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Exciton migration in pseudoisocyanine J-aggregates formed in polymer films

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Exciton transport efficiency in pseudoisocyanine (PIC) J-aggregates formed in PVA thin film has been studied using an exciton trap. As a trap, anionic cyanine dye DiD–C3S has been used. Luminescence spectra have been obtained using luminescence microscope that allows us to collect the spectra from very small areas within the film. Heterogeneous dye distribution has been found. Using Stern-Volmer equation for the J-aggregate luminescence quenching by the trap, it has been found that 50 % J-aggregate luminescence is quenched at the ratio PIC/DiD–C3S = 30:1. The obtained value is very small and points to the exciton migration over rather small distances.

Изучена эффективность экситонного транспорта в J-агрегатах псевдоизоцианина (PIC), сформированных в тонких пленках ПВС, при помощи экситонной ловушки. В качестве ловушки использован анионный цианиновый краситель DiD–C3S. Спектры люминесценции получены при помощи люминесцентного микроскопа, что позволило собирать спектры с очень маленьких участков пленки. Обнаружено неоднородное распределение красителей в пленке. Используя уравнение Штерна-Фольмера для тушения люминесценции J-агрегатов ловушкой, показано, что 50 % люминесценции J-агрегатов тушится в соотношении PIC/DiD–C3S = 30:1. Полученное значение очень мало и указывает на миграцию экситонов на малые расстояния.

1. Introduction

Luminescent molecular aggregates (so-called J-aggregates) take a special position among organic materials, due to very narrow absorption band, near resonant luminescence, giant oscillator strength, giant optical nonlinearities, high sensitivity of spectral properties to the microenvironment [1–4]. These features are caused by delocalization of the excitation over a molecular chain and Frenkel excitons appearing [1–4]. One of the fundamental questions in J-aggregates photophysics is exciton migration efficiency. There is a significant contradiction in the efficiency of exciton energy migration reported by different authors. According to some data the exciton migrates in J-aggregates over up to several hundred molecules [5–8], while other authors report the exciton motion over 10^4 molecules at room temperatures [9, 10]. Recently, using exciton traps we have shown the efficient exciton migration in J-aggregates of amphiphilic pseudoisocyanine (amphi-PIC) dye [7, 8]. However, to clear up the exciton migration features in J-aggregates it is important to deal with objects which are commonly known. Probably, the best candidates for this are J-aggregates of pseudoisocyanine (PIC) dye, which are the most investigated ones [1–4].

Even for PIC J-aggregates different data concerning its exciton migration efficiency could be found. For example, D.Mobius reported that 50 % PIC J-aggregate luminescence was quenched by eosin at the ratio of 1 eosin molecules per 2600 PIC molecules [1]. However, all our attempts to reproduce such results were unsuccessful: we haven't found conditions for PIC J-aggregate luminescence quenching by eosin in solutions.

Another estimation of exciton migration efficiency in PIC J-aggregates could be found in [11]. Authors studied PIC J-aggregates dispersed in thin polymer film using the NSOM technique. Analyzing single J-aggregate photobleaching behavior, they stated that upper limit of exciton migration is 50 nm [11]. To compare these two results, we could assume the PIC J-aggregates to be linear chains, which are composed of PIC dimers spaced 0.4 nm apart [12]. So, the upper limit for the exciton migration distance according to data [1] is 520 nm that is 10 times larger than that according to data [11].

Thus, the aim of present paper is to provide novel experimental results concerning the exciton transport in J-aggregates of PIC (Fig. 1a). For this purpose PIC J-aggregates has been formed in thin polymer film (polyvinyl alcohol, PVA) and another cyanine dye DiD–C3S (Fig. 1b) has been used as an exciton trap.

2. Experimental

Pseudoisocyanine (1,1′-diethyl-2,2′-cyanine iodide, PIC) dye was purchased from Sigma Aldrich (USA) and used as-received. DiD–C3S (1,1′-di(3-sulfopropyl)-3,3,3′,3′-tetramethylindodicarbocyanine sodium salt) dye was synthesized by Dr.I.A.Borovoy (Institute for Scintillation Materials NAS of Ukraine) with purity controlled by NMR and thin layer chromatography. PIC was dissolved at PVA water solution (2 mass.%) at the concentration of 10^{-2} mol/l. Thereupon DiD–C3S was added to the solution at required concentrations. To produce the thin polymer films the dye solution was heated to 70°C and drop of it was spin-coated onto a glass microscope slip cover at 2000 rpm. According to [11], using such a procedure the films of about 30 nm thickness could be obtained.

For spin-coating, lab centrifuge SM-12 (Russia) with home-made adapter for glass plates was used. Absorption spectra was registered using a microspectrometer USB4000 (OceanOptics, USA) supplied with an incandescent lamp. Luminescent images and spectra were obtained using luminescence microscope MIKMED-2 var.11 (LOMO, Russia) equipped with 5 Mpixels microscope digital camera DCM510 (Oplenic Optronics, China) and fiber-optic adapter for microspectrometer USB4000. Luminescence was excited at 450–480 nm and collected in the 520–700 nm spectral range. The equipment used allows collecting luminescent

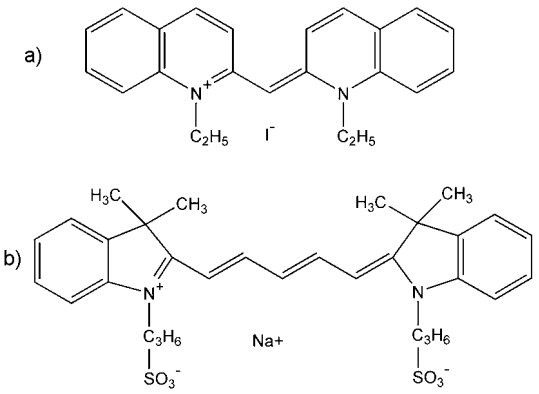

Fig. 1. Structural formulas of the dyes investigated: (a) PIC, (b) DiD–C3S.

spectra from the spots with a diameter less than 50 μm. Luminescence excitation spectra were recorded using a spectrofluorimeter on the base of two grating monochromators MDR-23 and a xenon lamp. One of the monochromators was used to select a required wavelength (FWHM ~ 0.5 nm), the other one was used for the luminescence collection.

3. Results and discussion

First of all, it was necessary to prove the PIC J-aggregates formation in PVA films. Indeed, in the work [11] the J-aggregates of cationic PIC was formed in the films of anionic poly(viny sulfate) (PVS) polyelectrolyte and electrostatic interactions were suggested to be one of the main factor of the dye aggregation. PVA is a neutral polymer and could not promote the aggregation. On the other hand, due to a very small amount of PVA in the solution (only 2 mass.%), enhanced concentration of the dye during the film formation takes place that is the key factor for the dye aggregation.

Luminescent image (Fig. 2) of PVA film with the dispersed PIC dye reveals a number of long thin fibers similar to PIC J-aggregate fibers, which are usually observed [11, 12]. In the luminescence spectrum of the film, a narrow band with the maximum at $\lambda = 583.2$ nm is clearly seen (Fig. 3a, solid line). At the same time, the absorption spectrum demonstrates a very narrow band (J-band) centered at $\lambda = 581.1$ nm, which is red-shifted as compared to the PIC monomer band ($\lambda_{max} = 525$ nm) (Fig. 3b, solid line). Thus, we could conclude the successful PIC J-aggregates formation in PVA film by spin-coating.

The next step is to check whether DiD–C3S dye can be an exciton trap for PIC

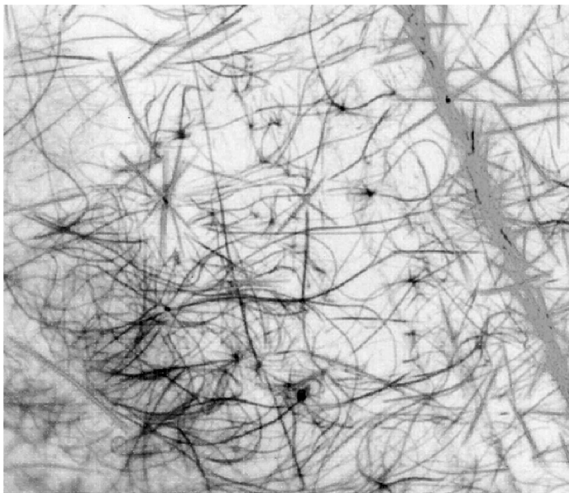

Fig. 2. Luminescence image of PIC J-aggregates spread within PVA film.

J-aggregates. There are several reasons to expect such results. First, DiD–C3S has the same chromophoric part as DiD dye, which was used as efficient exciton trap for J-aggregates of amphiphilic analogue of PIC-amphi-PIC dye. Second, DiD–C3S is an anionic dye and should efficiently interact with PIC dye due to Coulombic attraction. And third, due to strong concentration during the film formation, PIC and DiD–C3S have to come close together. Indeed, luminescence spectrum of the PIC J-aggregates with DiD–C3S in the PVA film at the ratio PIC/DiD–C3S = 50:1 reveals intense sensitized DiD–C3S band (λ_{max} = 680 nm) and PIC J-aggregates band quenching (Fig. 3a, dashed line). Note, we suggest that the dyes embedding into the film is proportional to it concentration in the solution. The luminescence excitation spectrum of DiD–C3S (λ_{reg} = 685 nm) reveals an intense band corresponding to PIC J-band (Fig. 3b, dashed line) that confirms energy transfer from PIC J-aggregates to DiD–C3S dye. Thus, DiD–C3S dye is indeed an exciton trap for PIC J-aggregates.

One of the ways to estimate the efficiency of the exciton migration, the J-aggregate luminescence quenching by the exciton trap could be analyzed using the well-known Stern-Volmer equation [13]:

$$F_0/F = 1 + K_{SV}[Q], \quad (1)$$

where F_0 and F are the J-aggregate luminescence intensities in the absence and presence of the trap, respectively, $[Q]$ is the quencher concentration and K_{SV} is the Stern-Volmer constant. The value $1/K_{SV}$

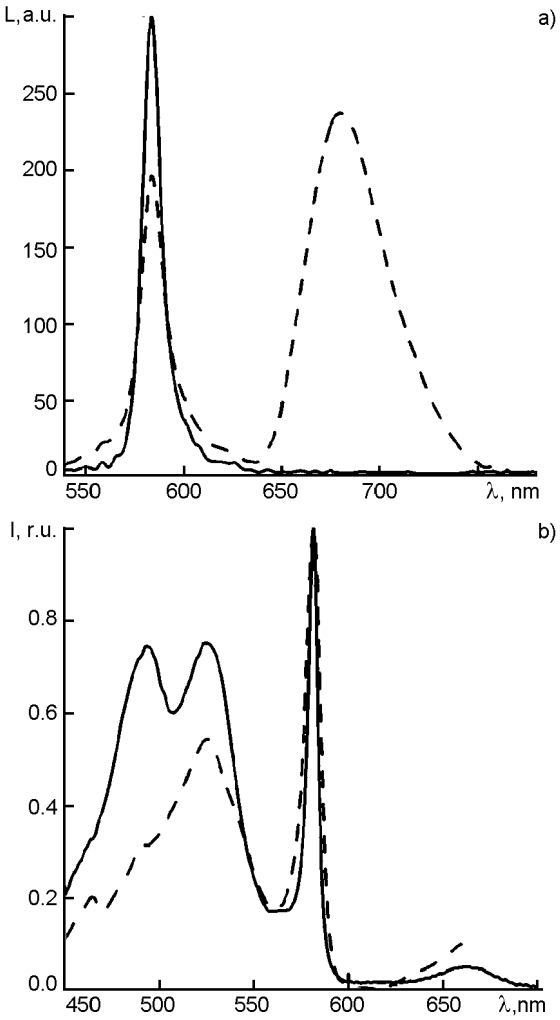

Fig. 3. a) Luminescence spectra of pure PIC J-aggregates (solid line) and PIC J-aggregates in presence of DiD–C3S at the ratio PIC/DiD–C3S = 50:1 (dashed line) in PVA film; b) Absorption (solid line) and DiD–C3S luminescence excitation (λ_{reg} = 685 nm, dashed line) spectra of PVA film containing PIC J-aggregates in presence of DiD–C3S at the ratio PIC/DiD–C3S = 50:1.

gives us the concentration of the trap that quenches 50 % of the J-aggregate luminescence.

However, collecting luminescence spectra from different areas within the films, the heterogeneous distribution of DiD–C3S dye have been found that appears as different ratios between the J-aggregates and traps luminescence bands (Fig. 4). Such a heterogeneous distribution was smaller at low DiD–C3S concentration and larger at high DiD–C3S concentration (like that, shown on Fig. 4). So, further we will take deal with estimation of exciton migration rather that

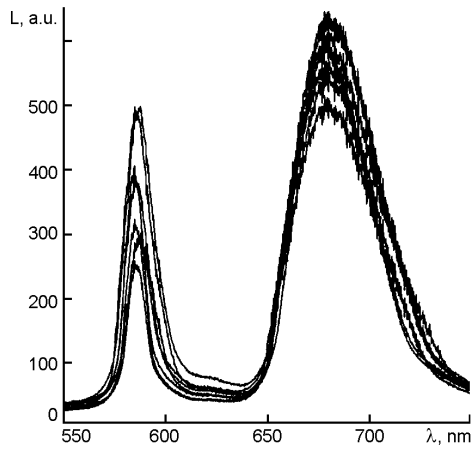

Fig. 4. Luminescence spectra of PVA film containing PIC J-aggregates in the presence of DiD–C3S (PIC/DiD–C3S = 50:1) from different areas of the film.

with strict quantitative analysis. For each film, luminescence spectra were recorded at least at 10 different areas and averaged. Such a procedure was carried out for the film contained different ratio PIC/DiD–C3S. As a result a family of luminescence spectra required for Stern-Volmer analysis has been obtained (Fig. 5a). The increase of the trap concentration leads to the redistribution of the J-aggregate and trap luminescence band intensities. The most efficient exciton energy transfer is achieved at the ratio PIC/DiD–C3S = 20:1. As one could see, at higher DiD–C3S concentration (the ratio PIC/DiD–C3S = 10:1), both PIC J-aggregates and DiD–C3S luminescence intensities decrease and the DiD–C3S band is redshifted as compared to that at the ratio PIC/DiDC3S = 20:1 (Fig. 5a). That points to the DiD–C3S concentration quenching, i.e. it associates formation [14].

Stern-Volmer plot appeared to be straight line (Fig. 5b). Note, that for amphi-PIC J-aggregates Stern-Volmer plot was not straight due to excitons not accessible to the quencher existing [7, 8]. So, it has been found that 50 % of the PIC J-aggregates luminescence is quenched at PIC/DiD–C3S = 30:1 (critical concentration). This value is much less as compared with amphi-PIC J-aggregates case (amphi-PIC/trap = 120:1) [8]. If we refer the result obtained to those reported in [1, 11] it could be postulated that it coincides with the exciton migration determined in [11], but not in [1]. So it could be stated that excitons in

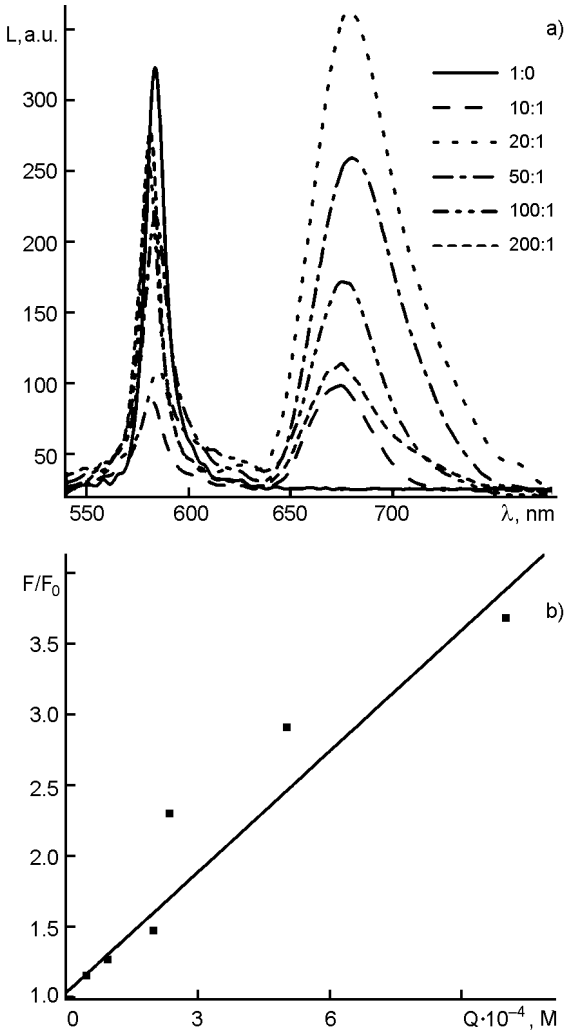

Fig. 5. a) Averaged luminescence spectra of the PIC J-aggregates with the DiD–C3S trap at different PIC/DiD–C3S ratios; b) Stern-Volmer plot of the J-aggregate luminescence quenching by the trap.

J-aggregates migrates over hundreds of molecules, but not over thousands ones.

4. Conlusions

PIC J-aggregates was successfully formed in thin PVA films by spin-coating. The DiD–C3S dye was used as the exciton trap for PIC J-aggregates. Spin-coating method of film preparation results in heterogeneous dye distribution in the films. The J-aggregates luminescence quenching analysis by Stern-Volmer equation yields the critical concentration equals to PIC/DiD–C3S = 30:1. It was concluded that excitons in J-aggregates migrates over hundreds of molecules but not over thousands ones.

References

1. D.Mobius, *Adv. Mater.*, **7**, 437 (1995).
2. J-Aggregates, ed. by T.Kobayashi, World Scientific Publishing, Singapore (1996).
3. B.I.Shapiro, *Russ. Chem. Rev.*, **75**, 433 (2006).
4. J.Knoester, V.M.Agranovich, Electronic Excitations in Organic Based Nanostructures. Thin Films and Nanostructures, ed. by V.M.Agranovich and G.F.Bassani, Elsevier, Amsterdam, Oxford (2003), v.31, p.1.
5. L.Lu, R.Helgeson, R.M.Jones et al., *J. Am. Chem. Soc.*, **124**, 483 (2002).
6. M.Sakomura, T.Takagi, H.Nakayama et al., *Coll. Surf. A*, **198–200**, 769 (2002).
7. R.S.Grynyov, A.V.Sorokin, G.Ya.Guralchuk et al., *J. Phys. Chem. C*, **112**, 20458 (2008).
8. A.V.Sorokin, I.I.Filimonova, R.S.Grynyov et al., *J. Phys. Chem. C*, **114**, 1299 (2010).
9. J.A.Tuszynski, M.F.Jorgensen, D.Mobius, *Phys. Rev. E*, **59**, 4374 (1999).
10. I.G.Scheblykin, O.Yu.Sliusarenko, L.S.Lepnev et al., *J. Phys. Chem. B*, **105**, 4636 (2001).
11. D.A.Higgins, P.F.Barbara, *J. Phys. Chem.*, **99**, 3 (1995).
12. H.von Berlepsch, C.Bottcher, L.Dahne, *J. Phys. Chem. B*, **104**, 8792 (2000).
13. J.R.Lakowicz, Principles of Fluorescence Spectroscopy, 2nd ed., Kluwer Academic/Plenum Publishers, New York, Boston, Dordrecht, London, Moscow (1999).
14. B.Valeur, Molecular Fluorescence. Principles and Applications, Wiley-VCH Verlag GmbH, Weinheim (2002).

Міграція екситонів в J-агрегатах псевдоізоціаніну, сформованих у полімерних плівках

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Вивчено ефективність екситонного транспорту в J-агрегатах псевдоізоціаніну (PIC), сформованих у тонких плівках ПВС, за допомогою екситонної пастки. В якості пастки використано аніонний ціаніновий барвник DiD–C3S. Спектри люмінесценції отримано за допомогою люмінесцентного мікроскопа, що дозволило збирати спектри з дуже маленьких ділянок плівки. Виявлено неоднорідний розподіл барвників у плівці. Використовуючи рівняння Штерна-Фольмера для гасіння люмінесценції J-агрегатів пасткою, показано, що 50 % люмінесценції J-агрегатів гаситься у співвідношенні PIC/DiD–C3S = 30:1. Отримане значення є дуже малим й указує на міграцію екситонів на невеликі відстані.