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PHOTONICS

Molecular Photonics of Polymethine Dyes in Complexes with Cucurbit[7, 8]urils

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Abstract—Thiacarbo- and thiadicarbocyanine indolenine and thiazoline polymethine dyes form host–guest complexes with cucurbit[7,8]urils in water. Cucurbit[7]uril forms preferentially 1 : 1 and 1 : 2 monomeric complexes and cucurbit[8]uril forms 2 : 1 and 2 : 2 dimeric complexes. On the basis of quantum-chemical calculations, the structure of monomeric and dimeric complexes has been suggested. The complexation manifested itself in absorption, prompt and thermally activated delayed fluorescence spectra, as well as in the triplet–triplet absorption spectra. Dimeric complexes in the triplet state are involved in one-electron oxidation and participate in triplet–triplet energy transfer.

Keywords: polymethine dyes, cucurbiturils, complex formation, absorption, prompt and delayed fluorescence, laser pulse photolysis, quantum-chemical calculations

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Currently, molecular photonics of polymethine (cyanine) dyes (**PD**) is a subject of much investigation. The widespread use of PD in various fields of science and technology accounts for a fixed interest to these compounds [1]. Polymethines are important class of organic synthetic dyes practically used in spectral sensitization of information registration [2, 3], in developing light-emitting diodes [4–6], in transforming the laser emission frequency [7, 8], and others. The dyes of this class are the subjects for the study of *trans–cis* photoisomerization [1, 9, 10], radiative and nonradiative energy loss of excited singlet and triplet states [10], electron transfer [11–16], and other processes of molecular photonics. Polymethine dyes are characterized by the ability to fluorescence and *trans–cis* photoisomerization occurring via excited singlet state [10]. The low quantum yield of intersystem crossing to the triplet state and the ability of the formation of dimers as simplest aggregates are the characteristic features of PD [10, 17, 18]. The increase in the intersystem crossing is attained at the expense of the heavy atom effect [19, 20], as a result of steric hindrance of the *trans–cis* photoisomerization, and PD dimerization [10, 21].

Recent attention is focused on the study of photonics of dye complexes with cavitands and particularly with cucurbit[*n*]urils [22, 23]. Cucurbit[*n*]urils ($C_{6n}H_{6n}N_{4n}O_{2n}$, $n = 5–10$) are organic macrocycles built from *n* glycoluril units connected by 2*n* methylene bridges. The van der Waals diameter of the inner cavity of cucurbiturils is 3.9–6.9 Å for $n = 6–8$ [24], which provides the inclusion of many organic molecules with formation of host–guest complexes. The formation of host–guest complexes of organic fluorophores with cucurbiturils usually is accompanied by a significant fluorescence enhancement [23, 25–31], affects the rate of the dark *cis–trans* photoisomerization and electron transfer [32]. In addition, the complex formation with cucurbiturils increases the photostability of the dyes that is important for their use as active laser media [33, 34].

In this manuscript, our results on molecular photonics of the host–guest complexes for thiacarbo- and thiadicarbocyanine indolenine and thiazoline dyes with cucurbit [7, 8]urils in water are summarized [28, 29, 31, 35–38].

COMPOSITION AND STRUCTURE OF COMPLEXES

The study of photonics was carried out on the host–guest complexes of thiacarbocycanine indolenine and thiazoline dyes with cucurbit [7, 8]urils in water. The complex composition was determined by the spectrophotometry and the Job method. The results of these study indicates that cucurbit [7]uril (**CB7**) forms preferentially 1 : 1 and 1 : 2 complexes, whereas cucurbit [8]uril (**CB8**) forms 2 : 1 and 2 : 2 dimeric complexes.

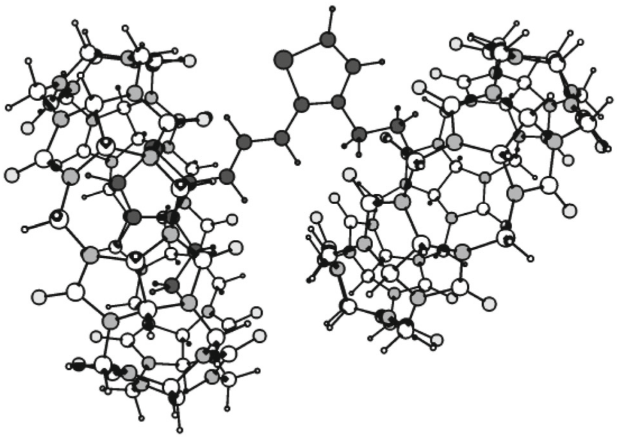

Fig. 1. Structure of the *trans*-TZCC@2CB7 complex optimized by the DFT/PBE method.

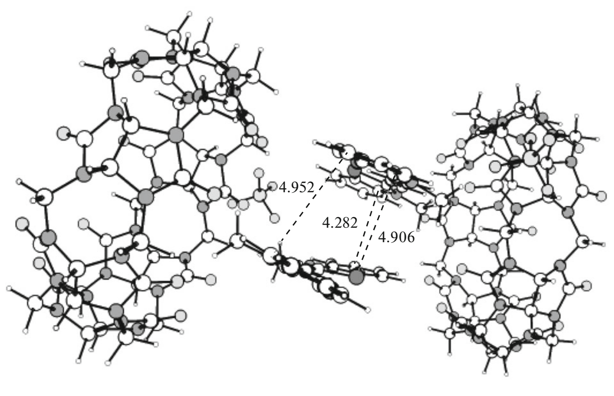

Fig. 2. The structure of the $(TCC)_2$@2CB7 dimeric complex calculated by the PM3 method. Distances are given in Å.

Host–Guest Complex of 3,3′-Diethylthiazolinecarbocyanine with CB7

The composition of the 1 : 2 complex for the 3,3'-diethylthiazolinecarbocyanine iodide (**TZCC**) with CB7 was determined by the Job method, from the changes of the fluorescence intensity on varying the TZCC and CB7 volumes, and from the absorbance changes of the complex solution with increasing concentration of CB7 [31]. The calculated value of the binding constant is $K = 1.31 \times 10^9$ M^{-2}. The calculation shows that only the *trans* isomer of the dye molecule can form the complex with two CB7 molecules to afford the *trans*-TZCC@2CB7 complex. The structure of the 1 : 2 complex optimized by the DFT/PBE method is shown in Fig. 1.

Host–Guest Complexes of 3,3′-Diethylthiacarbocyanine with CB7 and CB8

The possibility to form a monomeric host–guest complex of 3,3′-diethylthiacarbocyanine (**TCC**) with CB7 was shown on the basis of calculations made by a PM3 method. The energy of TCC^+ inclusion into the CB7 cavity is −21.4 kcal/mol, with only the benzene ring of the benzothiazole moiety of the dye being fixed in the CB7 cavity [35]. This result agrees with the data obtained by calculation of the complex of pseudoisocyanine dye (**PIC**) with CB7 by a DFT method with an exchange-correlation B3LYP/6-31G* functional, according to which only the benzene fragment of the PIC cation can be placed in the CB7 cavity [39].

The possibility of the formation of a dimeric host–guest complex of TCC with CB7 was considered in [35]. The results showed that the TCC dimer could not by placed inside the CB7 cavity. The structure of the dimeric complex $(TCC)_2$@2CB7 presented in Fig. 2 is the most energetically favorable. In this complex, two dyes molecules are oriented almost in parallel to one another.

The formation enthalpy of this complex is −20.1 kcal/mol. The presence of two counterions ClO_4^- is required for preventing the repulsion of two dye cations in the geometry optimization.

Thus, cucurbit [7]uril facilitates the fixation of the sandwich orientation of the dimer components, providing a hypsochromic shift of the absorption band caused by the π–π stacking interaction.

The formation of the complexes between TCC and CB7 affects substantially the photoprocesses in aqueous solutions. The steric hindrance to the rotation of the terminal benzothiazole groups enhances the fluorescence and intersystem crossing into the triplet state of the dye monomers. The possibility of the formation of the host–guest complexes between TCC and 3,3'-dimethylthiacarbocyanine (**MTCC**) with CB8 of different composition is considered in [40].

The processes occurring in aqueous solutions of TCC and MTCC are given in the scheme:

$$\begin{tikzcd}
\mathrm{M + M} \arrow[r, shift left, "(1)"] \arrow[d, shift left] & \mathrm{D} \arrow[l, shift left] \arrow[d, shift left] \\
\mathrm{M@CB8} \arrow[u, shift left, "\text{(2) CB8}"] \arrow[r, shift left, "\mathrm{M}"] \arrow[d, shift left] & \mathrm{M@CB8} \arrow[l, shift left] \arrow[u, shift left, "\text{CB8 (3)}"'] \arrow[d, shift left] \\
(\mathrm{M@CB8})_2 \arrow[u, shift left, "\text{(5) M@CB8}"] & \mathrm{D@2CB8}, \arrow[u, shift left, "\text{CB8 (4)}"']
\end{tikzcd}$$

where M is the dye monomer and D is the dye dimer.

Step (1) is the dimerization of the dyes. Step (2) is the complexation of the TCC and MTCC monomers to afford monomeric complexes MTCC@CB8 and TCC@CB8. Step (3) is the formation of the 2 : 1 complex between the dye dimers and CB8 due to the inclusion of the dimers into CB8. Step (4) characterizes the addition of the second CB8 molecule to D@CB8 to afford the 2 : 2 complex from the dye dimer and two

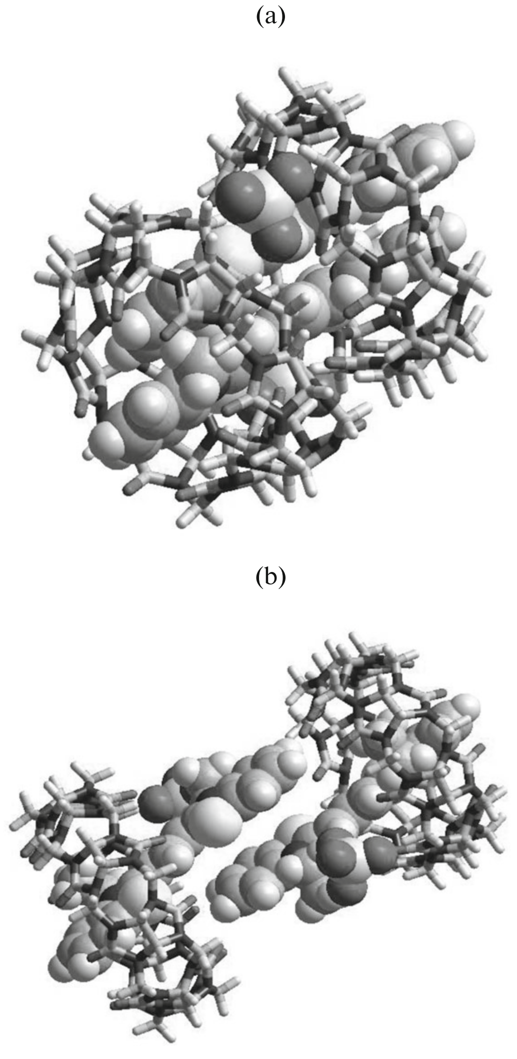

Fig. 3. Calculated optimized structures of the $(MTCC)_2@2CB8$ (a) and $(TCC)_2@2CB8$ (b).

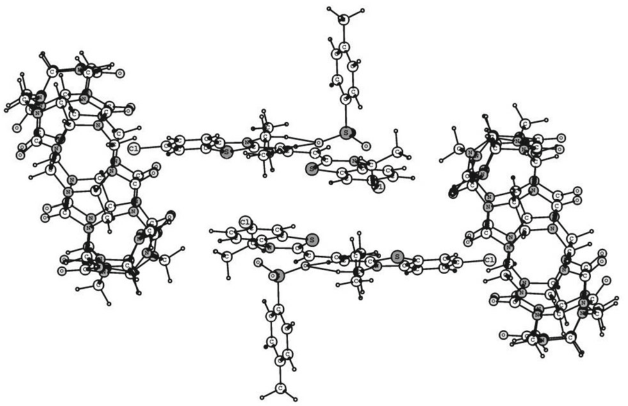

Fig. 4. The structure of (*trans*-DETC)$_2$@2CB7 dimeric complex.

CB8 molecules (D@2CB8). The possibility of the formation of these complexes follows, first, from the large volume of the CB8 cavity and, second, from comparison of the relative sizes of CB8 with MTCC and TCC. The height of the CB8 molecule is ~9 Å, whereas the van der Waals length of the MTCC and TCC molecules is twice longer, 18.5 Å, allowing the possibility of "putting on" the second CB8 molecule. Step (5) is the formation of the 2 : 2 complex via dimerization of monomeric 1 : 1 complexes.

It is important that the only TCC conformation corresponding to the energy minimum is the conformation with the ethyl groups oriented normally to the chromophore plane. This means that there is steric hindrance to the TCC dimerization, unlike the case of MTCC. As a consequence, the TCC molecules in $(TCC)_2@2CB8$ are shifted relative to one other (Fig. 3) and resemble the structure of the intensely fluorescing 2 : 2 complex of 3,3'-diethyl-5,5'-dichloro-9-ethylcarbocyanine with CB7 [28, 29].

The enthalpies of complex formation are listed in the table. It follows from the table that the enthalpies of MTCC and TCC dimerization in water are close in value, as well as the formation enthalpies as the complexes D@CB8 and D@2CB8. However, there is a difference in formation enthalpy between the M@CB8 and D@2CB8 complexes, which is due to the difference in the MTCC and TCC structures.

Host–Guest Complexes of 3,3'-Diethyl-5,5'-Dichloro-9-Ethylthiacarbocyanine with CB7

3,3'-Diethyl-5,5'-dichloro-9-ethylthiacarbocyanine (**DETC**) forms dimeric complexes with CB7 in aqueous solutions in the presence of alkali metal or ammonia cations. As follows from calculation, the 2 : 2 complex (*trans*-DETC)$_2$@2CB7, in which the dye is in the dimeric form, is more stable [28, 29]. The analysis of the complex structure shows that (1) with allowance for the van der Waals radii, the dye molecule enters the cavity of the closest CB7 molecule by 2.6 Å; (2) the minimal distance between the chromophore planes is 4.8 Å; and (3) the planes of the chromophores are displaced by 52° relative to the parallel configuration. According to the calculation of the transition energy by the ZINDO/S method, the displacement causes a hypsochromic shift of the (*trans*-DETC)$_2$@2CB7 absorption band by 21 nm relative to the *trans*-DETC@CB7 band. Thus, the partial inclusion of DETC into the cucurbit [7]uril cavity strengthens the dimeric complex. The structure of the (*trans*-DETC)$_2$@2CB7 dimeric complex is given in Fig. 4.

Host–Guest Complexes of Indocarbocyanines with CB7 and CB8

Cationic 3,3'-dimethylindocarbocyanine tetrafluoroborate (**ICC**) and 3,3',5,5',7,7'-hexamethylindo-

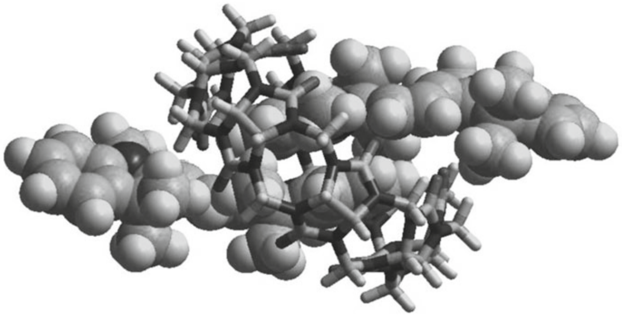

Fig. 5. The structure of the $(ICC)_2$@CB8 complex calculated by the PM6+D3 method.

carbocyanine iodide (**MICC**) dyes form 1 : 1 complexes with CB7 and preferentially 2 : 1 complexes with CB8 [36]. These complexes are characterized by a bathochromic shift of the absorption and fluorescence maximums. The fluorescence intensity increases for the ICC and MICC complexes with CB7 and decreases for the complexes with CB8.

The structure of ICC and MICC suggests that the dye molecules can be in both the *trans*- and *cis*-configurations. The full optimization of geometry for *trans*- and *cis*-ICC by the PM3 method has shown that the *trans*-configuration is thermodynamically more stable by 3.6 kcal/mol than the *cis*-configuration, thereby providing substantial prevalence of the *trans*-isomers in the mixture. In the presence of CB7, the monomeric complex *trans*-ICC@CB7 is formed with evolution of a significant amount of energy (−76.3 kcal/mol), indicating a substantial shift in equilibrium to the formation of *trans*-ICC@CB7.

The calculations show that the complexation of the dye with CB8 occurs at least in two steps. Due to the higher size of the cavity, the cavitand can accommodate two dye molecules; therefore, the 1 : 1 complex is formed in the first step and the 2 : 1 complex, in the second. The complex formation has a high enthalpy (−89.2 and −24.8 kcal/mol, respectively). The 2 : 1 complex has a structure of the ICC stacking dimer stabilized by getting into the cavitand cavity. Thus, the sizes of the dye and the cavity allow for the partial overlapping of the structures of two ICC molecules (Fig. 5), resulting in a decrease in the ICC fluorescence intensity.

SPECTRAL AND LUMINESCENT PROPERTIES OF THE COMPLEXES

Many of polymethine dyes are able to form dimers in aqueous solutions [2, 41]. In water, MTCC and TCC dyes are in the form of an equilibrium mixture of *trans*-monomers and *trans*-*trans*-dimers. The difference absorption spectrum between dye dimers and monomers exhibits two bands, which are due to the transition between the ground and two excited levels. The excited levels appear as a result of splitting of the excited singlet level of the monomer upon dimerization [42, 43]. The ratio of the absorbance of the long-wavelength band to that of the short-wavelength band in the difference spectrum is significantly lower than unity, indicating that the transition moments, which usually coincide with the direction of the principal molecular axis, are nearly parallel

In the presence of cucurbiturils, a shift of the absorption and fluorescence maximums and a change of in fluorescence intensity are observed.

A bathochromic shift of the maximums in the absorption and fluorescence spectra by 10 nm and a threefold increase in the fluorescence intensity were observed for the TZCC@2CB7 complexes. [31].

The cationic TCC dye in the phosphate buffer (pH 6.86) in the presence of cucurbit[7]uril occurs as a mixture of monomeric TCC@CB7 and dimeric $(TCC)_2$@2CB7 complexes [38]. The formation of the monomeric TCC@CB7 complex results in a bathochromic shift of the absorption and fluorescence maximums by 6 nm and in a sixfold increase in the fluorescence intensity. The formation of the dimeric complex increases the absorbance of the dimer band at 520 nm and results in the appearance of delayed fluorescence of type E with a lifetime of 1.6 ms.

Addition of CB7 to the solution of cationic DETC dye in the phosphate buffer (pH 6.86) results in the degradation of aqueous DETC dimers and the formation of monomeric DETC@CB7 complexes with the subsequent formation of dimeric $(DETC)_2$@2CB7 complexes [28, 29]. The complexation is accompanied by a sevenfold increase in the fluorescence intensity. The dimeric $(DETC)_2$@2CB7 complexes exhibit delayed fluorescence with a lifetime of 0.25 ms in air-saturated solutions.

The effect of CB8 on the spectral and luminescent properties of thiacarbocyanines TCC and MTCC were studied in [40]. The formation of the dimeric 2 : 1 and 2 : 2 complexes was established by spectrophotometric titration. The formation of the 2 : 1 complexes results in a decrease in the monomer absorption band, an increase in the dimer absorption band, and the disappearance of the fluorescence of the dye monomers. The 2 : 2 complexes are formed with an increase in the CB8 concentration. Their formation is manifested in the appearance of the short-wavelength absorbance for MTCC and an increase in the absorbance of the TCC dimeric band. Simultaneously with the changes in the absorption spectra, a new long-wavelength fluorescence band appears. Along with prompt fluorescence, thermally activated delayed fluorescence of type E with a lifetime of 4.4–4.6 ms was found for the MTCC and TCC 2 : 2 complexes with CB8 in oxygen-free solution. Annihilation delayed fluorescence of type P was not detected because of the low concentration of dimeric complexes in the triplet state. The delayed fluorescence indicates the existence of the triplet state of the MTCC and TCC dimeric complexes. The lifetime of the delayed fluorescence in air-saturated solutions of MTCC and TCC containing CB8 decreases down to 120 and 60 μs, respectively. The decrease is caused by the quenching of the dye triplet state by air oxygen. The longer lifetime of the delayed fluorescence for the MTCC dimeric complexes in comparison with the dimeric complexes for TCC in the presence of oxygen is presumably due to closer packing of $(MTCC)_2$@2CB8 restricting the oxygen diffusion inside the complex (Fig. 3).

The effect of CB7 and CB8 on the spectral and luminescent properties of indocarbocyanines ICC and MICC were studied in [36]. In the presence of cucurbiturils in the ICC and MICC solutions, the 1 : 1 and 2 : 1 complexes are formed with CB7 and CB8, respectively. This causes a bathochromic shift in absorption spectra by 5 nm. Luminescence measurements provide additional evidence for the complexation of indocarbocyanine dyes with cucurbiturils. The addition of CB7 to the ICC and MICC solutions results in a bathofluoric shift of the maximum by 7 nm in the fluorescence spectra and in an increase in the band intensity by factors of 1.5 and 1.2, respectively. The addition of CB8 to the ICC and MICC solution also results in a bathofluoric shift of the maximum by 7 nm in the fluorescence spectra and a decrease in the fluorescence intensity by 2.1 and 1.5 times, respectively. The increase in the fluorescence is due to the formation of the ICC and MICC 1 : 1 complexes with CB7, whereas the decrease in fluorescence is caused by the formation of the 2 : 1 complexes of ICC and MICC with CB8.

PHOTOISOMERIZATION OF COMPLEXES

We have found that polymethine dyes undergo *trans–cis* photoisomerization via the excited singlet state of a dye [10, 31–36]. The effect of cucurbiturils on the *trans–cis* photoisomerization of polymethine dyes was studied in [31, 36].

It has been shown that the lifetime of the *cis*-isomer for free 3,3’-diethylthiazolinecarbocyanine iodide is significantly shorter than the lifetime of the dye *cis*-isomer inside the CB7 cavity [31].

In the case of laser excitation of the ICC and MICC aqueous solution, short-term changes in the dye absorption spectrum were observed. [36]. Time-resolved differential absorption spectra of MICC caused by the photoinduced formation of the *cis*-isomer are given in Fig. 6. The difference absorption spectrum of *cis*-ICC agrees with the results reported in [46].

The decay curves of *cis* → *trans* transformations for ICC and for the ICC complex with CB8 in water are given in Fig. 6 (inset). The rate of the dark *cis* → *trans* reaction is described by a first-order equation with rate constants k of 2.5×10^5 and 2.1×10^5 s^{-1} for free ICC and MICC, respectively. For the ICC complexes with CB7 and CB8, the values of k decrease to 1.0×10^5 and 5.0×10^4 s^{-1}, respectively. For the MICC complexes with CB7 and CB8, the values of k are 1.3×10^5 and 1.1×10^5 s^{-1}, respectively. Thus, the complex formation of the dye molecules with cucurbiturils hinders *cis* → *trans* isomerization.

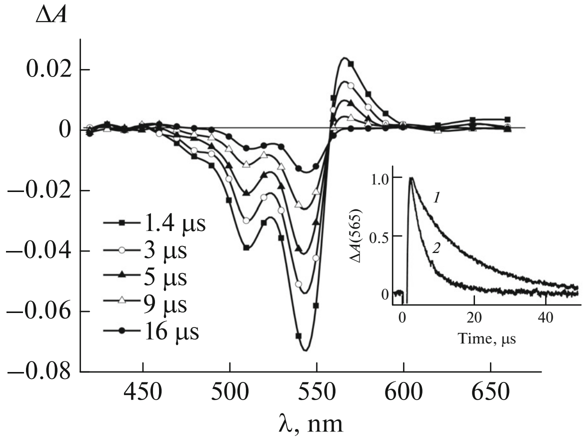

Fig. 6. Time-resolved difference absorption spectra of the MICC *cis*-isomer under laser excitation in water. Frame: the time of spectral measurements after the laser pulse; inset: decay curves of *cis* → *trans* transformations for (*1*) ICC and (*2*) the ICC complex with CB8 (1.0×10^{-5} mol/L) in water.

TRIPLET STATES OF THE COMPLEXES

Intersystem crossing to the triplet state has a very low quantum yield for the monomers of the polymethine dyes and is observed generally for the dyes with bulky substituents at the meso-position of the polymethine chain or in the presence of heavy atoms (Br, I) in the dye molecule [10, 17]. Unlike the monomers, the dimers of polymethine dyes [21] and bisindocarbocyanines [14, 44, 45] are capable of intersystem crossing to the triplet state.

The triplet states of the MTCC and TCC complexes with CB7 and CB8 were studied by examining triplet–triplet (T–T) absorption spectra obtained via nanosecond pulse laser excitation. The measurements of the TCC in the presence of CB7 showed the appearance of the T–T absorption of monomeric and dimeric 2 : 1 complexes with maximums at 650 and 540 nm, respectively. The lifetime of the triplet state of the monomeric complexes is 1.9×10^{-4} s, which exceeds significantly the lifetime of the triplet molecules for the free dye. The lifetime of the triplet state for the TCC dimeric complexes is 6.0×10^{-5} s.

The measurements for TCC in the presence of CB8 showed the appearance of the T–T absorption of the dimeric $(TCC)_2$@2CB8 complex, whose difference spectrum given in Fig. 7 [47]. In the case of laser exci-

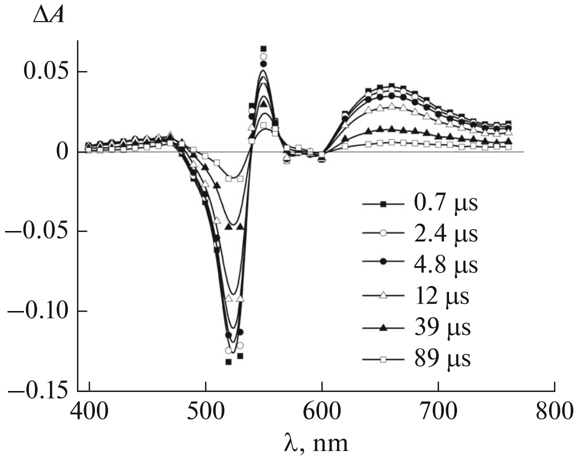

Fig. 7. Time-resolved difference absorption spectra of the TCC dimeric complex with CB8 (1.0×10^{-5} mole/L); frame: the time of the measurements of the spectra after the laser pulse.

tation of oxygen-free aqueous solution of the complex, the absorbance at 525 nm decreases and a relatively narrow band at 550 nm and a wide structureless band in the range of 620–700 nm with a maximum at ~665 nm appear (Fig. 7).

The decay kinetics of absorbance at 550 and at 650 nm is described by an exponential law with a deactivation rate constant of the lowest triplet state of $k = 1.2 \times 10^3$ s^{-1}. The lifetime depends on the presence of oxygen and is decreased to several microseconds by introducing air into the cell, a behavior that is typical of triplet dyes in water.

To account for the appearance of two bands in the difference spectrum of the TCC dimers in the presence of CB8, two models were suggested. According to the first model, not only the initial *trans*-isomers, but also the *cis*-isomers formed in the photoisomerization participate in the dimerization. The absorption of a light quantum by the *trans*-isomer in the dimer initially results in the formation of excited singlet *trans*-isomer followed by intersystem crossing competing with *trans* → *cis* isomerization. Thus, the *trans-trans* dimers in the triplet state and the *trans-cis* dimers in the ground state are formed. In this case, one of the band in the difference absorption spectrum of the dimers may be assigned to the triplet–triplet transition in the *trans-trans* dimers, and the other band can be attributed to the singlet–singlet transition in the *trans-cis* dimers. However, both bands are of a triplet origin, because their intensity decays with the same rate constant in the presence of air oxygen. Thus, the origin of one of the bands from the *trans-cis* dimers is improbable. An additional confirmation of the assignment of the two bands to the absorption of *trans-trans* dimers is the results obtained for covalently bonded indocarbocyanine *trans*-monomers (bis dyes) [10, 14, 45]. Two bands are also observed for the bis dyes in the difference triplet–triplet absorption spectrum. However, the formation of the *cis*-isomers in the *trans* → *cis* photoisomerization is almost impossible for the covalently bonded monomers because of steric hindrance due to the cyclic structure of the bis dye.

The second model is based on the possibility of population of both the triplet level of the dimeric complex itself and the dimeric complex with charge transfer in the triplet state. Earlier [10, 14, 45], it was assumed that the two bands in the difference triplet–triplet absorption spectrum of the covalently bonded monomers of indocarbocyanine dyes are caused by triplet level splitting. However, according to the theory of excitons [48–50], the value of the matrix element of exchange interaction for the triplet states of aromatic molecules, which are in close proximity in crystals, is ~10 cm^{-1}. This value is well below that observed in the present study (~3000 cm^{-1}); therefore, the bands observed in the triplet–triplet absorption spectrum cannot result from triplet level splitting. According to the theory of triplet excitons, the formation of triplet states with intermolecular charge transfer is possible [48–50]. The probability of optical transition to these states decreases with an increase in the distance between interacting fragments, and the corresponding bands in such systems will be broadened by interaction of the charge transfer states with surrounding molecules. Thus, we attributed the band at 550 nm to the triplet–triplet absorption of dimeric complexes. The band in the range of 620–700 nm may be due to the triplet–triplet absorption of the dimeric complexes with prevailing configurations with charge transfer between the fragments. The substantial broadening of the band is due to the dipole–dipole interaction with the environmental molecules.

The formation of the dimeric complexes of dyes with cucurbit [8]uril facilitates the population of their triplet level. Unlike a single band for monomers, the presence of two bands is typical of the triplet–triplet absorption spectrum of dimers and dimeric complexes.

PHOTOINDUCED ELECTRON TRANSFER WITH PARTICIPATION OF THE COMPLEXES

It is well documented that polymethine dyes adsorbed on the surface of silver halide materials participate in photoinduced electron transfer, the basic reaction of spectral sensitization [2]. Both dye monomers and dimers in the triplet state participate in the redox photoreactions of polymethine dyes [21, 51–53]. Electron transfer occurring via triplet state is detected and investigated by delayed fluorescence and the T–T absorption spectra.

In this study, the effect of cucurbit[7, 8]urils on electron transfer in thiacarbocyanine dyes is studied.

Table 1. Enthalpies of complexation (*ΔE)* of MTCC and TCC with CB8

Dye	ΔE, kcal/mol				
	step (1) Formation of dimer D in water	step (2) Formation of complex M@CB8	step (3) Formation of complex D@CB8	step (4) Formation of complex D@2CB8	step (5) Formation of complex M@2CB8
MTCC	−42.7	−67.8	−66.6	−113.34	−123.4
TCC	−38.5	−91.5	−57.3	−107.35	−36.9

Quenching of Delayed Fluorescence

In the presence of *p*-nitroacetophenone (electron acceptor), the delayed fluorescence of dimeric $(TCC)_2$@2CB7 complexes is quenched via the electron transfer mechanism with a rate constant of 7×10^8 L mol^{-1} s^{-1}. A decrease in the lifetime of delayed fluorescence is also typical of the dimeric $(MTCC)_2$@2CB8 and $(TCC)_2$@2CB8 complexes in the presence of *p*-nitroacetophenone. The measured quenching rate constants are 1.5×10^8 and 7.5×10^8 L mol^{-1} s^{-1} for $(MTCC)_2$@2CB8 and $(TCC)_2$@2CB8, respectively. The obtained data indicate the participation of dimeric complexes in electron transfer.

Deactivation of the Triplet State

In the presence of the electron acceptor *m*-dinitrobenzene (***m*-DNB**), the triplet state of the dimeric $(TCC)_2$@2CB8 complex is quenched in the one-electron oxidation to afford radical products of the reaction. The time-resolved difference absorption spectra of the dimeric $(TCC)_2$@2CB8 complexes in the presence of *m*-DNB after the laser excitation are given in Fig. 8.

As shown above, the absorption band at 540–700 nm is due to the T–T absorption of the dimeric complex and the band at 470–475 nm belongs to the radical product of TCC oxidation in the complex. The quenching of the T state is incomplete at an *m*-DNB concentration of 5×10^{-5} mol/L, as indicated by the presence of the T–T absorption for the complex. The T–T absorption decay kinetics in the presence of *m*-DNB (*2*) and the kinetics of the formation of the radical product of the dimeric complex oxidation and its further transformation (*1*) are given in Fig. 8 (inset). As follows from the comparison of the rate curves, the highest absorbance of the photoreaction products is attained 13 μs after the laser pulse, i.e., at the time of practically 100% decay of the triplet molecules. This finding unambiguously implies the involvement of the triplet state of the dimeric complex in the electron transfer.

TRIPLET–TRIPLET ENERGY TRANSFER

Triplet–triplet energy transfer with the participation of the dye complexes with CB8 was found for the system involving eosin (**Eo**) (free dye) as a donor of the triplet energy and the dimeric complex of 3,3'-diethylthiadicarbocycnine iodide (**TDCC**) as a triplet energy acceptor. Phosphorescence with a maximum at 677 nm and a lifetime of 0.6 ms is observed in the oxygen-free aqueous solution of Eo at room temperature. In the presence of the dimeric $(TDCC)_2$@CB8 complex, the Eo phosphorescence is quenched with a rate constant of 4×10^9 L mol^{-1}s^{-1} as a result of energy transfer. Eosin phosphorescence spectra in the presence and in the absence of CB8 are given in Fig. 9.

The formation of the TDCC triplet state is a consequence of the triplet energy transfer. However, we failed to record the phosphorescence spectrum of TDCC because of the very low quantum yields of phosphorescence in water at room temperature.

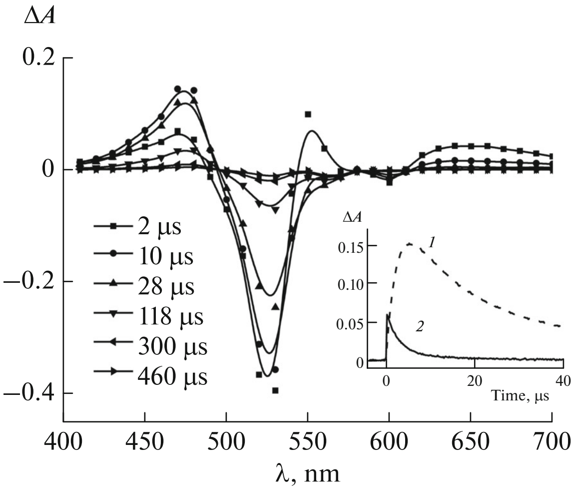

Fig. 8. Time-resolved difference triplet–triplet absorption spectra for the dimeric $(TCC)_2$@2CB8 complex in the presence of *m*-DNB and the radical product of complex oxidation. Frame: times of spectral measurements after the laser pulse; inset: (*1*) the formation and decay kinetics of the radical products of oxidation, 470 nm and(*2*) the kinetics of deactivation of the triplet state of the complex, 650 nm.

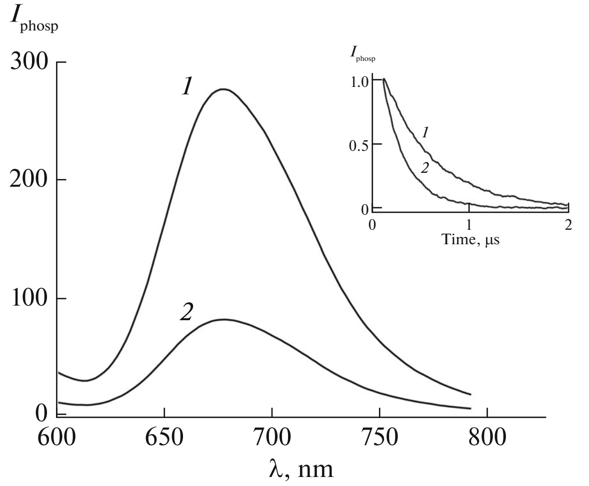

Fig. 9. Eosin phosphorescence in the (*1*) absence and (*2*) presence of CB8 (7×10^{-7} mol/L). Inset: the decay eosin phosphorescence in the(*1*) absence and (*2*) presence of CB8 (7×10^{-7} mol/L).

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REFERENCES

1. Mishra, A.R., Behera, K. Behera, P.K., et al., *Chem. Rev.*, 2000, vol. 100, p. 1973.
2. *The Theory of the Photographic Process*, James, T.H., Ed., New York: Macmillan, 1977.
3. Ying, L.-Q. and Branchaud, B.P., *Bioconjug. Chem.*, 2011, vol. 22, no. 5, p. 865.
4. Bourbon, S., Gao, M.Y., and Kirstein, S., *Synth. Met.*, 1999, vol. 101, nos. 1–3, p. 152.
5. Mal'tsev, E.I., Lypenko, D.A., Shapiro, B.I., and Vannikov, A.V., *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 2001, vol. 46, no. 1, p. 13.
6. Scheblykin, I.G., Lepnev, L.S., Vitukhnovsky, A.G., and Van der Auweraer, M., *J. Lumin.*, 2001, vol. 94/95, p. 461.
7. Sasaki, F. and Kobayashi, S., *J. Lumin.*, 1997, vols. 72–74, p. 538.
8. Markov, R.V., Plekhanov, A.I., Rautian, S.G., et al., *Opt. Spectrosc.*, 1998, vol. 85, no. 4, p. 588.
9. Tyutyulkov, N., Fabian, J., Mehlhorn, A., et al., *Polymethine Dyes*, Sofia: St. Kliment Ohridski Univ. Press, 1991.
10. Görner, H. and Chibisov, A.K., *CRC Handbook Organic Photochemistry and Photobiology*, Horspool, W.M. and Lenci, F, Eds., Boca Raton: CRC, 2004, 2nd ed., ch. 36.
11. Chibisov, A.K., *J. Photochem.*, 1977, vol. 6, no. 3, p. 199.
12. Mialocq, J.C., Doizi, D., and Gingold, M.P., *Chem. Phys. Lett.*, 1983, vol. 103, no. 3, p. 225.
13. Chibisov, A.K., Shvedov, S.V., and Görner, H., *J. Photochem. Photobiol., A*, 2001, vol. 141, no. 1, p. 39.
14. Chibisov, A.K. and Zakharova, G.V., *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1995, vol. 40, no. 6, p. 1.
15. Chatterjee, S., Davis, P.D., Gottschalk, P., et al., *J. Am. Chem. Soc.*, 1990, vol. 112, no. 17, p. 6329.
16. Tolmachev, A.I., Zaitsev, A.K., Koska, N., and Schuster, G.B., *J. Photochem. Photobiol., A*, 1994, vol. 77, p. 237.
17. Korobov, V.E. and Chibisov, A.K., *Usp. Khim.*, 1983, vol. 52, no. 1, p. 43.
18. Jia, K., Wan, Y., Xia, A., et al., *J. Phys. Chem. A*, 2007, vol. 111, no. 9, p. 1593.
19. Chibisov, A.K., Petrov, N.Kh., Voznyak, D.A., and Alfimov, M.V., *High Energy Chem.*, 2009, vol. 43, no. 1, p. 38.
20. Voznyak, D.A., Chibisov, A.K., Petrov, N.Kh., and Alfimov, M.V., *High Energy Chem.*, 2010, vol. 44, no. 1, p. 25.
21. Chibisov, A.K., *High Energy Chem.*, 2007, vol. 41, no. 3, p. 200.
22. Koner, A.L. and Nau, W.M., *Supramol. Chem.,* 2007, vol. 19, nos. 1/2, p. 55.
23. Dsouza, R.N., Pichel, U., and Nau, W.M., *Chem. Rev.*, 2011, vol. 111, no. 12, p. 7941.
24. Lagona, J., Mukhopadhyay, P., Cyakrabarti, S., and Isaacs, L., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, p. 4844.
25. Liu, Y., Li, C., Guo, D., et al., *Supramol. Chem.*, 2007, vol. 19, no. 7, p. 517.
26. Bhasikuttan, A.C., Mohanty, J., Nau, W.M., and Pal, H., *Angew. Chem., Int. Ed. Engl.*, 2007, vol. 46, no. 22, p. 4120.
27. Petrov, N.Kh., Ivanov, D.A., Golubkov, D.V., et al., *Chem. Phys. Lett.*, 2009, vol. 480, nos. 1–3, p. 96.
28. Zakharova, G.V., Zhizhimov, D.A., Avakyan, V.G., et al., *High Energy Chem.*, 2014, vol. 48, no. 2, p. 76.
29. Zakharova, G.V., Zhizhimov, D.A., Sazonov, S.K., et al., *J. Photochem. Photobiol., A*, 2015, vol. 302, p. 69.
30. Atabekyan, L.S., Vedernikov, A.I., Avakyan, V.G., et al., *J. Photochem. Photobiol., A*, 2013, vol. 253, p. 52.
31. Atabekyan, L.S., Kulemin, N.A., Avakyan, V.G., and Chibisov, A.K., *Izv. Akad. Nauk, Ser. Khim.*, 2013, no. 4, p. 966.
32. Yuan, L. and Macartney, D.H., *J. Phys. Chem. B*, 2007, vol. 111, no. 24, p. 6949.
33. Mohanty, J., Pal, H., Ray, A.K., et al., *Chem. Phys. Chem.*, 2007, vol. 8, no. 1, p. 54.
34. Mohanty, J. and Nau, W.M., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, no. 24, p. 3750.
35. Atabekyan, L.S., Avakyan, V.G., and Chibisov, A.K., *High Energy Chem.*, 2011, vol. 45, no. 2, p. 123.
36. Zakharova, G.V., Avakyan, V.G., Markelov, V.P., et al., *High Energy Chem.*, 2015, vol. 49, no. 6, p. 407.
37. Zakharova, G.V., Konstantinov, R.R., Odinokov, A.V., et al., *High Energy Chem.*, 2016, vol. 50, no. 2, p. 121.
38. Zakharova, G.V. and Chibisov, A.K., *High Energy Chem.,* 2016, vol. 50, no. 5, p. 368.
39. Gadde, S., Batchelor, E.K., Weiss, J.P., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 50, p. P. 17114.

40. Zakharova, G.V., Avakyan, V.G., Chibisov, A.K., and Alfimov, M.V., *High Energy Chem.*, 2017, vol. 51, no. 3, p. 195.
41. Herz, A.H., *Photogr. Sci. Eng.*, 1974, vol. 18, no. 3, p. 323.
42. Kasha, M., Rawls, H.R., and El-Bayoumi, M.A., *Molecular Spectroscopy*, London: Butterworths, 1965.
43. McRae, E.G. and Kasha, M., *Physical Processes in Radiation Biology*, London: Academic, 1964.
44. Chibisov, A.K., Zakharova, G.V., Görner, H., and Tolmachev, A.I., *Zh. Prikl. Spektrosk.*, 1995, vol. 65, no. 2, p. 57.
45. Chibisov, A.K., Zakharova, G.V., Görner, H., et al., *J. Phys. Chem.*, 1995, vol. 99, no. 3, p. 886.
46. Kuzmin, V.A. and Darmanyan, A.P., *Chem. Phys. Lett.*, 1978, vol. 54, no. 1, p. 159.
47. Zakharova, G.V., Gutrov, V.N., Plotnikov, V.G., et al., *High Energy Chem.*, 2017, vol. 51, no. 5, p. 345.
48. Jortner, J., Rice, S.A., Katz, J.L., and Choi, S., *J. Chem. Phys.*, 1965, vol. 42, no. 1, p. 309.
49. Choi, S., Jortner, J., Rice, S.A., and Silbey, R., *J. Chem. Phys.*, 1964, vol. 41, no. 1, p. 3294.
50. Davydov, A.S., *Teoriya tverdogo tela* (Theory of Solids), Moscow: Nauka, 1978.
51. Chibisov, A.K., Slavnova, T.D., and Görner, H., *Chem. Phys. Lett.*, 2004, vol. 386, nos. 4–6, p. 301.
52. Chibisov, A.K., Slavnova, T.D., Zakharova, G.V., and Görner, H., *High Energy Chem.*, 2007, vol. 41, no. 5, p. 344.
53. Zakharova, G.V. and Chibisov, A.K., *High Energy Chem.*, 2013, vol. 47, no. 6, p. 322.

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