

MOLECULAR SPECTROSCOPY

Kinetics of Long-lived Luminescence of Eosin in Langmuir–Blodgett Films

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Abstract—The spectral and kinetic properties of photoluminescence of mixed Langmuir–Blodgett (LB) films of eosin decyl ether and palmitic acid on a solid substrate are studied. The electronic absorption and fluorescence spectra of the films are identical to the spectra of the dye in ethanol. An increase in the dye concentration in a monolayer results in the appearance of a dimer absorption band, quenching of fluorescence of monomers, and the red shift of the spectral bands. At 90 K, the distinct phosphorescence and delayed fluorescence bands of LB films were observed. The decay kinetics of phosphorescence and delayed fluorescence is nonexponential. It is shown that the decay curve of delayed fluorescence is determined by triplet–triplet annihilation (TTA) and $T_1 \rightarrow S_1$ triplet–singlet intersystem crossing (IS). The initial nonexponential phosphorescence decay is caused by the dominant contribution of TTA to the decay of triplet molecules. The experimental data are interpreted based on the mechanisms of exchange–resonance and inductive–resonance annihilation. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Photophysical processes involving excited singlet states of dye molecules in Langmuir–Blodgett (LB) films have been studied in many papers (see review [1]). Most of the earlier studies, in which general problems of producing mono- and multilayers were analyzed and the spectral and luminescence properties of monomers and aggregates of luminophores in LB films were studied, were performed with cyanine dyes and azo dyes [2, 3]. Migration of the excitation energy over identical emission centers in LB films of rhodamine dyes was studied in detail in papers [4–8]. The application of the LB technology for fabrication of molecular systems of the specified structure for studying the Förster energy transfer was demonstrated in papers [9–11]. At the same time, the relaxation of the triplet states of dye molecules in LB films is poorly known. The study of this relaxation is of interest because the specific structure of LB films (close packing of particles and fixed mutual orientation of molecules) can affect in a certain way the efficiency of the intra- and intermolecular energy relaxation channels.

In this paper, we present the results of the study of relaxation of the triplet states of eosin decyl ether (EDE) molecules in LB films.

EXPERIMENTAL

Multimolecular films were fabricated on nonluminescent quartz substrates using a Langmuir–Blodgett setup. Twice-distilled deionized water was used.

The surface tension of water was 72.8 dyn/cm at pH = 5.6 and $T = 293$ K. The subphase was deposited on the surface using solutions of the dye and palmitic acid (PA) in chloroform. The luminophore and fatty acid were mixed in different molar ratios EDE:PA. The limiting value of the landing area for a dye molecule found from the π -A isotherms was $A = 50 \pm 5 \text{ \AA}^2$. This corresponds to the perpendicular arrangement of the plane of the chromophore part of the dye molecule with respect to the substrate plane. The conditions of fabrication of molecular eosin films on a solid substrate are described in more detail in [12].

The spectra and decay of the long-lived luminescence of LB films were measured with a photon-counting setup [13]. To obtain signals of the appropriate level, no less than 5000 signal accumulations were performed. The luminescence was excited by a pulsed neodymium laser at 532 nm. The pulse energy and duration were 3 mJ and 20 ns.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of samples with different molar EDE:PA ratios are shown in Fig. 1. The shape of the spectra and their position virtually coincide with those for solutions of eosin in ethanol. The absorption spectra of LB films exhibit a shoulder at 510 nm. The optical density of the absorption band of dimers increases compared to that of the monomer band with increasing concentration of the dye in the film.

The fluorescence of LB films of EDE is mainly determined by monomer molecules, whereas dimers do

not exhibit noticeable fluorescence. The most intense monomer fluorescence was observed for a sample with the EDE:PA ratio equal to 1 : 100. A further increase in the dye concentration in a monolayer resulted in fluorescence quenching. As the dye concentration was increased, the fluorescence band shifted to the red from 565 nm for the EDE : PA ratio equal to 1 : 100 to 585 nm for this ratio equal to 1 : 1. The fluorescence band also exhibited the red shift with increasing temperature from 293 to 90 K. The red shift of the fluorescence band is probably caused by migration of excitons over the inhomogeneously broadened S_1 levels of EDE, as in the case of LB films of rhodamine dyes [8].

The spectrum of long-lived luminescence of the films consists of the 570-nm delayed fluorescence band and the 700-nm phosphorescence band. The delayed fluorescence band coincides with the fluorescence band of the films, while the 700-nm band is similar to the phosphorescence band of eosin in ethanol. The integrated intensity of both bands increased with decreasing temperature from 293 to 90 K.

The total decay curve of delayed fluorescence and phosphorescence of the films is nonexponential. Analysis of the decay showed that at the initial stage after excitation ($t < 0.1$ ms), the decay curves are well described by a power dependence of the type $I_{PH} \sim t^{-n}$, while at $t > 0.5$ ms, the decay was exponential.

The table presents the exponents n of the power function describing the initial decay stage and the decay rates of delayed fluorescence (k_{DF}) and phosphorescence (k_{PH}) calculated from the exponential part of the decay curve. These data show that the triplet-state lifetime decreases with the increasing number of dye molecules in a monolayer. At the same time, the exponent of the power function describing the initial decay stage increases with the dye concentration.

The properties of the lower triplet state of eosin were studied in detail by Parker et al. [14]. It was found that the deactivation of the triplet state results in phosphorescence and delayed fluorescence, which is caused by the thermally induced back intersystem crossing from the T_1 state to the S_1 state. It was shown later that along with the thermally induced delayed fluorescence,

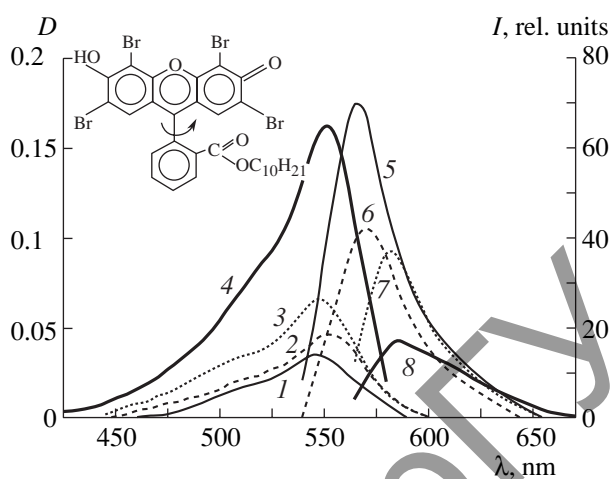


Fig. 1. Absorption (1–4) and fluorescence (5–8) spectra of LB films of EDE for different EDE : PA ratios: (1, 5) 1 : 100; (2, 6) 1 : 50; (3, 7) 1 : 10; (4, 8) 1 : 1. The fluorescence spectra are not corrected for the spectral sensitivity of the setup.

the delayed annihilation fluorescence of eosin could be observed under certain conditions in liquid or solid solutions [15, 16].

Therefore, the exponential decay of delayed fluorescence observed at large times ($t > 0.5$ ms) at low temperatures with the decay rate equal to the decay rate of phosphorescence demonstrates the existence of $T_1 \rightarrow S_1$ intersystem crossing. The initial part of the delayed fluorescence decay described by the power dependence is caused by triplet-triplet annihilation (TTA) in LB films. A similar form of the initial part of the phosphorescence decay curve suggests that TTA makes a dominant contribution to the deactivation of triplet eosin molecules at the initial stage after excitation. The increase in the exponent with increasing dye concentration shows that the role of pair annihilation in the decay of triplet states increases. The increase in the singlet-triplet splitting caused by the inhomogeneous broadening of the S_1 and T_1 levels probably favors the $T_1 \rightarrow S_1$ process at 90 K.

Values of the exponent n and the decay rate constants of phosphorescence (k_{PH}) and delayed fluorescence (k_{DF}) at different concentrations of the dye in the LB film

The ratio of dye and PA molecules	$I \sim t^{-n}$		$k \times 10^{-3}, s^{-1}$	
	$T = 90$ K		$T = 90$ K	
	n_{DF}	n_{PH}	k_{DF}	k_{PH}
1 : 100	0.54	0.40	0.33	0.23
1 : 50	0.58	0.49	0.32	0.35
1 : 10	0.84	0.80	0.36	0.40
1 : 1	0.87	0.82	0.61	0.68

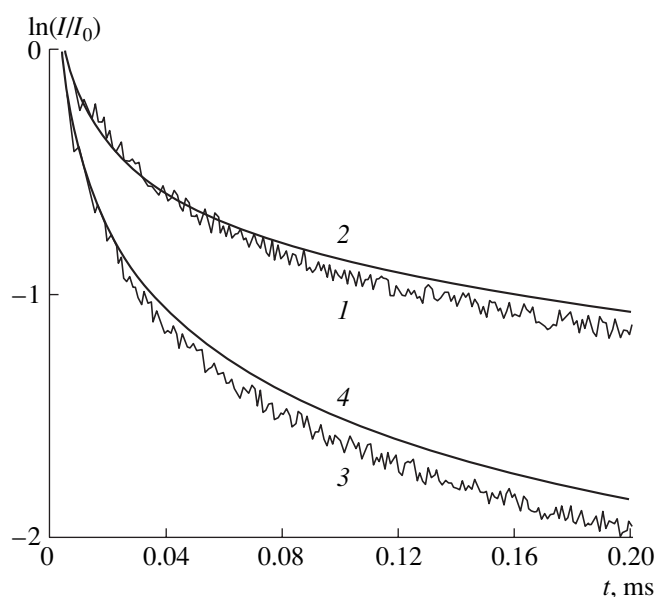


Fig. 2. Comparison of the experimental decay curves of delayed fluorescence of LB films of EDE with theoretical curves calculated using models [18] and [19] (see explanations in the text).

The annihilation of triplet molecules of dyes of the eosin type in solid solutions was studied in papers [17–20]. The model of static TTA [17, 18] explain the non-exponential decay of delayed fluorescence by the time dependence of the TTA rate constant. In papers [19, 20], the inductive-resonance mechanism of delayed annihilation fluorescence was considered.

Consider our results obtained for LB films of eosin using these models. We will compare with the theory only the initial nonexponential parts of decay curves, because at $t > 0.5$ ms the delayed annihilation fluorescence is strongly distorted by monomolecular thermally induced delayed fluorescence.

One can see from Fig. 2 that films with low dye concentration (1 : 100) demonstrate good agreement of the delayed fluorescence decay (curve 1) with the theoretical decay (curve 2) predicted by the inductive-resonance model of TTA [19]. The initial concentration of triplets $N_{0T} \approx 10^{13} \text{ cm}^{-3}$ used for the calculation of curve 2 was estimated from the laser pulse energy, the absorption coefficient of the film (1 : 100) at 532 nm, and the triplet-state quantum yield ϕ_T for eosin. The quantum yield of the eosin fluorescence $\phi_f = 0.45$ and $\phi_T = 0.50$ were taken from [14]. The critical radius R_0 of energy transfer and the triplet-state lifetime τ were measured to 50 Å and 4.3 ms, respectively.

At high concentrations of triplet molecules, the exchange-resonance static model of TTA better describes the experimental data (curves 3, 4) [17, 18]. Curve 4 was calculated, according to [18], using the

TTA parameters $U_0 = 8 \times 10^5 \text{ s}^{-1}$ and $L = 1.7 \text{ Å}$. The initial concentration of triplets (for the 1 : 1 LB film), the distance of the minimum approach of molecules, and the triplet-state lifetime were taken to be $N_{0T} \approx 10^{14} \text{ cm}^{-3}$, $r = 4 \text{ Å}$, and $\tau = 3 \text{ ms}$. The distance between molecules $r = 4 \text{ Å}$ was calculated assuming that the phenyl ring is located in the upper part of the chromophore (inset in Fig. 1). This takes place for the most close packing of molecules in a monolayer at high dye concentration.

The results obtained by us suggest that both the inductive-resonance and exchange-resonance TTA mechanisms take place in LB films. At low concentrations of dye molecules in a monolayer, when lumino-phore molecules are separated by a great number of fatty acid molecules, it is unlikely that there exists a great amount of triplet pairs with the distance between the particles required for the exchange interaction ($R \approx 10 \text{ Å}$). Therefore, the TTA decay is mainly determined by the inductive-resonance mechanism. As the concentration of dye molecules in a monolayer increases, the distance between the molecules decreases, and in the case of the most close packing this distance can be as small as 4 Å. In this case, the annihilation determining the delayed fluorescence decay is governed by the short-range exchange interaction.

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