction is unique.

Figure 6,*b* shows the fluorescence spectrum of *trans*-16 as a function of the Ca^{2+} concentration. Since photoexcitation of *trans*-16 leads to an increase in the electron density on the nitrogen atom, it may be assumed that in the excited state the equilibrium is shifted toward the complex in which the corresponding coordination bond is absent. This form of the complex seems to provide a main



Scheme 4

contribution to the fluorescence spectrum and therefore the position of the fluorescence band of *trans*-16 changes only slightly upon complexation.

It is known that butadienyl dyes are capable of generating laser radiation with a high efficiency [66]. Therefore, studies of the fluorescence characteristics, complexing ability and generating properties of dyes containing two double bonds and a crown-ether moiety are of great interest.

We investigated laser radiation of synthesized butadienyl dyes on excitation by the second harmonic (347.2 nm) of a ruby laser. It was found that the dyes of the type 17 generate laser radiation in the 687–730 nm spectral region. Substitution of the NMe₂ group by a crown-ether moiety results in an 8-fold increase in the efficiency of laser radiation. The fluorescence spectra of complexes of butadienyl dyes with Na⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ ions are similar to the spectra of free dyes; however, complexation leads to an increase in the fluorescence intensity. It is supposed that in this case recoordination also takes place, i.e., the breaking of the coordination bond between the nitrogen atom and the metal cation in the excited state of the complex (Scheme 4) [67].

The efficiency of laser radiation generation increases by a factor of 1.3–2.3 on complexation of butadienyl dyes with metal ions.

The data obtained by us reveal characteristics of the effects of the nature of a heterocyclic residue and crown-ether moiety, temperature and medium on the fluorescence of ionophores of the styryl and butadienyl series. This has provided the basis for a desired influence with the help of synthesis on their fluorescent parameters and cation-complexing ability.

7 Conclusions

The results of studies of crown-containing fluoroionophores discussed above show the potentialities of these compounds and variability in principles of their design. Certain of the compounds discussed are presently of little practical in-

terest. Other compounds are designed for practical use as selective fluoroionophores, including determination of cations of great ionic radius and small organic cations, ecological monitoring of environment, applications in medicine and biology, development of new systems for recording and reconstruction of information, new types of molecular photophysical and photochemical devices, and novel laser dyes with improved generation characteristics, etc. It may be safely suggested that photophysics and photochemistry of crown-containing fluoroionophores will be further developed and that these compounds will be widely used in the future.

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