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Peculiarities of excitonic energy transfer at the distance variation between *J*-aggregates and exciton traps

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Molecular aggregates called *J*-aggregates are excitonic systems which could be used as optical antennas. Preliminary experiments demonstrated an effective resonance energy transfer from *J*-aggregates to other dyes playing role of exciton traps by Forster mechanism. In the present study we report unexpected behavior of the distance dependence of the energy transfer in "*J*-aggregate-exciton trap" system. Contrary to typical Forster energy transfer dependence as ~ d^{-6}, the trap sensitized luminescence reveals nonmonotonic dependence with a maximum at ~ 10 nm distance between the *J*-aggregates and the exciton traps.

Keywords: *j*-aggregates, exciton, energy transfer, exciton trap, luminescence.

Молекулярные агрегаты, так называемые *J*-агрегаты, являются экситонными системами, которые могут использоваться в качестве оптических антенн. Предыдущие эксперименты показали эффективный перенос энергии с *J*-агрегатов на другие красители, которые играют роль экситонных ловушек, по механизму Ферстера. В данном исследовании наблюдается неожиданное поведение зависимости переноса энергии в системе "*J*-агрегат — экситонная ловушка" от расстояния. В противоположность зависимости ферстеровского переноса энергии ~ d^{-6}, сенсибилизированная люминесценция ловушек выявила немонотонную зависимость с максимумом на расстоянии ~ 10 нм между *J*-агрегатами и экситонными ловушками.

Особливості перенесення екситонної енергії при варіюванні відстані між *J*-агрегатами і екситонними пастками. *О.В.Сорокін, І.Ю.Ропакова, І.А.Боровой, С.Л.Єфімова, Ю.В.Малюкін.*

Молекулярні агрегати, так звані *J*-агрегати, є екситонними системами, які можуть використовуватися як оптичні антени. Попередні експерименти показали ефективне перенесення енергії з *J*-агрегатів на інші барвники, що грають роль екситонних пасток, за механізмом Ферстера. У даному дослідженні спостерігається неочікувана поведінка залежності перенесення енергії у системі "*J*-агрегат — екситонна пастка" від відстані. На протилежність залежності ферстерівського перенесення енергії ~ d^{-6}, сенсибілізована люмінесценція пасток виявила немонотонну залежність з максимумом на відстані ~ 10 нм між *J*-агрегатами і екситонними пастками.

1. Introduction

J-aggregates are luminescent well-ordered organic nanoclusters formed by polymethine, porphyrine and some other dye molecules [1–6]. Due to high order degree of molecular chain packing, electronic excitations are delocalized within some molecular chain fragments and Frenkel excitons appear [1–6]. That results in the appearance of a new very narrow and intense absorption band (called J-band) bathochromically shifted with respect to the monomeric absorption band and a near resonant luminescence band. In some cases, depending on mutual arrangement of molecules, excitonic band is hypsochromically shifted (H-band) [1–6]. Due to excitonic nature of electronic excitations, J-aggregates reveal a number of unique spectral properties, such as abnormally high extinction coefficient (up to 10^6 $cm^{-1}\cdot M^{-1}$) and the excitons migration over considerable distances [1–6]. Thus J-aggregates can be used as an optical antenna for energy delivery purposes or for significant pumping of dyes gaining their bright luminescence [7].

In a number of articles, for various types of J-aggregates the exciton transport was studied using exciton traps [7–13]. As exciton traps, organic molecules were used, which the first excited singlet level lays below the bottom of the exciton band [7–13]. As it was demonstrated, the concentration dependence of the J-aggregates luminescence quenching by the exciton traps followed the modified Stern-Volmer law [11–13]. At the increase of the traps concentration, the stronger quenching the J-aggregates luminescence was observed [11–13]. Such dependence caused by combination of two effects, namely the exciton migration along the molecular chain and the resonance energy transfer of the exciton excitation to the trap. The Stern-Volmer law of the aggregate luminescence quenching supposes the Forster mechanism of the energy transfer to the exciton traps [14]. Indeed, that was confirmed in the experiments of the dye pumping by J-aggregates [7]. Therefore, keeping in mind the distance dependence for the Forster energy transfer as d^{-6} [14], one may assume a significant restriction of the J-aggregate application as optical antenna due to necessity to locate the exciton traps into the J-aggregates or in their close vicinity.

From other hands, recently it has been shown that for the J-aggregates formed in thin polymer films due to strong exciton-photon interaction surface exciton polaritons can appear which possess similar properties to localized plasmons in metallic nanoparticles [15, 16]. Moreover, the subwavelength field-confinement and the nanoscale luminescence enhancement for thin films J-aggregates were predicted [15, 16]. Such features can strongly affect the energy transfer process.

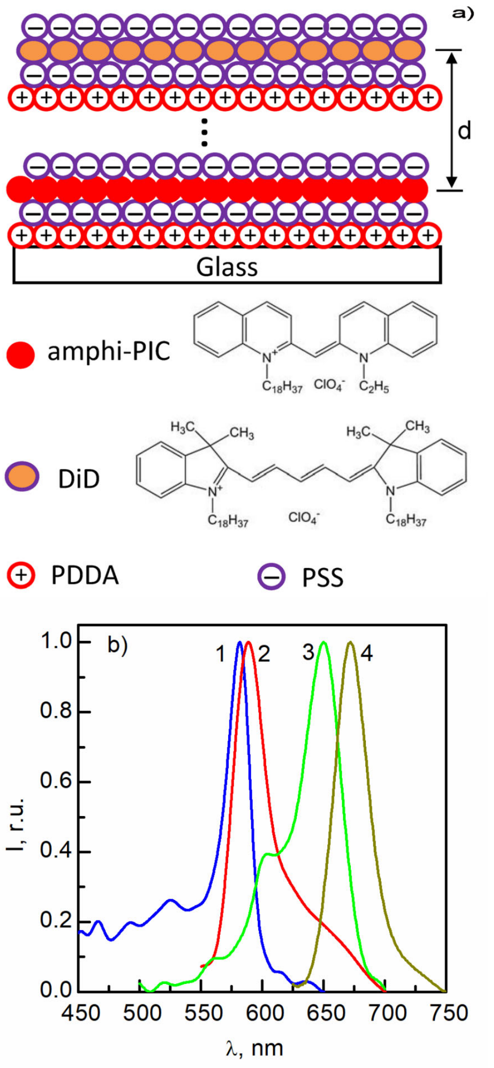

Fig. 1. a) Scheme of composite films containing amphi-PIC J-aggregates and DiD dye as exciton traps. b) Absorption (*1*, *3*) and luminescence (*2*, *4*) spectra of amphi-PIC J-aggregates (curves *1* and *2*) and DiD dye (curves *3* and *4*) in polymer films.

Thus, the goal of this letter was to study the energy transfer from the J-aggregates to the exciton traps in thin polymer films controlling the distance between them. For this purpose, the system of amphi-PIC J-aggregates and DiD dye as the exciton trap was chosen as well studied previously both in solutions [8, 13, 17] and polymer films (with a direct interaction between the J-aggregates and the traps) [12].

2. Experimental

DiD dye (1,1′-dioctadecyl-3,3,3′,3′-tetramethylindodicarbocyanine perchlorate, Fig. 1a), anionic polyelectrolyte PSS

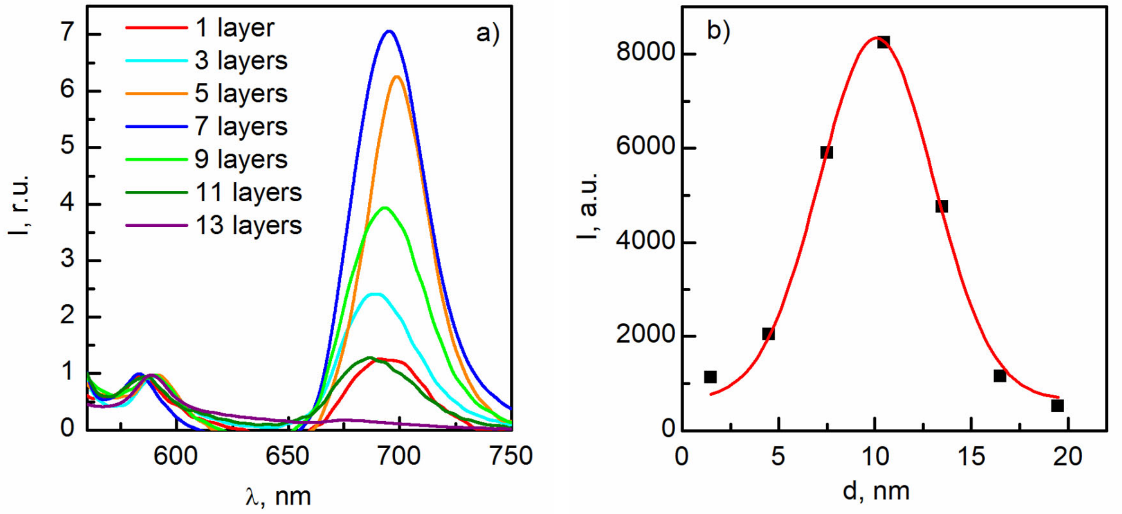

Fig. 2. a) Luminescence spectra (λ_{exc} = 530 nm) of the polymer films containing as separated layers amphi-PIC *J*-aggregates and DiD as exciton traps, depending on the number of spacing polymer layers. The spectra are excited to the corresponding *J*-band and normalized to *J*-aggregate luminescence intensities; b) The distance dependence of the trap luminescence intensity, which is fitted for illustration purpose only.

(poly(sodium 4-styrenesulfonate), average M_w ~ 70000 g/mol, powder) and cationic polyelectrolyte PDDA (poly(diallyldimethylammonium chloride), average M_w < 100000 g/mol, solution 35 wt. % in H_2O) were purchased from Sigma Aldrich (USA) and used as-received. Amphi-PIC dye (1-methyl-1′-octadecyl-2,2′-cyanine perchlorate, Fig. 1a) was synthesized by Dr. Igor Borovoy with purity controlled by NMR and thin layer chromatography.

Amphi-PIC *J*-aggregates were prepared by the dye dissolution in dimethyl formamide (DMF) to get a stock solution with concentration of 10^{-3} M. Then doubly distilled water was added to obtain a binary solution with 90 % water content. Thus, amphi-PIC concentration in final solution (DMF:water = 1:9) was 10^{-4} M. DiD (10^{-4} M) dye was used in DMF solution.

To prepare polymer film containing amphi-PIC *J*-aggregates and exciton traps (DiD) the layer-by-layer assembly (LbL) was used [6, 18]. In the LbL technique alternative multilayered polymer films can be deposited by means of electrostatic attraction onto an electrically charged substrate [6, 18]. Its main advantage is a controllable composite formation of dense thin (about 1.5 nm) layers of polymers and other species with a possibility of distance variation between different components [6, 18]. In particular, the LbL technique was successfully used for layered films formation containing *J*-aggregates [6, 19–23]. For the film preparation, a substrate glass plate was preliminarily cleaned with piranha acid (H_2SO_4 + hydrogen peroxide), that gives a negatively charged surface of glass. Then, the substrate is dipped into a water solution of polycation PDDA (1 wt.%) for coating with a positively charged film. Then, the glass plate was immersed into the polyanion PSS water solution (1 wt.%) resulting in negatively charged polymer coating. Then, the glass plate with polyelectrolyte films was immersed in the *J*-aggregate water solution. The *J*-aggregate layer was successively covered by PSS layer and then by DiD dye layer (Fig. 1). Finally, PSS layer covered the whole assembly. To change the distance between the *J*-aggregates and traps layers, the number of polymer layers between them was varied due to alternation of PSS and PDDA layers (Fig. 1) similar to *J*-aggregates — metal nanoparticles composites [21–23]. The single layer was deposited for 30 minutes. Between the adsorption cycles, the composite was washed three times with deionized water followed with drying by a stream of air.

Absorption spectra was registered using a microspectrometer USB4000 (OceanOptics, USA) supplied with an incandescent lamp. Luminescence spectra were recorded with the luminescence spectrometer Lumina (Thermo Scientific, USA) using a solid sample holder. Luminescence decay curves were collected using FluoTime 200 fluorescence lifetime spectrometer (PicoQuant, Germany) equipped with 531 nm picosecond pulsed laser diode head. An instrument response function (IRF) width for the whole setup was 100 ps. For decay curves analysis FluoFit software (PicoQuant, Germany) was used.

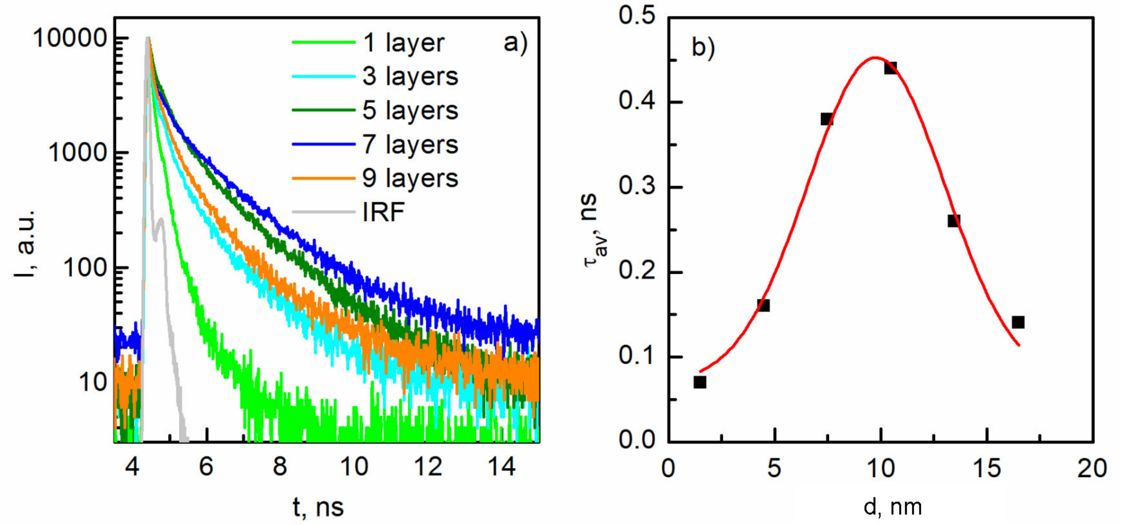

Fig. 3. a) Luminescence decays of DiD (λ_{exc} = 531 nm) depending on the distance to amphi-PIC J-aggregates layers in polymer films at the excitation into corresponding J-band; b) The distance dependence of the traps luminescence decay times, which is fitted for illustration purpose only.

3. Results and discussion

Due to long hydrophobic tail of amphi-PIC molecules (Fig. 1a) their J-aggregates possess cylinder-like structure [13]. It was found that amphi-PIC J-aggregates affected by significant static disorder leading to different exciton localization effects [5, 6, 13, 24]. As a result even in solutions with high water content, these J-aggregates reveal very wide J-band ($\Delta\nu_{FWHM}$ = 650 cm^{-1}) and a very small luminescence quantum yield (η ~ 0.3) in combination with short decay time (τ ~ 60 ps) [13]. From other hand, amphi-PIC J-aggregates preserve their structure in LbL film and demonstrate only small changes of it optical properties with J-band ($\Delta\nu_{FWHM}$ = 700 cm^{-1}) positioning at λ_J = 581 nm and the luminescence band (τ^{LbL} ~ 40 ps) positioning at λ_{lum} = 588 nm (Fig. 1b) [12]. Because of very small luminescence decay time, it changing due to energy transfer will not be analyzed below.

Previously, for exciton migration studying in amphi-PIC J-aggregates, DiD dye (Fig. 1) was successfully used as the exciton trap [8, 12, 13, 17]. It is caused by red shifted absorption (λ_{abs} = 650 nm) and luminescence (λ_{lum} = 675 nm) bands of DiD relatively to these of amphi-PIC J-aggregates (Fig. 1b). Hence, the excited singlet level of the exciton traps lays below the bottom of the exciton band. In addition, a good spectral overlap of the J-aggregate luminescence band and the trap absorption (Fig. 1b) provides quite large overlap integral and so, efficient energy transfer [14]. In LbL film the DiD decay curve is non-exponential with an average decay time (amplitude weighted) τ ~ 0.21 ns. Both in solution and in the LbL film DiD dye was used as the trap embedded into amphi-PIC J-aggregates allowing the exciton migration analyzing by Stern-Volmer method [12, 13].

For present study, the bilayer LbL film structure was created in which the J-aggregates and traps were in the different polymer layers separated by the inert polymer spacer with different thickness (Fig. 1a). In previous experiments, it was demonstrated that such structure of LbL film indeed allows to control the distance between metal nanoparticles and J-aggregates with high accuracy providing the single spacer layer thickness ~ 1.5 nm [21–23, 25].

The steady-state measurements of the luminescent properties of the created bilayer polymeric structures demonstrate distinctive evidence of energy transfer from the J-aggregates to the exciton traps at the condition of the direct J-aggregate excitation (Fig. 2a). The trap luminescence intensity as a function of the distance between the J-aggregates and the traps is shown on Fig. 2b. Assuming the Forster mechanism of the energy transfer between direct excited J-aggregates and the exciton traps, one would expect that the intensity of the traps luminescence should decrease according to the law ~ d^{-6} with increasing the distance d between the layer of aggregates and the layer of traps [14]. However, the data presented in Fig. 2 show that this law is not valid in our case.

Indeed, at the direct excitation into the *J*-aggregate absorption band and the increasing the distance between *J*-aggregates and exciton traps at the same its concentration, the intensity of the traps emission grows, reaches a maximum, and then decreases (Fig. 2b). Simultaneously, the luminescence decay time of the exciton traps varies according to the same dependence (Fig. 3). It is important to note that both the luminescence intensity and decay time reach their maximum at the same distance d (~ 10 nm) (Figs. 2 and 3).

Similar distance dependence for the luminescence of different species in vicinity of metal nanoparticles is well-known [21–23, 25–28]. Therefore, we could suppose that the trap luminescence enhancement is caused by plasmon-like effect of exciton-enhanced luminescence. However, for plasmon-enhanced luminescence the decay time quenching have to be expected with the maximum quenching at maximal luminescence enhancement [21–23, 25–28]. Contrary, for our case the trap luminescence decay time is increasing (Fig. 3b) synchronously with the luminescence intensity (Fig. 2b). Up to now, we didn't find the model which can explain the observed effect. As the exciton enhancement of the trap luminescence is a very promising phenomenon for using *J*-aggregates as the optical antenna, the further experiments and theoretical modeling are necessary.

4. Conclusions

At the direct excitation of amphi-PIC *J*-aggregates into J-band and the increase of the inert layer thickness, the nonmonotonic variation of the traps luminescence was observed, which did not follow the expected law ~ d^{-6}. Instead, the trap luminescence increases reaching a maximum at ~ 10 nm thickness of separating layer and then drops. The decay time of the traps reaches the maximum value at the same condition and then drops as well. The observed effect can't be explained within current models of energy transfer, so the further experiments are needed.

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