

Features of exciton transport in J -aggregates of amphi-PIC

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The experimental results concerning the efficiency of exciton migration under the exciton selective excitation within the amphi-PIC J -aggregate absorption band at different temperatures are presented. To detect the exciton migration, the luminescence of exciton traps, which are molecules capable of energy capturing as an exciton approaches has been used. Exciton states have been shown to exhibit different mobility within the J -aggregate absorption band. Excitons in the J -band absorption maximum provide an effective energy transfer to the trap. The efficiency does not change within 20–70 K temperature range and decreases monotonously in the 70–300 K one. At the longer-wavelength edge of the absorption J -band, excitons are strongly localized. In the 70–300 K range, energy transfer to traps reveals a complicated temperature dependence and activation character.

Представлены экспериментальные результаты исследования эффективности миграции экситонов при их селективном возбуждении в пределах полосы поглощения J -агрегатов amphi-PIC при разных температурах. Для детектирования миграции экситонов использовалась люминесценция экситонных ловушек-молекул, способных перехватывать энергию при приближении экситона. Показано, что экситонные состояния в пределах полосы поглощения J -агрегатов обладают разной подвижностью. Экситоны в максимуме полосы поглощения обеспечивают эффективный перенос энергии, который остается неизменным в диапазоне температур 20–70 К и монотонно спадает при изменении температуры в диапазоне 70–300 К. На длинноволновом краю полосы поглощения экситоны сильно локализованы, в диапазоне температур 70–300 К перенос энергии к ловушкам носит активационный характер и имеет сложную немонотонную температурную зависимость.

Since their first discovery by Jelley and, independently, Scheibe in the mid thirties, molecular aggregates named J -aggregates or S -polymers in honor of their discoverers draw a keen interests in both fundamental and applied aspects. J -aggregates are specific assemblies of non-covalently coupled organic dye molecules organized in the form of linear or closed molecular chains which, in their turn, form complex cylindrical patterns [1–3]. These supramolecular assemblies are characterized by a narrow intense absorption band red-shifted with respect to the relevant monomer band, that reflects the exciton nature of electronic excitations

in J -aggregates [1]. Due to the chain arrangement, optical and luminescence properties of J -aggregates are well described within the 1D Frenkel exciton model [1]. Recently, J -aggregates have attracted a great attention as a new type of luminescent probes to control mitochondrial membrane potential in living cells [4] and as an artificial analogue of light-harvesting (LH) complexes [5].

The works devoted to the exciton transport in J -aggregates [1, 6–12] are not numerous. In [1, 6], authors declared a high efficiency of the exciton transport, since the quenching of J -aggregate exciton lumi-

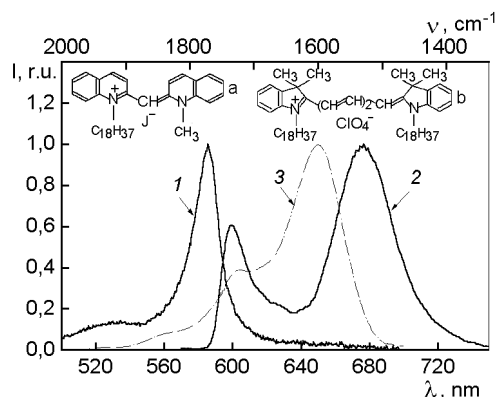


Fig. 1. Absorption (1) and luminescence (2) spectra of *J*-aggregates with traps, $T = 290$ K; DiD absorption spectra in DMFA(3). The insets show amphi-PIC (a) and DiD (b) structural formulas.

nescence by traps is achieved even at the ratio of $1 \cdot 10^6$ (one trap molecule per 10^6 monomer dye molecules). The exciton-exciton annihilation experiments revealed complex non-monotonous temperature dependence of exciton migration in *J*-aggregates [10]. The exciton energy transfer was shown to occur over 10^7 monomer molecules that indicates coherent mechanism of exciton transport and high order of molecular packing in the *J*-aggregates. The exciton transport parameters stated in these papers are very promising for nanoelectronics. It should be noted in this connection that in our experiments with amphi-PIC *J*-aggregates, exciton migration has been found to occur over 10^2 monomer molecules. Thus, our results differ essentially from the above-mentioned ones. This contradiction stimulates a detailed investigation of exciton transport in *J*-aggregates. Thus, complete understanding of exciton transport mechanisms and their dependence on a *J*-aggregate arrangement and system parameters is still required.

In this work, we report the study of the temperature dependence of exciton transport in *J*-aggregates of 1-methyl-1'-octadecyl-2,2'-cyanine iodide (amphi-PIC) under selective excitation of excitonic states in the absorption band. Another amphiphilic dye 1,1'-dioctadecyl-3,3',3'-tetramethylindodicarbocyanine perchlorate (DiD) having the first excited singlet level located 1850 cm^{-1} lower of the bottom of the *J*-aggregate exciton band (Fig. 1 and Fig. 2) was used as an exciton trap. The inset in Fig. 1 presents structural formulas of used dyes. DiD molecules are known to form non-lumi-

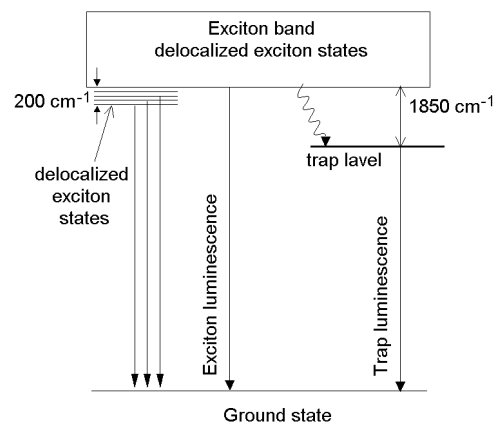


Fig. 2. Simplified scheme of exciton *J*-band and energy levels of traps, localized and free excitons.

nescent associates in water solutions [13], but their intense sensitized luminescence is observed in a water solution containing *J*-aggregates under the excitation at the absorption band of *J*-aggregates (Fig. 1). As the concentration of DiD molecules was small enough ($\sim 10^{-6}$ M), we were not able to record the DiD absorption band (Fig. 1). In the DiD luminescence excitation spectrum, a band corresponding to the absorption of *J*-aggregates is observed. This band we will hereinafter refer to as "excitation *J*-band" by analogy with absorption *J*-band.

Amphi-PIC molecules are known to form *J*-aggregates in a binary dimethylformamide : water (DMFA:W) solution at water content exceeding 30 % [14]. The sample solutions containing amphi-PIC *J*-aggregates with traps were prepared as follows. DiD (0.014 mM) and amphi-PIC (1 mM) were dissolved in DMFA under moderate heating to form a mixture at the ratio 1:70, then doubly distilled water was added to obtain a binary solution with 75 % water content. While temperature decreases down to vitrifying temperature ($T_{vitr} = 265$ K), this binary solution forms a homogeneous vitrescent matrix. Luminescence and luminescence excitation spectra were recorded using a spectrofluorometer on the base of two monochromators MDR-23 and a xenon lamp. One of the monochromators was used to select the required excitation wavelength (FWHM $\sim 20 \text{ cm}^{-1}$), whereas the other one was used to record luminescence. At low temperature experiments, a liquid helium cryostat was used. The solutions were placed into an 1mm thick cell and cooled down to liquid helium temperature. Then

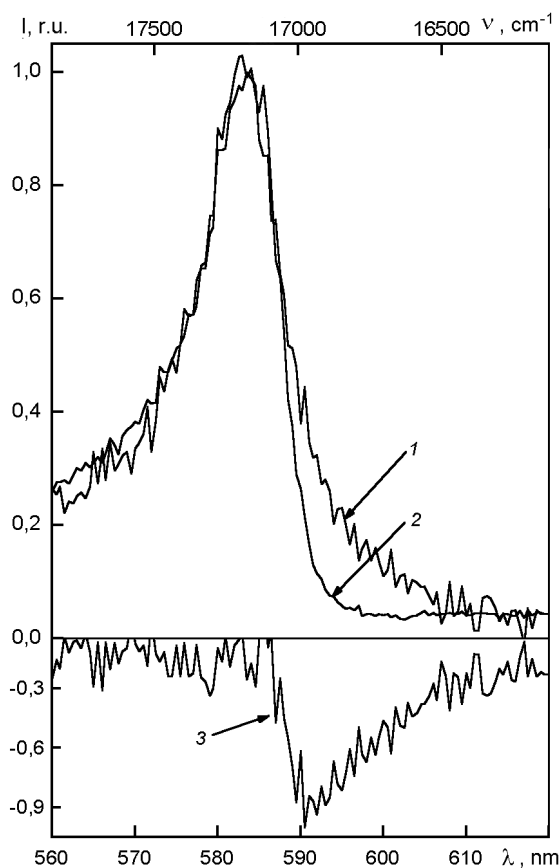


Fig. 3. Amphi-PIC absorption J -band (1) and trap luminescence excitation band (2); (3) — spectral difference. $T = 77$ K.

the recording monochromator was adjusted to the trap luminescence maximum. Under the temperature increasing, the luminescence intensity was measured at 5 K steps. The temperature was controlled within 1 K or better.

J-band structure and the role of static disorder. The exciton migration is substantially affected by static disorder, i.e. J -aggregate structure imperfection. Optical properties of J -aggregates are usually considered taking into account only diagonal disorder [1, 12, 16, 17], that is, the scatter in transition frequencies of individual monomer molecules in a J -aggregate. However, it was shown in [15] that the non-diagonal disorder, i.e. randomness in either molecular orientation or molecular positions, also plays an important role in optical properties of amphi-PIC J -aggregates. The presence of the non-diagonal disorder is manifested as changing of the shape of the low-frequency edge of J -aggregate absorp-

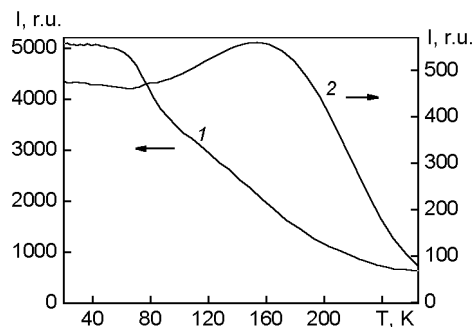


Fig. 4. Temperature dependence of exciton trap luminescence intensity at the excitation in different sides of the J -aggregate absorption band: 1 — excitation at absorption maximum ($\lambda_{exc} = 580$ nm); 2 — excitation at the long-wavelength edge ($\lambda_{exc} = 590$ nm).

tion band at low temperature from Gaussian, that is typical for J -aggregates with a prevalence of diagonal disorder [15–17], to Lorentzian one [15]. The degree of non-diagonal disorder in amphi-PIC J -aggregates was shown to be controllable by changing the water content in a DMFA:W solution [18]. While the water content increases, the non-diagonal disorder extent reduces [18]. However, Lorentzian shape of low-frequency edge of the absorption J -band at 77 K (Fig. 3, curve 1) observed in our experiments indicates that at high concentration of amphi-PIC molecules used (1 mM), 75 % water content is still insufficient.

In [15], strong exciton localization at the edges of the absorption band was predicted in the case of non-diagonal disorder. To verify this statement, the absorption J -band shape has been compared with that of the trap luminescence excitation band at 77 K (Fig. 3). It has been revealed that in contrast to the absorption J -band, the long-wavelength edge of the excitation J -band is steeper and fits well to the Gaussian contour. This means that excitons formed under the excitation at the long-wavelength absorption edge are localized and do not actually reach the trap. The absorption and excitation line shape comparison (curves 1 and 2, Fig. 3) shows that the localized exciton states are located about 200 cm^{-1} lower of the bottom of the free exciton band (Fig. 2). Excitons formed at the J -band maximum excitation are delocalized and reach the trap. Thus, the effect of static disorder provokes a complex structure of the absorption J -band, which consists really of two parts: low-frequency edge where localized excitons are formed and high-energy part where free

mobile excitons are formed (Fig. 3). Using selective excitation of different states in the J -band, we can study peculiarities of localized and delocalized exciton transport in the same conditions.

Delocalized exciton migration. Fig. 4 presents temperature dependence of exciton trap luminescence intensity ($\lambda_{reg} = 690$ nm) at the excitation in the absorption J -band maximum (curve 1, $\lambda_{exc} = 580$ nm) and in the long-wavelength edge of the J -band (curve 2, $\lambda_{exc} = 590$ nm). As is seen, the investigated temperature range can be divided into two temperature intervals: 20–70 K where the trap luminescence intensity is temperature-independent and 70–300 K where a strong temperature dependence of trap luminescence intensity is observed for both localized and delocalized excitons. The same temperature ranges where strong changes of exciton transport characteristics occur were mentioned in [10].

Let us consider the temperature dependence of delocalized exciton migration (Fig. 4, curve 1). In the 80–300 K temperature range, the monotonic temperature dependence of the trap luminescence intensity fits well by the $T^{-1/2}$ law. Such temperature dependence is a characteristic feature of coherent exciton transport [19]. In the case of coherent motion, the exciton diffusion constant where m is 0 to 1.5, depending on the specific parameters of the exciton-phonon system, and is due to exciton scattering on optical phonons [19]. At $T < 70$ K, the trap luminescence intensity is temperature-independent that seems to correspond to $D = const$. The pattern of diffusion coefficient temperature dependence is known to change near $T = 3.6$ K (m^*/m_0) where m^* is the effective exciton mass and m_0 is the electron mass in vacuum [19]. So, the effective mass of delocalized excitons is estimated to be $m^* \sim 17m_0$.

Localized exciton migration. At $T > 70$ K, the trap luminescence intensity starts to increase (Fig. 4, curve 2) that is a characteristic feature of incoherent "hopping" exciton migration and is due to the thermal activation of the localized excitons [19]. At $T \sim 160$ K, the temperature dependence of the trap luminescence exhibits a maximum that is due to the competition of two processes influencing the localized exciton motion. On the one hand, thermal activation of localized excitons promotes their mobility, but on the other hand, scattering on phonons rebounds the exciton motions. This

statement is confirmed by the fast luminescence intensity decrease under further temperature increasing (curve 2, Fig. 4).

Similarly to the case of delocalized excitons, the trap luminescence intensity does not depend on temperature (Fig. 4, curve 2) in the temperature interval 20–70 K. It should be noted that in this case, the luminescence intensity is much less than that for delocalized excitons (Fig. 4). The fact that the trap luminescence does not decay down to zero seems to be due to the localized exciton is formed in immediate proximity to the trap and energy transfer is possible. According to [12], for localized excitons, the exciton migration is strongly hindered at $T < T_0 = 0.4\beta(\Delta/\beta)^{1.36}$ where β is the hopping integral and Δ characterized diagonal disorder. For amphi-PIC J -aggregates, $\beta \sim 840$ cm⁻¹ and $\Delta \sim 300$ cm⁻¹ [18]. So, $T_0 \sim 80$ K. Thus, as it was predicted in [12], in the temperature range 20–70 K, localized excitons in J -aggregates of amphi-PIC remain motionless.

Thus, static disorder has been shown to affect the complex structure of the absorption exciton band of amphi-PIC J -aggregates. At the long-wavelength edge of the absorption J -band, motionless localized exciton states are formed. For localized excitons, the energy transfer to traps is observed in the temperature range 70–300 K and reveals an activation character. The energy levels of localized excitons are located 200 cm⁻¹ lower of the mobility boundary. At higher-energy side with respect to the localized exciton states, mobile "free" excitons are formed. Temperature dependence of free exciton migration efficiency points to a coherent transfer mechanism.

References

1. D.Mobius, *Adv. Matter.*, **7**, 437 (1995).
2. H.Berlepsch, C.Bottcher, A.Ouart et al., *J. Phys. Chem. B*, **104**, 5255 (2000).
3. H.Berlepsch, C.Bottcher, S.Dahne, *J. Phys. Chem. B*, **104**, 8792 (2000).
4. M.Reers, T.Smith, L.Chen, *Biochemistry*, **30**, 4480 (1991).
5. G.McDermott, S.M.Prince, A.A.Freer et al., *Nature*, **374**, 517 (1995).
6. D.Mobius, H.Kuhn, *J. Appl. Phys.*, **64**, 5138 (1988).
7. H.Fidder, J.Terpstra, D.A.Wiersma, *J. Phys. Chem.*, **94**, 6895 (1991).
8. J.Moll, S.Daehne, J.R.Durrant, D.A.Wiersma, *J. Phys. Chem.*, **102**, 6362 (1995).
9. M.A.Drobizhev, M.N.Sapozhnikov, I.G.Schelykin et al., *Chem. Phys.*, **211**, 455 (1996).

10. I.G.Scheblykin, O.Yu.Sliusarenko, L.S.Lepnev et al., *J. Phys. Chem. B*, **105**, 4636 (2001).
11. G.S.Katrich, K.Kemnitz, Yu.V.Malyukin, *Mol. Cryst. and Liquid Cryst.*, **348**, 15 (2000).
12. A.V.Malyshev, V.A.Malyshev, F.Dominguez-Adame, *Chem. Phys. Lett.*, **371**, 417 (2003).
13. Yu.V.Malyukin, S.L.Efimova, K.Kemnitz, *J. Lumin.*, **94–95**, 239 (2001).
14. Yu.V.Malyukin, S.L.Efimova, A.V.Sorokin, A.M.Ratner, *Functional Materials*, **10**, 715 (2003).
15. H.Fidder, J.Knoester, D.A.Wiersma, *J. Chem. Phys.*, **95**, 7880 (1991).
16. J.Klafter, J.Jortner, *J. Chem. Phys.*, **68**, 1513 (1978).
17. M.Schreiber, Y.Toyozaawa, *J. Phys. Soc. Japan*, **51**, 1528 (1981).
18. Yu.V.Malyukin, O.G.Tovmachenko, G.S.Katrich, K.Kemnitz, *Low Temp. Phys.*, **24(12)**, 1171 (1998).
19. V.M.Agranovich, M.D.Galanin, *Electronic Excitation Energy Transfer in Condensed Matter*, North-Holland Publishing Company, Amsterdam (1982).

Особливості екситонного транспорту в *J*-агрегатах *amphi*-PIC

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Представлено експериментальні результати дослідження ефективності міграції екситонів при їх селективному збудженні у межах смуги поглинання *J*-агрегатів *amphi*-PIC при різних температурах. Для детектування міграції екситонів використовувалася люмінесценція екситонних пасток — молекул, що здатні перехоплювати енергію при наближенні екситону. Показано, що екситонні стани у межах смуги поглинання *J*-агрегатів мають різну рухливість. Екситони у максимумі смуги поглинання забезпечують ефективний перенос енергії, який залишається незмінним у діапазоні температур 20–70 К та монотонно спадає при зміні температури у діапазоні 70–300 К. На довгохвильовому краї смуги поглинання екситони сильно локалізовані, у діапазоні температур 70–300 К перенос енергії на пастки носить активаційний характер та має складну немонотонну температурну залежність.