

Reviews

Molecular meccano for light-sensitive and light-emitting nanosized systems based on unsaturated and macrocyclic compounds

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The review presents the results of the development of an universal approach to the molecular design of light-sensitive and light-emitting nanosized systems with desired properties based on unsaturated and macrocyclic compounds. Within the same class of compounds, various nanosized systems were constructed using a limited number of structural fragments. These nanosized systems are susceptible to all main types of photoprocesses, such as fluorescence, photodissociation, photoisomerization, photocycloaddition, photoelectrocyclization, excimer formation, charge-transfer complex formation, the formation of the twisted intramolecular charge-transfer state (TICT state), and the electron transfer. The use of photostructural transformations for controlling the complexation and mechanical movements in molecular devices and machines is discussed. The prospects of application of the new strategy are exemplified by the design of the previously unknown types of molecular switches, materials for optical chemosensors, optical data recording and storage media, photo-switchable molecular devices, and photocontrolled molecular machines.

Key words: *trans*—*cis* photoisomerization, [2+2] photocycloaddition, charge transfer, photo-induced electron transfer, unsaturated compounds, crown compounds, cucurbiturils, molecular devices, molecular machines, molecular meccano.

Introduction

The bottom-up design, which is also known as the molecular design or molecular assembly, is one of the main fields of investigation in nanotechnology.¹ Important aims of nanotechnology are to predict the properties of compounds in nanosized systems and develop procedures for their assembly. Nowadays the new scientific engineering field called the molecular engineering has started to de-

velop. This field is aimed at designing various-destination molecular devices and machines. The bottom-up molecular assembly resulting in the selective formation of nanosized structures and the presence of light-sensitive fragments are prerequisites for the design of light-controlled molecular devices and machines.

Molecular devices are defined as structurally organized and functionally integrated molecular systems,^{2–6} which can perform certain tasks to achieve useful results.

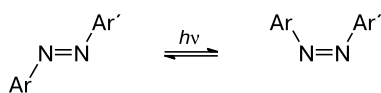
Devices operating as a result of the mechanical movement of components relative to each other are commonly assigned to molecular machines.^{3,7–12} For this purpose, the components should not be linked by strong chemical bonds. These types of nanosized systems can be used for designing molecular mechanisms and machines for energy generation, conversion, and transformation, as well as for nanoscale motion, and for constructing nanodevices for control and diagnostics of nanoscale amounts of materials and compounds. The above-mentioned fields are of considerable interest from the point of view of their application in supramolecular technology and nanotechnology.^{3,13–15} In Russia, they were assigned to critical technologies, *i.e.*, the synthesis and investigation of new classes of compounds having physicochemical characteristics promising for this purpose, as well as the development of an approach to the design of these compounds, are urgent problems.

It is most convenient to control molecular devices and machines by light, whose wavelength and quantity can easily be varied.^{16–21}

Light-sensitive systems, which can be considered as prototypes of molecular devices and machines, play a great role in living nature. For example, these systems enable photosynthesis, vision, phototropism in plants, and bacterial phototaxis. Natural light-sensitive systems consist of two main units: a photoantenna absorbing a light quantum and a functional unit, which perceives changes in the photoantenna after absorption of the light quantum. Hence, in natural light-sensitive systems, the light acts as a trigger for a number of vitally important processes.^{22,23}

Artificial light-sensitive systems are built up in an approximately the same manner. Although photochromic derivatives of bisanthracenes²⁴ and spiro compounds²⁵ were studied as photoantennae, azobenzene derivatives were most often used for this purpose.²⁶ However, the latter compounds have a principal drawback. Thus, they can be involved only in *trans*–*cis*- and *cis*–*trans*-photoisomerization reactions (Scheme 1).²⁷

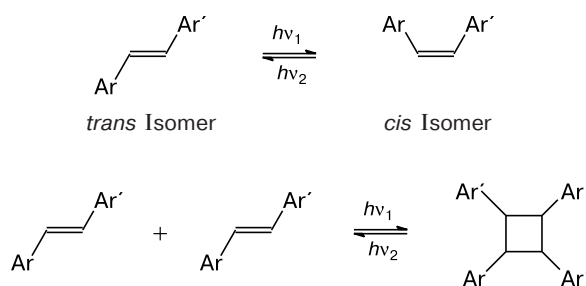
Scheme 1



In this respect, compounds containing a carbon–carbon double bond have certain advantages. The main advantage is that they can be involved not only in photoisomerization but also, for example, in [2+2] photocycloaddition (PCA) giving rise to cyclobutane derivatives (Scheme 2).^{28–31}

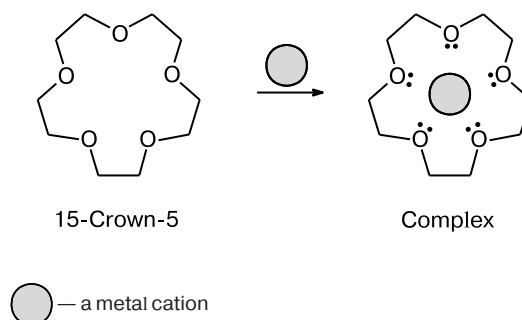
Crown compounds are most often used as functional units in artificial light-sensitive systems. These are mac-

Scheme 2

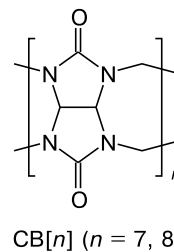


rocyclic compounds containing heteroatoms bearing lone electron pairs, which can form coordination bonds with metal ions. One of the fundamental properties of these molecules is that they can undergo self-assembly in solution with ions or other molecules to form more complex systems^{32,33} (Scheme 3).

Scheme 3



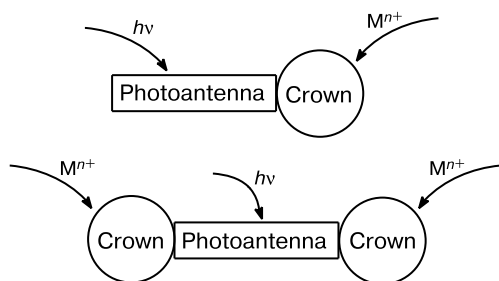
The complexation properties of cucurbit[*n*]urils (CB[*n*]) belonging to the relatively new class of macrocyclic compounds have been extensively investigated in recent years.^{34,35} These compounds have a hydrophobic electron-donor cavity. The ability of CB[*n*] to form stable complexes with positively charged organic molecules in aqueous media is of particular interest.



Therefore, photoswitchable molecular devices based on compounds capable of undergoing photostructural (photochromic) transformations and crown compounds can be represented as follows: these are hybrid molecules, which should contain a fragment of unsaturated compounds adsorbing a light quantum as a photoantenna and one or two crown ether moieties capable of binding metal ions (Scheme 4).

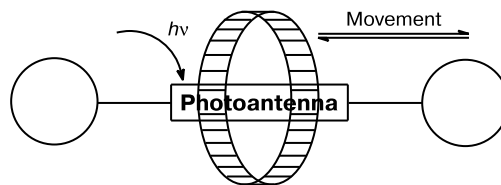
If fragments of a crown ether and a photochromic compound are linked to each other by covalent bonds in such a way that at least one heteroatom of the macrocycle is conjugated with the chromophore,

Scheme 4

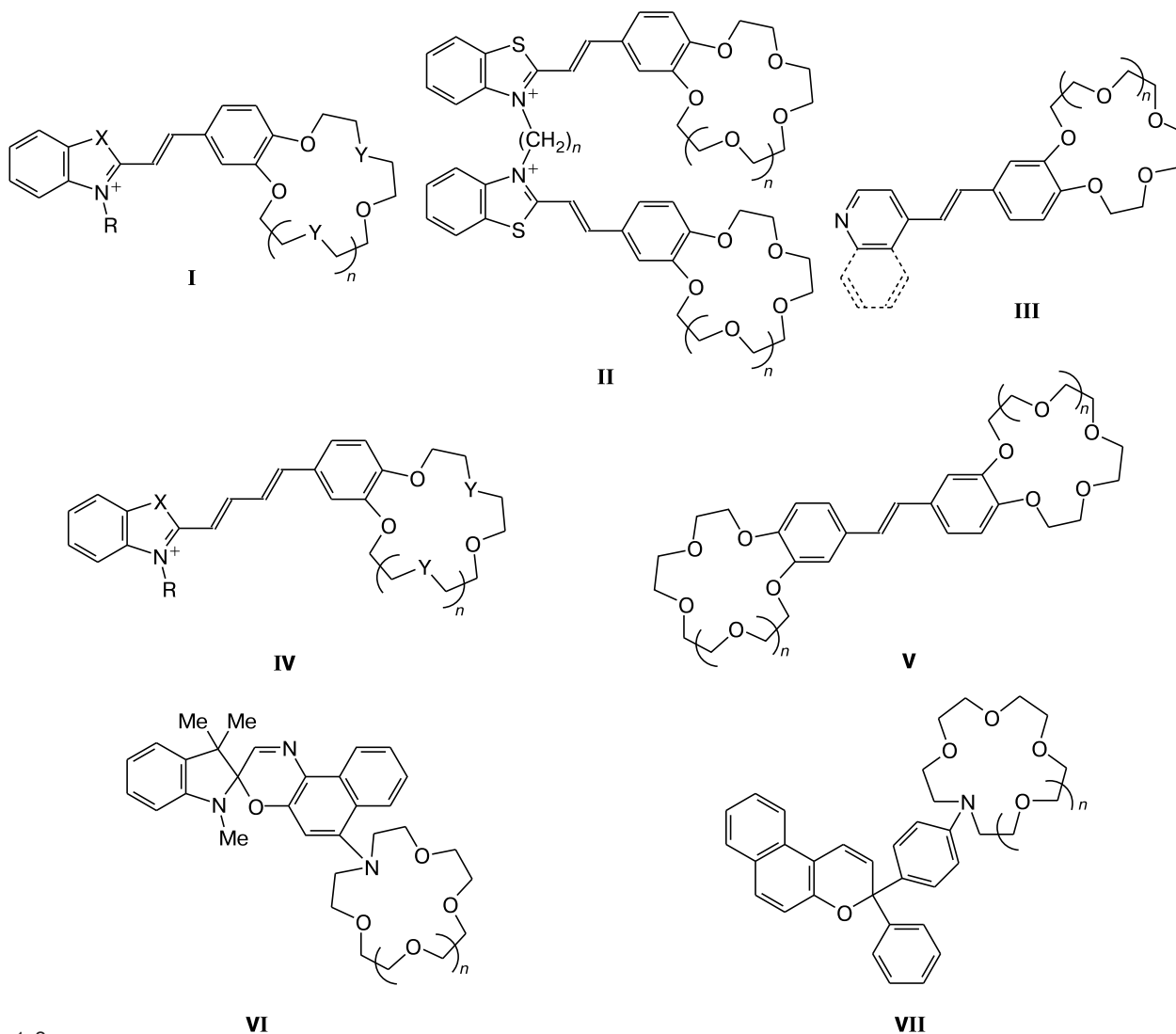


the self-assembly in solution giving rise to supramolecular structures would allow changes in the spectroscopic and photochemical characteristics of the photochromic fragment of the molecule, and the self-assembly of such crown-containing molecules can, in turn, be controlled by light.

Scheme 5



New types of artificial light-sensitive systems based on the previously unknown crown-containing and crown ether-free styryl, bis-styryl, and butadienyl dyes, heptarylphenylethylenes, dihetarylethylenes, and stilbenes


$$n = 1, 2$$

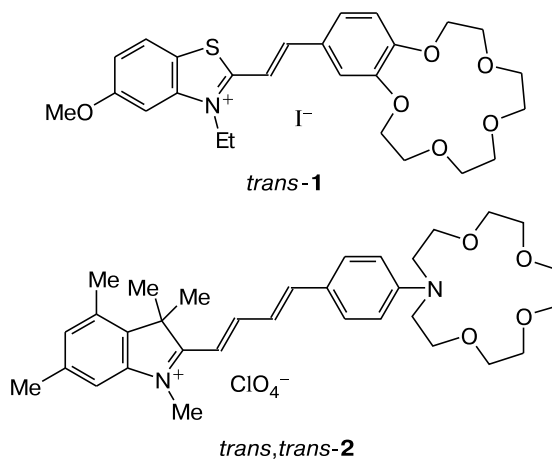
containing a photoswitchable carbon-carbon double bond, as well as spironaphthoxazines and naphthopyrans capable of being involved in photoinduced electrocyclic reactions, satisfy the above-mentioned conditions.

In the first type of systems, *viz.*, in crown-containing styryl dyes **I**, we varied the heterocyclic moiety, the substituents at the nitrogen atom of the heterocyclic moiety, and the size and nature of the crown ether moieties. The second type of systems includes bis-crown-containing styryl dyes **II**, in which two fragments of the dye are covalently bridged. In this case, both crown ether moieties can simultaneously be involved in complexation. Crown-containing hetarylphenylethylenes **III** containing various heterocyclic fragments and crown ether moieties belong to the third type of light-sensitive systems. The fourth type includes crown-containing butadienyl dyes **IV**, in which heterocyclic fragments, the substituent at the nitrogen atom, and crown ether moieties were varied. In bis-crown-containing stilbenes **V**, spironaphthoxazines **VI**, and naphthopyrans **VII**, we varied the size of the crown ether moieties.

Structures of unsaturated dyes

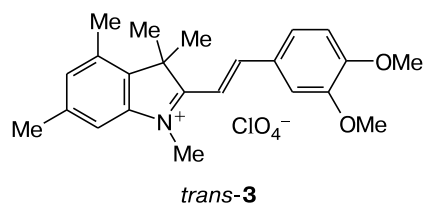
X-ray diffraction studies of a large series of compounds revealed two characteristic features for the type of unsaturated dyes under consideration. The distances between groups and atoms of the dye moiety are smaller than the sums of their van der Waals radii, which is indicative of substantial steric strain in the chromophoric systems (for example, in styryl dye **1** (Fig. 1)).³⁶ In spite of this fact, the chromophoric systems remain planar due to a high degree of conjugation between different unsaturated fragments of the dyes, as exemplified by butadienyl dye **2** (Fig. 2).³⁷

The three-dimensional structure of the crown ether moiety can be described as a distorted crown (see Figs 1 and 2).



Complexation reaction

In the first step of investigations performed by our research group, the self-assembly of crown-containing styryl dyes involving metal ions was studied. The difference between crown ether-free dye **3** and crown-containing dye **4** was found after the addition of metal ions to solution.³⁸



Large hypsochromic (toward shorter wavelengths) shifts of the long-wavelength maximum were observed³⁸ in the absorption spectra of crown-containing dye **4** (Scheme 6).

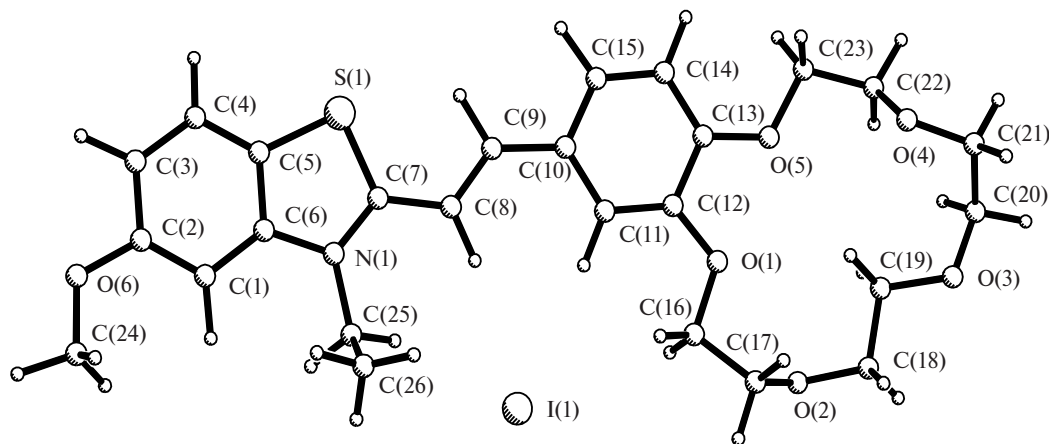


Fig. 1. Structure of styryl dye *trans*-**1** projected onto the plane of smallest overlap.

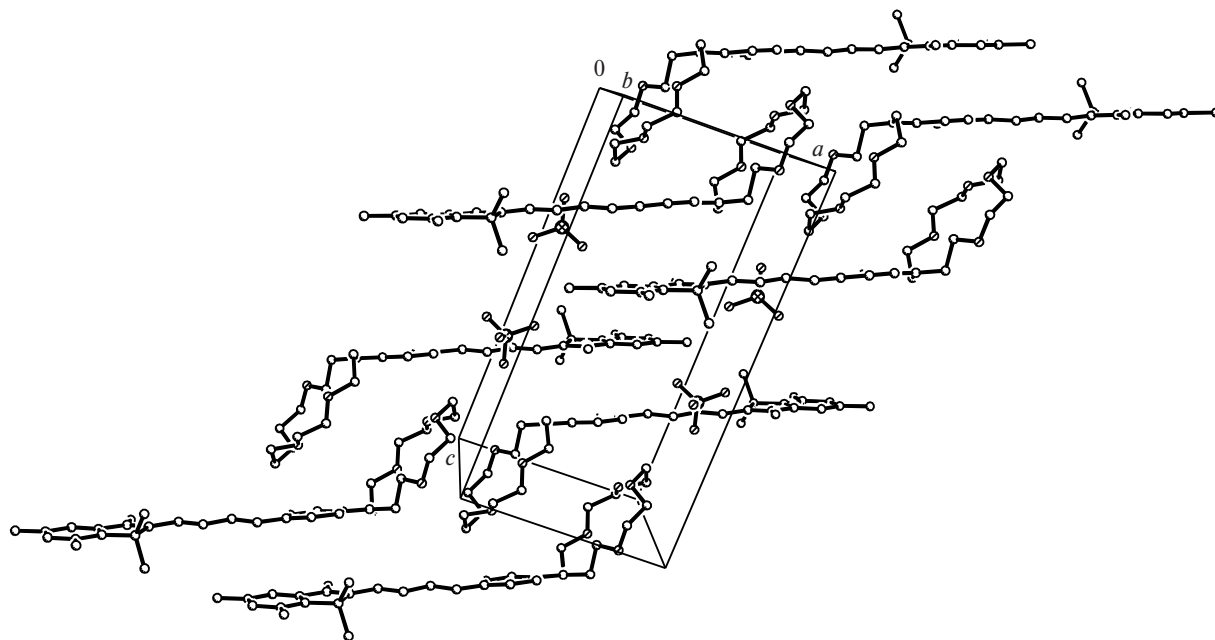
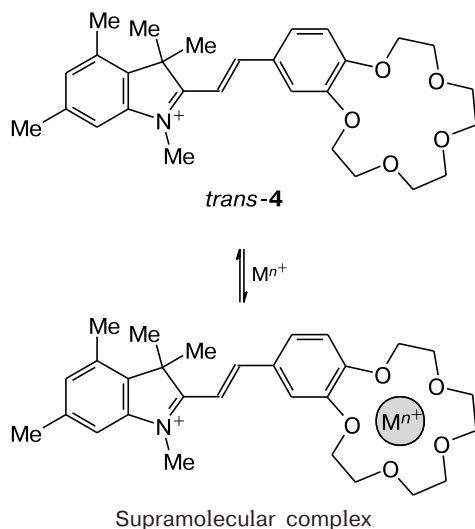


Fig. 2. Crystal packing of the structural units of butadienyl dye *trans,trans*-2.

Scheme 6



These hypsochromic shifts depend on the nature of metal ions added to solution.^{38–46} For the dye under consideration, the largest shift was observed in the presence of magnesium ions; the smallest shift, in the presence of barium ions (Fig. 3).³⁸

A more detailed study of this effect for two crown-containing dyes (**4** and **5**) and a series of singly, doubly, and triply charged metal cations revealed the largest shifts for the highest surface charge density, *i.e.*, for triply charged cations (Table 1). In a series of cations with the same charge, the largest shifts were observed for compounds, in which the diameter of the metal ion best

matches the cavity size of the crown ether moiety. For example, the largest shift for dye **4** was observed in the presence of magnesium ions; for dye **5**, in the presence of europium ions. Interestingly, the second dye virtually does not give a hypsochromic shift upon complexation with a magnesium ion.⁴¹

Table 1. Changes in the long-wavelength absorption maxima ($\Delta\lambda$) of crown-containing dyes *trans*-**4** and *trans*-**5** upon complexation with various metal ions in MeCN and MeOH

$M^{n+}(X^-)_n$	$\Delta\lambda^*/\text{nm}$		
	<i>trans</i> - 4	<i>trans</i> - 5	
	MeCN	MeCN	MeOH
LiClO ₄	15	1	0
NaClO ₄	11	8	8
KClO ₄	8	13	2
KSCN	3	11	3
CsClO ₄	3	5	4
NH ₄ ClO ₄	4	13	4
Mg(ClO ₄) ₂	42	1	2
Ca(ClO ₄) ₂	39	26	4
Sr(ClO ₄) ₂	33	29	23
Ba(ClO ₄) ₂	28	27	27
Eu(ClO ₄) ₃	2	44	3
Tb(ClO ₄) ₃	1	34	2

* $\Delta\lambda = \lambda_L - \lambda_{LM}$ (λ_L and λ_{LM} are the long-wavelength absorption maxima of the dye and its complex with the metal ion, respectively).

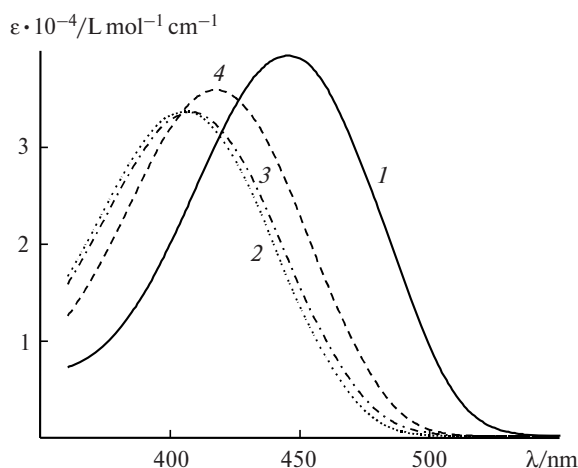
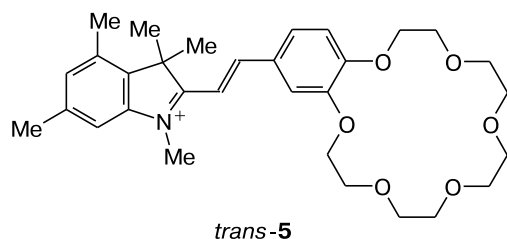


Fig. 3. Absorption spectra of crown-containing dye *trans*-4 (1) and its complexes with magnesium (2), calcium (3), and barium (4) cations in MeCN.



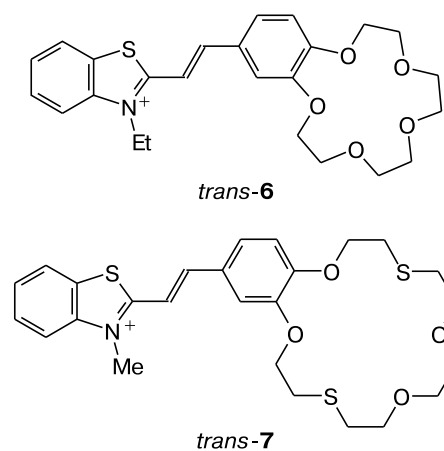
We hypothesized that the hypsochromic shift depends on the efficiency of metal-ion binding to the dye, which is known to be quantitatively characterized by the stability constant. Measurements of the stability constants for a series of complexes of crown-containing styryl dyes with metal ions, which were synthesized by our research group, showed that the constants change in parallel with the hypsochromic shifts.⁴⁷ This was exemplified by dye *trans*-6. The stability constants (K_1) for the complexes with *trans*-6 and the changes in the long-wavelength maxima ($\Delta\lambda$) upon complexation with various metal perchlorates are given below.

M^{2+}	$\log K_1$	$\Delta\lambda/\text{nm}$
Mg^{2+}	4.5	39
Ca^{2+}	4.0	36
Ba^{2+}	3.7	28

Therefore, the hypsochromic shift can serve as a good qualitative indicator of the efficiency of metal-ion binding to dyes.

However, this is not true for dyes containing other heteroatoms in the macrocycle in addition to oxygen. As an example, let us refer to dithiacrown-containing styryl dye 7.

For this dye, the hypsochromic shift upon the addition of mercury ions is 25 nm, whereas the stability constant is very high ($\log K = 18$).^{45,48}



Fluorescence and excimer formation

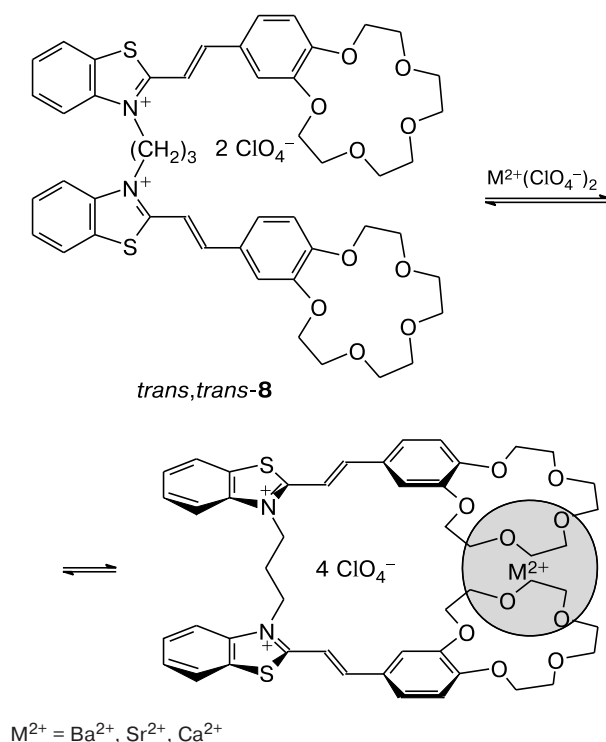
Crown-containing styryl dyes have intense deep color attributed to the presence of an oxygen or nitrogen atom of the crown ether moiety in the *para* position with respect to the double bond and the conjugation of these atoms with the chromophoric fragment.⁴³ These compounds exhibit weak fluorescence in solution at room temperature (the fluorescence quantum yield $\phi_f = 0.002\text{--}0.1$).^{49,50} On the contrary, *cis* isomers of styryl dyes show no fluorescence at all. The fluorescence intensity of dyes is substantially higher in viscous solutions or polymeric matrices and increases with decreasing temperatures (up to $\phi_f = 0.6$ at 173 K).⁴⁹

Our research group obtained interesting results when studying the complexation of bis-crown-containing dyes. In this case, two crown ether moieties can simultaneously be involved in binding of ions with large ionic radii, such as barium, strontium, and calcium ions, to form sandwich complexes^{51,52} (Scheme 7).

Such molecules are called molecular pincers. It should be noted that data on sandwich complexes, in which the crown ether moieties are bound to chromophores, are lacking in the literature. It should also be noted that the chromophoric systems in the above-mentioned sandwich complex are located one above another. This leads to their interactions, which is reflected in absorption spectra. Hence, the hypsochromic shifts upon complexation are abnormally large.

Two-component fluorescence is observed also for the sandwich complex of 8 with Ba^{2+} . The spectroscopic properties of the fast component indicate that this component is associated with radiative deactivation of the excited state of one of the chromophoric fragments involved in the complex. The long-lived component belongs to an intramolecular excimer that is formed as a result of an interaction between two chromophoric fragments of the sandwich complex (the excited fragment and the fragment in the ground state).⁵²

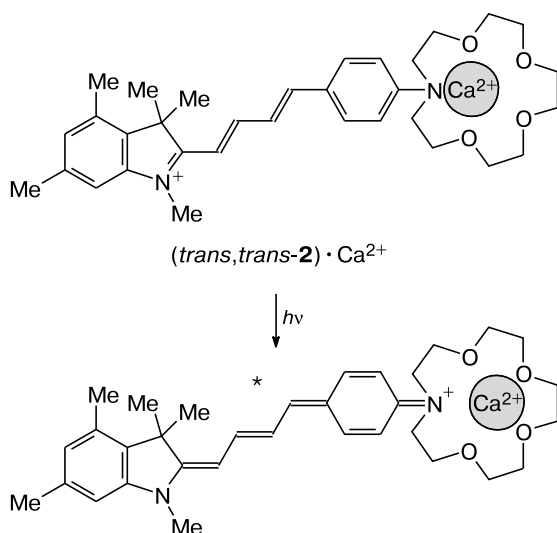
Scheme 7



Recoordination reaction

In a series of butadienyl dyes, we found a photocontrolled molecular device with a switching time of 20 ps. In the complex of dye **2**, the calcium ion forms coordination bonds with all heteroatoms (Scheme 8). However, the Ca—N bond is cleaved under light irradiation as

Scheme 8



a result of photodissociation, and this bond is again formed after the transition from the excited to the ground state.

Therefore, the Ca—N bond formation is a controlled function in this photoswitchable molecular device.^{37,53–56}

trans—*cis* Photoisomerization

Anion-"capped" complexes. In the first step of investigation of our research group, we compared the ability of a crown-containing dye and a dye containing two methoxy groups, whose donor effect reproduces the donor effect of the crown ether moiety, to act as molecular photoswitches. It should be noted that the photochromic characteristics of styryl dyes have not been described. We showed that both styryl dyes are efficient molecular photoswitches. The forward and backward reactions proceed with nearly theoretical yields ($\phi_{tc} = 0.5$).⁵⁷ Only in some cases, the geometrical isomerization is accompanied by the competitive formation of the twisted intramolecular charge-transfer state (TICT state), which can be efficiently suppressed by complexation.⁵⁸ In addition, it was found that the long-wavelength maxima of the *trans* and *cis* isomers differ by only 10–15 nm. Hence it follows that the photostationary state is always formed under irradiation.³⁸ However, we succeeded in overcoming this drawback.

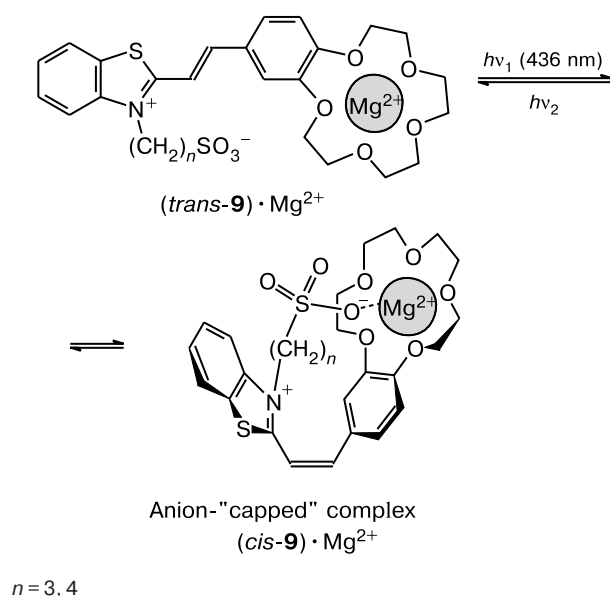
We observed an interesting behavior of styryl dye **9**, which contains the substituent with the terminal sulfo group having ligand properties at the nitrogen atom. This group in the *trans* isomer of the dye cannot "reach" the metal ion located in the crown ether cavity. However, this group in the *cis* isomer forms a rather strong coordination bond with the metal ion. This anion-"capped" complex is stable at room temperature⁵⁹ (Scheme 9).

The long-wavelength maxima of the *trans* and *cis* isomers are substantially different (by almost 70 nm; Fig. 4) enabling the complete molecular photoswitch from the *trans* to the *cis* isomer and back with high quantum yields ($\phi \approx 0.5$).⁵⁹

Yet another interesting property of this dye is that its *cis* isomer can bind metal ions 500 times more stronger than the *trans* isomer. As a result, the complexation, which is not photosensitive by itself, can be controlled by light. These supramolecules are commonly called photocontrolled or photoswitchable molecular devices. Therefore, we have synthesized the previously unknown photoswitchable molecular devices based on crown-containing styryl dyes.^{57,60–65}

The characteristics of photoswitchable molecular devices can be controlled by varying the structure of the dyes.^{47,66–69} For example, the stability of anion-"capped" complexes can be varied by varying the length and nature of the substituent at the nitrogen atom. It should be noted

Scheme 9



that the formation of anion-"capped" complexes is the ion-selective reaction. For example, dye **10** forms the stable anion-"capped" complex with a calcium ion (Scheme 10), but it does not give an analogous complex with a magnesium ion.⁷⁰ Dithiacrown-containing dye **11** forms the anion-"capped" complex with a mercury ion, but it does not give the complex with a calcium ion having a similar size.^{48,71}

We obtained particularly impressive results for azacrown-containing styryl dye **12**. In this case, the com-

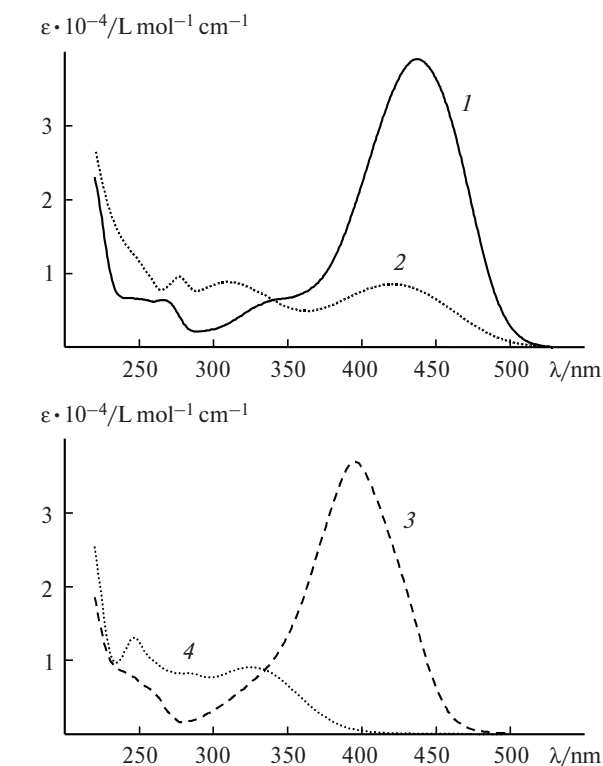
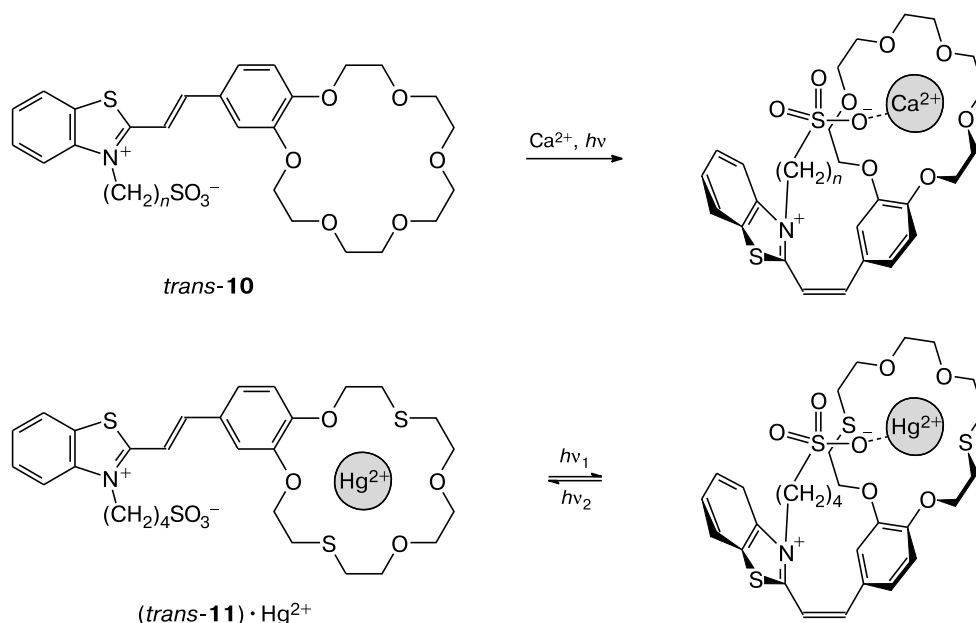


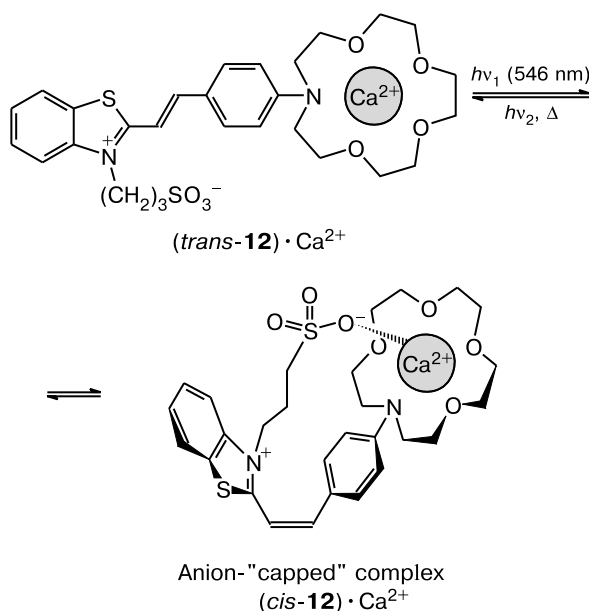
Fig. 4. Absorption spectra of dyes *trans*-**9** (1) and *cis*-**9** (2) and their complexes with a magnesium cation, (*trans*-**9**)· Mg^{2+} (3) and (*cis*-**9**)· Mg^{2+} (4), in MeCN ($n = 3$).

plexation constant increases by more than three orders of magnitude on going from the *trans* to the *cis* isomer, and a change in the position of the long-wavelength maximum is as large as 160 nm (Scheme 11).^{72,73}

Scheme 10

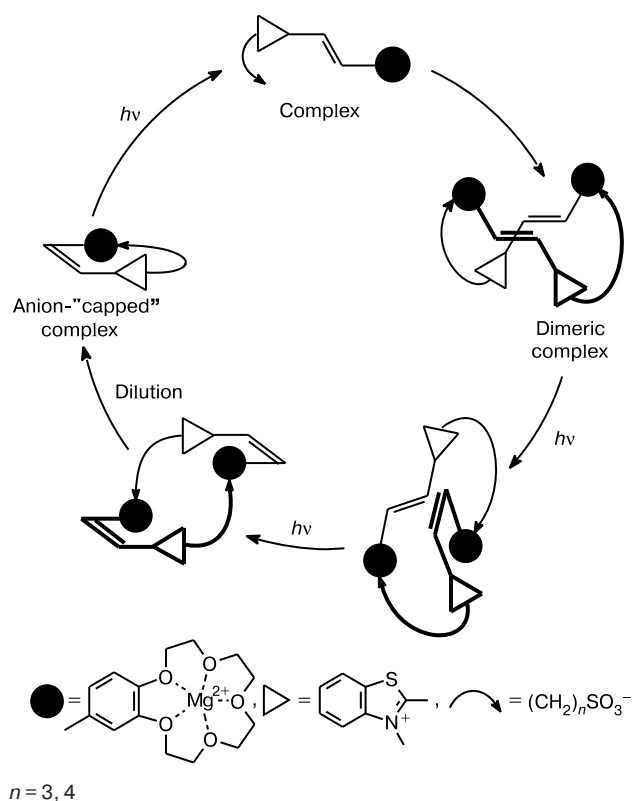


Scheme 11



A more detailed study of the behavior of crown-containing styryl dyes in the presence of metal ions and under irradiation showed that the processes in solution are rather complex (Scheme 12). In the presence of metal ions,

Scheme 12

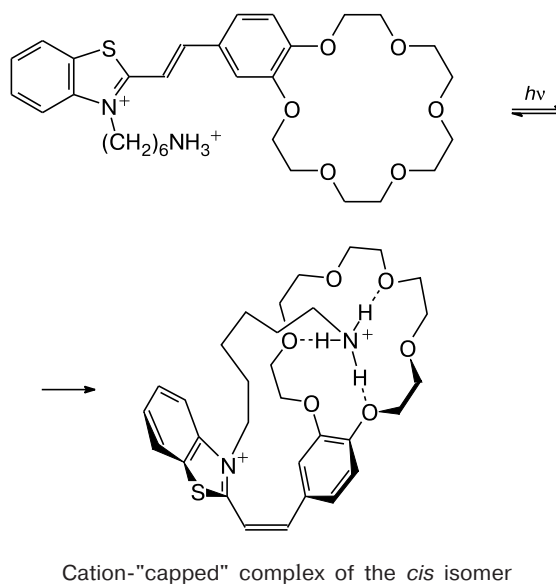


the dyes are self-assembled to form dimeric complexes, in which styryl dyes undergo photoisomerization, two light quanta being required for the complete isomerization of the dimeric complexes to anion-"capped" complexes. The resulting anion-"capped" complexes can again be converted into the *trans* isomers under light irradiation at shorter wavelengths.^{18–20,47}

In the second step of investigation, we studied, the self-assembly of nanosized systems from crown-containing styryl dyes through hydrogen bonding.

Cation-"capped" complexes. Crown ethers are known to bind primary ammonium ions *via* three hydrogen bonds with the ammonium group. The introduction of a long alkylammonium substituent at the nitrogen atom of the heterocyclic moiety of styryl dyes enables the synthesis of stable cation-"capped" complexes in solution as a result of intramolecular complexation with the involvement of hydrogen bonds and in the absence of metal ions (Scheme 13).⁷⁴

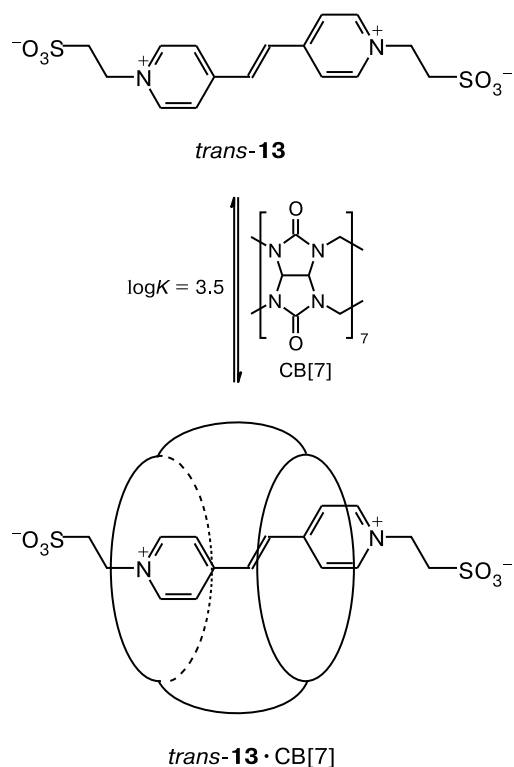
Scheme 13



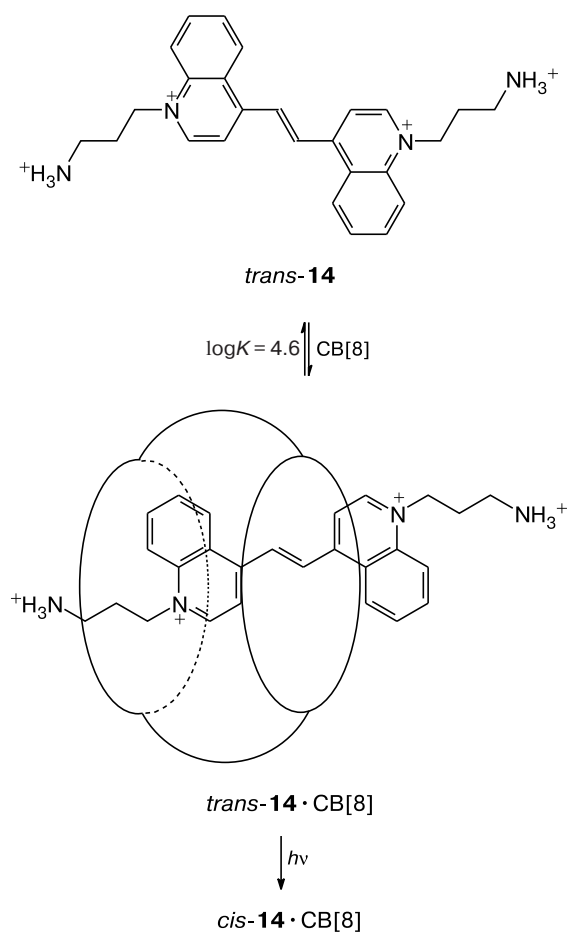
Pseudorotaxane complexes. A new field of our research is concerned with the self-assembly of photoswitchable molecular machines based on unsaturated and macrocyclic compounds. Pseudorotaxane complexes of cucurbiturils and unsaturated viologen analogs can serve as prototypes of such molecular machines. It appeared that cucurbiturils form rather stable complexes with these compounds (Scheme 14).⁷⁵

We studied the three-dimensional structure of the pseudorotaxane complex by X-ray diffraction (Fig. 5). It should be noted that the macrocycle can be mechanically moved along the axis of the guest molecule.⁷⁵ It was of interest to examine the possibility of photocontrolling

Scheme 14



Scheme 15



these mechanical movements. This was done for the pseudorotaxane complex of cucurbituril with a diquinolyethylene derivative. Under light irradiation, the *cis* isomer of the unsaturated compound with cucurbituril, *viz.*, *cis*-**14** · CB[8], was formed (Scheme 15).⁷⁶

The three-dimensional structure of this complex was studied by X-ray diffraction (Fig. 6), and it was shown

that the mechanical movement in the cavity of the macrocycle can easily be performed.⁷⁶

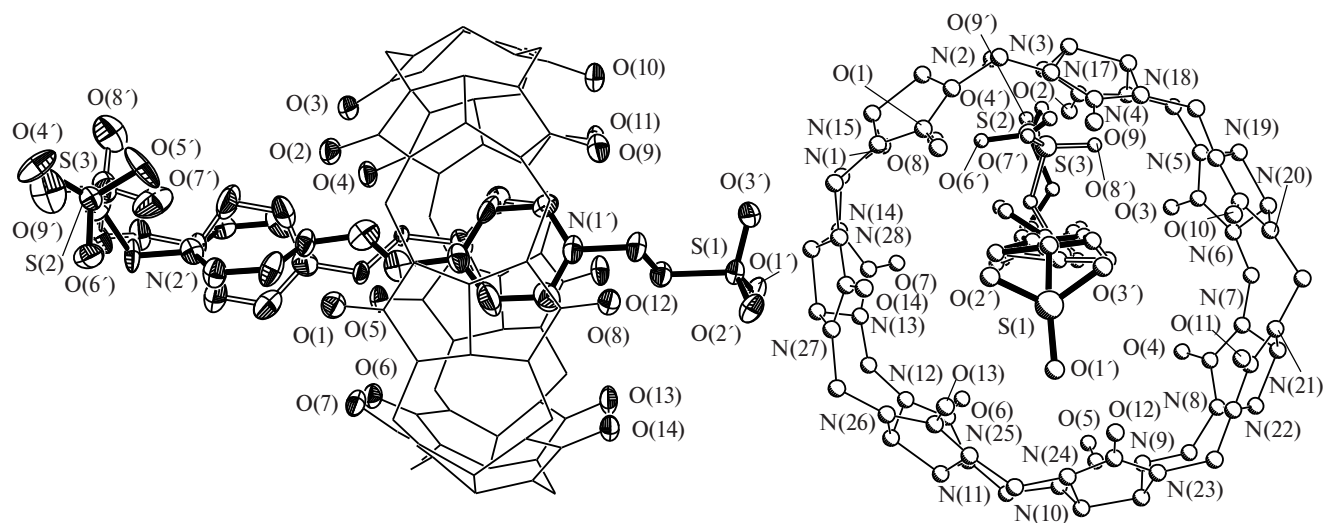


Fig. 5. Structure of the complex *trans*-**13** · CB[7] in two projections (molecule **13** is disordered over two positions).

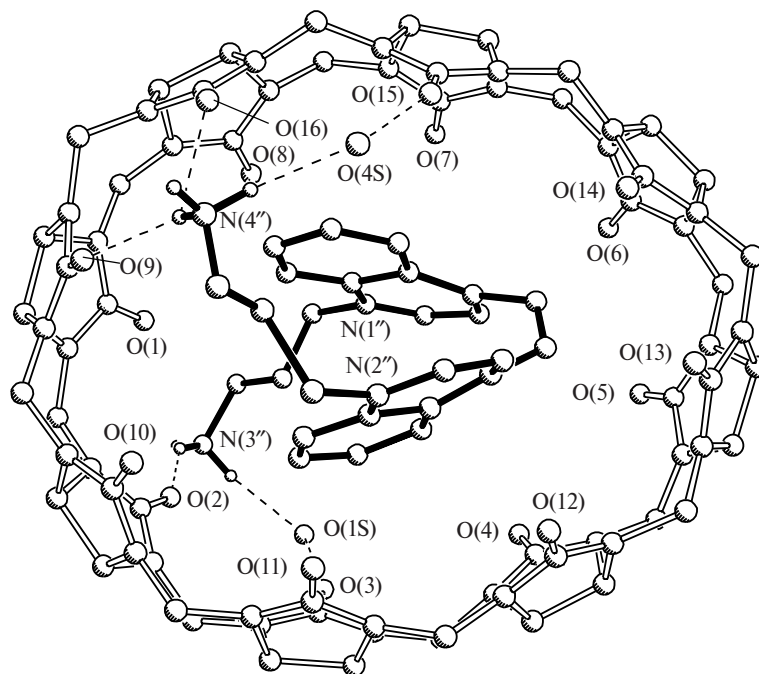


Fig. 6. Structure of the complex *cis*-14 • CB[8].

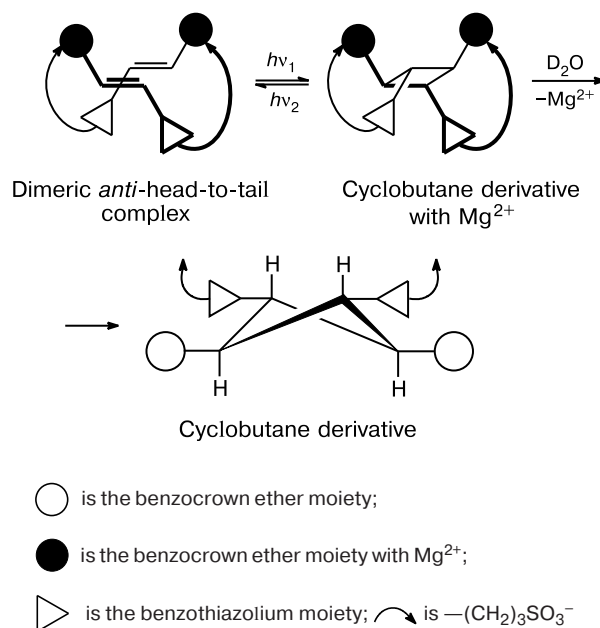
[2+2] Photocycloaddition reactions

Dimeric and pseudodimeric complexes. In solution, the complexes of *trans* isomers of dyes exist as dimers.^{62,77} Hence, we hypothesized that the double bonds in these complexes can be located in proximity to each other. Consequently, the [2+2] cycloaddition would be expected to proceed under photoirradiation. Actually, we obtained a photoproduct after prolonged irradiation. According to the NMR data, this compound is a cyclobutane derivative (Scheme 16). The UV spectrum of the cyclobutane derivative, which was prepared by photolysis of the complex of *trans*-9 with a Mg^{2+} cation, is shown in Fig. 7. In this case, the only isomer of eleven theoretically possible isomers was produced, *i.e.*, the reaction was completely stereospecific.^{78,79}

The cyclobutane derivative was found to be quantitatively recovered to the starting dimeric complex after photoirradiation at shorter wavelength. In addition, the complexation constant of the cyclobutane derivative with the metal ion was found to be substantially larger than that of the *trans* isomer of the dye. Therefore, in this case the complexation is controlled by light, *i.e.*, the dimeric complex is also a photoswitchable molecular device with the controlled complexation function. Unlike the anion-"capped" complex, the resulting cyclobutane derivative belongs to a new type of ditopic host molecules.

The total cycle of transformations of cyclobutane derivatives in solution is presented in Scheme 17. There-

Scheme 16



fore, using metal ions, we can assemble dimeric complexes, perform the PCA reaction in these complexes, and again disassemble, if desired, nanosized systems to the starting components.^{18–20,80,81}

It is interesting that the formation giving rise to cyclobutane derivatives is very sensitive to slightest structural changes of the starting dyes (Scheme 18).⁷⁰

Scheme 17

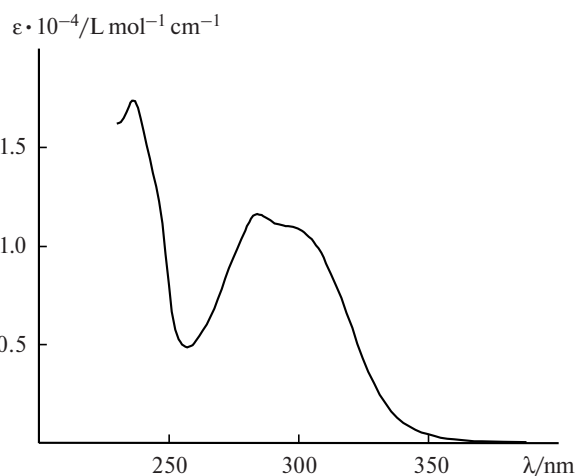
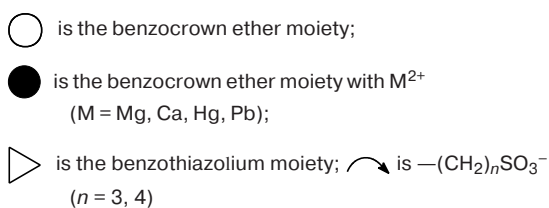
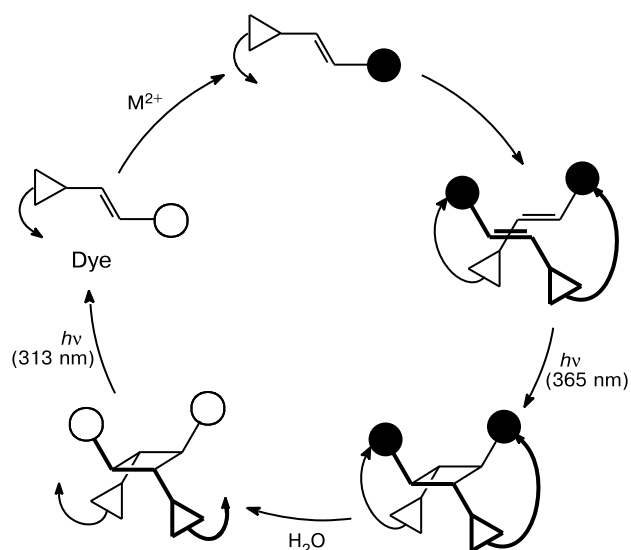


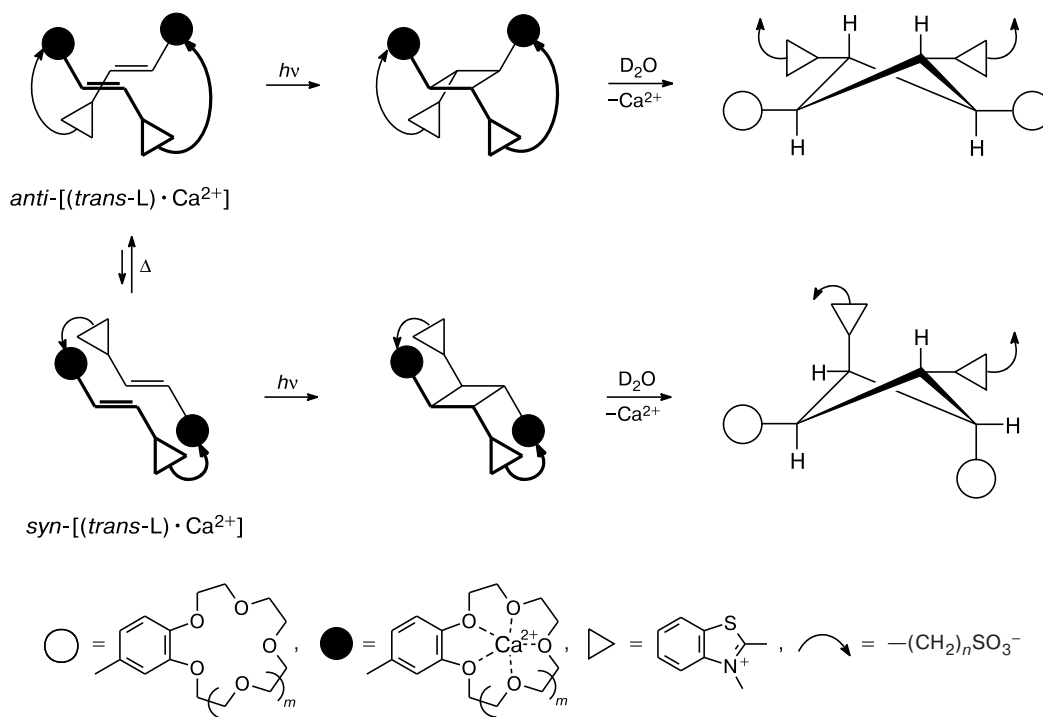
Fig. 7. Absorption spectrum of the cyclobutane derivative prepared by photolysis of the complex of *trans*-9 ($n = 3$) with a magnesium cation at a wavelength $\lambda = 365$ nm in MeCN.

The quantum yields of the PCA reaction of the complexes of styryl dyes with the Ca^{2+} cation (see Scheme 18) are given below.

n	m	Φ	n	m	Φ
3	1	0.001	3	2	0.0004
4	1	0.01	4	2	0.06

It can be seen that the change in the length of the substituent at the nitrogen atom of the heterocyclic

Scheme 18



$m = 1, 2; n = 3, 4$

moiety by only one methylene group leads to a change in the quantum yield of the PCA reaction by a factor of 150.⁷⁰

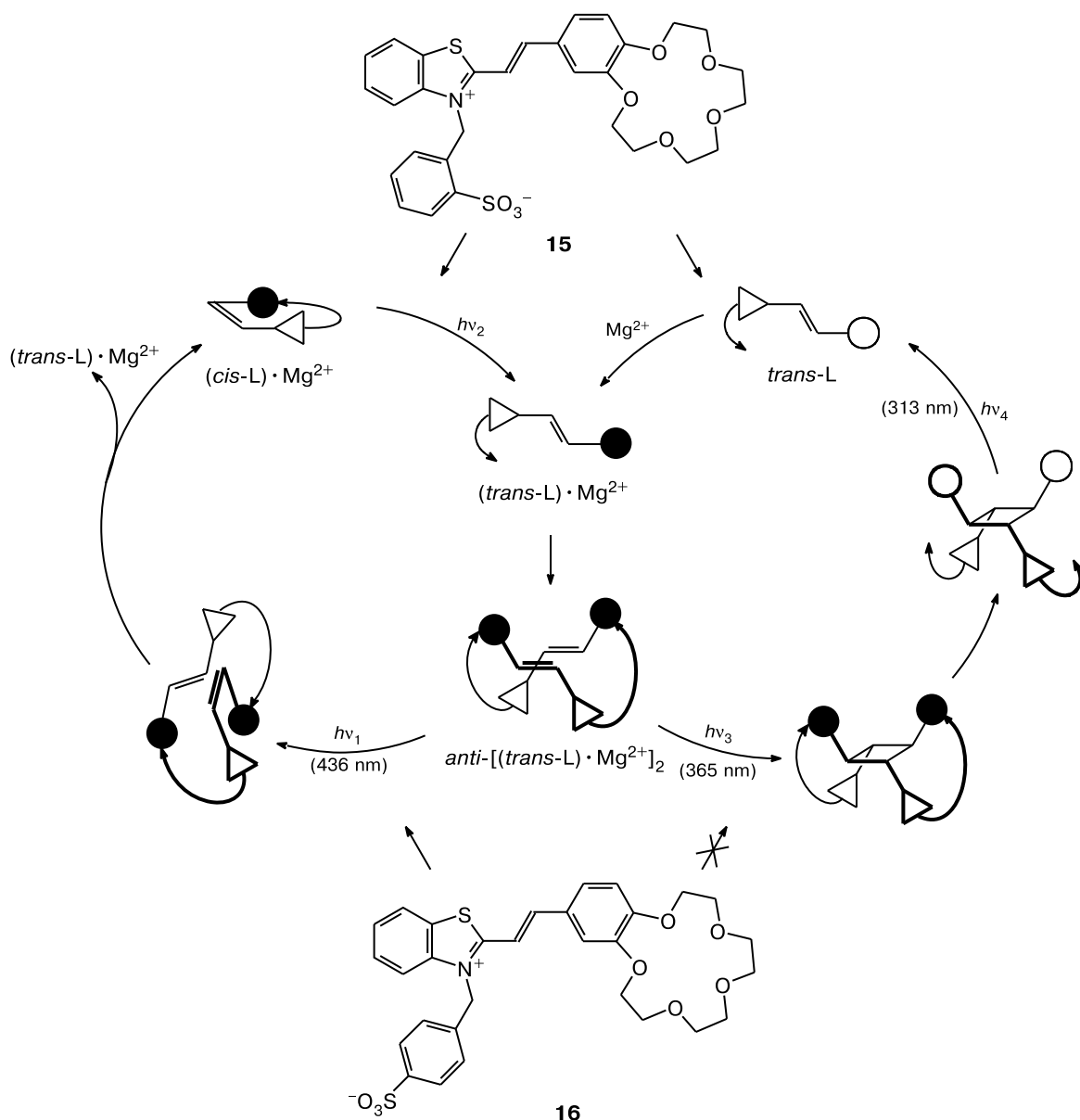
Therefore, for the cycloaddition reaction to be efficient, the position of one dye molecule with respect to another one in a nanosized system should be very finely adjusted.

From the point of view of using styryl dyes in molecular electronics, it is extremely important that the compounds can be involved in various photochemical transformations, *i.e.*, they should have multiphotochromic properties. We synthesized and studied such molecules.^{68,69} Dye **15**, which can form an anion-"capped"

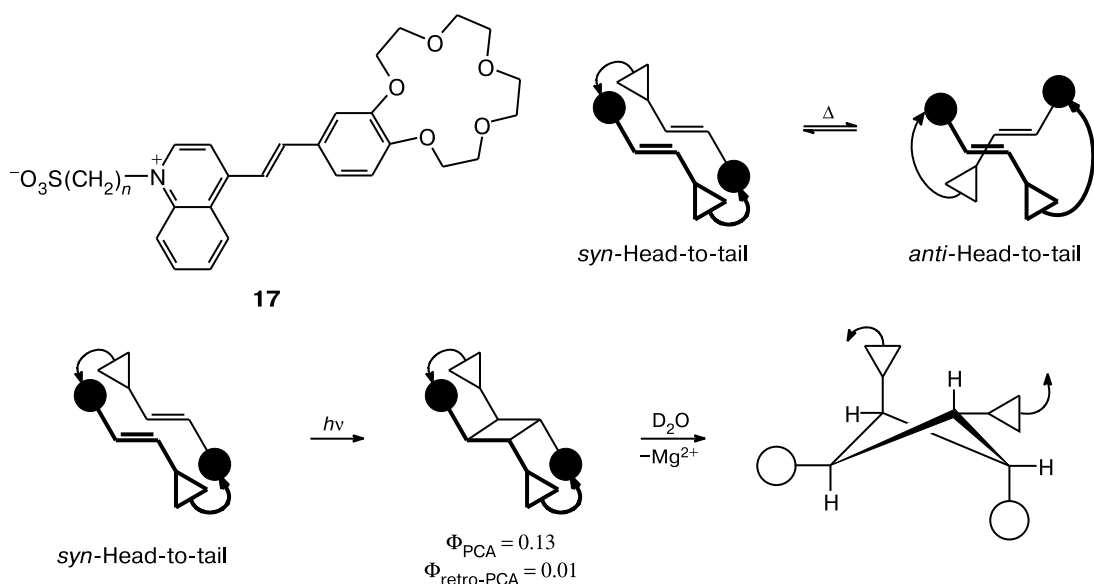
complex and can be involved in the PCA reaction, and dye **16**, which can give only an anion-"capped" complex, are shown in Scheme 19.

We studied crown-containing styryl dyes **17**, which give only cycloaddition products and do not form anion-"capped" complexes upon photoirradiation (Scheme 20).^{58,82} It appeared that these dyes give only one cyclobutane derivative of eleven theoretically possible isomers, *i.e.*, the reactions are stereospecific; however, the three-dimensional structures of these cyclobutanes differ from those described above. We attempted to reveal the factors responsible for this behavior. The NMR study of the reaction mixture showed that this mixture

Scheme 19



Scheme 20

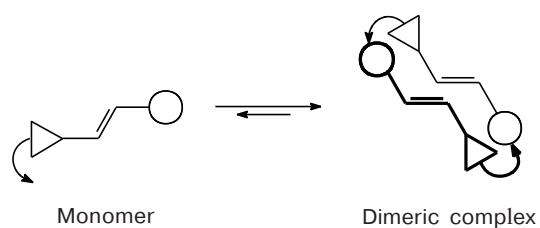
 $n = 2-4$

contains both types of dimeric complexes (*syn*-head-to-tail and *anti*-head-to-tail). However, only the former complex gives the cycloadduct upon photoirradiation.

Studies of the three-dimensional structures of these dimeric complexes by molecular mechanics methods showed that the most favorable arrangement of the double bonds with respect to each other is observed only in the first type of complexes. In the second type of dimeric complexes, not only the double bonds but also the planes of the dyes are mutually perpendicular, *i.e.*, these dimeric complexes cannot be involved in the [2+2] cycloaddition reaction for steric reasons.^{79,83}

The introduction of an alkylammonium substituent at the nitrogen atom of the heterocyclic moiety of styryl dyes allows the preparation of dimeric complexes in the absence of metal ions as a result of spontaneous self-assembly of dye molecules in solution (Scheme 21).^{84,85}

Scheme 21



The structure of the dimeric complex was confirmed by NMR data. The formation of the dimeric complexes is accompanied by upfield shifts of almost all proton signals of the double bonds and aromatic fragments of the dyes.

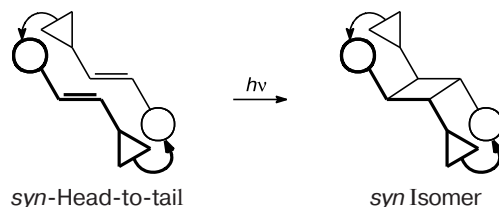
This is possible only if the fragments of the dyes are located one above another. The competitive titration showed that all styryl dyes under study exist in solution as dimeric complexes. Their high stability ($\log K_d$ up to 8.03) is apparently attributed primarily to hydrogen bonding.^{84,85}

The three-dimensional structures of the dimeric complexes were established by X-ray diffraction. It should be noted that the conjugated fragments of the dyes are nearly or almost parallel to each other and that the arrangement of the double bonds in the molecules is favorable for the PCA reaction. Figure 8 exemplifies the dimeric complex of dye **18**.⁸⁴

It is not surprising that attempts to perform the stereospecific PCA reaction of this dye and its closest structural analogs in solution failed (Scheme 22). Our investigations showed that the presence of the propylammonium substituent, the pyridine or quinoline fragments, and the 18-crown-6-ether moiety is most favorable for this reaction (Table 2).^{84,85}

The dimeric complex of dye **18** was involved in the PCA reaction without decomposition by irradiating

Scheme 22



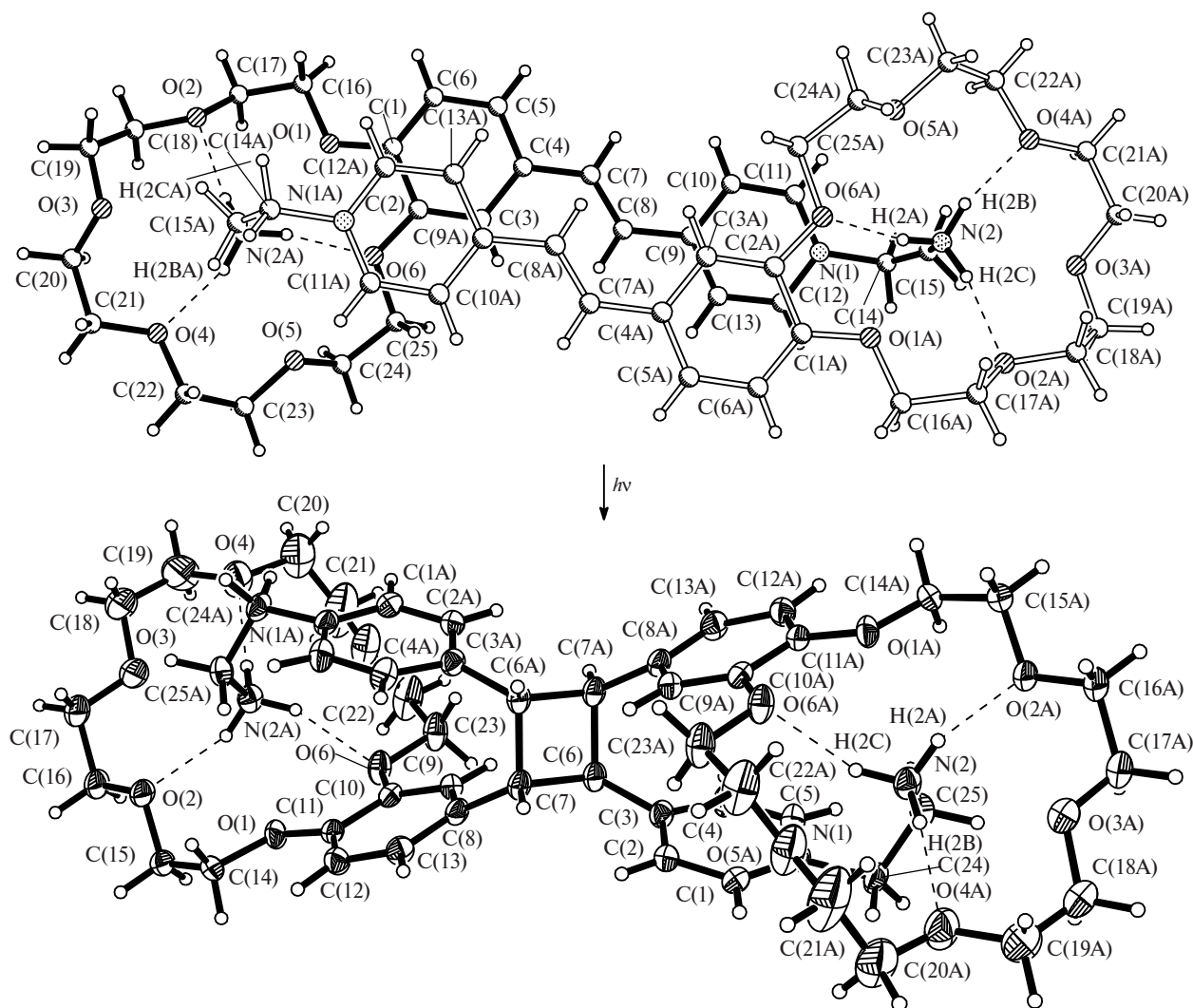


Fig. 8. Structures of the dimeric complex of dye **18** with the cyclobutane derivative prepared by the topochemical reaction.

a single crystal of the complex. This is a rare case for topochemical reactions, which is apparently associated with the fact that the space occupied by the starting dimeric complex is rather large and suitable in shape for the formation of cyclobutane (see Fig. 8). Taking into account this property, one would expect that crystals of these new photosensitive nanosized systems can be used for data recording and storage.^{84,86}

We suggested that a sufficient condition for the construction of nanosized systems, in which the PCA reaction can be performed, is that one component of the complex contains an alkylammonium substituent. Apparently, the stacking interactions in such pseudodimeric complexes provide the favorable orientation of the unsaturated fragments of the components for their involvement in the PCA reaction.

Actually, the addition of one component to another led to substantial upfield shifts of almost all proton signals of the double bonds and aromatic fragments in

the NMR spectra of the dyes, which indicates that the components in the complex are located one above another (Scheme 23).^{85,87}

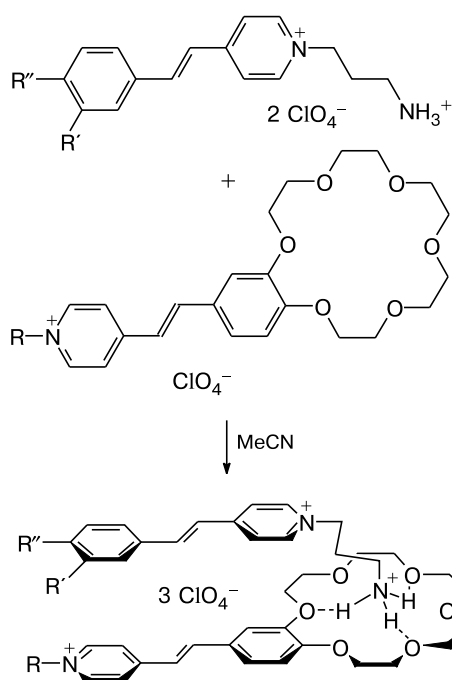
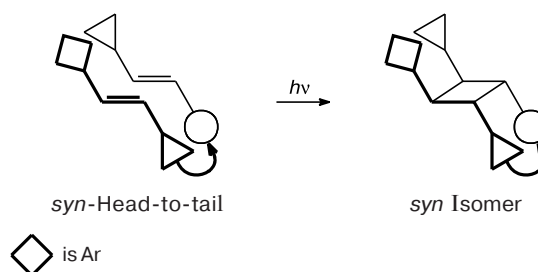
Measurements of the stability constants of the pseudodimeric complexes showed that these constants depend only slightly on the nature of the substituents in the benzene ring of the propylammonium derivatives of styryl dyes. The stability constants are sufficiently high for the PCA reaction to proceed efficiently.

Under irradiation, pseudodimeric complexes gave cyclobutane derivatives, one of numerous possible isomers being obtained in all cases (Scheme 24). This is indicative of a decisive role of the supramolecular preorganization for the stereospecific photoreaction.

It was of interest to study the influence of the second C=C bond in crown-containing butadienyl dyes on their complexation ability and photochemical properties. The addition of magnesium ions to these dyes afforded complexes, which undergo *trans*—*cis* isomerization un-

Table 2. Yields of cyclobutane derivatives after irradiation of dyes in MeCN (the duration of irradiation was 4 h)

Dye	Yield (%)	Dye	Yield (%)
	100		33
	100		0
	40		0

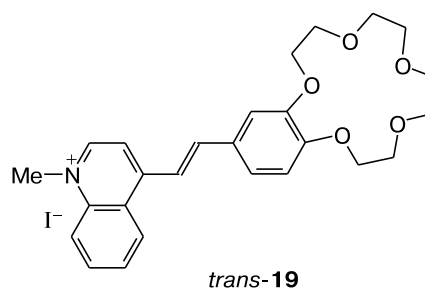
Scheme 23**Scheme 24**

ation of these complexes causes the regio- and stereospecific PCA reaction (Scheme 26). This reaction proceeds with the involvement of only one double bond of the butadienyl dye and affords only one of numerous possible cyclobutane isomers. The quantum yields of the reaction (up to 0.35) are substantially higher than the yields of the reactions with styryl dyes.⁹⁰

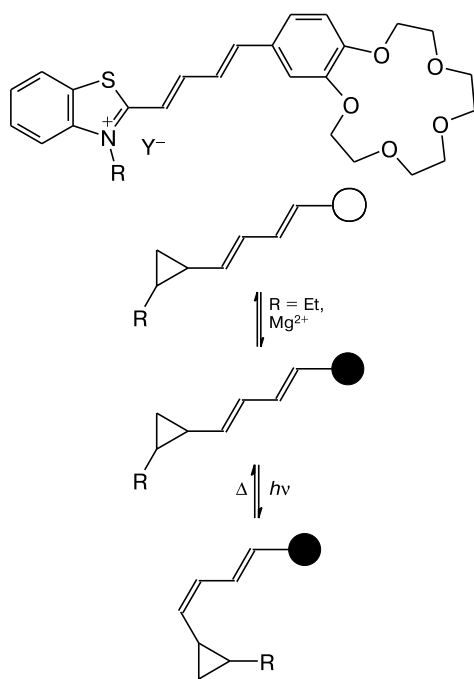
Sandwich, bis-sandwich, and pseudosandwich complexes. We obtained interesting results in studies of sandwich complexes of bis-crown-containing dyes and their photo-

der light irradiation (Scheme 25).^{88,89} The NMR study showed that the photoisomerization proceeds at the double bond adjacent to the heterocyclic moiety.

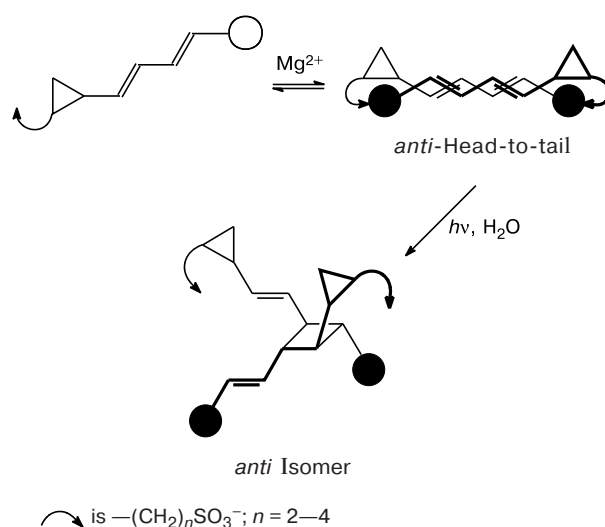
The addition of magnesium ions to butadienyl dyes containing a substituent with the terminal sulfo group at the nitrogen atom of the benzothiazole fragment of the dyes gives rise to dimeric complexes. The light irradi-



Scheme 25



Scheme 26



chemical reactions. We succeeded in performing the PCA reaction of the sandwich complex of crown-containing styryl dye **19** with a potassium ion (Fig. 9).

The conjugated fragments of this complex are located one above another due to stacking interactions,⁹¹ which should assist the PCA reaction.

Actually, irradiation of the complex of bis-crown-containing styryl dye **8** with a barium ion gives rise to two isomeric cyclobutanes and results in a stronger binding of the metal ion (Scheme 27). The molecular pincer is transformed into the molecular trap. The photoirradiation of

cyclobutane derivatives at the absorption maximum induces the reverse reaction giving rise to the starting sandwich complex. The quantum yield of the reverse reaction ($\Phi_{\text{retro-PCA}} = 0.3$) appeared to be much higher than that of the forward reaction ($\Phi_{\text{PCA}} = 0.001$), which is apparently associated with steric strain in the resulting cyclobutanes.⁵¹

It was found that the presence of a covalent bridge between two unsaturated fragments of the compounds is not a necessary prerequisite for the PCA reaction. The addition of ions with a large ionic radius to hetarylphenylethylenes also gives rise to sandwich complexes with the predominant conformation (Scheme 28). The light irradiation of the latter complexes gives rise to a mixture of two cyclobutanes containing the *syn* isomer as the major product with high quantum yield. The ratio be-

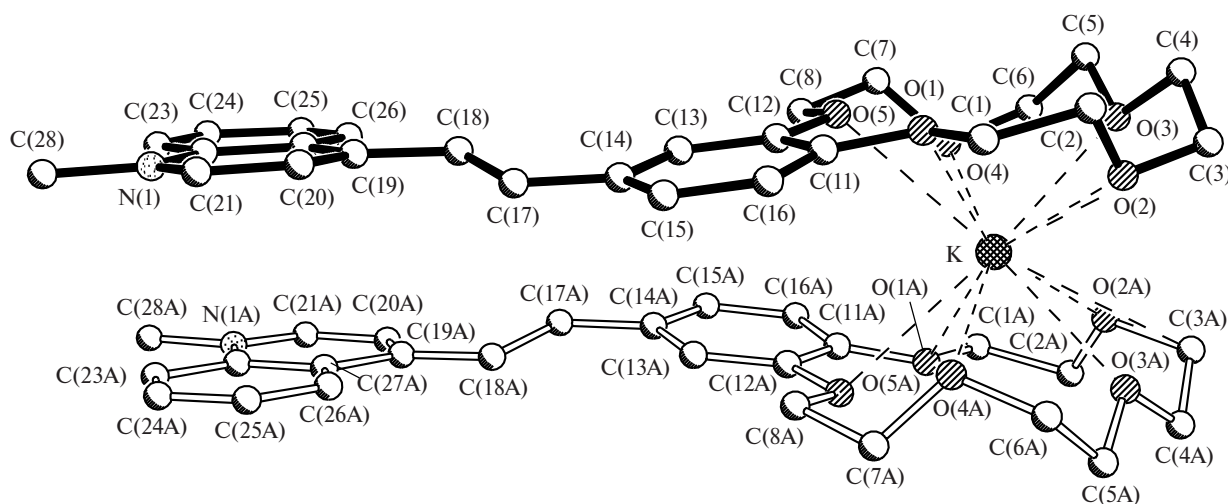
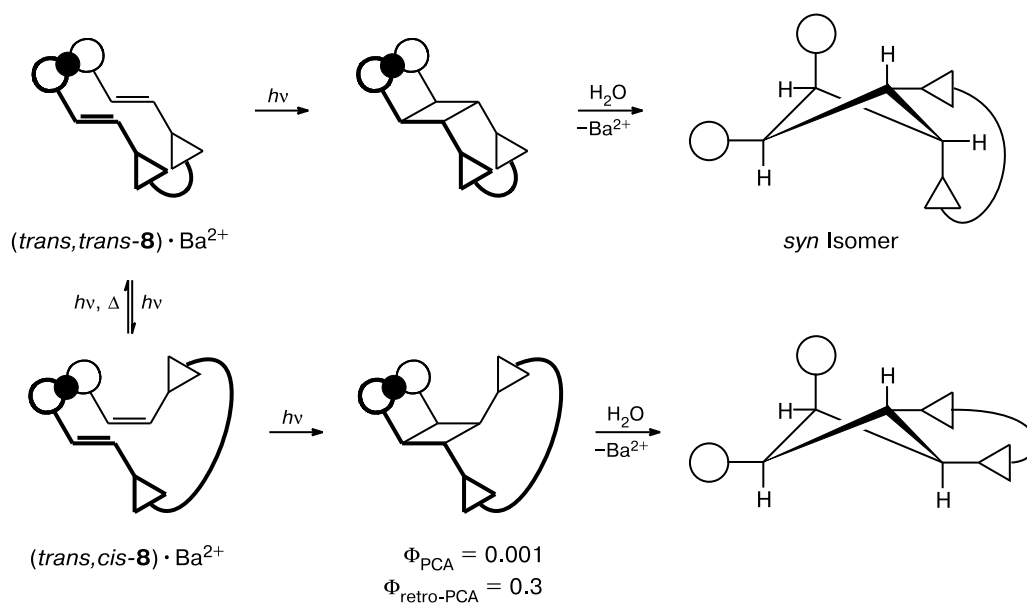


Fig. 9. Frontal projection of the complex of *trans*-**19** with KI.

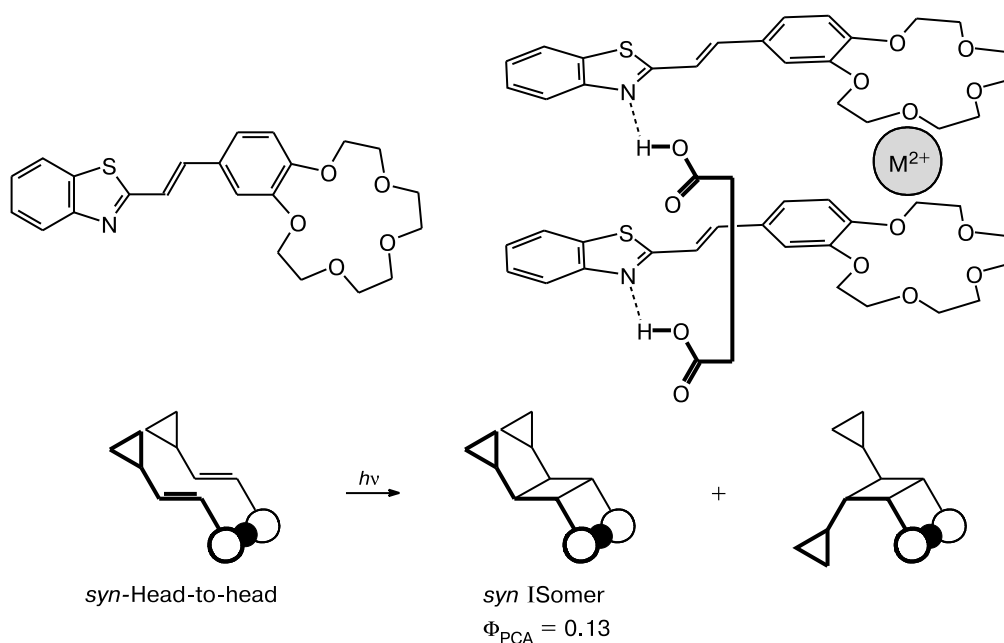
Scheme 27

● = Ba^{2+}

tween the isomers of cyclobutanes in the mixture can be efficiently influenced by adding dibasic acids to the starting solution, which leads to a substantial increase in the percentage of the *syn* isomer. The observed effect is

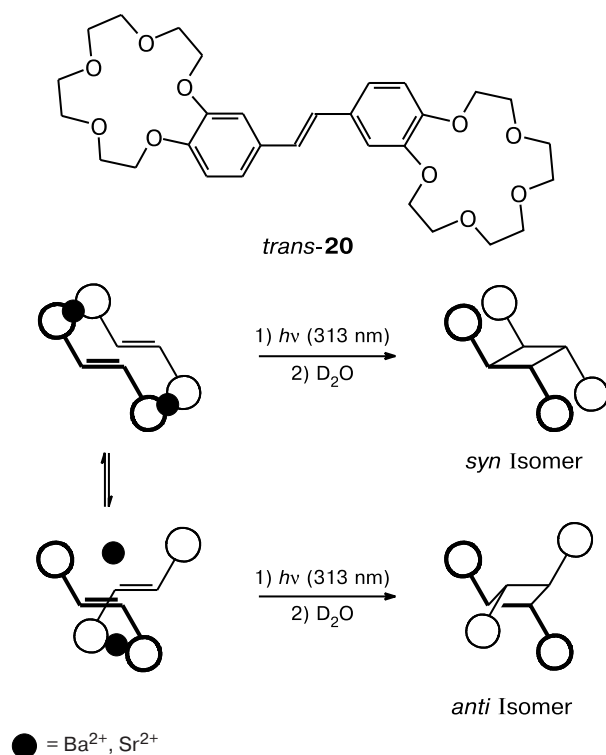
apparently associated with the fact that the conformation of the sandwich complex favorable for the PCA reaction is additionally stabilized by the acid molecule through two hydrogen bonds.⁹²

Scheme 28

● = Ba^{2+} , Sr^{2+}

New possibilities of the self-assembly of light-sensitive nanosized systems were found in studies of the complexation of bis-crown-containing stilbene **20**. The reactions with magnesium and calcium ions afford 1 : 1 and 1 : 2 complexes. In the presence of ions with a larger ionic radius, the reactions apparently afford double sandwich complexes (Scheme 29). The structures of these complexes can be suggested based on NMR data. The complexation results in upfield shifts of most of the proton signals for the double bonds and aromatic fragments of stilbene. This can occur only if the protons of one component are in the shielding cones of another component, *i.e.*, if the components are located one above another.⁹³

Scheme 29

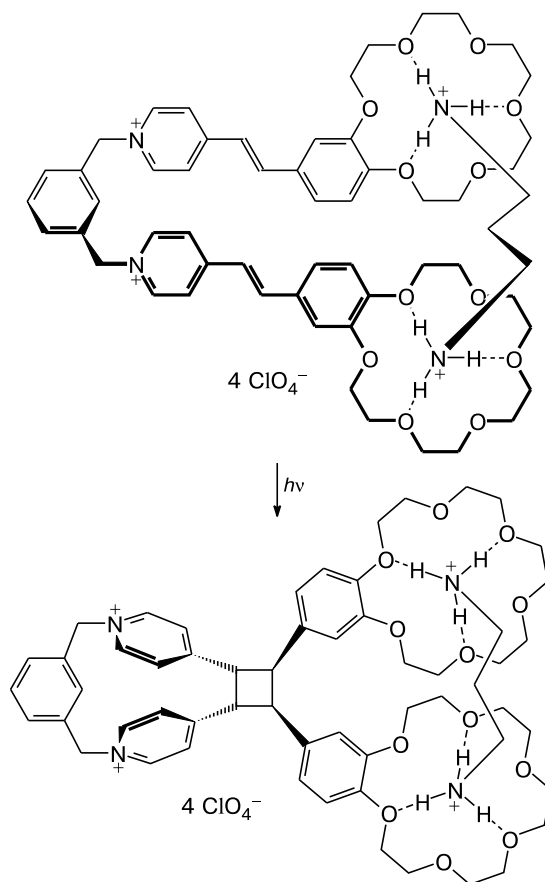


The additional data on the structures of this type of complexes were obtained in the studies of the [2+2] cycloaddition of bis-crown-containing stilbene **20**. The light irradiation of stilbene complexes with ions having a larger ionic radius gives rise to mixtures of two isomeric cyclobutanes, with the *syn* isomer substantially prevailing.⁹³

Studies of bis-crown-containing styryl dyes revealed two promising possibilities for the self-assembly of light-sensitive nanosized systems with the involvement of hydrogen bonds.^{94,95} For example, the addition of propanediammonium perchlorate to a dye of this type affords a pseudosandwich complex through hydrogen

bonding with two crown ether moieties. The irradiation of this pseudosandwich complex gives rise to only one cyclobutane derivative as the *syn* isomer (according to the NMR data; Scheme 30).⁹⁵

Scheme 30



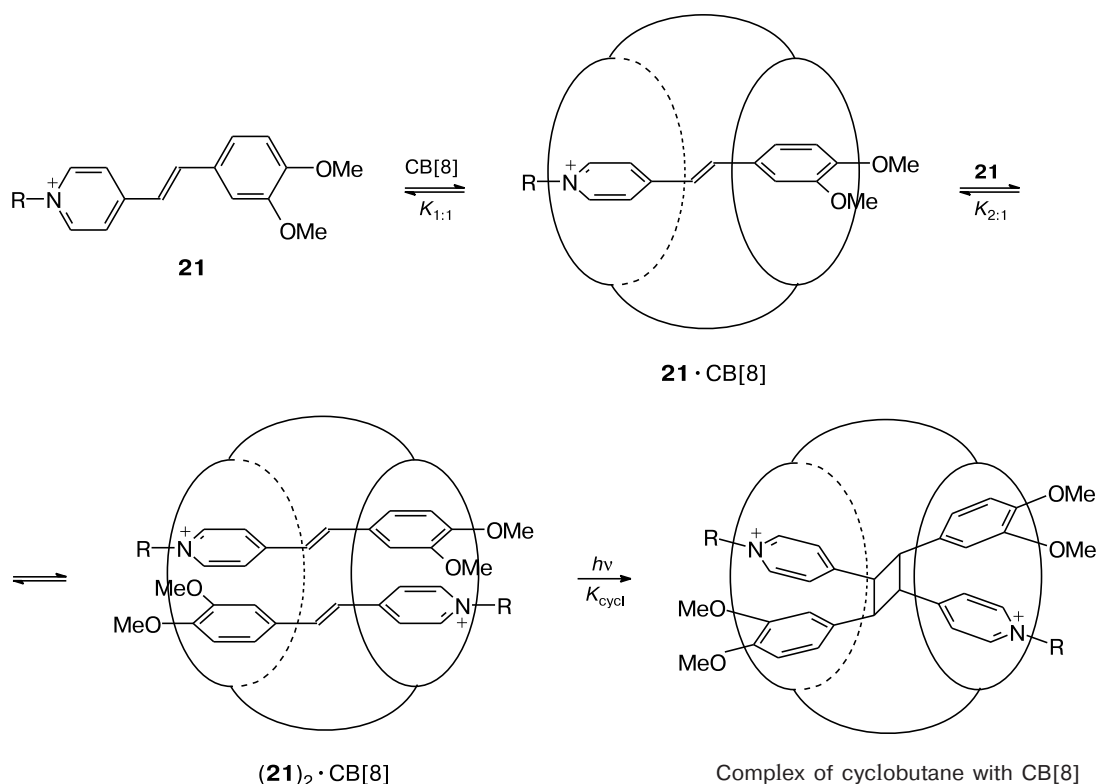
Trimolecular pseudorotaxane complexes. It appeared that the cavity of cucurbituril CB[8] can encapsulate two molecules of styryl dye **21**, due to which this dye can be involved in the [2+2] cycloaddition under irradiation (Scheme 31).

Measurements of the stability constants of the inclusion complexes (Table 3) showed that the cyclobutane is

Table 3. Stability constants of the pseudorotaxane-like complexes of dyes **21** (K) and their cyclobutane derivatives (K_{cycl}) with CB[8]

R	$\log K_{1:1}$	$\log K_{2:1}$	$\log K_{cycl}$
Et	4.9	4.1	4.3
$(CH_2)_3NH_3^+$	5.0	4.4	4.8
$(CH_2)_3SO_3^-$	4.0	2.6	3.2

Scheme 31



stronger bound to cucurbituril compared to the starting components. Therefore, not only mechanical movements within the macrocycles of molecular machines but also the binding strength of the components can be controlled.⁹⁶

Charge transfer and photoinduced electron transfer

Charge-transfer bimolecular and trimolecular complexes. We suggested that the hydrogen bonding can be used to substantially increase the stability of charge-transfer complexes (CTC) and to achieve the spatial preorganization of the components of the complex for more efficient interactions.^{97,98} Derivatives of viologen analogs⁹⁹ containing ammonium groups were used as acceptor components because ammonium groups are known to form stable complexes with crown ethers through hydrogen bonding.¹⁰⁰ Bis-crown-containing stilbene **22** capable of forming ditopic complexes was chosen as the donor component. After mixing of colorless solutions of these components, the reaction mixture turned dark-brown, which is indicative of the interaction of the components giving rise to CTC **23** (Scheme 32).^{97,101–103}

Actually, the absorption spectrum shows a characteristic intense charge-transfer band at 500 nm (Fig. 10).

The structures of CTCs can be determined by NMR spectroscopy. The complexation is accompanied by upfield shifts of the proton signals of the double bonds and aromatic fragments. This is possible only if the protons of one component are in the shielding cones of another component, *i.e.*, if the components are located one above another.

The addition of barium or calcium ions to solutions of CTCs results in the displacement of the acceptor compo-

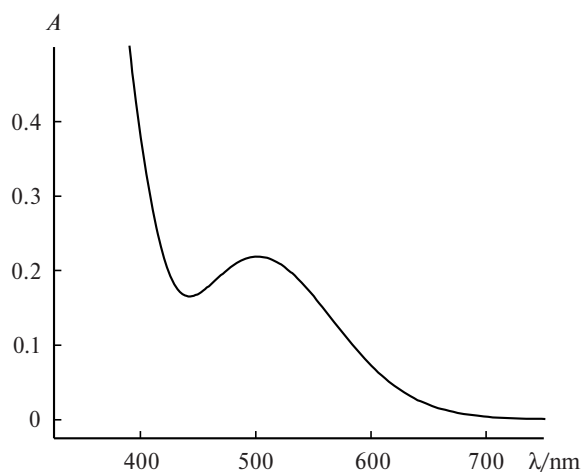
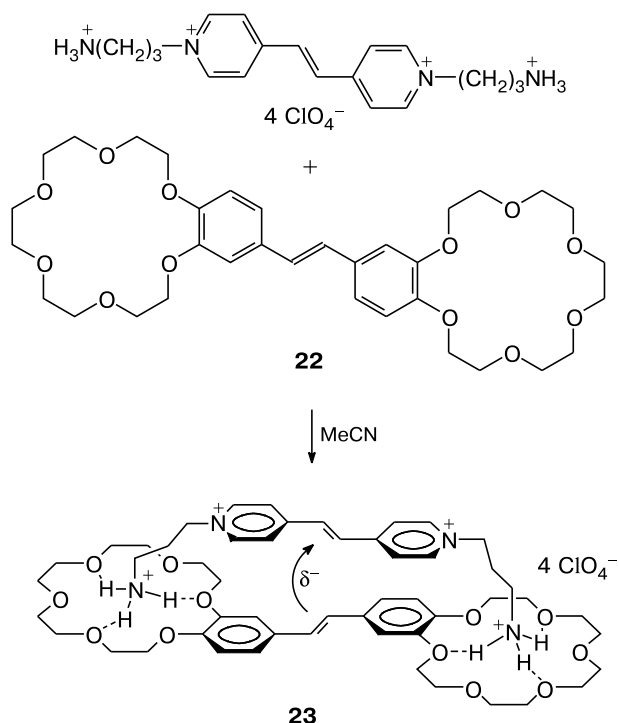
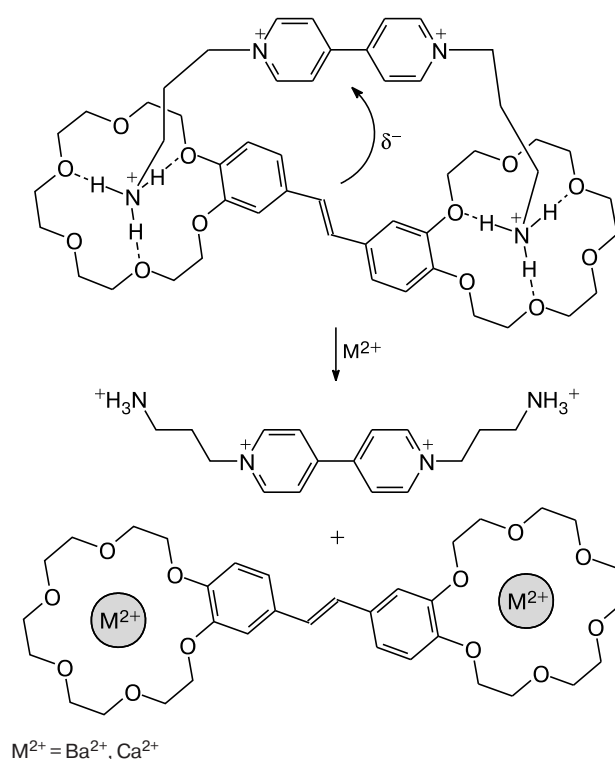


Fig. 10. Absorption spectrum of charge-transfer complex **23** in MeCN.

Scheme 32



Scheme 33

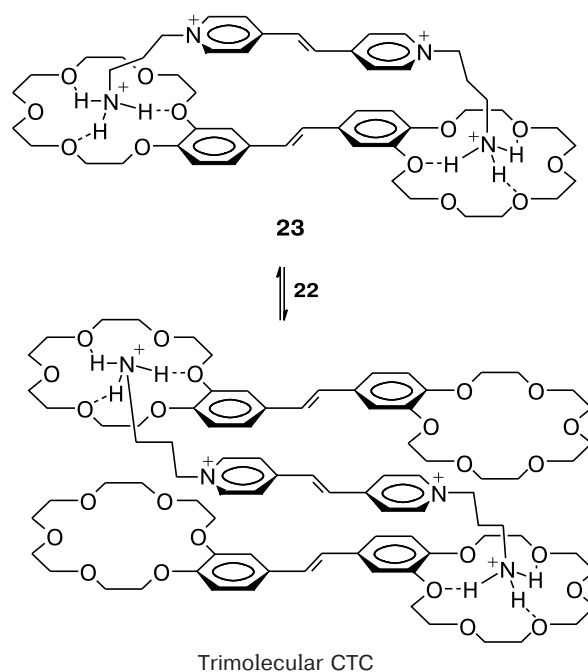


nent and the formation of crown-containing stilbene complexes with metal ions (Scheme 33). This process is accompanied by the disappearance of the long-wavelength charge-transfer band. The most interesting changes are observed in the fluorescence spectra. The starting CTCs do not exhibit fluorescence. However, the addition of barium or calcium ions leads to a substantial fluorescence enhancement due to complexation of stilbene with metal ions. Since this reaction is ion-selective, charge-transfer complexes can be used as fluorescent molecular sensors for the detection of barium and calcium ions.¹⁰⁴

The stabilization by hydrogen bonding is so high that rather exotic trimolecular CTCs can be prepared (Scheme 34). Actually, the addition of crown-containing stilbene **22** to complex **23** led to a substantial increase in the intensity of the long-wavelength charge-transfer band at 500 nm.¹⁰⁴ We established the three-dimensional structure of one trimolecular CTC by X-ray diffraction. The results confirmed the earlier suggestion¹⁰⁵ that the ammonium groups of the acceptor component are coordinated to the crown ether moieties of two stilbene molecules.

We studied the dynamics of the excited states of bimolecular (**23**) and trimolecular CTCs by femtosecond spectroscopy.¹⁰⁶ The excitation at the absorption maximum of CTCs with the composition 1 : 1 gives rise to the lowest electron-transfer excited state. After very fast internal vibrational relaxation, the excited state decays into the ground state as a result of the reverse electron

Scheme 34

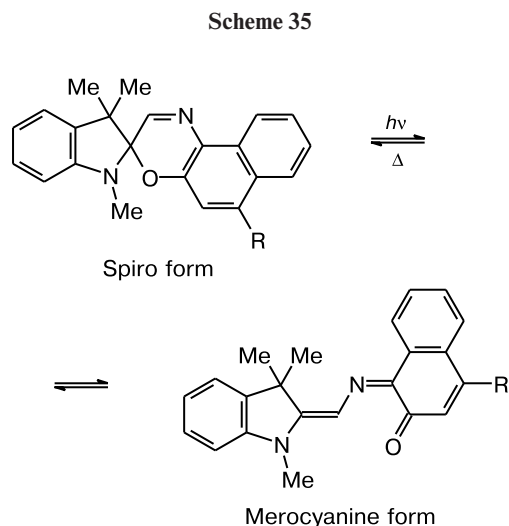


transfer with a time constant of 540 fs. The excited state of the trimolecular complex exhibits very similar dynamics, but the reverse electron transfer in this case is two times

slower, which is apparently attributed to greater electron delocalization.

Photoinduced electrocyclic reaction

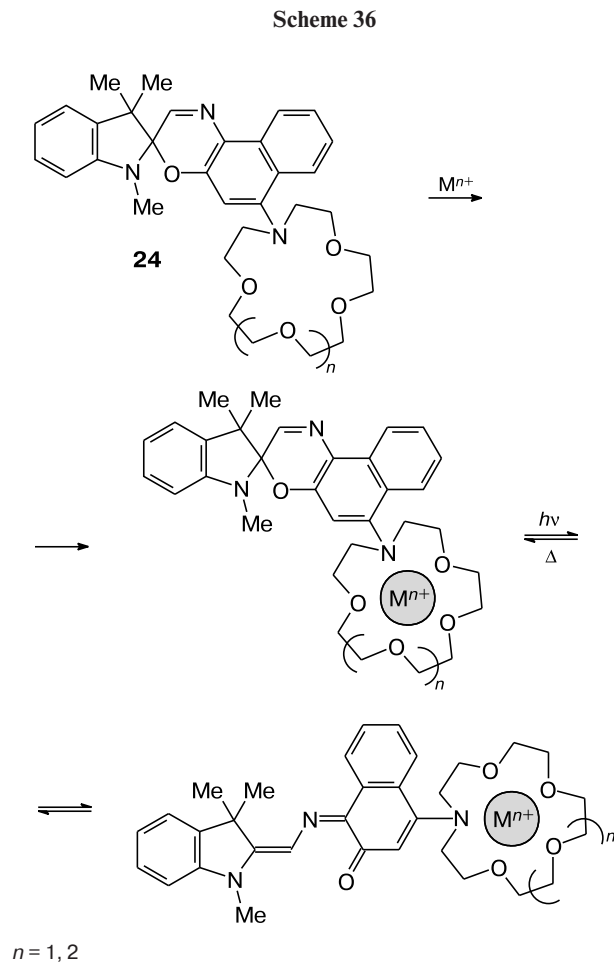
Complexes of merocyanine and open forms. Spiro-naphthoxazines are known^{107,108} to be strongly photochromic and highly stable to photodegradation, due to which these compounds are promising for practical use. Crown-containing spironaphthoxazines, which undergo photo-induced isomerization between the neutral spiro form and the zwitterionic merocyanine form (Scheme 35), would be expected to change the complexation ability.



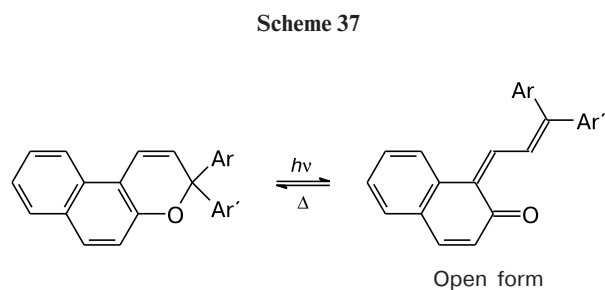
Spironaphthoxazines containing a crown ether moiety conjugated with a chromophoric fragment (**24**) are of considerable interest because the substantial influence on their spectroscopic and photochemical properties would be expected to occur. The addition of alkali or alkaline-earth metal cations results in complexation at the crown ether moiety (Scheme 36). The light irradiation of the resulting complexes leads to their photoisomerization from the spiro to the merocyanine form, which is characterized by a decrease in the rate of the reverse thermal transformation into the spiro form, *i.e.*, the complexation stabilizes the merocyanine form.¹⁰⁹

The stability constants of the complexes of the merocyanine form appeared to be smaller than the corresponding constants of the spiro form. Therefore, the photoisomerization of compound **24** leads to a decrease in its ability to bind metal cations.

In recent years, naphthopyrans have attracted considerable interest due to their use in photochromic optical lenses and as promising materials for data recording and storage.¹¹⁰ As in the case of spironaphthoxazines, the photochromism of naphthopyrans involves the O—C

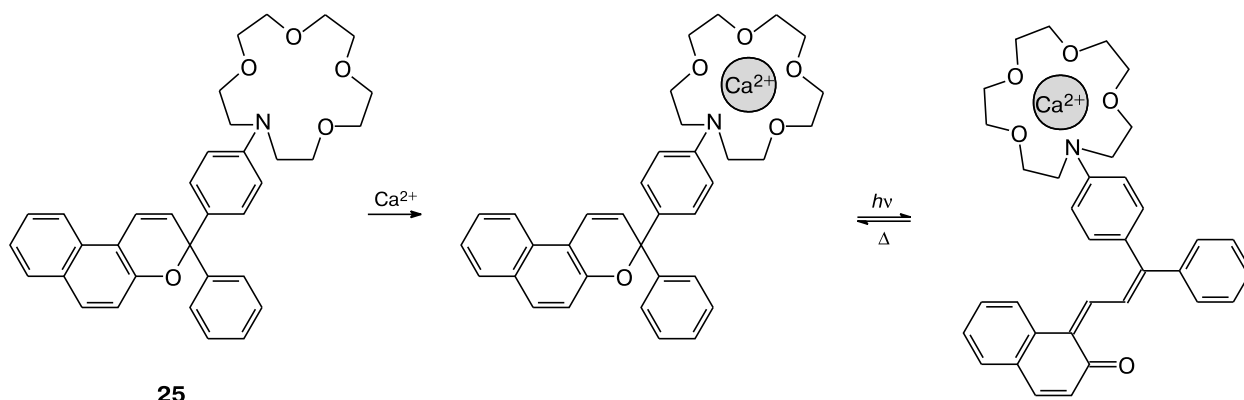


bond cleavage of the pyran ring as a result of the electrocyclic reaction (Scheme 37).



Among crown-containing naphthopyrans, compounds containing the crown ether moiety in the aryl group are of most interest because irradiation of these compounds gives rise to the open form containing the conjugated crown ether moiety in closest proximity to the chromophore. The addition of calcium cations to naphthopyran **25** leads to their binding by the crown ether moiety. Under irradiation, the colored open form of the complex was obtained (Scheme 38), the rate constant of the dark bleaching being smaller.¹¹¹

Scheme 38



We measured the complexation constant of the open form with a calcium cation. This constant appeared to be almost an order of magnitude smaller than that of the starting naphthopyran **25**.

Hence, the photoisomerization of naphthopyran, like that of spironaphthoxazine, leads to a decrease in the binding ability of metal cations.

Conclusions

In conclusion, let us note that the previously unknown hybrid structures based on unsaturated and macrocyclic compounds were found to have a unique combination of characteristics necessary for the design of light-sensitive and light-emitting nanosized systems. These hybrid structures 1) are available from the standpoint of organic synthesis, 2) can act as efficient molecular photoswitches, 3) can undergo various photochemical transformations depending on the structure, and 4) can undergo spontaneous organization to form various nanosized architectures. These facts suggest that these compounds can be used for the design of *molecular meccano*, which allows the construction of light-sensitive and light-emitting nanosized systems, photoswitchable molecular devices, and photocontrolled molecular machines with the desired properties.

Taking into account the above-considered results, crown-containing unsaturated compounds and their complexes would be expected to find wide application as selective chromo- and fluoroionophores^{18–20,38,41,43,46} binding small organic molecules and metal cations, for the design of photochromic and photofluorescent materials,^{18–20,80,84} as photochromic ionophores in the photocontrolled ion transport through membranes,¹¹² in polymeric^{42,113} and photoswitchable Langmuir–Blodgett films,^{114–119} as materials for the optical data recording and storage,^{18–20,84} for the photocontrolled extraction of metal ions from water, in molecular electron-

ics for the design of photoswitchable molecular devices,^{18–20,80} as laser dyes,⁵³ as photoswitchable artificial enzymes in photodynamic cancer therapy, and in nanotechnology for the design of photocontrolled molecular machines.^{75,76,96}

I thank the Russian Academy of Sciences awarding the 2007 Butlerov prize for studies summarized in the present review.

This study was financially supported by the Presidium and the Division of Chemistry and Materials Science of the Russian Academy of Sciences, the Ministry of Education and Science of the Russian Federation, the Russian Foundation for Basic Research, the Government of Moscow, the International Science Foundation (ISF), the INTAS, the US Civilian Research and Development Foundation (CRDF), the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), the Royal Society of Chemistry (Great Britain), and the National Center for Scientific Research (Centre National de la Recherche Scientifique, CNRS, France).

References

1. E. Landre, *Rossiiskie nanotekhnologii*, 2007, **2**, 8 [*Nanotechnologies in Russia*, 2007, **2** (Engl. Transl.)].
2. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, 1995.
3. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, J. Wiley and Sons, Chichester, 2000, Vol. **1**, **2**.
4. J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153.
5. A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature*, 1993, **364**, 42.
6. M. A. Fox, *Acc. Chem. Res.*, 1999, **32**, 201.
7. V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405.
8. J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611.
9. R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445.

10. J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero, J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477.
11. K. Kinbara, T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
12. *Topics in Current Chemistry*, Ed. T. R. Kelly, Springer, Berlin, 2005, **262**.
13. *Nanotechnology Research Directions: IWGN Workshop Report. Vision for Nanotechnology R&D in the Next Decade*, Eds M. C. Roco, R. S. Williams, P. Alivisatos, Kluwer Acad. Publ., Dordrecht, 2000.
14. C. P. Poole, F. J. Owens, *Introduction to Nanotechnology*, J. Wiley and Sons, New York, 2003.
15. N. Kobayashi, *Vvedenie v nanotekhnologiyu* [Introduction to Nanotechnology], Binom, Moscow, 2005 (Russian translation from Japanese).
16. V. Balzani, F. Scandola, in *Comprehensive Supramolecular Chemistry*, Ed. J.-M. Lehn, Pergamon Press, New York, 1996, **10**, 687.
17. K. Kimura, *Coord. Chem. Rev.*, 1996, **148**, 41.
18. S. P. Gromov, *Rossiiskaya nauka: vystoyat' i vozrodit'sya* [Russian Science: Withstand and Revive], Nauka, Moscow, 1997, 187 (in Russian).
19. S. P. Gromov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 641 [*Russ. Chem. Bull.*, 1997, **46**, 611 (Engl. Transl.)].
20. S. P. Gromov, *Ros. Khim. Zh.*, 2001, **45**, 116 [*Mendeleev Chem. J.*, 2001, **45** (Engl. Transl.)].
21. S. P. Gromov, *Rossiiskie nanotekhnologii*, 2006, **1**, 29 [*Nanotechnologies in Russia*, 2006, **1** (Engl. Transl.)].
22. D. E. Metzler, *Biochemistry. The Chemical Reactions of Living Cells*, Academic Press, New York, 1977, **3**.
23. R. P. Wayne, *Principles and Applications of Photochemistry*, Oxford University Press, Oxford, 1988.
24. H. Bouas-Laurent, A. Castellán, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.*, 2001, **30**, 248.
25. K. Kimura, H. Sakamoto, M. Nakamura, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 225.
26. S. Shinkai, in *Comprehensive Supramolecular Chemistry*, Ed. J.-M. Lehn, Pergamon Press, New York, 1996, **1**, 671.
27. *Organicheskie fotokhromy* [Organic Photochromes], Ed. A. V. El'tsov, Khimiya, Leningrad, 1982, 120 (in Russian).
28. J. A. Barltrop, J. D. Coyle, *Excited States in Organic Chemistry*, J. Wiley and Sons, London, 1975.
29. *Photochromism: Molecules and Systems*, Eds H. Dürr, H. Bouas-Laurent, Elsevier, Amsterdam, 1990.
30. V. F. Razumov, M. V. Alfimov, *Zhurn. nauch. i prikl. fotografii* [*J. Sci. Appl. Photography Cinematography*], 2003, **48**, 28 (in Russian).
31. *Molecular Switches*, Ed. B. L. Feringa, Wiley-VCH Verlag GmbH, Weinheim, 2001.
32. *Cation Binding by Macrocycles*, Eds Y. Inoue, G. W. Gokel, Marcel Dekker, New York, 1990.
33. *Host Guest Complex Chemistry Macrocycles. Synthesis, Structure, Applications*, Eds F. Vögtle, E. Weber, Springer-Verlag, Berlin, 1985.
34. K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96.
35. J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621.
36. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, V. V. Tkachev, L. O. Atovmyan, *Dokl. Akad. Nauk SSSR*, 1991, **319**, 1141 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
37. S. P. Gromov, S. A. Sergeev, S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, L. G. Kuz'mina, A. V. Churakov, J. A. K. Howard, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 530 [*Russ. Chem. Bull.*, 1999, **48**, 525 (Engl. Transl.)].
38. S. P. Gromov, M. V. Fomina, E. N. Ushakov, I. K. Lednev, M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1990, **314**, 1135 [*Dokl. Chem.*, 1990 (Engl. Transl.)].
39. S. P. Gromov, M. V. Fomina, G. K. Chudinova, V. A. Barachevskii, M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 739 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
40. K. Lednev, M. V. Fomina, S. P. Gromov, O. B. Stanislavsky, M. V. Alfimov, J. N. Moore, R. E. Hester, *Spectrochim. Acta*, 1992, **48A**, 931.
41. S. P. Gromov, M. V. Fomina, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1625 [*Russ. Chem. Bull.*, 1993, **42**, 1561 (Engl. Transl.)].
42. M. V. Alfimov, S. P. Gromov, V. B. Nazarov, O. M. Pilyugina, M. V. Fomina, *Dokl. Akad. Nauk*, 1993, **330**, 453 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
43. S. P. Gromov, O. A. Fedorova, M. V. Fomina, M. V. Alfimov, Pat. RF 2012574; *Byul. izobret. [Inventor Bull.]*, 1994, No. 9 (in Russian).
44. S. P. Gromov, D. E. Levin, K. Ya. Burshtein, V. A. Krasnovskii, S. N. Dmitrieva, A. A. Golosov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 999 [*Russ. Chem. Bull.*, 1997, **46**, 959 (Engl. Transl.)].
45. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, Yu. V. Fedorov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1007 [*Russ. Chem. Bull.*, 1997, **46**, 967 (Engl. Transl.)].
46. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, O. V. Eshcheulova, Yu. V. Fedorov, M. V. Alfimov, Pat. RF 2176256; *Byul. izobret. [Inventor Bull.]*, 2001, No. 33 (in Russian).
47. O. B. Stanislavskii, E. N. Ushakov, S. P. Gromov, O. A. Fedorova, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 605 [*Russ. Chem. Bull.*, 1996, **45**, 564 (Engl. Transl.)].
48. M. V. Alfimov, S. P. Gromov, Yu. V. Fedorov, O. A. Fedorova, A. I. Vedernikov, A. V. Churakov, L. G. Kuz'mina, J. A. K. Howard, S. Bossmann, A. Braun, M. Woerner, D. F. Sears, J. Saltiel, *J. Am. Chem. Soc.*, 1999, **121**, 4992.
49. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2003 [*Russ. Chem. Bull.*, 1995, **44**, 1922 (Engl. Transl.)].
50. S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, M. V. Alfimov, S. P. Gromov, O. A. Fedorova, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1995, **107**, 721.
51. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, A. V. Buevich, I. I. Baskin, Y. V. Pershina, B. Eliasson, U. Edlund, M. V. Alfimov, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1323.
52. E. N. Ushakov, S. P. Gromov, O. A. Fedorova, Y. V. Pershina, M. V. Alfimov, F. Barigelletti, L. Flamigni, V. Balzani, *J. Phys. Chem. A*, 1999, **103**, 11188.
53. S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, S. P. Gromov, S. A. Sergeev, M. V. Alfimov, *J. Fluorescence*, 1999, **9**, 33.
54. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2505 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2646].
55. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Int. J. Quantum Chem.*, 2004, **100**, 617.
56. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1981 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2042].
57. M. V. Alfimov, S. P. Gromov, in *Supramolecular Chemistry*, Eds V. Balzani, L. De Cola, NATO ASI Ser. C, 1992, 343.

58. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, I. I. Baskin, A. V. Buevich, E. N. Andryukhina, M. V. Alfimov, D. Johnels, U. G. Edlund, J. K. Whitesell, M. A. Fox, *J. Org. Chem.*, 2003, **68**, 6115.
59. M. V. Alfimov, S. P. Gromov, I. K. Lednev, *Chem. Phys. Lett.*, 1991, **185**, 455.
60. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, I. K. Lednev, M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
61. K. Lednev, S. P. Gromov, E. N. Ushakov, M. V. Alfimov, J. N. Moore, R. E. Hester, *Spectrochim. Acta, Part A*, 1992, **48**, 799.
62. A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova, M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.
63. I. I. Baskin, K. Ya. Burshtein, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Dokl. Akad. Nauk*, 1992, **325**, 306 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
64. I. I. Baskin, K. Ya. Burshtein, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *J. Mol. Struct.*, 1992, **274**, 93.
65. I. I. Baskin, K. Ya. Burshtein, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Zh. Strukt. Khim.*, 1993, **34**, 39 [*Russ. J. Struct. Chem.*, 1993, **34**, 208 (Engl. Transl.)].
66. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 104 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
67. S. P. Gromov, A. A. Golosov, O. A. Fedorova, D. E. Levin, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 129 [*Russ. Chem. Bull.*, 1995, **44**, 124 (Engl. Transl.)].
68. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, I. I. Baskin, A. V. Lindeman, E. V. Malysheva, T. A. Balashova, A. S. Arsen'ev, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 99 [*Russ. Chem. Bull.*, 1998, **47**, 97 (Engl. Transl.)].
69. E. N. Ushakov, S. P. Gromov, A. V. Buevich, I. I. Baskin, O. A. Fedorova, A. I. Vedernikov, M. V. Alfimov, B. Eliasson, U. Edlund, *J. Chem. Soc., Perkin Trans. 2*, 1999, 601.
70. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, A. V. Buevich, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 693 [*Russ. Chem. Bull.*, 1996, **45**, 654 (Engl. Transl.)].
71. M. V. Alfimov, A. I. Vedernikov, S. P. Gromov, Yu. V. Fedorov, O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2213 [*Russ. Chem. Bull.*, 1997, **46**, 2099 (Engl. Transl.)].
72. E. N. Ushakov, S. P. Gromov, O. A. Fedorova, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 484 [*Russ. Chem. Bull.*, 1997, **46**, 463 (Engl. Transl.)].
73. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, V. A. Soldatenkova, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1192 [*Russ. Chem. Bull.*, 1997, **46**, 1143 (Engl. Transl.)].
74. A. I. Vedernikov, D. V. Kondratuk, N. A. Lobova, T. M. Valova, V. A. Barachevsky, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 264.
75. A. I. Vedernikov, N. A. Lobova, L. G. Kuz'mina, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Rossiiskie nanotekhnologii*, 2007, **2**, 56 [*Nanotechnologies in Russia*, 2007, **2** (Engl. Transl.)].
76. L. G. Kuz'mina, A. I. Vedernikov, N. A. Lobova, J. A. K. Howard, Y. A. Strelenko, V. P. Fedin, M. V. Alfimov, S. P. Gromov, *New J. Chem.*, 2006, **30**, 458.
77. E. N. Ushakov, O. B. Stanislavskii, S. P. Gromov, O. A. Fedorova, M. V. Alfimov, *Dokl. Akad. Nauk*, 1992, **323**, 702 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
78. M. V. Alfimov, S. P. Gromov, O. B. Stanislavskii, E. N. Ushakov, O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1449 [*Russ. Chem. Bull.*, 1993, **42**, 1385 (Engl. Transl.)].
79. I. I. Baskin, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Dokl. Akad. Nauk*, 1994, **335**, 313 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
80. M. V. Alfimov, S. P. Gromov, *Applied Fluorescence in Chemistry, Biology, and Medicine*, Eds W. Rettig, B. Strehmel, S. Schrader, H. Seifert, Springer-Verlag, Berlin, 1999, 161.
81. O. A. Fedorova, Y. V. Fedorov, A. I. Vedernikov, S. P. Gromov, O. V. Yescheulova, M. V. Alfimov, M. Woerner, S. Bossmann, A. Braun, J. Saltiel, *J. Phys. Chem. A*, 2002, **106**, 6213.
82. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, A. V. Buevich, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2225 [*Russ. Chem. Bull.*, 1995, **44**, 2131 (Engl. Transl.)].
83. A. Ya. Freidzon, I. I. Baskin, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2185 [*Russ. Chem. Bull.*, 1998, **47**, 2117 (Engl. Transl.)].
84. S. P. Gromov, A. I. Vedernikov, N. A. Lobova, L. G. Kuz'mina, S. N. Dmitrieva, O. V. Tikhonova, M. V. Alfimov, Pat. RF 2278134; *Byul. izobret. [Inventor Bull.]*, 2006, No. 17 (in Russian).
85. A. I. Vedernikov, S. P. Gromov, N. A. Lobova, S. N. Dmitrieva, S. K. Sazonov, O. V. Tikhonova, P. S. Loginov, E. N. Ushakov, M. V. Alfimov, L. G. Kuz'mina, J. A. K. Howard, *XXX Int. Symp. on Macrocyclic Chemistry (July 17–21, 2005, Drezden, Germany)*, Drezden, 2005, **A33**, 113.
86. A. I. Vedernikov, S. P. Gromov, N. A. Lobova, L. G. Kuz'mina, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1896 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1954].
87. A. I. Vedernikov, S. K. Sazonov, P. S. Loginov, N. A. Lobova, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 29.
88. S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, L. G. Kuz'mina, A. V. Feofanov, V. G. Avakyan, A. V. Churakov, Yu. S. Alaverdyan, E. V. Malysheva, M. V. Alfimov, J. A. K. Howard, B. Eliasson, U. G. Edlund, *Helv. Chim. Acta*, 2002, **85**, 60.
89. E. N. Ushakov, S. P. Gromov, L. G. Kuz'mina, A. I. Vedernikov, V. G. Avakyan, J. A. K. Howard, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1491 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1549].
90. A. I. Vedernikov, E. N. Ushakov, L. G. Kuz'mina, S. Yu. Zaitsev, M. S. Kapichnikova, Yu. A. Strelenko, M. V. Alfimov, A. V. Churakov, T. I. Sergeeva, J. A. K. Howard, D. Johnels, U. G. Edlund, K. Gloe, S. P. Gromov, *XVII Mendeleev Congress on General and Applied Chemistry (September 21–26, 2003, Kazan)*, Kazan, 2003, 45.
91. L. G. Kuz'mina, A. V. Churakov, J. A. K. Howard, O. A. Fedorova, S. P. Gromov, M. V. Alfimov, *Kristallografiya*, 2003, **48**, 664 [*Crystallogr. Repts*, 2003, **48**, 613 (Engl. Transl.)].
92. S. P. Gromov, A. I. Vedernikov, Yu. V. Fedorov, O. A. Fedorova, E. N. Andryukhina, N. E. Shepel, Yu. A. Strelenko, D. Johnels, U. G. Edlund, J. Saltiel, M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1524 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1569].
93. S. P. Gromov, A. I. Vedernikov, N. A. Lobova, S. S. Basok, Yu. P. Strokach, L. G. Kuz'mina, T. M. Valova, E. I. Ivanov, J. A. K. Howard, M. V. Alfimov, *XXX Int. Symp. on Macrocyclic Chemistry (July 17–21, 2005, Drezden, Germany)*, Drezden, 2005, **A34**, 114.

94. A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Kiselev, M. V. Alfimov, S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 656 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 666].
95. A. I. Vedernikov, N. A. Lobova, E. N. Ushakov, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2005, **15**, 173.
96. A. I. Vedernikov, S. K. Sazonov, N. A. Lobova, A. A. Botsmanova, L. G. Kuz'mina, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *XVIII Mendeleev Congress on General and Applied Chemistry (23–28 September, 2007, Moscow)*, Moscow, 2007, 2265.
97. S. P. Gromov, E. N. Ushakov, A. I. Vedernikov, N. A. Lobova, M. V. Alfimov, Y. A. Strelenko, J. K. Whitesell, M. A. Fox, *Org. Lett.*, 1999, **1**, 1697.
98. E. N. Ushakov, S. P. Gromov, A. I. Vedernikov, E. V. Malyshova, A. A. Botsmanova, M. V. Alfimov, B. Eliasson, U. G. Edlund, J. K. Whitesell, M. A. Fox, *J. Phys. Chem. A*, 2002, **106**, 2020.
99. L. G. Kuz'mina, A. V. Churakov, J. A. K. Howard, A. I. Vedernikov, N. A. Lobova, A. A. Botsmanova, M. V. Alfimov, S. P. Gromov, *Kristallografiya*, 2005, **50**, 266 [*Crystallogr. Repts*, 2005, **50**, 234 (Engl. Transl.)].
100. A. I. Vedernikov, S. S. Basok, S. P. Gromov, L. G. Kuz'mina, V. G. Avakyan, N. A. Lobova, T. V. Titkov, Yu. A. Strelenko, E. I. Ivanov, J. A. K. Howard, M. V. Alfimov, *Zh. Org. Khim.*, 2005, **41**, 864 [*Russ. J. Org. Chem.*, 2005, **41**, 843 (Engl. Transl.)].
101. I. S. Alaverdian, A. V. Feofanov, S. P. Gromov, A. I. Vedernikov, N. A. Lobova, M. V. Alfimov, *J. Phys. Chem. A*, 2003, **107**, 9542.
102. Yu. S. Alaverdyan, A. V. Feofanov, S. P. Gromov, A. I. Vedernikov, N. A. Lobova, M. V. Alfimov, *Optika Spektroskopiya*, 2004, **97**, 589 [*Optics Spectrosc.*, 2004, **97**, 560 (Engl. Transl.)].
103. K. P. Butin, A. A. Moiseeva, S. P. Gromov, A. I. Vedernikov, A. A. Botsmanova, E. N. Ushakov, M. V. Alfimov, *J. Electroanal. Chem.*, 2003, **547**, 93.
104. S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Botsmanova, S. S. Basok, L. G. Kuz'mina, A. V. Churakov, Y. A. Strelenko, M. V. Alfimov, E. I. Ivanov, J. A. K. Howard, D. Johnels, U. G. Edlund, *New J. Chem.*, 2005, **29**, 881.
105. A. I. Vedernikov, L. G. Kuz'mina, N. A. Lobova, E. N. Ushakov, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 151.
106. E. N. Ushakov, V. A. Nadtochenko, S. P. Gromov, A. I. Vedernikov, N. A. Lobova, M. V. Alfimov, F. E. Gostev, A. N. Petrukhin, O. M. Sarkisov, *Chem. Phys.*, 2004, **298**, 251.
107. S. M. Aldoshin, *Usp. Khim.*, 1990, **59**, 1144 [*Russ. Chem. Rev.*, 1990, **59** (Engl. Transl.)].
108. V. A. Lokshin, A. Sama, A. V. Metelitsa, *Usp. Khim.*, 2002, **71**, 1015 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].
109. Yu. P. Strokach, O. A. Fedorova, S. P. Gromov, A. V. Koshkin, T. M. Valova, V. A. Barachevskii, M. V. Alfimov, V. A. Lokshin, A. Samat, R. Guglielmetti, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2002, 56 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 58].
110. *Organic Photochromic and Thermochromic Compounds*, Eds J. C. Crano, R. J. Guglielmetti, Plenum Press, New York, 1999, 1.
111. E. N. Ushakov, V. B. Nazarov, O. A. Fedorova, S. P. Gromov, A. V. Chebun'kova, M. V. Alfimov, F. Barigelletti, *J. Phys. Org. Chem.*, 2003, **16**, 306.
112. V. P. Tsybyshev, V. A. Livshits, B. B. Meshkov, O. A. Fedorova, S. P. Gromov, M. V. Alfimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1997, 1296 [*Russ. Chem. Bull.*, 1997, **46**, 1239 (Engl. Transl.)].
113. I. R. Nasimova, E. N. Ushakov, E. E. Makhaeva, O. A. Fedorova, S. P. Gromov, M. V. Alfimov, A. R. Khokhlov, *Vysokomol. Soedin., Ser. A*, 2002, **44**, 2171 [*Polym. Sci., Ser. A*, 2002, **44**, 1313 (Engl. Transl.)].
114. T. I. Sergeeva, S. Yu. Zaitsev, M. S. Tsarkova, S. P. Gromov, A. I. Vedernikov, M. S. Kapichnikova, M. V. Alfimov, T. S. Druzhinina, D. Möbius, *J. Colloid Interface Sci.*, 2003, **265**, 77.
115. S. Yu. Zaitsev, T. I. Sergeeva, D. Möbius, A. I. Vedernikov, M. S. Kapichnikova, S. P. Gromov, M. V. Alfimov, *Mendeleev Commun.*, 2004, **14**, 199.
116. A. A. Turshatov, M. L. Bossi, D. Möbius, S. W. Hell, A. I. Vedernikov, S. P. Gromov, N. A. Lobova, M. V. Alfimov, S. Yu. Zaitsev, *Thin Solid Films*, 2005, **476**, 336.
117. T. I. Sergeeva, S. P. Gromov, A. I. Vedernikov, M. S. Kapichnikova, M. V. Alfimov, V. T. Lieu, D. Möbius, M. S. Tsarkova, S. Yu. Zaitsev, *Colloids Surf. A*, 2005, **255**, 201.
118. T. I. Sergeeva, S. P. Gromov, A. I. Vedernikov, M. S. Kapichnikova, M. V. Alfimov, D. Möbius, S. Yu. Zaitsev, *Appl. Surf. Sci.*, 2005, **246**, 377.
119. T. I. Sergeeva, S. P. Gromov, A. I. Vedernikov, M. S. Kapichnikova, M. V. Alfimov, D. Möbius, S. Yu. Zaitsev, *Colloids Surf. A*, 2005, **264**, 207.

Received January 18, 2008;
in revised form April 21, 2008