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Reviews

Photonics of supramolecular nanostructures*

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The results of studying optical and photochemical properties of organic supramolecular nanostructures capable of self-organizing due to specific intermolecular interactions are generalized in the review. The linear and nonlnear optical properties of supramolecular nanostructures of the "guest—host" type based on cyclodextrins, intramolecular and intermolecular complexes of crown-containing styryl dyes with metal cations, and aggregates of carbocyanine dyes are described. Photolysis reactions in supramolecular nanostructures, including photoisomerization, photocycloaddition, and formation of excimeric and charge-transfer complexes are presented. A possibility of controlling photochemical transformations in these systems by the light and cations of metal salts is shown.

Key words: nanophotonics, supramolecular nanosystems, linear and nonlinear optical properties, aggregates of cyanine dyes, cyclodextrin complexes, styryl dyes, photochemistry, complexation.

Introduction

Nanophotonics, a science dealing with optical characteristics of materials formed of nanoparticles, is a new vigorously developing area of studies.[1] Evidently, results obtained by nanophotonics can form a basis for future informational technologies, because they allow one to create informational systems of smaller units working at higher frequencies than those operating today.

Two directions of studies can be distinguished in nanophotonics. The first direction concerns processes initiated in a substance by excitation with a light beam focused to nanometer sizes. An object itself can be of rather long sizes (longer than the exciting light wavelength). A necessary decrease in the size of the surface area on which the light is focused requires a special technique. Therefore, these studies are mainly related to the use of near-field microscopy.

The second direction is related to studies of the optical properties (linear and nonlinear) of thermodynamically stable nanoparticles and photoinitiated transformations in these particles. In these studies, the exciting light spot can be of any size but the object under study either

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consists of nanoparticles or has nanosizes in at least one direction.

Two technologies for obtaining nanodimensional systems are known. The first technology of constructing nanosystems, the so-called "top—down" procedure, is the fragmentation of a macroobject into nanoparticles. The second procedure concerns assembling of a nanodimensional objects of particular molecules or atoms ("top—down" procedure). This technology is widely used in living nature (for example, complex protein structures are formed of twenty comparatively simple molecules of amino acids).

We hope that one can build nanodimensional supramolecular systems of molecules and create new generations of related devices for informational technologies by the use of intermolecular interactions (dipole-dipole and donor-acceptor interactions, "stacking" interactions, hydrogen bonds, *etc.*).

The approach developed at the Center of Photochemistry of the Russian Academy of Sciences is that processes of self-organization of molecules are used to form photochemically active sites and then to create new materials of different design from these pre-organized supramolecular systems. In this route, the main task is the design and synthesis of stable supramolecular systems, whose composition and structure provide required optical and photochemical characteristics. The number of molecules in a supramolecular system can vary in wide limits (in particular, a system can consist of two molecules in the simplest case).

To solve the problem stated, the following questions should be elucidated: (1) what should be structural features of an organic molecule to be appropriate for forming related supramolecular nanosystems and (2) what should be the architecture of supramolecular systems to possess optical and photochemical characteristics significant in practice?

This article presents the results of studying the optical properties of organic supramolecular nanostructures obtained at the Center of Photochemistry of the Russian Academy of Sciences and the results of studying the photochemical properties of these structures.

1. Linear and nonlinear optical properties of supramolecular nanostructures

Linear and nonlinear optical properties of substances in the condensed phase are determined by the photochemical properties of active sites (admixture sites) in these substances, the concentration of these sites, and their spatial arrangement. For molecular solutions of dyes, an active site is a dye molecule surrounded by solvent molecules. As known, the interaction of dye molecules with surrounding molecules results in a situation when their optical spectra in solutions are often structureless. For a long time, the exception was optical spectra of organic molecules in the Shpolsky matrices (normal paraffins)[2] in which optical spectra have the high-resolution vibrational structure at 77 K and both high-resolution vibrational and phonon structures at lower temperatures. This is caused by the nonuniform broadening of spectral lines in the Shpolsky matrices is small. In normal matrices, the nonuniform broadening decreases the resolution of optical spectra. The nonuniform broadening is related to the fact that molecules in solution exist in different molecular environments, resulting in a scatter of frequencies of electron transitions of molecules. Thus, the nonuniform broadening can be decreased if rigorously the same atomic environment around photochemically active molecules is formed in a solution (matrix). The uniform broadening is caused by the interaction of an electron-excited molecule with intramolecular vibrations and, unlike the nonuniform broadening, decreases with a decrease in the temperature of the substance.

When considering that an active (admixture) site contains a photochemically active molecule and surrounding solvent molecules, which affect the nonuniform broadening, the task of creating a material with optical spectra characterized by a small nonuniform broadening is reduced to the construction of molecular ensembles with rigorously the same composition and architecture or an ensemble of similar supramolecular nanostructures.

Controlling the composition and structure of such a supramolecular site, one can decrease or increase the nonuniform broadening of optical spectra. This controlling is impossible in homogeneous solutions.

One of the approaches to create optical sites with the same structure is the use of supramolecular systems of the "guest—host" type in which a dye serves as a "guest" molecule and a "host" molecule is the "environment." In these systems, the more rigid the structure of the "host" molecule and the better the correspondence of the shape of the "guest" molecule to the shape of the "host" molecule cavity in which the "guest" molecule should be localized, the lower is the nonuniform broadening compared to that in solutions.

Other known examples of photochemically active supramolecular sites are dimers or aggregates of dye molecules formed, under certain conditions, in solid and liquid solutions from molecules in the ground or electron-excited state.

Using specific intermolecular interactions, one can construct supramolecular optical sites (dimers, aggregates) with a specified structure. As shown by calculations,[3] the position, shape, and width of the absorption band in a dimer depend strongly on the mutual arrangement of its molecules. If the molecules are arranged exactly above each other, then sublevels from intramolecular vibrations disappear in the spectrum and a strong hypsochromic shift of the band of the 0—0-transition occurs mainly due to the interaction of orbitals through the space. If the molecules are strongly displaced relatively to each other, the spectrum does not either contain vibrational sublevels and a bathochromic shift is observed, which is caused by the interaction of dipole moments of electron transitions. These two extreme dimeric forms are separated by a sufficiently large area of intermediate structures in which the interaction of dipole moments of transitions of monomers is weak and the shape of the absorption band is almost the same as that of the monomers.

Thus, the design and directed synthesis (pre-organization) of supramolecular systems ("guest—host," dimers, aggregates) on the basis of specific intermolecular interactions make it possible to create active sites with various optical properties: positions and shapes of absorption bands, fluorescence, intensities of electron transitions, *etc.*

1.1. Structure and dynamic and optical properties of nanosystems of the "guest—host" type based on cyclodextrins

When "guest—host" complexes based on cyclodextrins were constructed, naphthalene, octadeuterionaphthalene, phenanthrene, fluorene, and bases of styryl dyes were used as "guest" molecules, and substituted and unsubstituted β-cyclodextrins (β-CD) served as molecule-"hosts."

Using mathematical simulation methods (molecular mechanics, quantum chemistry), we showed[4] that the aromatic compounds listed form stable 1 : 1 complexes (Fig. 1, *a*). The complexes are formed due to hydrophobic interactions. The calculations show that a molecule in the cavity can occupy different positions; this implies that a set of different optical sites can be obtained from one "host" molecule and one "guest" molecule.

The nonuniform broadening of such a photochemically active spectrum can be decreased by the restriction of the mobility of an aromatic molecule in the cyclodextrin cavity, for instance, by the addition of one more molecule to the cyclodextrin cavity. The structures of ternary complexes β-cyclodextrin—naphthalene—adamantane (or methyladamantane, cyclohexane) with different compositions (see Fig. 1, *a*, *b*) were calculated. The calculations showed that the ternary complexes in which cyclohexane or adamantane was used as the third molecule are highly stable, and organic molecules inside the cyclodextrin cavity occupy a rigidly certain position. Ternary complexes are optical sites characterized by narrow lines of optical electron transitions.

In these experiments, the most informative optical characteristics of cyclodextrin complexes are fluorescence and phosphorescence spectra.

The phosphorescence spectra of naphthalene in hexane and diethyl ether and the phosphorescence spectra of the binary and ternary naphthalene complexes with β-cyclodextrin in aqueous solutions are presented in Fig. 2. The measurements were carried out on cooling to 77 K. It is seen that the band of the 0—0-transition (ν_{00}) and vibrational bands in the phosphorescence spectrum of the cyclodextrin complexes are narrower than those in the spectra of solutions of aromatic molecules. The narrowest bands are experimentally observed for the ternary complexes.

The spectral data for the binary and ternary complexes with different compositions are presented in Table 1. It is seen that the effect of maximum narrowing of bands in the phosphorescence spectrum is observed for the ternary complex containing cyclohexane as a "fixing" molecule. For phenanthrene, the band of the 0—0-transition in the complex is 2.5-fold narrower, and that for naphthalene is 2.0-fold narrower than those for the same compounds in solutions. Cooling of the sample containing a phen-

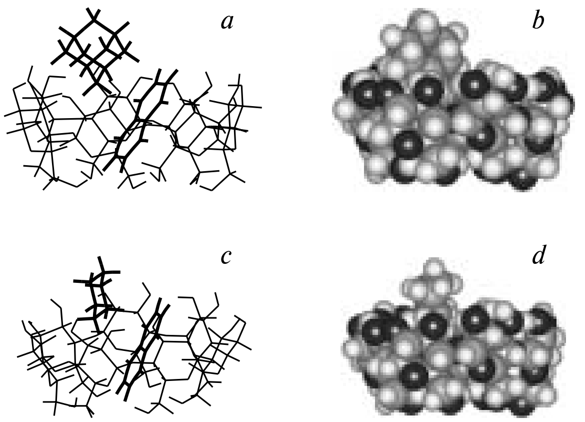


Fig. 1. Structures of cyclodextrin complexes calculated by the PM3 method: *a*, *b* are the β-cyclodextrin—naphthalene—adamantane complex; *c*, *d* are the β-cyclodextrin—naphthalene—cyclohexane complex.

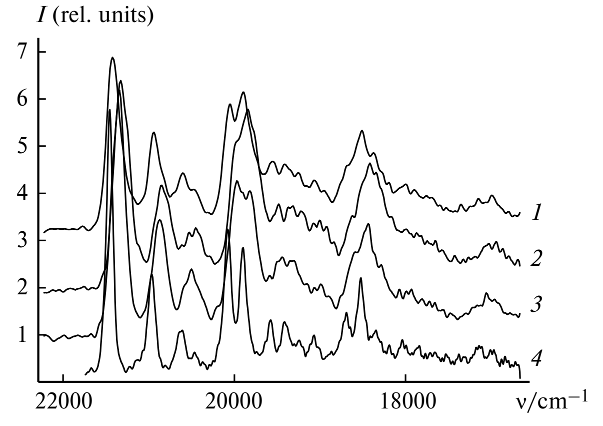


Fig. 2. Fluorescence spectra at 77 K of the complexes of naphthalene-d_8 with β-cyclodextrin (*1*), naphthalene-d_8 in hexane (*2*), naphthalene-d_8 in diethyl ether (*3*), and the ternary complex naphthalene-d_8—β-cyclodextrin—cyclohexane (*4*). The spectral gap width is 1 nm.

Table 1. Spectral characteristics of the complexes (frequency of the band of the 0—0-transition (ν_{00}) and its width ($\delta\nu$))

Complexes	ν_{00}	$\delta\nu$	τ/s*
	cm^{-1}		
Phenanthrene—cyclohexane	21535	210	3.9
Phenanthrene—Et_2O	21703	205	4.1
Phenanthrene—β-CD	21539	290	4.3
Phenanthrene—β-CD—cyclohexane	21657	120	4.44
Phenanthrene—β-CD—cyclohexane*	21850	110	4.2
Phenanthrene—β-CD—cyclohexane**	21850	110	3.2
Naphthalene-d_8—hexane	21327	220	20.5
Naphthalene-d_8—Et_2O	21340	188	21.3
Naphthalene-d_8—β-CD	21422	200	21.7
Naphthalene-d_8—β-CD—isooctane	21452	136	23.8
Naphthalene-d_8—β-CD—adamantane	21437	135	20.4
Naphthalene-d_8—β-CD—cyclohexane	21422	120	24.9

* At 60 K.

** At 8 K.

anthrene molecule down to 8 K only insignificantly narrows the band of the 0—0-transition (see Table 1). This indicates that the band width is completely determined by the nonuniform broadening. It remains unclear whether a greater narrowing of the 0—0-band can be achieved by a more similar environment or not.

It should be mentioned that the encapsulation of aromatic molecules in the β-cyclodextrin cavity shields them from the interaction with surrounding solvent molecules and molecules of dissolved substances, thus preventing quenching of excited states of molecules encapsulated in the β-cyclodextrin cavity. The effect observed is most significant for phosphorescence of aromatic hydrocarbons, which possess long-lived phosphorescence in ternary complexes in aqueous solutions at room temperature in the presence of oxygen.[6,7]

An optical site consisting of two naphthalene molecules can be constructed from cyclodextrins. It is known that upon the photolysis of concentrated solutions of naphthalene its molecules in the excited singlet state form excimers (excited dimers) with non-excited naphthalene molecules. The dimer fluoresces in a longer-wave spectral region (λ_{max} = 500 nm) than the monomer does.[8] The calculations show that in the naphthalene—cyclodextrin system both the 1 : 1 and 2 : 2 complexes are stable, and in the latter the naphthalene molecules are arranged one above another, *i.e.*, their packing is close to that postulated for the naphthalene excimers (Fig. 3, *a*).

Based on β-cyclodextrins, one can construct a supramolecular system in which naphthalene molecules are pre-organized to form a structure corresponding to an excimer. The fluorescence spectra of naphthalene solutions in water and concentrated solutions of naphthalene and β-cyclodextrin are presented in Fig. 3, *b*. The fluorescence spectrum of solutions with β-cyclodextrins contains a band with a maximum at 400 nm (~25000 cm^{-1}), which can be ascribed to the excimeric fluorescence of the naphthalene dimers.[9]

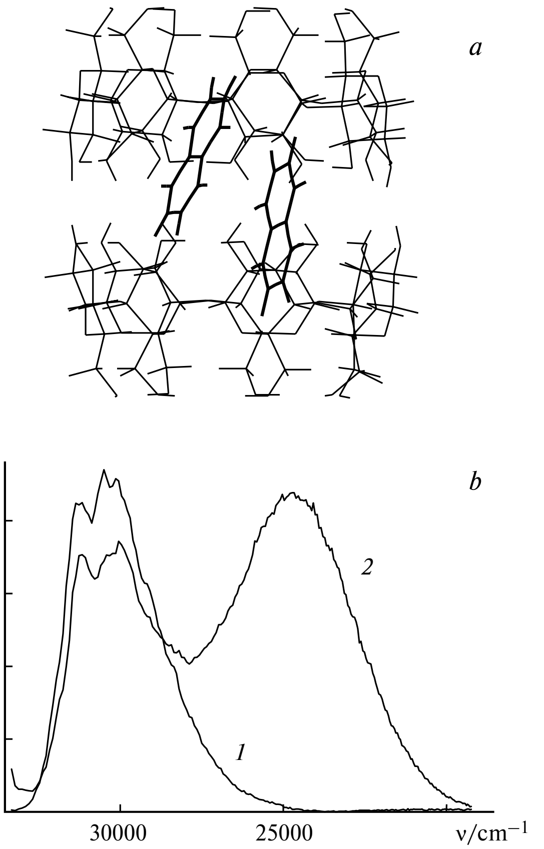


Fig. 3. (*a*) Structure of the 2 : 2 complex of β-cyclodextrin with naphthalene calculated by the quantum-chemical PM3 method; (*b*) fluorescence spectra of naphthalene in an aqueous solution (*1*); excimeric fluorescence spectrum (~25000 cm^{-1}) of the 2 : 2 complex of β-cyclodextrin with naphthalene in an aqueous solution (*2*).

Thus, based on complexes of naphthalene and β-cyclodextrin, one can construct active sites (complexes) with different structures, which possess luminescence spectra different from those of naphthalene molecules in solutions containing no β-cyclodextrin.

The dynamic characteristics of the behavior of molecule-guests in the cyclodextrin cavity can differ considerably from the dynamic behavior of these molecules in a solvent. This makes it possible to control the dynamic properties using supramolecular systems.

Molecules in liquid solutions can rotate and transfer. If a molecule is incorporated into the β-cyclodextrin cavity, it can perform the translational motion only together with β-cyclodextrin, while it can rotate both together with β-cyclodextrin and individually, moving inside the cavity relatively to the β-cyclodextrin walls. This complicated dynamics of the behavior of molecules can exert a significant effect on the dynamics of fluorescence, photochemi-

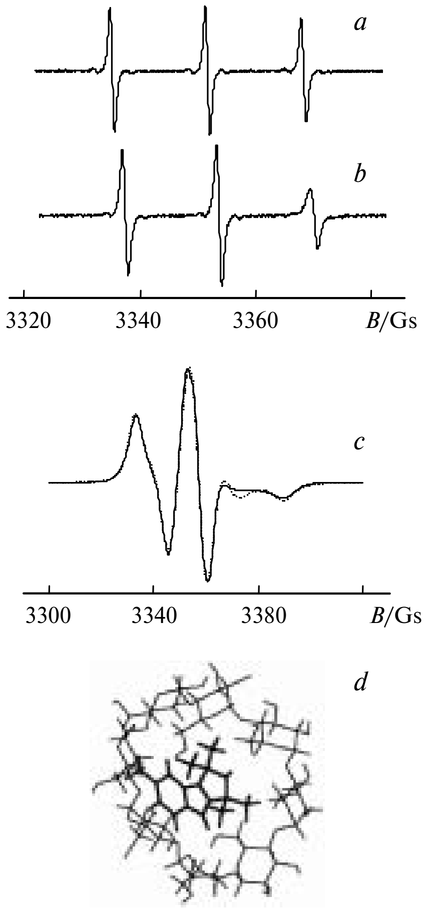


Fig. 4. ESR spectra of the spin probe in water (*a*), a complex of the spin probe with β-cyclodextrin in water (*b*) and in the solid phase (*c*), and the structure of a complex of the spin probe with β-cyclodextrin (*d*). Rotational correlation time $\tau_R \sim 10^{-10}$ (*a*), $3.5 \cdot 10^{-10}$ (*b*), and $3 \cdot 10^{-9}$ s (*c*).

cal transformations, dynamics of fluorescence depolarization, *etc.*

To study the dynamic behavior of the "guest" in the β-cyclodextrin cavity, we used ESR, and a paramagnetic spin probe served as a "guest" molecule. The ESR spectra of the spin probe in the solvent and in the β-cyclodextrin cavity are shown in Fig. 4.

The analysis of the spectra shows that complex formation increases the correlation time of probe rotation. This indicates that the mobility of molecules is restricted inside the β-cyclodextrin cavity.[9] This fact shows that the quantum yield of photoisomerization of organic molecules inside β-cyclodextrin should be lower than that in a solution, and the quantum yield of competitive fluorescence of organic molecules in β-cyclodextrins, on the contrary, should be higher. Thus, the theoretical and experimental results show that the creation of "guest—host" complexes of dyes is one of possible directions for developing active sites with unique optical properties.

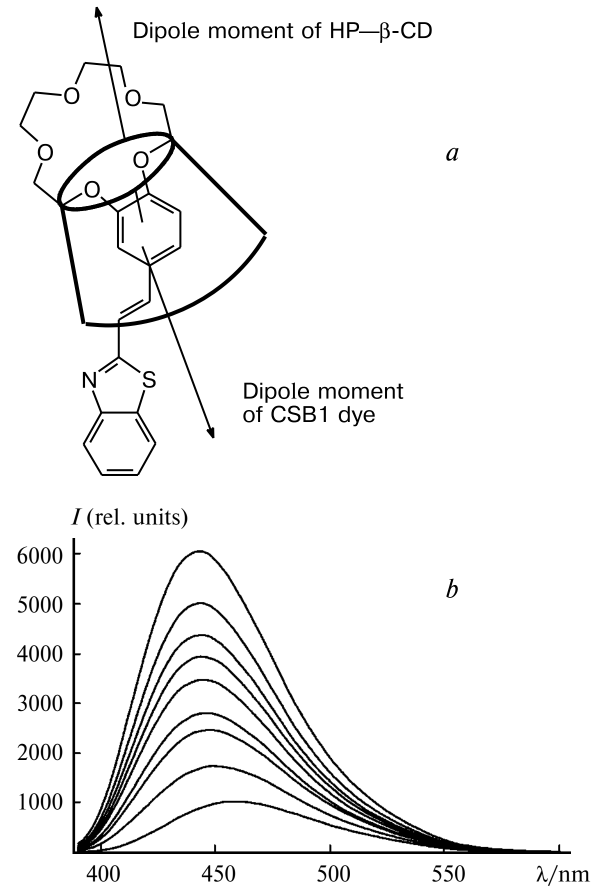


Fig. 5. (*a*) Structure of a complex of the crown-containing dye CSB1 with cyclodextrin HP—β-CD and (*b*) the plot of the fluorescence intensity (*I*) of an aqueous solution of the dye *vs.* concentration of β-cyclodextrin in a solution: 0 (*1*)...0.1 mol L^{-1} (*9*).

The experimental results on an increase in the fluorescence intensity of solutions of crown-containing 2-styrylbenzothiazoles upon the addition of β-cyclodextrin to the solution are presented in Fig. 5.

1.2. Optical properties of intramolecular and intermolecular complexes of crown-containing styryl dyes with metal cations

Another type of a supramolecular system, whose optical properties differ from the properties of its molecules, is presented by complexes of crown-containing dyes. To build even the simplest supramolecular systems with specified structures, it is necessary for molecules in the composition of this supramolecular system to have specifically interacting groups. The structure and position of these groups mainly determine the structure of the supramolecular system.

In this Section, we present examples of creating supramolecular systems (complexes, dimers, trimers) from styryl dyes modified by special complex-forming groups.

Molecules with ionophoric groups are known to form stable complexes with metal cations in solutions, and some cations are capable of selective binding. When a molecule has two ionophoric groups, one can expect that in solutions it forms complexes with cations in which the cation binds simultaneously two ionophoric groups of the same molecule. If the molecule is flexible, complexation can significantly change the molecular structure compared to the structure of the initial molecule. It can be expected that the new conformation of the molecule would change the conjugation system in the molecule and, as a consequence, its optical properties.[10]

The chemical structures and absorption spectra of the initial molecule and complex are presented in Fig. 6. The intensity of the long-wave transition decreases more than tenfold upon complexation (the long-wave absorption band disappeared), which indicates weakening of the conjugation between two parts of the molecule. The quantum-chemical calculations of the dependence of the energy of electron transitions on the rotation angles about the ordinary bonds connecting the double bond and heterocycles confirmed the experimentally observed phenomena.[11]

Another example for changing the optical properties of a molecule due to a change in the conformation of molecules upon complexation was obtained for bisstyryl dyes.[12] In these dyes, two similar fragments are linked by a chain of methylene bonds, whereas in solutions both fragments do not interact with each other (absorption spectra of these molecules in a solution coincide with the absorption spectra of the monomers). The addition of cations to the solution produces sandwich complexes in which the fragments are arranged above each other. The optical properties of these pre-organized molecules can possess excimeric fluorescence, which is observed in experiment (Table 2).

Organic charge-transfer complexes are widely studied because of investigations of the charge transfer dynamics. As a rule, charge-transfer complexes are weakly bonded systems formed upon the random collision of a donor and an acceptor in solutions. It is of interest to study the charge transfer dynamics in a supramolecular system in which the donor and acceptor are preliminarily remote at a close distance from each other. It has recently been shown that in acetonitrile solution biscrown-containing stilbene (S) and viologen salt (V^{4+}) form stable 1 : 1 ($[S\cdot V]^{4+}$) and 2 : 1 ($[S\cdot V\cdot S]^{4+}$) complexes.[13,14] The absorption spectra of solutions of these complexes in MeCN contain a broad charge-transfer absorption band (Fig. 7).

The studies of the charge transfer dynamics by femtosecond spectroscopy showed that both complexes are characterized by the two-exponential quenching of the in-

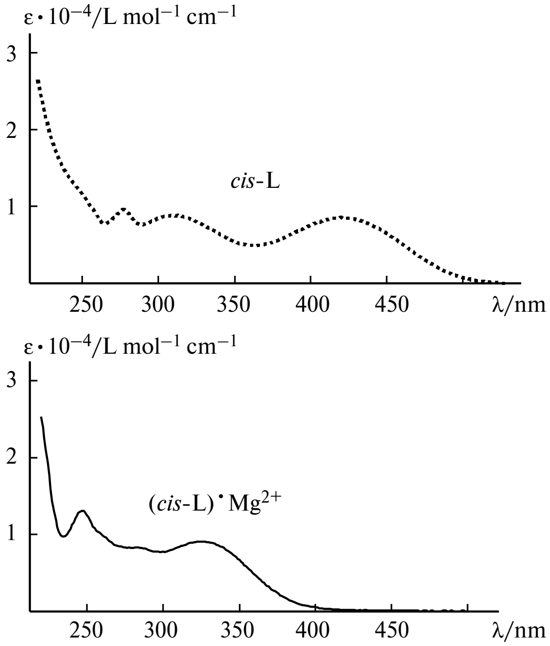


Fig. 6. Absorption spectra of the *cis*-form of the crown-containing dye and a complex of the *cis*-form of the dye with the magnesium cation.

Scheme 1

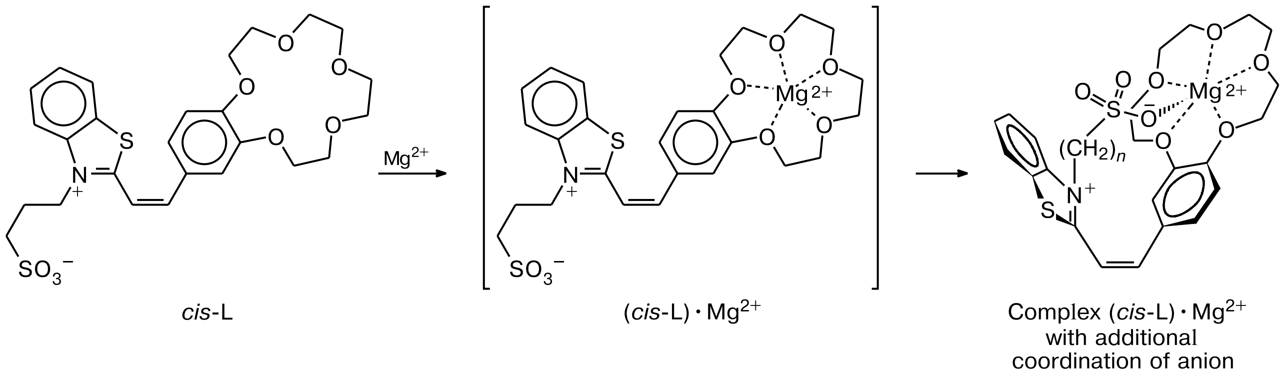
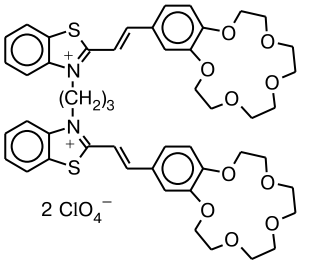
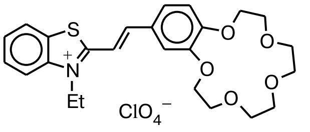
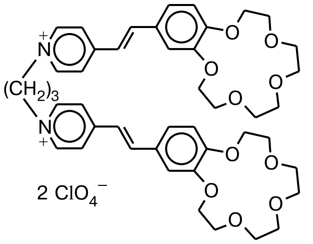
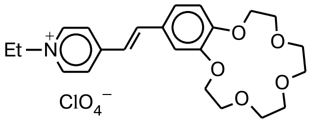


Table 2. Spectral characteristics of bisstyryl dyes and their complexes with cations

Compound	Absorption		Fluorescence			
	λ_{max}	Shift	λ_{max}	Shift	Quantum yield	τ*/ps
	nm		nm			
	432	−41	554	−36	0.0062	70
Ba^{2+}	391		518		0.0032	40 and 1400
	429	−28	544	−34	0.0078	65
Ba^{2+}	401		510		0.0035	35
	406	−38	556	−7	0.054	330
Ba^{2+}	368		549		0.032	1300
	399	−30	546	−38	0.098	650
Ba^{2+}	329		508		0.048	260

* Lifetime.

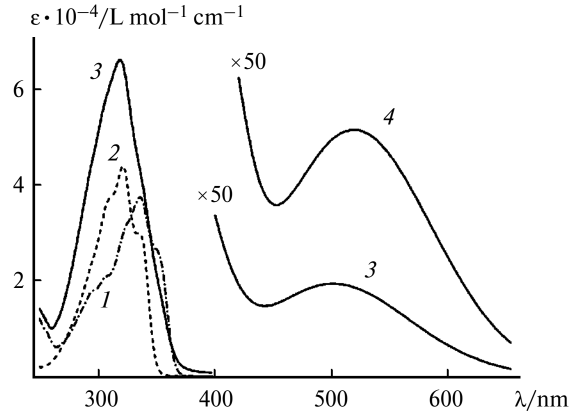
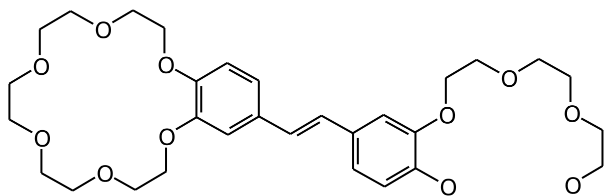


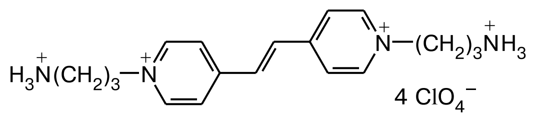
Fig. 7. Absorption spectra of the donor (S) (*1*), acceptor (V^{4+}) (*2*), and their complexes $[S \cdot V]^{4+}$ (*3*) and $[S \cdot V \cdot S]^{4+}$ (*4*) in MeCN solutions.

duced optical absorption at the charge-transfer band upon the femtosecond pulse excitation (616 nm, duration 70 fs) of the system.[14] The fast component (150—200 fs) was ascribed to the relaxation to the lowest excited state of charge transfer, while the second component (540 fs) was attributed to the backward electron transfer from the donor to acceptor part. For the trimolecular complex, the backward electron transfer is twofold longer than that of the bimolecular complex, which is probably related to a greater electron delocalization.

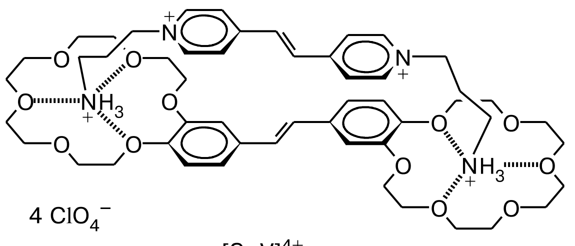
These examples show that the preliminary modification of molecules by special groups capable of linking molecules with each other due to intermolecular interactions is an efficient method for the directed construction of supramolecular systems with specified structures and optical properties.



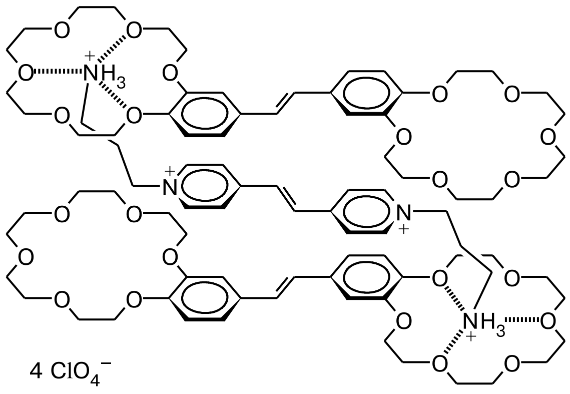
S



V^{4+}



[S · V]$^{4+}$



[S · V · S]$^{4+}$

1.3. Linear and nonlinear optical properties of aggregates of carbocyanine dyes

Polymethine dyes attract attention of researchers due to their ability to form aggregates with different compositions and structures in solutions. The properties of these aggregates differ from the properties of individual molecules in solutions (dimers, H- and J-aggregates). A special attention is given to the investigation of J-aggregates, which are characterized by narrow absorption bands and high oscillation forces of electron transitions.

Below we present the results of studying the linear and nonlinear characteristics of liquid and solid solutions of carbocyanine dyes. The theoretical calculations[15] of the spectra of the dimers showed that the optical characteristics of their absorption spectra (band shapes and positions of absorption maxima) depend on the dimer structure. The theoretical results obtained for simple structures of the dye[16] agree well with experiment.

The results of calculations of the optical absorption spectra of aggregates with different compositions (four and nine molecules), for which the structure of molecular packing of the "brickwork" type in the aggregate was accepted, show that the absorption band of the aggregate shifts toward the long-wave spectral region with an increase in the number of molecules in the aggregate. It follows from the results presented that the optical properties of the aggregates depend rather strongly on both the structure and composition of the aggregate. The development and mastering of the technology of constructing dye aggregates with specified compositions and structures provide syntheses of active sites with linear and nonlinear optical properties and production of related new optical materials.

The structure of the dye under study and its absorption and fluorescence spectra in aqueous solutions are presented in Fig. 8.

The absorption spectrum of an aqueous solution of the aggregate obtained at 21 °C contains several absorption bands: an intense band with a maximum at 638 nm and

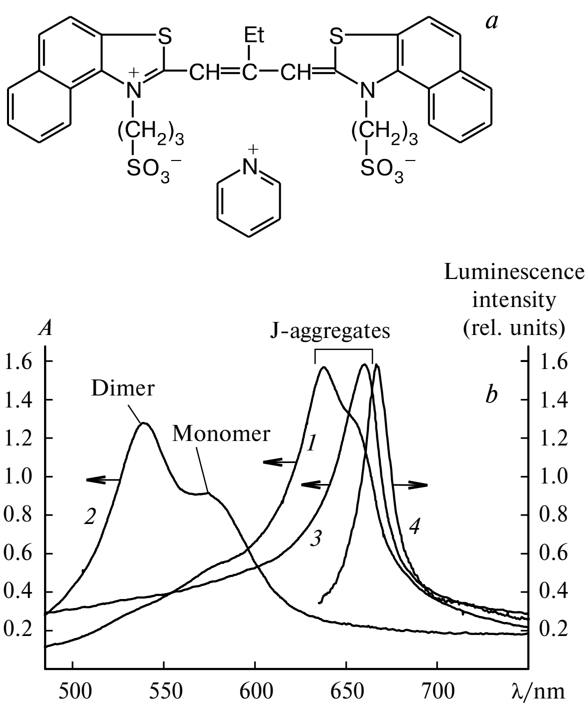


Fig. 8. Dye structure (*a*) and absorption spectra (*A*) of dye solutions (*b*) at different temperatures: 21 (*1*), 60 °C (*2*), and after cooling of the solution heated to 60 °C (*3*); fluorescence spectrum (*4*).

two shoulders at 628 nm and 659 nm and low-intensity short-wave bands with maxima at 575 and 538 nm, the first of which belongs to monomers, and the second band belongs to dimers. The long-wave absorption of solutions of polymethine dyes is usually ascribed to J-aggregates of dyes. When the temperature of an aqueous solution increases to 60 °C, the intensity of the long-wave absorption band decreases and the intensities of the short-wave bands at 538 nm and 575 nm increase, indicating that the J-aggregates decompose on heating to form monomers and dimers.

The analysis of the above-described processes by NMR spectroscopy of solutions allows us to conclude that at 60 °C in DMSO solutions the dye forms true solutions of the monomer. In the NMR spectrum of an aqueous solution at 60 °C, some lines of protons change strongly their position compared to those in the NMR spectra of DMSO solutions. Especially strong upfield chemical shifts (0.36—0.82) are observed for protons of the ethylene group, aromatic protons, and protons of methylene groups. The data of the NMR spectra show that aqueous solutions contain dimers along with monomers. The changes in the NMR spectra characterized by the upfield shifts of the lines indicate the anisotropic effect related to the fact that protons fall to the region of shielding of closely arranged substituents or individual molecules with unsaturated fragments. Therefore, the above-mentioned specific features of changing the chemical shifts of some protons of the dye suggest that the sandwich structure of the dimer is most probable. Two planar molecules of the dye are retained in the pile due to weak dipole-dipole intermolecular interactions. Thus, an aqueous solution of the dye simultaneously contain monomers, dimers, and aggregates of a higher order (J-aggregates).

Based on the analysis of the complicated absorption band in the long-wave spectral region, we proposed the existence of three different J-aggregates (with absorption maxima at 628, 638, and 659 nm, respectively). Since heating of solutions results in the consecutive transformation of the bands (with maxima at 628, 638, and 659 nm) one into another with isosbestic points, we concluded that these transformations are related to the transformation of the aggregate structure with an unchanged molecular composition.

In addition to studies of the absorption and luminescence spectra of this dye under weak irradiation, we studied the optical absorption spectra of solutions under excitation with short intense laser pulses.

The experimental procedure has been described.[17] When solutions of the dye in ethanol containing only monomers and dimers (aggregates are not formed) are excited with femtosecond pulses from a chromium—forsterite laser (1260 nm, 70 fs), optical signals upon pumping are virtually absent. When aggregates are formed along with monomers and dimers, two peaks are observed: one peak corresponds to the double frequency of a pumping laser, and the second peak corresponds to the triple pumping frequency of the femtosecond laser used (Fig. 9). The appearance of these peaks was ascribed to the third harmonic generation and two-photon fluorescence of the dye aggregates, respectively.[18]

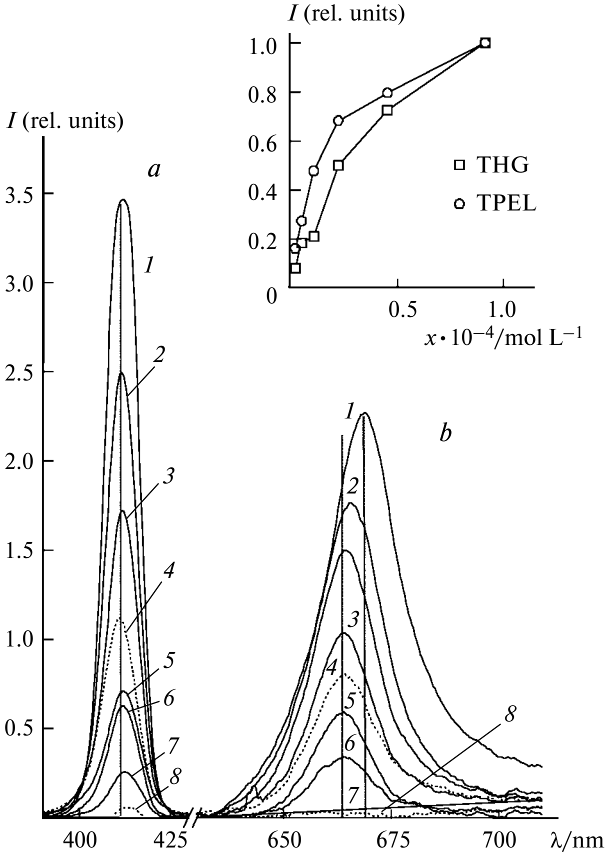


Fig. 9. Spectrum of the third harmonic generation (*a*) and two-photon luminescence of a solution of the dye (*b*), whose structure is shown in Fig. 8, *a*: dye concentration, mol L^{-1}: $1 \cdot 10^{-4}$ (*1*), $0.5 \cdot 10^{-4}$ (*2*), $0.25 \cdot 10^{-4}$ (*3*), $1 \cdot 10^{-5}$ (*4*), $0.12 \cdot 10^{-4}$ (*5*), $0.06 \cdot 10^{-4}$ (*6*), and $0.03 \cdot 10^{-4}$ (*7*).

The intensity of optical signals upon pumping increases with an increase in the dye concentration in solutions. The intensity of signals of the third harmonic increases with an increase in the pumping intensity, and the dependences are nonlinear.

The results presented show that optical sites with different optical properties can be obtained by constructing aggregates with different compositions and structures (dimers, J-aggregates) from molecules of some dye.

2. Photochemistry of supramolecular nanostructures

The efficiency of photochemical reactions is known to depend on the phase state of the substance. For instance, for stilbene-like molecules in liquid solutions, three types of photochemical reactions are observed: photoisomerization, photocyclization, and [2+2] photocycloaddition. Photoisomerization in solutions occurs rather efficiently (the quantum yield of the process can achieve 1.0), while [2+2] photocycloaddition and photocyclization occur with relatively low quantum yields. In solid solutions of these molecules, the photoreactions listed above occur with a low efficiency. In crystals of stilbene-like molecules, [2+2] photocycloaddition is rather highly efficient if the molecules in the crystalline cell are packed in such a way that the ethylene bonds of adjacent molecules are parallel to each other and remote at a distance of ~4 Å. These facts indicate that this is precisely the pre-organization of the reaction center that determines the direction and efficiency of photochemical transformations in this reaction center.

One can hope that the rate of the desired photochemical reaction can be controlled by the formation of reaction centers, *i.e.*, building supramolecular systems in which reactants are pre-organized to form structures providing the efficient occurrence of this or another photochemical reaction. To study the efficiency of this approach, we synthesized crown-containing styryl and butadiene dyes, whose molecules were capable of self-organizing to form supramolecular systems with different specified structures.

The results of studying photoisomerization, photocyclization, and [2+2] photocycloaddition in the pre-organized supramolecular systems of crown-containing dyes are presented below.

2.1. Photoisomerization of crown-containing styryl dyes organized to supramolecular systems

It is known that the fluorescence and photoisomerization of stilbene-like molecules are competitive processes. An increase in the solvent viscosity restricts the freedom of motion of a photoactivated molecule and, as a result, decreases the isomerization quantum yield. Therefore, when creating a supramolecular system in which the mobility of the photoisomerizing molecule is restricted compared to that in a liquid solution, the isomerization quantum yield in this system should decrease, while the fluorescence quantum yield should increase. The efficiency of this approach was demonstrated above for the complexes of crown-containing dyes with β-cyclodextrins.

It was shown that the addition of metal salts to solutions of crown-containing dyes, whose structures contain two ionophoric groups, leads to the formation of 2 : 2 intermolecular complexes with the metal cations in which each cation is coordinated with two ionophoric groups of the dye. The study of these complexes showed that the fluorescence lifetime of the dimeric complex is several times longer than that of the 1 : 1 complex.[19] This indicates the restricted possibility of conformational rearrangements of a molecule in the complex, resulting in the inhibition of *trans*-*cis*-isomerization and the appearance of fluorescence.

Thus, creating supramolecular systems of photochemically active molecules in solutions, one can control the efficiency of competitive fluorescence and photoisomerization processes. It has been shown in several works that the photoisomerization mechanism can change when photoisomerizing molecules are included into a supramolecular system.[20]

2.2. [2+2] Photocycloaddition in binary complexes of crown-containing styryl dyes

It is known that the photolysis of solutions of ethylene derivatives results in the formation of different cyclobutane derivatives due to [2+2] photocycloaddition, although the efficiency of the formation of cyclobutanes is low. This is caused by the fact that approaching of double bonds and their parallel orientation are needed for the reaction to occur. However, the selectivity and efficiency of [2+2] photocycloaddition can be high in a supramolecular system, whose reacting molecules were pre-organized to form a complex with the configuration required for the reaction.

2.3. Photolysis of solutions of "head-to-head" type bimolecular complexes of crown-containing dyes with metal cations

When metal salts are added to a solution of 2-styrylbenzothiazole in acetonitrile, dye bicomplexes of the "head-to-head" type are formed (Scheme 2: [2+2] photocycloaddition of crown-containing styrylbenzothiazole, Fig. 10). This structure was proposed from the data on studying the NMR spectra of these complexes).

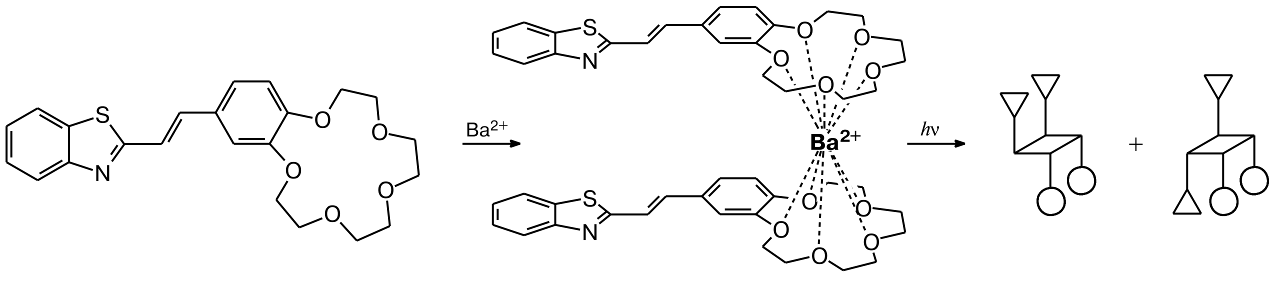
The absorption band of the complex disappears upon prolonged photolysis, and a short-wave band appears. The NMR analysis of products obtained by photolysis showed that cyclobutanes with two different structures are accumulated in the solution (see Fig. 10 and Scheme 2).

The fraction of the first product increases when complexes of dicarboxylic acids are added to the solution. This can be caused by the fact that the additional coordination of heterocyclic fragments of dyes due to hydrogen bonds with carboxyl groups results in further bringing together of the ethylene bonds, which favors a more efficient occurrence of cycloaddition.

2.4. Photolysis of solutions of bimolecular complexes of benzothiazole and quinoline dyes, containing crown-ether and sulfonate groups, with metal cations

The structures of the bimolecular complexes were calculated by the quantum-chemical methods. The results of

Scheme 2



▷ is benzothiazole, ○ is crown ether

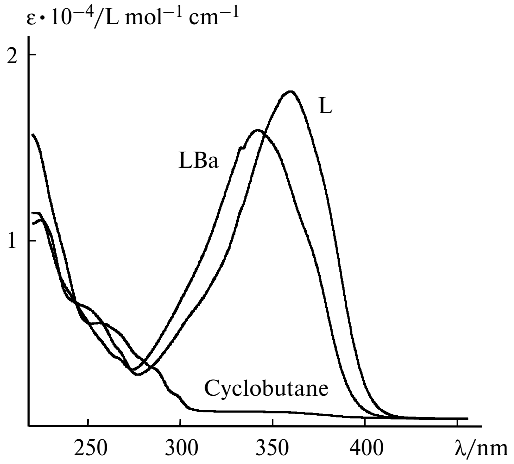


Fig. 10. UV spectra of the starting compound (L), complex (L·Ba), and the product (substituted cyclobutane) of [2+2] photocycloaddition of crown-containing styrylbenzothiazole (see Scheme 2).

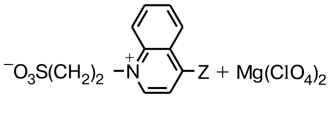
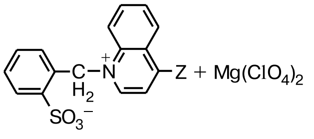
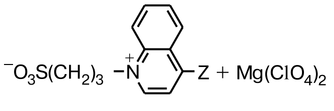
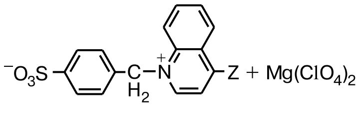
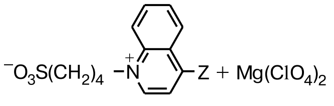
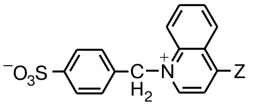
calculations show that the complexes have the "head-to-tail" structures. The photolysis of solutions of these complexes affords cyclobutanes in high quantum yields. The quantum yield of [2+2] photocycloaddition depends on the length and rigidity of the sulfonate substituent and the size of the crown ether cavity (Table 3).

The experiments for quinoline substituents with two ionophoric groups gave similar results.

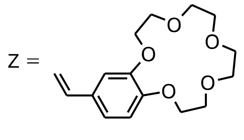
2.5. Control of photochemical transformations of styryl dyes with two ionophoric groups by light and cations of metal salts

A set of photochemical transformations of the styryl dyes with two ionophoric groups in solutions with additives of metal cations is presented in Fig. 11. It is seen that the variation of the cation concentration and wavelength of the exciting light changes the direction of the photochemical transformations.

Table 3. Quantum yields of photocycloaddition*

Reaction	$\varphi_{t\text{-}c}$	φ_{PCA}	φ_{PD}	Reaction	$\varphi_{t\text{-}c}$	$\varphi_{c\text{-}t}$	φ_{PCA}	φ_{PD}
	0.08	0.20	0.019		—	—	0.024	0.011
	0.10	0.13	0.010		0.20	0.42	<0.001	—
	0.14	0.073	0.010		0.009	0.49	—	—

* Solutions in MeCN, room temperature, dye concentration $1.2 \cdot 10^{-5}$ *M*, $Mg(ClO_4)_2$ concentration $1.2 \cdot 10^{-4}$ *M*; $\varphi_{t\text{-}c}$ and $\varphi_{c\text{-}t}$ are the quantum yields of *trans—cis-* and *cis—trans*-isomerization, φ_{PCA} is the quantum yield of photocycloaddition, and φ_{PD} is the quantum yield of adduct photodissociation.



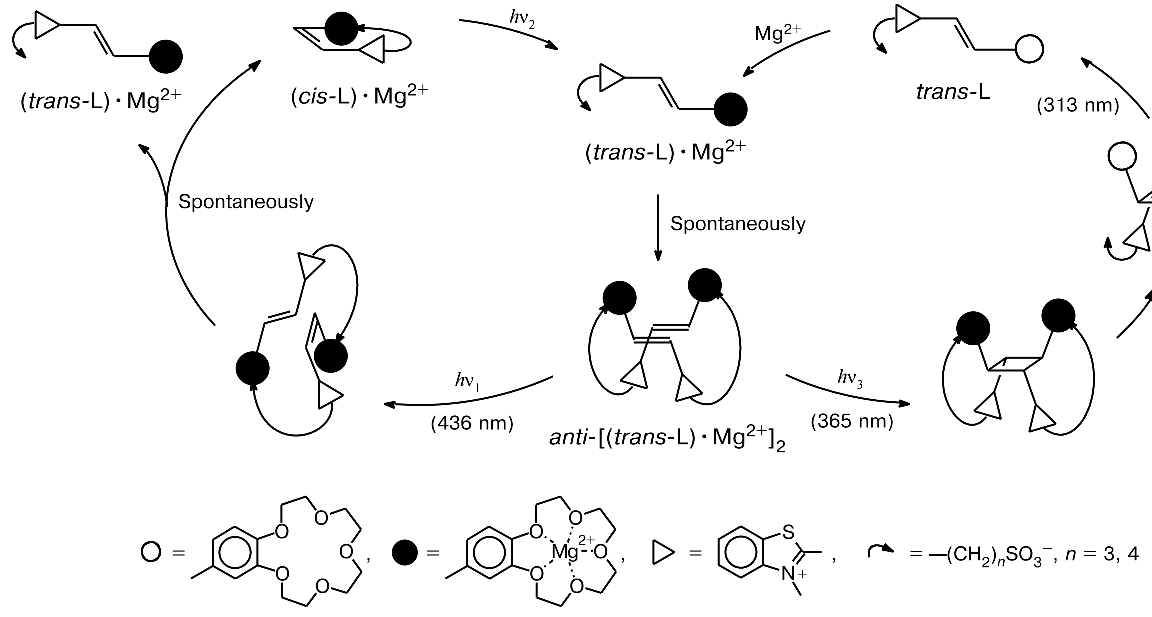


Fig. 11. Sequence of photochemical transformations of crown-containing dyes in solutions in the presence of metal cations.

Conclusion

The examples presented for organic supramolecular structures show that the syntheses of nanostructures from organic molecules can provide nanosystems with specified optical and photochemical properties.

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