

Features of exciton migration in pseudoisocyanine *J*-aggregates

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Exciton migration in pseudoisocyanine (PIC) *J*-aggregates has been studied via luminescence quenching by an exciton trap. It has been shown that in PIC *J*-aggregates excitons migrate by coherent mechanism. Exciton diffusion coefficient and diffusion length have been obtained using classical approach developed for molecular crystals. Both of them are much smaller in comparison with exciton diffusion parameters for molecular crystals.

Исследована миграция экситонов в *J*-агрегатах псевдоизоцианина (PIC) по тушению их люминесценции экситонными ловушками. Показано, что в *J*-агрегатах PIC экситоны мигрируют по когерентному механизму. При помощи классического подхода, развитого для молекулярных кристаллов, получены коэффициент диффузии и длина диффузии экситонов. Оба параметра намного меньше, чем параметры экситонной диффузии для молекулярных кристаллов.

1. Introduction

Highly ordered molecular aggregates, called *J*-aggregates (Jelley aggregates) or Scheibe aggregates in honor of their inventors, last year celebrated 75 years of their discovering [1–3]. Their intriguing optical properties like very narrow bandwidth, extremely large extinction coefficients, giant cubic susceptibility, effective energy migration are attracted a great interest of a number of scientists [3–6]. Such properties caused by delocalisation of electronic excitation over segments of molecular chains due to strong dipole-dipole interaction between molecules and Frenkel excitons appearing [7]. Frenkel excitons appeared to be highly mobile and revealed an effective exciton transport [8–11]. As a result *J*-aggregates could be used as optical antennas that absorb a light and transfer an energy obtained to the target. Indeed soon after their discovering and up to now *J*-aggregates have applied as the best photo-sensitizers for silver halides microcrystals [6]. Recently it

was found that optical properties of light-harvesting complexes (LHC), which provide extremely fast and efficient energy transport of the absorbed sun light to the photochemical reaction centres of plants and photosynthetic bacteria, also associated with Frenkel excitons [12, 13]. That is additionally stirs up an interest to excitonic properties of *J*-aggregates as the most perspective candidates to mimic LHC exciton properties [14, 15].

However despite the big interest to the exciton transport in the *J*-aggregates experimental data reported are different and some times contradict each other. For example, Sundstrom et al. studying exciton transport in pseudoisocyanine (PIC) *J*-aggregates by means of exciton-exciton annihilation conclude of exciton migration over $2\text{--}5\cdot 10^4$ molecules [16]. Mobius reports about exciton migration over 2600 PIC molecules based on Scheibe data of PIC *J*-aggregate luminescence quenching by eosin molecules [4]. And finally from direct observation of spatial extent of photobleach-

ing Higgins and Barbara found that upper limit of exciton migration in PIC *J*-aggregates is ~50 nm, i.e. taking into account ~4 Å [3] distance between PIC molecules in molecular chain exciton can move just over ~125 molecules [17].

Recently we have reported on exciton transport in amphi-PIC *J*-aggregates studied using exciton traps (energy acceptors) [11]. Despite the high energy disorder which takes place in that type of *J*-aggregates it reveals the energy migration over 120 molecules which we consider as a quite effective. And now we intend to spread out our approach on PIC *J*-aggregates which are the most famous and investigated ones. A number of different dyes including eosin reported in [4] have been tested for luminescence quenching of PIC *J*-aggregates in solution without success. Finally we have chosen the anionic cyanine dye DiD-4CS as the exciton trap for pseudoisocyanine *J*-aggregates. First attempt to study exciton migration in PIC *J*-aggregates has been done on the aggregates spread in PVA polymer film [18]. But in a such case the large heterogeneity of the dyes distribution has been revealed which strongly misrepresented the data obtained [18].

2. Experimental

Pseudoisocyanine (1,1'-diethyl-2,2'-cyanine iodide, PIC, Fig. 1a) dye was purchased from Sigma Aldrich (USA) and used as-received. DiD-4CS (1,1'-di(3-sulfobutyl)-3,3,3',3'-tetramethylindodicarbocyanine sodium salt, Fig. 1b) dye was synthesized by Dr.I.A.Borovoy (Institute for Scintillation Materials of NAS of Ukraine) with purity controlled by NMR and thin layer chromatography. PIC *J*-aggregates were prepared by dissolving the dye PIC (0.5 mM) in an aqueous NaCl (0.2 M) solution under moderate heating (<80°C). Then the solution was cooled down to room temperature. DiD-4CS at required concentrations was mixed with portion of PIC dye before aqueous solution adding. As one of the way to do this all components were dissolved in chloroform and mixed with consequent chloroform full evaporation.

Absorption spectra were registered using a spectrophotometer Specord 200 (Analytik Jena, Germany). Luminescence and luminescence excitation spectra at room temperature were recorded using fluorescence spectrometer Lumina (Thermo Scientific, USA). As PIC *J*-aggregates have a high extinction

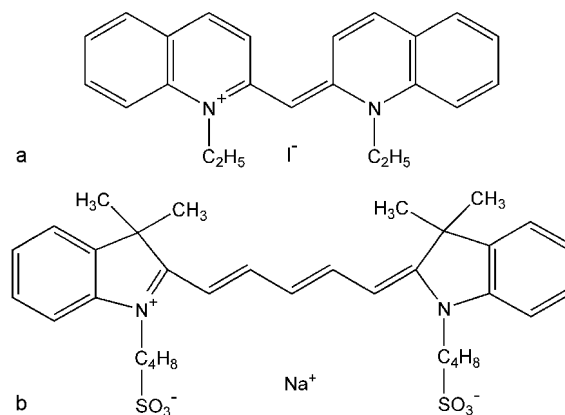


Fig. 1. Structural formulas of the dyes investigated: (a) PIC, (b) DiD-4CS.

coefficient the measurements have been done using solid sample holder and thin (3 mm) cuvette to avoid reabsorption. Low temperature measurements have been done using spectrofluorimeter based on two grating monochromators MDR-23 and a xenon lamp. A drop of sample solution deposited between two glass plates has been placed into a cryostat and cooled down to liquid nitrogen temperature. Luminescence intensity was measured in the temperature range of 80–240 K with a step of 5 K. The temperature was controlled within 1 K.

3. Results and discussion

DiD-4CS dye is good soluble in water so the main attractive force that could bring it in contact with PIC *J*-aggregates is Coulombic force. NaCl salt, which presenting in water solution facilitates PIC *J*-aggregates formation at relatively small dye concentration due to electrostatic repulsion screening [19], results in further promotion of DiD-4CS interaction with *J*-aggregates. So, when DiD-4CS dye has been added to PIC *J*-aggregates solution it results in some spectral change (Fig. 2). First of all, there is sensitized luminescence of DiD-4CS ($\lambda_{max} = 679$ nm) which appeared at the excitation ($\lambda_{exc} = 530$ nm) within the *J*-aggregates absorption band (called *J*-band, $\lambda_{max} = 574$ nm), whereas PIC *J*-aggregates luminescence band ($\lambda_{max} = 574.5$ nm) is quenched (Fig. 2b). Note, that in water solution the luminescence band of DiD-4CS is much weaker than *J*-aggregates one (Fig. 2b) in contrast to the case of PVA polymer film [18]. This could be associated with much less *J*-aggregates luminescence quantum yield in the polymer film. In luminescence excitation spectrum of DiD-4CS ($\lambda_{reg} = 685$ nm) the band corresponding to

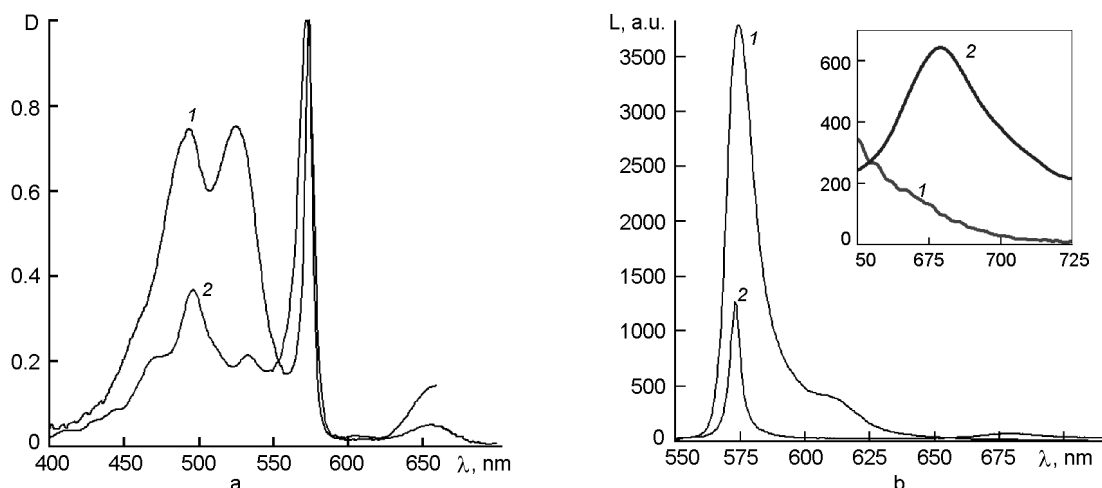


Fig. 2. a) (1) Absorption and (2) DiD-4CS ($\lambda_{reg} = 680$ nm) excitation spectra of PIC *J*-aggregates with DiD-4CS (PIC/DiD-4CS = 1:20); b) luminescence ($\lambda_{exc} = 530$ nm) spectra of (1) PIC *J*-aggregates and (2) PIC *J*-aggregates with DiD-4CS (PIC/DiD-4CS = 1:20).

J-band is clearly seen which intensity is much higher comparing with band corresponding to its own absorption band ($\lambda_{max} = 655$ nm) (Fig. 2a). Furthermore, the band corresponding to PIC *J*-aggregates *H*-band ($\lambda_{max} = 494$ nm) (hypsochromically shifted band [3, 6, 20]) is appeared to be more intense than band corresponding to PIC monomers band ($\lambda_{max} = 525$ nm) (Fig. 2a). So we could conclude effective energy transfer from *J*-aggregates to DiD-4CS as a result of their strong interaction. One more fact which further supports our supposition about strong PIC *J*-aggregate and DiD-4CS dye interaction is that the absorption and luminescence spectra of DiD-4CS dye in the same water solution in absence of PIC *J*-aggregates appeared to be shifted in blue region with maxima: $\lambda_{abs} = 641.5$ nm and $\lambda_{lum} = 666.5$ nm (Fig. 3).

To estimate the efficiency of exciton transport in PIC *J*-aggregates we have analyzed a quenching luminescence of *J*-aggregates by the exciton traps (DiD-4CS dye) as it has been done for amphi-PIC *J*-aggregates previously [11, 21]. For this purpose a series of luminescence spectra of PIC *J*-aggregates in presence of different DiD-4CS dye concentrations has been obtained (Fig. 4a). As it could be seen increasing DiD-4CS amount lead to successive *J*-aggregate luminescence quenching and the trap luminescence building-up (Fig. 4a, inset). It should be noted, that at high concentrations of DiD-4CS (ratio PIC:DiD-4CS < 10:1, Fig. 4a) a maximum of the trap luminescence band is shifted to $\lambda_{lum} = 666.5$ nm that is corresponded to free molecules (Fig. 3).

Moreover, in absorption spectrum a width of the *J*-band became increased with simul-

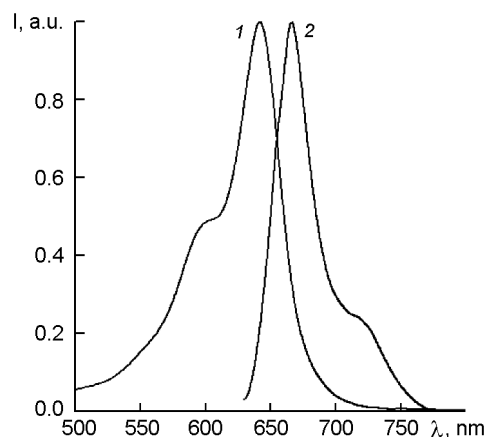


Fig. 3. (1) Absorption and (2) luminescence ($\lambda_{exc} = 625$ nm) spectra of DiD-4CS in the aqueous NaCl (0.2 M) solution.

taneous blue shift of the *J*-band maximum (not shown). Similar picture was observed for amphi-PIC *J*-aggregates previously and corresponds to *J*-aggregate destroying [11]. So, hereafter we will use smaller DiD-4CS concentrations (ratio PIC:DiD-4CS \geq 10:1) for the analysis.

The next step was analysis of the *J*-aggregate luminescence quenching using Stern-Volmer equation [11, 22]:

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

where F_0 and F are *J*-aggregate luminescence intensities in the absence and presence of the trap, respectively, $[Q]$ is the

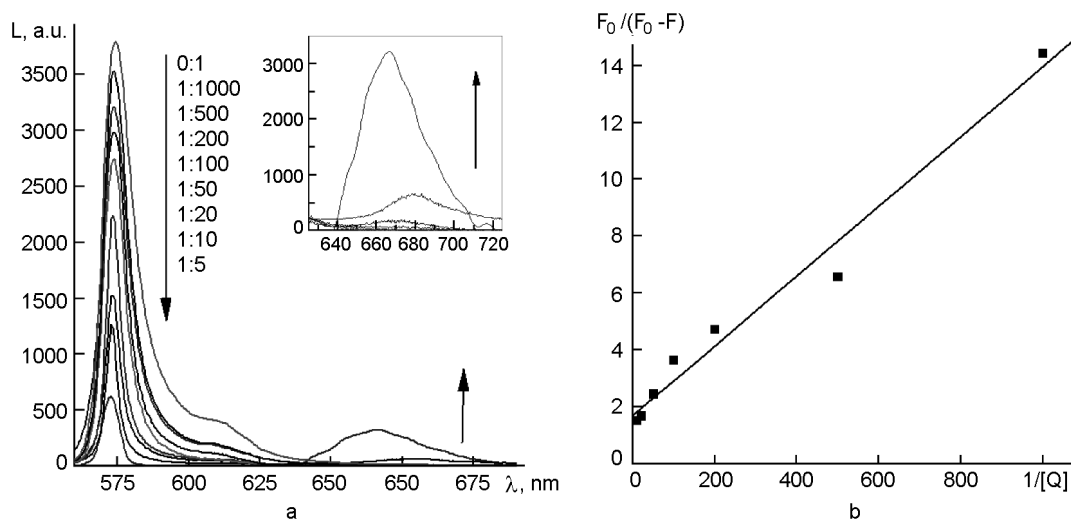


Fig. 4. a) Luminescence ($\lambda_{exc} = 530$ nm) spectra of J -aggregates with the trap at different PIC/DiD-4CS ratios; b) modified Stern-Volmer plot of PIC J -aggregate quenching by DiD-4CS dye.

quencher concentration and K_{SV} is Stern-Volmer constant. The value $1/K_{SV}$ gives us the concentration of the trap that quenches 50 % of J -aggregate luminescence [11, 22].

As in the case of amphi-PIC J -aggregates [11, 21] the plot F_0/F against $[Q]$ does not follow the linear law and shows downward curvature toward X-axis (not shown) and the modified Stern-Volmer equation was used [11, 22]:

$$\frac{F_0}{F_0 - F} = \frac{1}{f_q \cdot K_{SV} \cdot [Q]} + \frac{1}{f_q}, \quad (2)$$

where f_q is the fraction of the initial fluorescence which is accessible to a quencher. The plot of $F_0/(F_0 - F)$ versus $1/[Q]$ for PIC J -aggregate luminescence quenching is linear and yields $1/f_q$ as the intercept and $1/(f_q \cdot K_{SV})$ as the slope (Fig. 4b). So, we obtain $f_q = 0.70$, i.e. 70 % of excitons in PIC J -aggregates are trapped by DiD-4CS trap. This value is much larger in comparison with that obtained for amphi-PIC J -aggregates luminescence quenching by DiD trap (only 30 %) [11]. Previously we supposed that such small value of f_q for amphi-PIC J -aggregates is associated with very short radiation decay time (about 40 ps) for this type of aggregates. As a result significant portion of exciton could relax radiatively before they trapped by DiD molecules [11]. For PIC J -aggregates much bigger radiation decay time $\tau \sim 1.4$ ns has been obtained. So, parameter f_q shouldn't be considered as the

portion of excitons reaching the trap only. Another parameter, namely an association constant for complex formation, should be also taking into account. One could suppose the latter has the main contribution to the f_q parameter in the case of PIC J -aggregates.

Expressing the trap concentration in mole fraction units we obtained Stern-Volmer constant $K_{SV} = 110$, i.e. 1 DiD-4CS molecule quenches 50 % luminescence of 110 PIC molecules forming J -aggregate. This value appeared to be unexpectedly low. Indeed, it is comparable with the one for amphi-PIC J -aggregates [11], which reveal much larger static disorder degree and, correspondingly, much smaller delocalization length [23]. Regarding to different estimates of exciton migration in PIC J -aggregates, namely 10^4 molecules [16], 10^3 molecules [4] and 10^2 molecules [17], the result obtained corresponds to the smallest one [17].

For an exciton diffusion in molecular crystals it is possible to obtain an exciton diffusion coefficient using following expression [24, 25]:

$$K_{SV} \sim 4\pi \cdot D \cdot R_{trap} \cdot \tau_0 n_d, \quad (3)$$

where D is the exciton diffusion coefficient, R_{trap} is the radius of exciton capture (usually it takes as $\sim 10^{-9}$ m [24]), τ_0 is the exciton lifetime in absence of a trap ($\tau_0 = 1.4$ ns in our case) and n_d is the number density of host molecules per m^3 . To obtain the latter parameter we used PIC J -aggregate structure proposed in [26] based on cryo-TEM data. According it PIC J -aggregates are

long rodlike particles with rod diameter ~ 2.3 nm consisting of six double strands stacked together [26]. Thus in cross-section we have 12 molecules and a distance between molecules in the strand is about 0.5 nm, i.e. an elementary volume of the rod has a volume ~ 2 nm³. Hence, we could estimate n_d as 12 molecules per 2 nm³, which is about 6 nm⁻³.

So, from Eq.3 we can obtain $D \sim 10^{-9}$ m²s⁻¹ = 10^{-5} cm²c⁻¹, which is much smaller than the exciton diffusion coefficient in classical molecular crystals, such as anthracene ($D \sim 5 \cdot 10^{-3}$ cm²c⁻¹ [24]) or naphthalene ($D \sim 10^{-4}$ cm²c⁻¹ [24]). For 1D diffusion, which is supposed for PIC J -aggregates, we can find a diffusion length [25]:

$$l = \sqrt{2D\tau_0}. \quad (4)$$

Thus in our case we obtain $l \sim 1.7 \cdot 10^{-9}$ m = 1.7 nm. The value obtained is too small and it seems to be not reasonable. It could be caused, for example, by strong exciton localization in 1D molecular chain despite large exciton delocalization length, weak exciton-phonon coupling and small static disorder [27].

To verify such assumption we investigate a temperature dependence of the trap sensitized luminescence like it was done for amphi-PIC J -aggregates [10] (Fig. 5). PIC J -aggregates with the traps has been cooled to liquid nitrogen temperature and excited into the short-wavelength edge of J -band near the maximum (to exclude excitation of long-wavelength edge where localized excitons could appear [10]).

The temperature dependence of the trap luminescence (Fig. 5) clearly demonstrates a monotonic decreasing within the 80–240 K temperature range which is characteristic for the coherent exciton motion [10]. Thus exciton localization is not the reason for a very small diffusion length. Other unaccounted physical processes leading to underestimation of diffusion length should be considered in further analysis like exciton trapping in small cages caused by potential barriers [25] or something else.

4. Conclusions

Exciton migration in pseudocyanine J -aggregates has been studied using another cyanine dye DiD-4CS as exciton traps. DiD-4CS interaction with PIC J -aggregates causes strong quenching the J -aggregates luminescence which has been analyzed using Stern-Volmer equation. As it

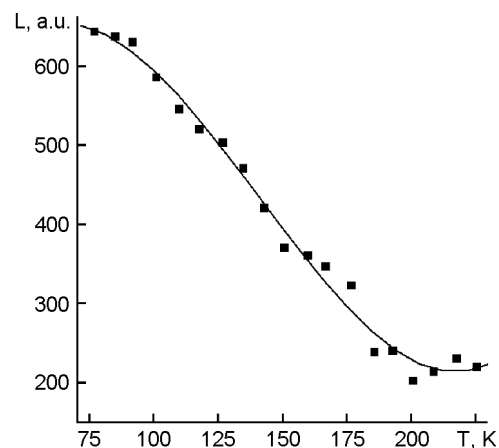


Fig. 5. Temperature dependence of exciton trap luminescence ($\lambda_{reg} = 680$ nm) intensity at excitation on J -band ($\lambda_{exc} = 567$ nm).

was found previously for J -aggregates of another dye amphi-PIC, modified Stern-Volmer equation which takes into account a fraction of donor inaccessible for quenching should be used for PIC J -aggregates. It has been determined that 50 % of J -aggregates luminescence quenched in ratio 1 DiD-4CS molecule per 100 PIC molecules. Using value obtained exciton diffusion coefficient $D \sim 10^{-9}$ cm²c⁻¹ and diffusion length $l \sim 1.7 \cdot 10^{-9}$ m have been found. Both of them are very low in comparison with the exciton diffusion in molecular crystals. The values obtained contradict to coherent mechanism of exciton diffusion in PIC J -aggregates and are subjects of further discussion.

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Особливості екситонної міграції у *J*-агрегатах псевдоізоціаніну

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Досліджено міграцію у *J*-агрегатах псевдоізоціаніну (PIC) по гасінню їх люмінесценції екситонними пастками. Показано, що у *J*-агрегатах PIC екситони мігрують за когерентним механізмом. За допомогою класичного підходу, що було розвинуто для молекулярних кристалів, отримано коефіцієнт дифузії та довжина дифузії екситонів. Обидва параметри набагато менші за параметри екситонної дифузії для молекулярних кристалів.