

Triplet Energy Transfer from Polymethine Dimers in the Complexes with Cucurbit[8]urils

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Abstract—Effect of cucurbit[8]uril on the efficiency of triplet–triplet energy transfer between the donor dimer and the acceptor monomer or dimer has been studied. The efficiency depends on the rate constant of quenching of donor delayed fluorescence by the triplet energy acceptor, on the lifetime of the donor triplet state in the absence of a quencher, and on the acceptor concentration. Triplet–triplet energy transfer between the 3,3'-diethylthiacarbocyanine dimer (donor) and indodicarbocyanine (acceptor) occurs with a rate constant of $1.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. Replacing the indodicarbocyanine monomer by the thiadicarbocyanine dimer decreases the energy transfer rate constant by a factor of 4.5. In the case of the 3,3'-dimethylthiacarbocyanine dimer as a donor, the quantum yield of energy transfer to the indodicarbocyanine monomer decreases four-fold.

Keywords: triplet–triplet energy transfer, carbo- and dicarbocyanines, eosin, delayed fluorescence, phosphorescence, triplet–triplet absorption

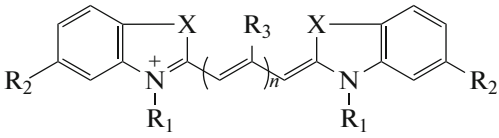
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The capability of organic molecules in the triplet state for nonradiative energy transfer was revealed by Dexter [1], Ermolaev and Terenin [2–5], and several other authors [6–8]. Triplet–triplet energy transfer (T–T) was observed in vapors, liquid and solid solutions, and crystals of a number of aromatic and heterocyclic compounds at ambient and low temperatures [9]. Triplet–triplet energy transfer was used for population of the triplet level of molecules with a low quantum yield of intersystem crossing and for the establishment of the mechanisms of photochemical reactions, in particular, for revealing the nature of the excited state involved in photoprocesses. A great variety of photochemical reactions occur in liquid solutions where the translational diffusion of a triplet energy donor or acceptor is frequently hindered by certain factors. These conditions may be attained in supramolecular systems such as host–guest complexes formed between cavitand molecules (cyclodextrins, cucurbiturils) and the donor and acceptor molecules. The phenomenon of triplet–triplet energy transfer in supramolecular systems was studied. For example, the appearance of sensitized fluorescence as a result of T–T energy transfer was observed in the fluorene– β -cyclodextrin–acetone supramolecular system [10]. The T–T energy transfer from eosin to the thionine monomer in the complex with cucurbit[7]uril and to

the thionine dimer in the complex with cucurbit[8]uril was studied in [11]. Self-assembled aggregates of dye molecules of various classes, particularly polymethine dyes, also belong to supramolecular systems [12–17]. The dimers formed from thiadicarbocyanine monomers and related polymethines are the simplest aggregates. It has been shown [18–22] that the dimers of sulfonated thia- and oxa-derivatives of polymethines are produced via the spontaneous dimerization of the dyes in aqueous solutions. The dimers undergo intersystem crossing in oxygen-free solutions with a lifetime of 10–60 μs [18, 21, 22]. In this paper, we present the results of the study on the effect of cucurbit[8]uril on T–T energy transfer involving the dimers of polymethine dyes in complexes with cucurbit[8]uril using T–T absorption, phosphorescence, and delayed fluorescence data.

EXPERIMENTAL

The objects of the study were thia- and indodicarbocyanine dyes, eosin, and cucurbit[8]uril (Aldrich). Triplet–triplet absorption spectra and triplet state deactivation kinetics were measured on a nanosecond laser photolysis setup [23]. Dye solutions were irradiated by pulses from an yttrium–aluminum garnet laser (Nd : YAG, Solar, $\lambda = 532 \text{ nm}$) with a pulse duration of 10 ns and an energy up to 70 mJ. Spectra and decay

Table 1. Donors (D) and acceptors (A) of triplet energy


Dye	<i>n</i>	X	R ₁	R ₂	R ₃
Dye1 (D)	1	S	C ₂ H ₅	H	H
Dye2 (D)	1	S	C ₂ H ₅	H	CH ₃
Dye3 (D)	1	S	CH ₃	H	H
Dye4 (A)	2	C(CH ₃) ₂	CH ₃	H	H
Dye5 (A)	2	S	C ₂ H ₅	H	H
Dye6 (D)	1	S	C ₃ H ₆ SO ₃ ⁻	OCH ₃	C ₂ H ₅

kinetics of delayed fluorescence and phosphorescence were measured on a Cary Eclipse spectrofluorimeter. The spectra of delayed fluorescence and phosphorescence were recorded 100 μs after switching off a pulse lamp as an excitation source (spectrofluorimeter option). The spectra of delayed fluorescence and phosphorescence of thiocarbocyanines in the presence of cucurbit[8]uril were measured in oxygen-free aqueous solutions at room temperature. The phosphorescence spectra of thiocarbocyanines in acetonitrile were measured at 77 K. The air oxygen was removed by bubbling the argon gas through the solution. Absorption spectra were recorded on an Agilent 8453 spectrophotometer. Water was purified using a Direct-Q3 Millipore system.

RESULTS AND DISCUSSION

The efficiency of triplet–triplet (T–T) energy transfer from thiocarbocyanines dimers (**Dye1**, **Dye2**,

and **Dye2**) in the 2 : 2 complexes with cucurbit[8]uril (**CB8**) to the indocarbocyanine (**Dye4**) monomer or to the thiadcarbocyanine (**Dye5**) dimer in the 2 : 2 complex with CB8 was studied. In the absence of CB8, the eosin (**Eo**) monomer and a 3,3'-disulfopropyl-5,5'-dimethoxy-9-ethylthiocarbocyanine (**Dye6**) dimer were used as free energy donors. The general formula of monocarbo- and dicarbocyanines is given in Table 1.

Dimers of Dye1 and Dye3 in the complex with CB8 (2Dye1@2CB8, 2Dye3@2CB8) in oxygen-free aqueous solutions exhibit delayed fluorescence [24], whereas the dimer of Dye2 in the complex with CB8 (2Dye2@2CB8) phosphoresces. The rate constant of energy transfer was determined from the dynamic quenching of the delayed fluorescence of the 2Dye1@2CB8, 2Dye3@2CB8 complexes and the phosphorescence of the 2Dye2@2CB8, complex, as well as of eosin, by the energy acceptors Dye4 and 2Dye5@2CB8. The energy transfer from the 2Dye6 dimer to Dye4 was observed by following the disappearance of the T–T absorption of 2Dye6 in the presence of the acceptor. Figure 1 presents decay rate curves of the delayed fluorescence of 2Dye1@2CB8 in the absence and in the presence of $(3-8) \times 10^{-6}$ mol/L of Dye4. The inset shows the graphical determination of the energy transfer rate constant (k_T is the decay rate constant of delayed fluorescence). The calculated rate constants of energy transfer for all of the systems under study are listed in Table 2.

Evidence for the energy transfer is the finding that the energy acceptor exhibits triplet–triplet absorption. The rate curves illustrating energy transfer in the dimer 2Dye6 (donor)–Dye4 (acceptor) system are given in Fig. 2. The acceptor Dye4 undergoes *trans*–*cis* isomerization upon pulse laser irradiation. Curve 1 shows the formation kinetics of the Dye4 *cis*-isomer and the kinetics of its thermal conversion into the *trans*-form. In the presence of the energy donor

Table 2. Position of the triplet level in energy donors (E_T^D), quenching rate constants (energy transfer, k_{ET}), decay rate constants of delayed fluorescence (phosphorescence) for the energy donor ($1/\tau_T$) in the absence of a quencher

D	A	E_T^D , cm ⁻¹	k_{ET} , L mol ⁻¹ s ⁻¹	$1/\tau_T$, s ⁻¹
2Dye1@2CB8	Dye4	13700*	1.5×10^8	6.5×10^2
2Dye1@2CB8	2Dye5@2CB8	–	3.4×10^7	–
2Dye2@2CB8	Dye4	14880*	1.7×10^8	2.0×10^3
2Dye3@2CB8	Dye4	13230*	3.8×10^7	2.3×10^2
2Dye1@2CB8	2Dye5@2CB8	13670*	3.4×10^7	6.5×10^2
(2Dye6) ²⁻	Dye4	13950*, 13330*	5.0×10^9	3.0×10^5
Eo ²⁻	Dye4	14730**	6.7×10^9	2.13×10^3
Eo ²⁻	2Dye5@2CB8	–	2.4×10^9	–

* Calculated from the dye phosphorescence spectra in acetonitrile at 77 K.

** Calculated from the oxygen-free aqueous solution of Eo at room temperature.

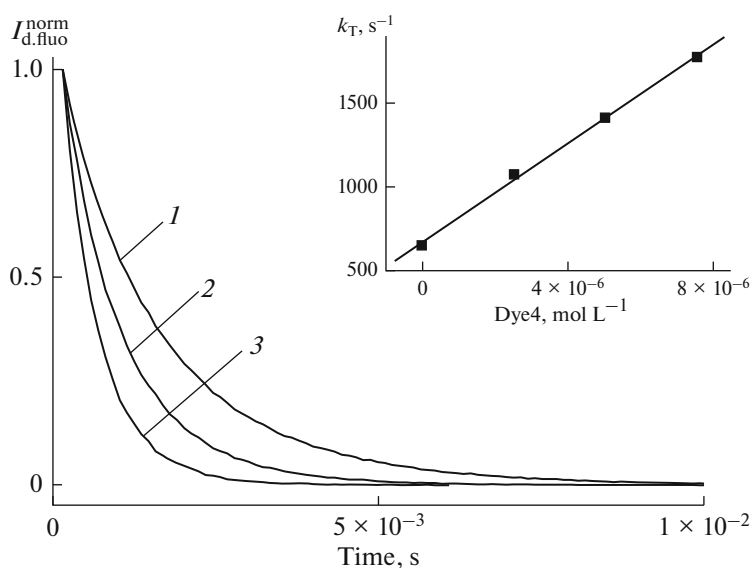


Fig. 1. Kinetics of delayed fluorescence quenching for 2Dye1@2CB8 dimer in the (1) absence and presence of Dye4 in concentrations of (2) 3×10^{-6} and (3) 3×10^{-6} mol L $^{-1}$. Inset: graphical determination of the energy transfer rate constant.

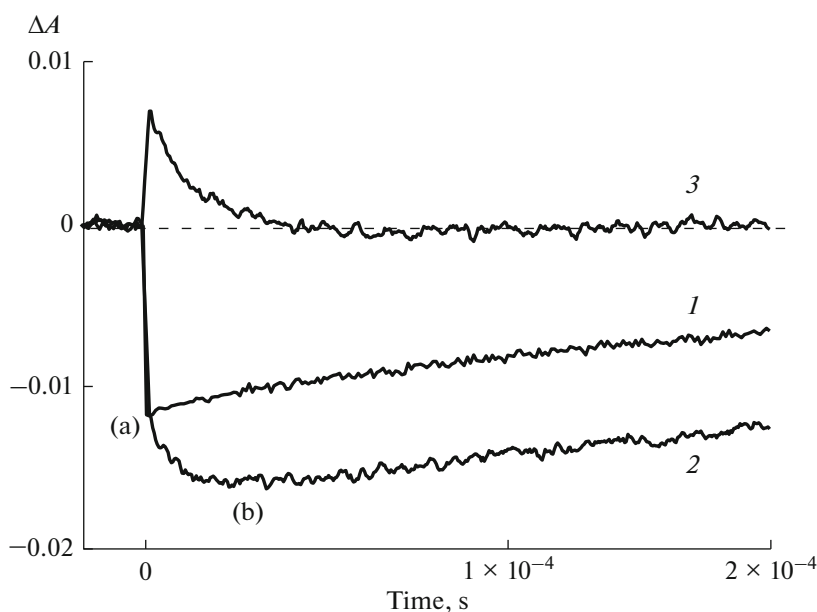


Fig. 2. Kinetics of (1) absorption changes for Dye4 in photoisomerization and (2) population of the T level at 540 nm. (3) Kinetics of the T state deactivation for the 2Dye6 dimer in the presence of Dye4 at 615 nm

2Dye6, T–T absorption is observed along with the *cis*-isomer. This absorption is displayed in curve 2 as the a–b portion. The formation kinetics of the T state of Dye4 coincides with the decay kinetics of the T state of the energy donor, the 2Dye6 dimer (3).

It follows from the data in Table 2:

(1) The rate constants for energy transfer from the thiocarbocyanine dimers 2Dye1@2CB8, 2Dye2@2CB8, and 2Dye3@2CB8 to the thiocarbocyanine monomer

Dye4 range within $(0.38–1.7) \times 10^8$ L mol $^{-1}$ s $^{-1}$. Dye2 has the highest value of k_{ET} , and Dye3 has the lowest value. The value of k_{ET} decreases by a factor of 4.4 on passing from 2Dye2@2CB8 to 2Dye3@2CB8 and decreases fourfold on passing from 2Dye1@2CB8 to 2Dye4@2CB8. The low values of k_{ET} for the transfer between the dimeric complexes of carbocyanines with CB8 and Dye4 are the result of the shielding action of CB8 on the overlapping of frontier orbitals of the energy

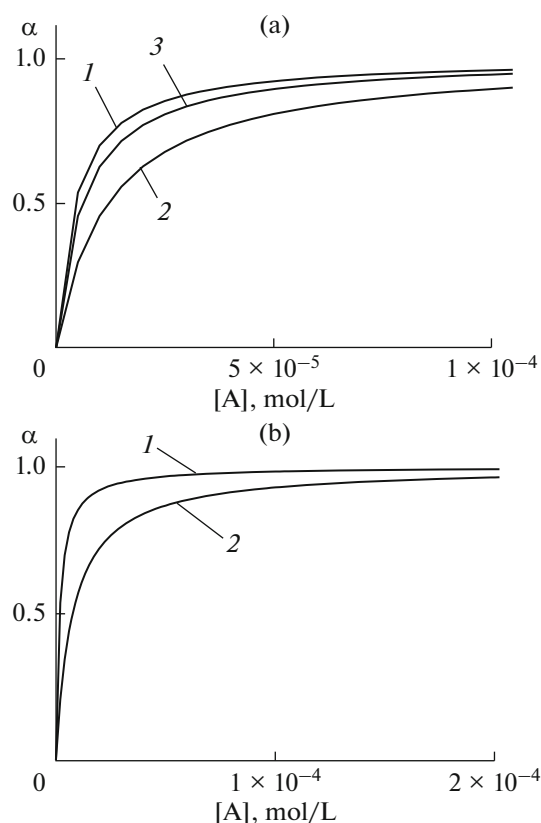


Fig. 3. Plot of the efficiency of energy transfer vs the energy acceptor concentration for the systems: (a) (1) 2Dye1@2CB8–Dye4, (2) 2Dye2@2CB8–Dye4, and (3) 2Dye3@2CB8–Dye4 and (b) (1) 2Dye1@2CB8–Dye4 and (2) 2Dye1@2CB8–2Dye5@2CB8.

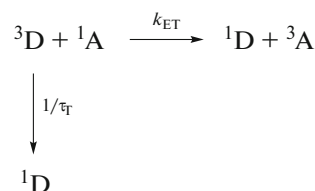
donor and acceptor. The decrease in the rate constant k_{ET} in the order row 2Dye2@2CB8, 2Dye1@2CB8, and 2Dye3@2CB8 is due to the difference in structure between the dimeric complexes. According to quantum-chemical calculations, the Dye3 dimer has a plane-parallel structure and is almost completely located in the cavities of the two CB8 molecules [24]. A horizontal displacement of the dye monomers relative to one another takes place on the complexation of 2Dye2 and 2Dye1 dimers with CB8, with the displacement being greater for Dye1 [24]. The horizontal displacement of the monomeric molecules in the dimeric complexes with CB8 increases the distance between the CB8 molecules in the complex, thereby decreasing the shielding action of CB8 on the overlapping of the frontier orbitals of the energy donor and acceptor and increasing the rate constant of energy transfer.

(2) A decrease in the k_{ET} by a factor of 4.4 occurs in the energy transfer from 2Dye1@2CB8 and the replacement of the acceptor monomer Dye4 by the dimer of Dye5 in the complex with CB8 (2Dye5@2CB8). Shielding by CB8 affects both energy donor and acceptor.

(3) In the energy transfer from the Eo monomer and the replacement of the acceptor Dye4 by the 2Dye5@2CB8 dimer, the transfer rate constant decreases by a factor of 2.8. In this case, the shielding action of CB8 manifests itself only for the acceptor.

(4) Energy transfer from the 2Dye6 dimer to Dye4 in the absence of CB8 is characterized by a high transfer rate constant ($5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) close to the rate constant of energy transfer from Eo to Dye4 ($6.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$).

The splitting of the excited singlet level into two levels located higher and lower relative to that of the free monomer (Davydov splitting) is typical of the monomers forming dimers [25]. The splitting of the dimer excited singlet level ΔE^S is usually $(1-3) \times 1000 \text{ cm}^{-1}$, significantly exceeding the splitting of the triplet level of the dimer ΔE^T [12] equal to $\sim 10 \text{ cm}^{-1}$ [26]. Thus, the positions of the triplet level of monomers and dimers listed in Table 2 practically coincide. The process of energy transfer is schematized below.



The scheme suggests the following expression for the efficiency (α) of triple–triplet energy transfer:

$$\alpha = \frac{k_{ET} [{}^1\text{A}]}{1/\tau_T + k_{ET} [{}^1\text{A}]} \quad (1)$$

As follows from Eq. (1), $\alpha = 1$ and is independent of $[{}^1\text{A}]$ if $1/\tau_T \ll k_{ET} [{}^1\text{A}]$. When $1/\tau_T \gg k_{ET} [{}^1\text{A}]$, $\alpha = \tau_T k_{ET} [{}^1\text{A}]$ and, hence, is proportional to $\tau_T k_{ET} [{}^1\text{A}]$. Figure 3 shows the plots of the efficiency of T–T energy transfer as a function of the energy acceptor concentration for the systems: the dimer in the complex with CB8 (2Dye1@2CB8, 2Dye2@2CB8, 2Dye3@2CB8)—monomer Dye4 (Fig. 3a) and the dimer in the complex with CB8 (2Dye1@2CB8)—monomer Dye4 and the dimer in the complex with CB8 (2Dye5@2CB8) (Fig. 3b). As follows from Fig. 3a, there is a difference in α at close rate constants of energy transfer between 2Dye1@2CB8 and Dye4 (1) and between 2Dye2@2CB8 and Dye4 (2), which is due to the difference in the lifetime of donor molecules in the T state between 2Dye1@2CB8 and 2Dye2@2CB8. There is also a difference in α in the case of coincidence of the triplet lifetimes but different k_{ET} values (Fig. 3b).

Thus, α depends on both the triplet lifetime of the donor—the dye dimer in the complex with CB8—and the concentration of the acceptor of triplet energy. The effect of cucurbit[8]uril primarily reduces to the formation of the dye dimer capable of intersystem cross-

ing to the T state with a characteristic lifetime τ_T . In addition, cucurbit[8]uril affects the rate constant of energy transfer k_{ET} , which ranges within 3.4×10^7 – 5.0×10^9 L mol⁻¹ s⁻¹ (Table 2). It follows from the scheme that the energy transfer competes with deactivation of the T-state of the dye dimer in the complex with CB8. Since the rate of energy transfer depends not only on k_{ET} , but also on the energy acceptor concentration [¹A], the efficiency of energy transfer can be varied by varying [¹A].

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