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Interlayer Triplet–Triplet Energy Transfer in Nanosized Molecular Layers

N. Kh. Ibrayev, A. K. Aimukhanov, and E. V. Seliverstova

Karaganda State University, ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan

e-mail: nibraev@ksu.kz

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Abstract—The results of the study of interlayer triplet–triplet energy transfer from anthracene molecules to Nile Red molecules in Langmuir–Blodgett films are presented. The observed sensitized delayed fluorescence of the energy acceptor is shown to be due to annihilation of migrating triplet excitons. It has been found that the decay kinetics of delayed fluorescence of the donor and the acceptor has a complex form and is described by a combination of the power and exponential functions. The dependence of the energy transfer efficiency on the distance between the donor and acceptor layers was studied.

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Triplet–triplet (T–T) energy transfer is one of fundamental problems of physics of the condensed state and has always attracted the attention of researchers [1, 2]. It follows from the exchange-resonance nature of T–T energy transfer that the energy transfer efficiency should depend on the distance and relative orientation of the energy donor and acceptor. The review of early experimental studies of this problem is presented in the book of Ermolaev et al. [1].

A new theory of electronic excitation energy transfer has been developed [3–5], which is based on the quantum-chemical approach. According to this model, the orientation dependence of the energy transfer rate constant has more complex character than in the Förster–Dexter theory.

To study experimentally the effect of the orientation and distance factors on the intermolecular energy transfer efficiency, the Langmuir–Blodgett (LB) technique [6] can be used, which permits the formation of donor–acceptor systems in which the distance between the molecules and their relative orientation are predictable. The first such studies applied to singlet–singlet energy transfer were performed by Kuhn et al. [7–9].

In spite of a great number of publications on the study of photoprocesses in LB films of organic molecules, the works on the study of intermolecular transfer involving triplet states are practically lacking [10]. This work presents the results of the study of interlayer T–T energy transfer from anthracene molecules to Nile red molecules in LB films.

EXPERIMENTAL

Anthracene molecules were chosen as the triplet energy donor, and Nile red molecules served as the acceptor. Nile red was chosen as the acceptor because its quantum yield to the triplet state is practically zero [11], which excludes direct population of its triplet states.

The samples studied were prepared by the following procedure. The mixed LB film consisting of amphiphilic poly(*N*,*N*-diallyl-*N*-octadecylamine-alt-maleic acid) (PDOAM) and anthracene in the ratio 3:1 was deposited onto the surface of a nonluminescent quartz substrate. Then the mixed LB film of Nile Red and PDOAM with different dye concentrations was deposited onto the anthracene film. The mixed LB films based on PDOAM and dyes were shown to possess a number of advantages [12, 13]. First, it is related to their thermal and mechanical stability and good luminescent properties. The surface tension of water was 72.8 mN m^{-1} at pH 5.6 and T = 20°C. Twice distilled deionized water was used. The control of cleanness of the water surface was performed by the method of temporal monitoring of the surface pressure. The dye and PDOAM were dissolved separately in chloroform, mixed in the necessary molar ratios, and the mixture was deposited onto the water surface. The transfer of monolayers onto the substrate by the Y type was performed at the pressure of 28 mN m^{-1} for the dye and 30 mN m^{-1} for anthracene; the dipping speed of the plate was 0.02 mm s^{-1}. The number of monolayers in the LB films was ten. Multilayers of the donor and the acceptor were separated by monolayers of palmitic acid (PA).

The spectral and kinetic characteristics of the samples were measured on an automated apparatus with detection in the photon counting regime. The registering unit of the apparatus consisted of an H7421 photomultiplier tube and an M8784 (Hamamatsu) counting board. The samples were placed into an evacuated optical cryostat to perform measurements in a wide temper-

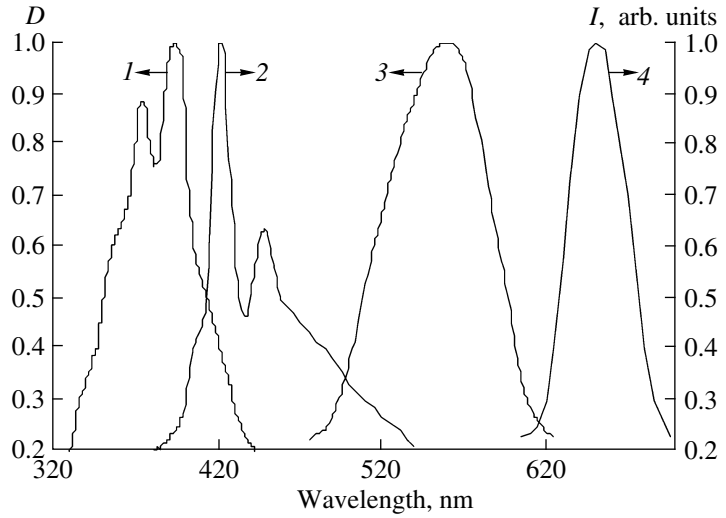

Fig. 1. (*1–3*) Absorption and (*2–4*) fluorescence spectra of LB films of (*1–3*) anthracene and (*2–4*) Nile red.

ature range. Photoexcitation was performed with radiation of a nitrogen laser (with the radiation wavelength $\lambda = 337.2$ nm, the pulse energy $E = 3$ mJ, and the pulse duration $\tau = 10$ ns). To eliminate the signal of conventional fluorescence, the system with a rotating mechanical seal was used, which closed the slit of a registration monochromator at the moment of action of a laser pulse. The time of beginning the measurement after arrival of the laser pulse was 1 μs. To obtain signals at a satisfactory level, no less than 2000 acquisitions were performed. The control over the apparatus and the collection and subsequent analysis of the signals were performed by a computer.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and fluorescence spectra of LB films of anthracene and Nile red on a quartz substrate. The spectral and luminescent properties of LB films of aromatic molecules were studied in the works [14, 15], and those of Nile red in the works [11, 16]. The absorption and fluorescence spectra of LB films of anthracene and Nile red overlap very slightly, which excludes the possibility of singlet–singlet energy transfer from anthracene to Nile red molecules. The fluorescence spectra do not overlap, which permits their separate identification.

Upon pulse excitation of the sample with nitrogen laser radiation ($\lambda = 337.2$ nm), triplet excitons will be generated in the molecular layer of anthracene. The migrating excitons can reach the surface of the film and encounter with a molecule of Nile Red embedded in the structure of the LB film. As the result of the T–T energy transfer reaction

$$T_1^D + S_0^A \longrightarrow S_0^D + T_1^A, \quad (1)$$

triplet molecules of the dye will be formed in the LB film.

Figure 2 shows the spectra of delayed luminescence of the anthracene–Nile red heterostructure. The excitation was performed at the energy donor absorption band . To preclude the processes of quenching by uncontrollable impurities and defects, the spectra were measured at a sample temperature of $T = 90$ K.

The spectrum consists of the band of delayed annihilation fluorescence (DAF) of the anthracene monomers ($\lambda_{max} = 420$ nm) and excimers ($\lambda_{max} = 500$ and 530 nm) [14] and the emission band with $\lambda_{max} = 650$ nm, which coincides in its spectrum with the fluorescence band of Nile red [16]. An increase in the acceptor concentration (c_A) in the monolayer leads to quenching of energy donor emission.

Figure 3 shows the decay curves of anthracene emission at different Nile red concentrations in the LB film. It can be seen that an increase in the number of anthracene molecules in the monolayer decreases the emission lifetime of the energy donor. The emission lifetime (τ) calculated from the exponential portion of the kinetics varies from 2.3 to 1.3 ms upon changing the concentration of Nile red from 10 to 50 mol %.

It was shown that the DAF decay kinetics of LB films of aromatic molecules was described by a combination of the power and exponential functions [14, 15]. Figure 4 shows the initial portions of the kinetic curves of anthracene DAF upon changing the acceptor concentration from 10 to 50 mol %. The curves obtained are well described by the power function of the form $I_{DAF} \sim t^{-n}$. The exponent varies from 0.2 to 0.5 upon changing the acceptor concentration. The table presents the parameters describing the features of the decay kinetics of the energy donor upon changing the acceptor concentration.

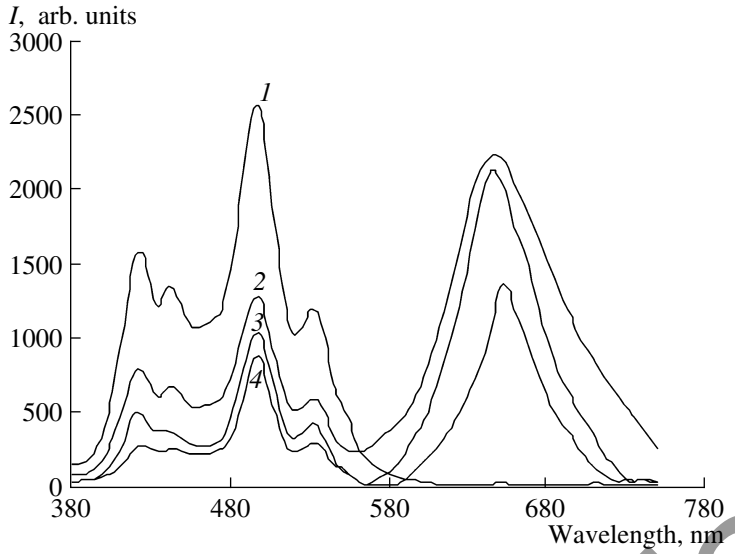

Fig. 2. Delayed emission spectra of anthracene–Nile Red LB films at different acceptor concentrations: (*1*) 0, (*2*) 10, (*3*) 25, and (*4*) 50 mol %.

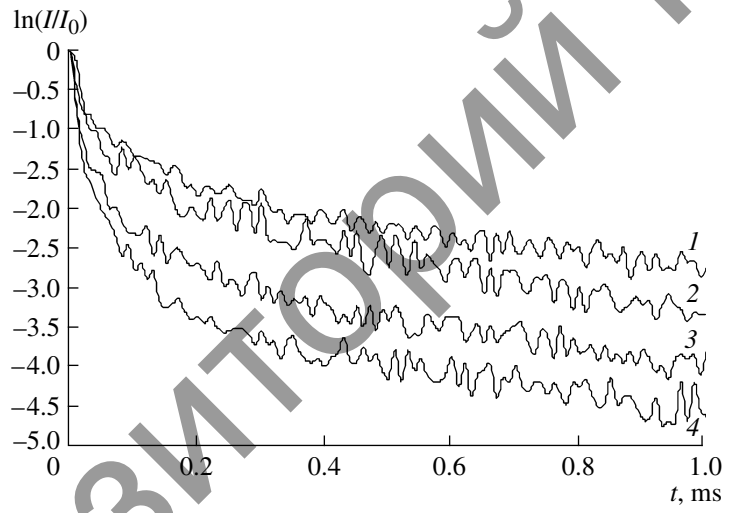

Fig. 3. Decay kinetics of anthracene DAF at different Nile Red concentrations: (*1*) 0, (*2*) 10, (*3*) 25, and (*4*) 50 mol %.

As noted above, intersystem crossing from the excited singlet state (S_1) to the triplet state (T_1) is forbidden in Nile red. Upon direct photoexcitation of LB films of the dye at the long-wavelength absorption band with radiation of the second harmonic of a neodymium laser (λ_{gen} = 532 nm), population of the triplet state did not take place, as demonstrated by the lack of any delayed emission in the green and red spectral regions. Hence, the appearance of emission whose spectrum coincides with the spectrum of fluorescence of the dye points to population of the triplet levels of Nile red as the result of nonradiative T–T energy transfer from anthracene molecules to Nile red molecules.

Since the probability of $S_1 \longrightarrow T_1$ intersystem crossing is low for the dye studied, thermostimulated delayed fluorescence is practically not observed in the absence of external heavy atoms. The low temperature of the films (T = 90 K) has also a negative effect on the population of vibrational sublevels of the triplet state.

Parameters describing the features of the decay kinetics of the energy donor upon changing the concentration of Nile red

Donor	c_A, mol %	τ, ms	n
Anthracene	0	2.3	0.2
	10	2	0.3
	25	1.5	0.4
	50	1.3	0.5

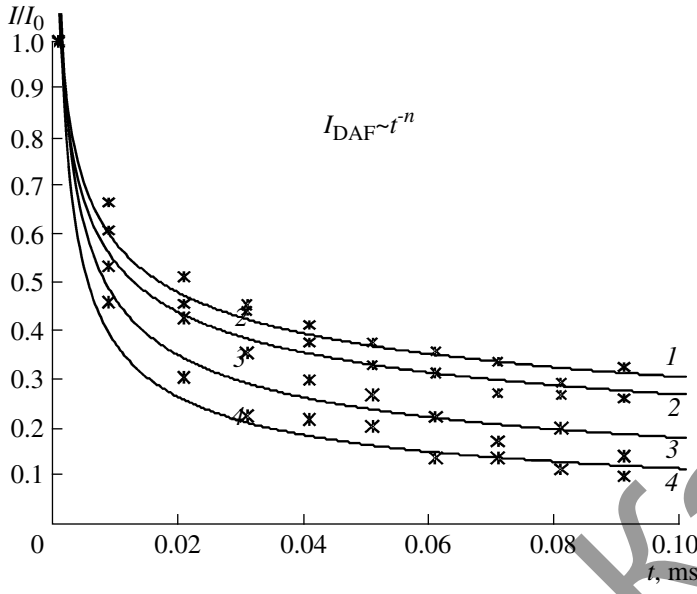

Fig. 4. Initial portions of the decay kinetics of anthracene DAF at different acceptor concentrations: (*1*) 0, (*2*) 10, (*3*) 25, and (*4*) 50 mol %.

Since the spectrum of sensitized luminescence observed coincides with the band of fluorescence of the dye, this emission should be assigned to DAF of Nile red.

DAF can be observed both at the expense of annihilation of triplet excitons of the acceptor (2) and upon heteroannihilation of triplet excitons of anthracene and Nile red (3):

$$T_1^A + T_1^A \longrightarrow S_1^A + S_0^A \longrightarrow 2S_0^A + h\nu_{DAF}, \quad (2)$$

$$T_1^D + T_1^A \longrightarrow S_1^A + S_0^D \longrightarrow S_0^A + S_0^D + h\nu_{DAF}. \quad (3)$$

In the case of the triplet pairs composed of molecules of anthracene-like aromatic hydrocarbons and dyes, as a rule, emission of dye molecules is observed [17, 18]. Therefore, it is difficult to decide unambiguously, which reaction, (2) or (3), is dominating in this case. In general, simultaneous occurrence of both reactions is possible.

To study experimentally the effect of the distance factor on the T–T transfer efficiency, the influence of the distance between the layers of the donor and the acceptor on the quenching efficiency of triplet energy donor emission was studied. The distance between the donor and acceptor layers was varied by changing the number of PA monolayers. The direct contact between the energy donor and acceptor through holes in the layer separating the donor and the acceptor is insignificant, because the holes constitute a negligible portion of the surface. Figure 5 shows the change in the anthracene DAF intensity upon changing the distance between the energy donor and acceptor. As can be seen from the figure, the strongest quenching of the triplet states of the donor is observed at the direct contact of the donor layer with the layer of acceptor molecules. Growing the number of PA monolayers between the donor and the acceptor decreases the energy transfer efficiency. At the distance $R \approx 70$–80 Å the DAF intensity of the donor is completely restored to the initial value.

The dependence obtained shows that quenching of the donor triplets occurs at distances much longer than the action radii of exchange interactions [1]. One of possible explanations for the results obtained may be occurrence of the energy transfer by the inductive-resonance mechanism [19]. We may not completely exclude also the additional quenching of delayed fluorescence of donor molecules at the expense of long-range energy transfer over the singlet levels [20]. For more complete interpretation of the phenomena observed, additional studies are necessary.

CONCLUSIONS

The experimental data obtained indicate the occurrence of interlayer T–T energy transfer from anthracene molecules to Nile red molecules, which are located in different layers of the LB film. The observed sensitized delayed luminescence of the acceptor appears as the result of annihilation of triplet excitations of the dyes. The dependence of donor luminescence quenching on the distance between the donor and acceptor layers shows that the energy transfer occurs at distances much

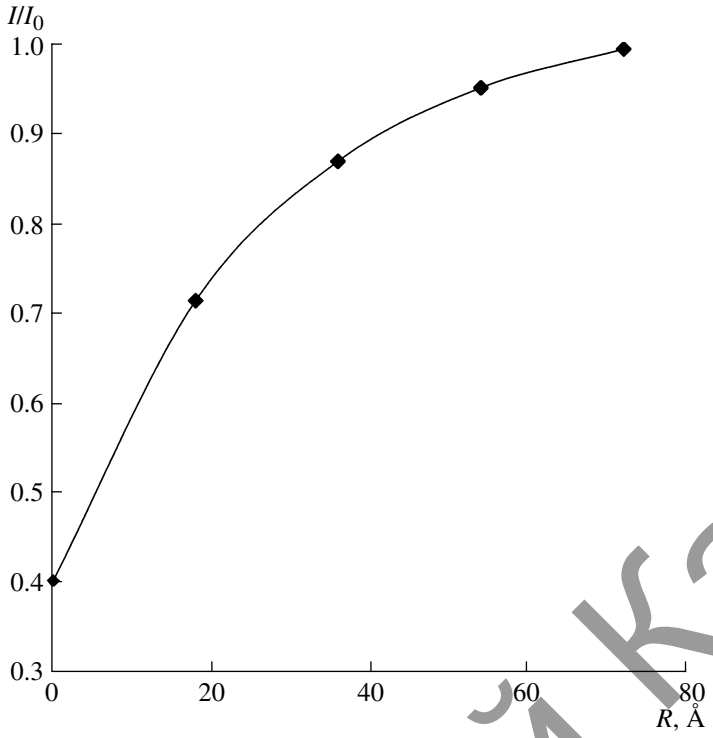

Fig. 5. Dependence of the anthracene DAF intensity upon changing the distance between the energy donor and acceptor.

longer than those followed from the exchange-resonance nature of T–T energy transfer.

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