

ANTHRACENE-SENSITIZED LONG-DELAYED RHODAMINE C FLUORESCENCE OF THE LANGMUIR–BLODGETT FILMS

N. Kh. Ibrayev

UDC 535.37

Results of investigation into the triplet-triplet energy transfer from a vacuum-deposited anthracene film to the Langmuir–Blodgett rhodamine dye film are presented. It is demonstrated that the observed long-delayed sensitized dye fluorescence is caused by annihilation of migrating triplet excitons.

The triplet-triplet energy transfer is one of the fundamental problems in condensed state physics that always attracts attention of researchers [1, 2]. From the exchange-resonant nature of the triplet-triplet energy transfer it follows that the efficiency of energy transfer must depend on the separation and mutual orientation of the energy donor and acceptor. A review of experimental studies of this problem was presented in [1].

In [3–5], a new theory of electronic excitation energy transfer was developed based on the quantum-chemical approach. According to this model, the orientational dependence of the energy transfer rate constant has a more complicated character than in the Ferster–Dexter theory.

To investigate experimentally the influence of the orientational and separation factors on the efficiency of intermolecular energy transfer, we took advantage of the Langmuir–Blodgett technology [6] which allowed donor-acceptor systems to be formed with predicted separation and mutual orientation of molecules. Such investigations were first performed by Kuhn *et al.* [7–9] for the singlet-singlet energy transfer.

Despite many publications devoted to the photoprocesses in the Langmuir–Blodgett (LB) films of organic molecules, in the scientific literature there are no studies devoted to the intermolecular energy transfer with allowance for the triplet states. The present work studies the interlayer energy transfer in a molecular glass – LB film system.

The anthracene molecules were chosen as triplet energy donors, and the heptadecyl ether rhodamine C molecules served as energy acceptors [10]. The choice of rhodamine C for the acceptor is caused by the fact that its quantum yield in the triplet state is close to zero [11], which excludes direct population of its triplet states.

The examined samples were prepared as follows. On the surface of the substrate made from nonluminescent quartz, an anthracene film was deposited in vacuum. Then a mixed rhodamine C and stearic acid LB film was deposited on the anthracene film. Doubly distilled deionized water was used. The surface water tension was 72.8 dyn/cm at pH = 5.6 and a temperature of 20°C. The dye and stearic acid were dissolved separately in chloroform, mixed in the required molar ratios, and the mixture was put on the water surface. Stearic acid was purified by means of recrystallization from an ethanol solution. Monolayers were deposited on the substrate using the Y-type transportation at a pressure of 28 dyn/cm for a plate immersion rate of 0.02 mm/s. The number of monolayers in the LB film was equal to 20.

Spectral and kinetic characteristics of samples were measured using an automated facility with registration in the photon counting regime [12]. The samples were put into an evacuated optical cryostat to perform investigations in a wide temperature interval. Nitrogen-laser radiation (with radiation wavelength $\lambda = 337.2$ nm, energy per pulse $E = 3$ mJ, and pulse duration $\tau = 10$ ns) was used for photoexcitation. A system of electronic photomultiplier triggering was used to eliminate a conventional fluorescence signal. Measurements started 10 μ s after the laser pulse arrival. No less than 5,000 signals were accumulated to obtain satisfactory signal levels. Operation of the facility, signal

E. A. Buketov Karaganda State University, Karaganda, Kazakhstan, e-mail: nIbrayev@kargu.krg.kz. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 7, pp. 60–63, July, 2008. Original article submitted September 11, 2007.

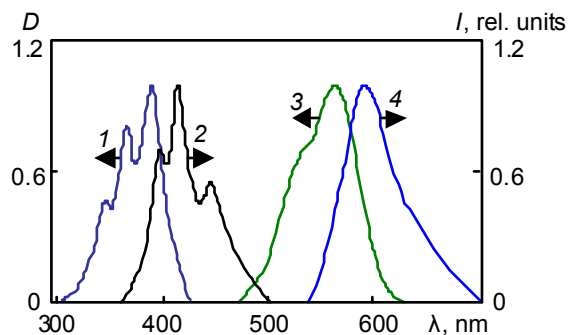


Fig. 1. Absorption (curves 1 and 3) and fluorescence spectra (curves 2 and 4) of anthracene (curves 1 and 2) and rhodamine C films (curve 3 and 4) on the quartz substrate.

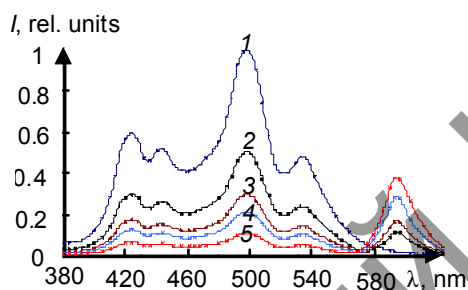


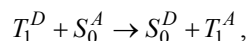
Fig. 2. Long luminescence spectrum of the anthracene–rhodamine C heterostructure for acceptor concentrations of 0 (curve 1), 10 (curve 2), 25 (curve 3), 50 (curve 4), and 75 mol% (curve 5).

accumulation, and subsequent signal processing were controlled by a computer.

Figure 1 shows the absorption and fluorescence spectra of anthracene and LB heptadecyl ether rhodamine C films on the quartz substrate. In [10] it was demonstrated that the attachment of long alkyl groups does not change the position and maximum of the absorption and fluorescence spectra of initial luminophores.

From Fig. 1 it can be seen that the anthracene fluorescence and absorption rhodamine C spectra overlap only slightly, which excludes effective singlet-singlet energy transfer from anthracene to rhodamine C. The fluorescence spectra are not overlapped, which allows us to identify them separately.

In the sample excited by nitrogen-laser radiation ($\lambda = 337.2$ nm), triplet excitons are generated in the deposited anthracene layer. Migrating excitons can reach the film surface and collide with the rhodamine C molecule incorporated in the LB-film structure. As a result of the energy transfer reaction



the triplet rhodamine C molecules will be formed in the LB film.

Figure 2 shows the spectra of long luminescence of the anthracene–rhodamine C heterostructure. Excitation was performed, as indicated above, into the absorption band of the energy donor. The spectra were registered 50 μ s after the beginning of excitation. To exclude the processes of luminescence quenching by uncontrollable impurities and defects, the spectra were measured at the sample temperature $T = 90$ K.

The spectrum comprises long-delayed annihilation anthracene monomer ($\lambda_{\max} = 420$ nm) and excimer fluorescence bands ($\lambda_{\max} = 500$ and 530 nm) [13] and the luminescence band at $\lambda_{\max} = 595$ nm whose spectrum coincides

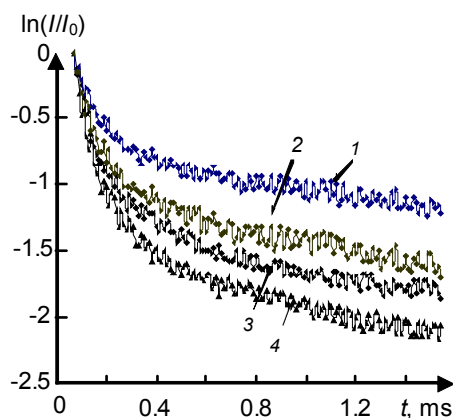


Fig. 3. Kinetics of donor luminescence quenching for rhodamine C concentrations of 10 (curve 1), 25 (curve 2), 50 (curve 3), and 75 mol% (curve 4).

with that of the rhodamine C fluorescence band. An increase in the dye concentration in the monolayer leads to quenching of the energy donor luminescence and build-up of the long-wavelength band.

Figure 3 shows curves of anthracene luminescence quenching for the indicated rhodamine C concentrations. It can be seen that the increase in the number of acceptor molecules in the monolayer results in the decrease of the luminescence time of the energy donor.

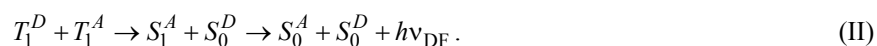
The luminescence time calculated from its exponential decay decreased from $\tau = 2.04$ ms to $\tau = 0.86$ ms when the rhodamine C concentration increased from 10 to 75 mol%.

The entire kinetics of rhodamine C luminescence quenching was nonexponential in character. The acceptor luminescence time depended on the dye concentration and was $\tau = 1.82$ ms for $C = 50$ mol% and $\tau = 0.68$ ms for $C = 75$ mol%.

As indicated above, the intercombination transition from the singlet excited S_1 state to the triplet T_1 state is forbidden. During direct photoexcitation of the LB rhodamine C films into the long-wavelength absorption band by the second harmonic of a neodymium laser ($\lambda = 532$ nm), the triplet state was not populated. This was testified by the absence of any long luminescence in the green and red ranges of the spectrum. Therefore, the occurrence of the luminescence with the spectrum coinciding with that of the fast dye fluorescence testifies to the occupation of rhodamine C triplet energy levels due to nonradiative triplet-triplet energy transfer from anthracene to rhodamine C.

Since the probability of the $S_1 \rightarrow T_1$ intercombination transition for rhodamine C dye is low, the long-delayed thermally stimulated fluorescence is virtually not observed without external heavy atoms [14]. The low film temperature ($T = 90$ K) also influences negatively the population of the vibrational sublevels of the triplet states. Since the spectrum of the observed sensitized luminescence coincides with that of the fast dye fluorescence band, the luminescence should be interpreted as the long-delayed rhodamine C annihilation fluorescence.

The long-delayed annihilation fluorescence can be due to annihilation of triplet acceptor excitons (I) and heteroannihilation of anthracene and rhodamine C triplet excitons (II):



As a rule, for the triplet pairs formed by molecules of aromatic hydrocarbons of anthracene type and dyes, the luminescence of dye molecules is observed [15, 16]. Therefore, it is difficult to determine unambiguously which reaction – (I) or (II) – is dominant in this case. In principle, both reactions can occur simultaneously.

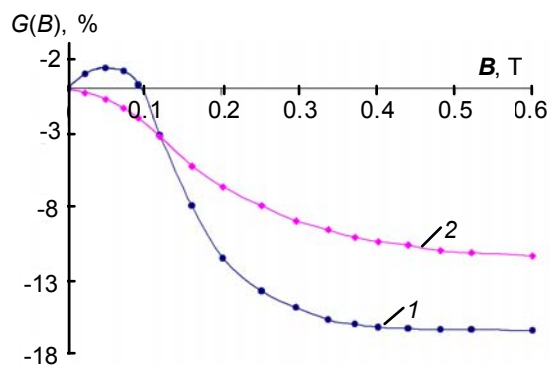


Fig. 4. Influence of the magnetic field on the long-delayed fluorescence intensity of anthracene (curve 1) and rhodamine C (curve 2).

To elucidate this question, the effect of the external magnetic field on the triplet-triplet annihilation should be considered. In [17, 18] it was demonstrated that the magnetic effect caused by the heterogenic annihilation of the triplet excitation was stronger than that caused by the annihilation of the triplet molecules of the same compound.

Figure 4 illustrates our experimental data on the influence of the external magnetic field on the properties of the long luminescence of the energy donor and acceptor. The magnetic effect magnitude was estimated from the relative changes of the long-delayed fluorescence intensity.

The dependence for anthracene was similar to that for vitreous chrysene films [19]. The limiting magnitude of the negative magnetic effect was 16.3% at 0.5 T. The magnetic field influenced to a lesser degree the sensitized dye luminescence intensity. The maximum magnitude of the magnetic effect for rhodamine C was 11.3%.

The influence of the external magnetic field on the long-delayed sensitized rhodamine C fluorescence intensity testifies to the fact that this luminescence is due to annihilation of triplet excitons. A lower magnitude of the magnetic effect in comparison with the field influence on the anthracene luminescence can be due to the dominant contribution of rhodamine C triplet self-annihilation.

Thus, the results obtained testify to the occurrence of the interlayer triplet-triplet energy transfer from anthracene to rhodamine C molecules in heterostructures of the deposited film (donor) – LB film (acceptor) type. The long sensitized luminescence of the triplet energy acceptor has the annihilation nature.

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