

Migration of Frenkel Excitons in PIC J-aggregates

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Using luminescent exciton traps, an efficiency of the exciton migration in J-aggregates of pseudoisocyanine dye in solutions has been investigated. Applying a modified Stern-Volmer equation for an analysis of the J-aggregates luminescence quenching by the trap, the quenching of 50% of PIC J-aggregates luminescence at the ratio PIC/trap = 70:1 has been found. To increase the exciton migration efficiency, the J-aggregate structure was improved by the formation of a "J-aggregate-surfactant" complex. It results in 35% enhancement of the exciton migration efficiency in PIC J-aggregates.

Keywords: J-aggregate, Exciton transport, Exciton trap, Luminescence quenching, Modified Stern-Volmer equation.

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Aggregation of dye molecules is often accompanied by spectral shifts or new spectral bands appearing, due to strong interactions between the chromophores. Outstanding example of the latter case is well-ordered luminescent molecular assemblies called J-aggregates. Due to excitonic nature of electronic excitations, J-aggregates reveal a number of unique spectral properties, one of which is exciton migration over hundreds of monomers [1-4]. Thus J-aggregates can be used as an optical antenna for energy delivery purposes [5, 6]. Indeed, exciton properties of J-aggregates are similar to those of light-harvesting complexes (LHC), which provide extremely fast and efficient energy transport of the absorbed sun light to the photochemical reaction center of plants and photosynthetic bacteria [7]. Pseudoisocyanine (PIC) dye (Fig.1a) is the most investigated cyanine dye forming J-aggregates, which have attracted considerable attention because of their high nonlinear optical properties, ultrafast optical response, and large molecular hyperpolarizability arising from the actions of the aligned molecules [8]. Due to their remarkable physical properties, PIC J-aggregates have received continuous interest through the years. But despite such interest experimental data concerning the exciton transport in PIC J-aggregates are different and some times contradict each other. For example, Sundström et al. studying an exciton transport in pseudoisocyanine (PIC) J-aggregates by means of an exciton-exciton annihilation conclude of exciton migration over $2\cdot 5 \times 10^4$ molecules [9]. Möbius reports about exciton migration over 2600 PIC molecules based on Scheibe data of PIC J-aggregate luminescence quenching by eosin molecules. And finally from direct observation of spatial extent of photobleaching Higgins and Barbara found that upper limit of exciton migration in PIC J-aggregates is ~ 50 nm (~ 125 molecules) [10]. So the purpose of present article is an alternative investigation of exciton transport in PIC J-aggregates. In view of our previous experience, it was clear that the most promising way of introduction molecules / exciton traps to the J-aggregates of PIC is using Coulombic interac-

tion between molecules of PIC and traps. Therefore, anionic cyanine dye DiD-4CS (1,1'-di(3-sulfobutyl)-3,3,3',3'-tetramethylindodicarbocyanine sodium salt) has been chosen as the exciton trap (Fig.1b).

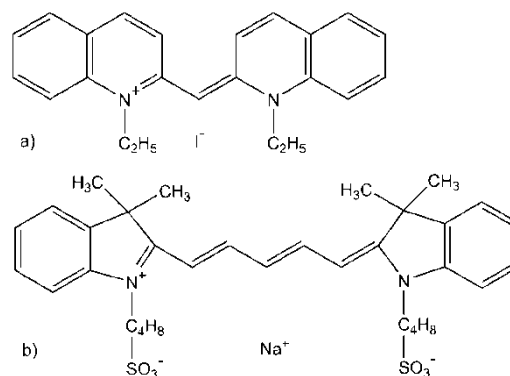


Fig. 1 – Structural formulas of the dyes: (a) PIC; (b) DiD-4CS

The DiD-4CS dye is well dissolved in water and reveals quite narrow absorption ($\lambda_{\max} = 640$ nm) and luminescence ($\lambda_{\max} = 665$ nm) bands (Fig. 2).

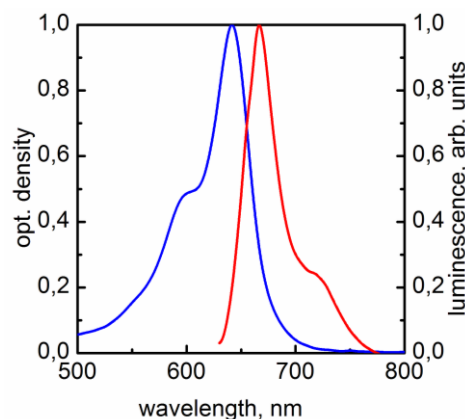


Fig. 2 – Absorption (blue) and luminescence (red) spectra of DiD-4CS dye in water

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DiD-4CS dye addition to PIC J-aggregates solution results in some spectral change (Fig.3). 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.3b). In luminescence excitation spectrum of DiD-4CS ($\lambda_{reg} = 685$ nm) the band corresponding to J-band is clearly seen which intensity is much higher comparing with band corresponding to its own absorption band ($\lambda_{max} = 655$ nm) (Fig. 3a). So we could to conclude effective energy transfer from J-aggregates to DiD-4CS as a result of their strong interaction.

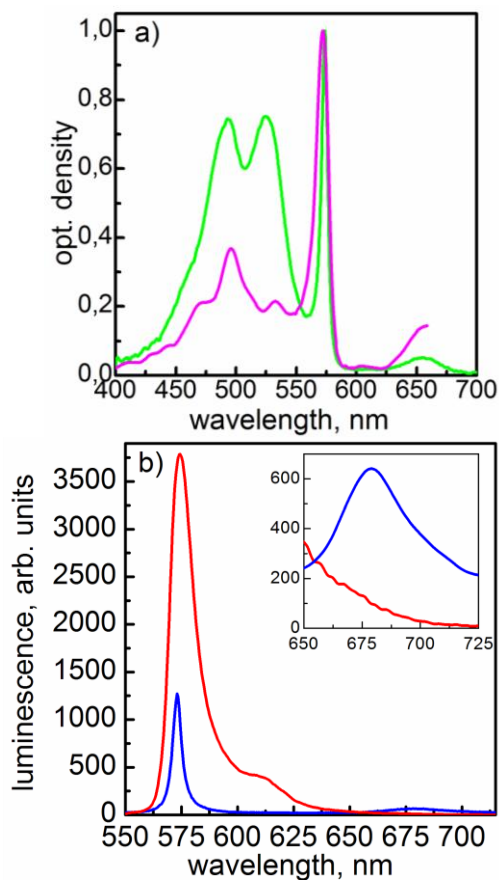


Fig. 3 - a) Absorption (green) and the DiD-4CS luminescence excitation (purple, $\lambda_{reg} = 690$ nm) and b) luminescence ($\lambda_{exc} = 530$ nm) spectra of PIC J-aggregates with the DiD-4CS trap (PIC/trap = 20:1) (blue) and without the trap (red)

So to investigate the exciton migration efficiency in PIC J-aggregates the concentration of DiD-4CS was varied. The increase of the DiD-4CS portion leads to the redistribution of J-band and DiD-4CS luminescence band intensities (Fig.4). Since J-aggregate luminescence quenching and sensitized DiD-4CS dye luminescence are observed even at very small ratio PIC/DiD-4CS = 1000:1 (Fig.4), we consider DiD-4CS to be a very effective exciton trap.

To find the efficiency of the exciton transport in the PIC J-aggregates, the luminescence quenching was analyzed using the Stern-Volmer equation [11]:

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

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 $1/K_{sv}$ gives us the concentration of the trap that quenches 50% of the J-aggregate luminescence [11].

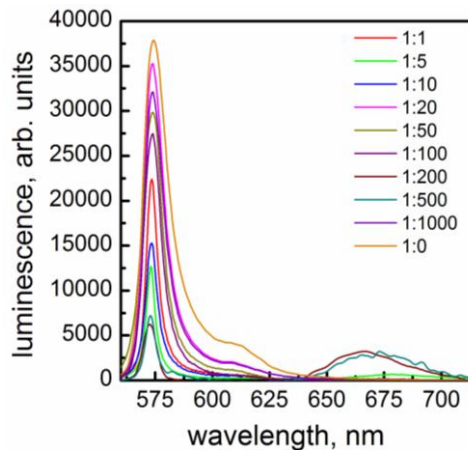


Fig. 4 - Luminescence spectra of the J-aggregates with the DiD-4CS trap at different PIC/DiD ratios

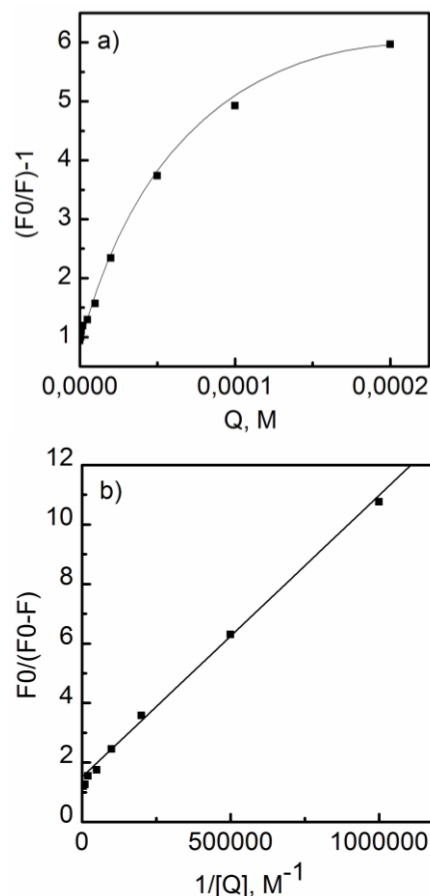


Fig. 5 - (a) Stern-Volmer and (b) modified Stern-Volmer plots for PIC J-aggregate luminescence quenching by the DiD-4CS trap

The Stern-Volmer plot does not follow the linear law and shows downward curvature toward the X-axis (Fig.5a). Such behaviour points to an existence of exci-

tons, which are not accessible to the trap, and is characterized by the modified Stern-Volmer equation [11]:

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

where f_q is the fraction of the initial J-aggregates luminescence, which is accessible to the exciton trap. The modified Stern-Volmer plot is appeared to be linear and yields $1/f_q$ as the intercept and $1/(f_q \cdot K_{SV})$ as the slope (Fig. 5b). So, we obtain $f_q = 0.75$, i.e. about 80% of excitons is trapped by DiD-4CS. Stern-Volmer constant is $K_{SV} = 1.4 \cdot 10^5 \text{ M}^{-1}$, so taking into account that the concentration of PIC in a binary solution is $5 \cdot 10^{-4} \text{ M}$, we obtain that 1 DiD-4CS molecule quenches 50% luminescence of 70 PIC molecules forming the J-aggregate. This value appeared to be unexpectedly low. Regarding to different estimates of exciton migration in PIC J-aggregates, namely 10^4 molecules [9], 10^3 molecules [1] and 10^2 molecules [10], the result obtained corresponds to the smallest one.

"J-aggregates – surfactant" complex. The question arises can we increase the exciton mean free path in J-aggregates? It could be supposed that the main parameter, which may affect the exciton transport, is structural perfection of molecular chain or minimal static disorder. Recently, it was found that formation of a "J-aggregate-surfactant" complex could lead to decreasing static disorder in a number of J-aggregates [12]. So, it was interesting to analyze how this complex formation will affect the exciton transport in PIC J-aggregates.

The DiD-4CS sensitized luminescence intensity is revealed to be much intense in the J-aggregates-surfactant complex (Fig.6).

The Stern-Volmer plot of J-aggregate luminescence quenching by the DiD-4CS trap in the presence of CPB does not follow the linear law (Fig.7) and the modified Stern-Volmer equation (2) was used.

We have obtained next values: $f_q = 0.9$, $K_{SV} = 1.9 \cdot 10^5 \text{ M}^{-1}$. Accordingly 1 DiD-4CS molecule quenches 50% luminescence of 95 PIC molecules forming PIC J-aggregate. So, the surfactant shell formation around the J-aggregates indeed resulted in increasing efficiency of exciton transport in PIC J-aggregates about on 30%, but this increasing wasn't significant and we still stand within the lowest estimation of exciton migration ability.

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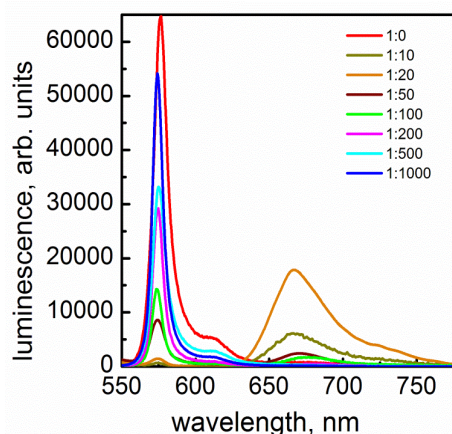


Fig. 6 – Luminescence spectra of the J-aggregate with the trap at different PIC/DiD-4CS ratios in the presence of CPB

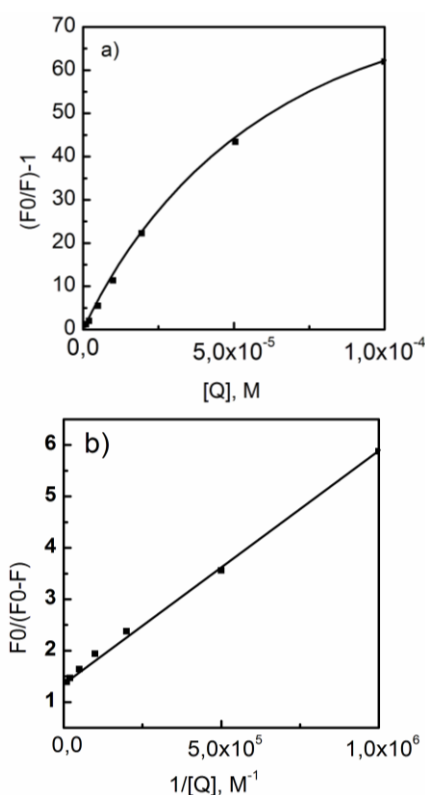


Fig. 7 – (a) Stern-Volmer and (b) modified Stern-Volmer plots for PIC J-aggregate luminescence quenching by the DiD-4CS trap in presence of CPB surfactant