

Comparison of two polymethine dyes used as exciton traps for amphi-PIC J-aggregates

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Two polymethine dyes of different types (cyanine and squaraine) which possess hydrophobic properties have been used as exciton traps (energy acceptor) for amphi-PIC J-aggregates. Both dyes are found to interact with J-aggregates and reveal strong sensitized luminescence. The comparison of the two dyes has been done to find the most effective trap for incorporation into amphi-PIC J-aggregates. A number of advantages of the squaraine dye over cyanine one have been revealed. This dye is proposed as an effective exciton trap to study the exciton transport in J-aggregates.

Два полиметиновых красителя разных типов (цианиновый и сквариновый), которые обладают гидрофобными свойствами, использованы в качестве экситонных ловушек (акцепторов энергии) для J-агрегатов amphi-PIC. Установлено, что оба красителя взаимодействуют с данными J-агрегатами и выявляют интенсивную сенсibilizированную люминесценцию. Проведено сравнение свойств данных красителей в качестве ловушек, чтобы определить наиболее подходящий краситель для внедрения в J-агрегаты amphi-PIC. Обнаружено, что сквариновый краситель обладает рядом преимуществ по сравнению с цианиновым красителем. Данный краситель предложен для использования в качестве эффективной экситонной ловушки для исследования экситонного транспорта в J-агрегатах.

Recently, optical properties of organic nanoparticles have attracted growing attention [1–6]. J-aggregates (or Scheibe aggregates) stand out among a large family of organic nanoparticles. J-aggregates are luminescent well-ordered nanoclusters of non-covalently coupled luminophores, which are typically cyanines, porphyrines, or merocyanines [5–11]. Due to high ordering degree of molecular packing in the J-aggregate and a strong dipole-dipole interaction between molecules forming the J-aggregate, an electronic excitation is delocalized within a molecular chain. That causes the formation of excitonic states (Frenkel excitons) and results in unique optical properties of J-aggregates: extremely narrow (for organic molecules) spectral width of the absorption

band, resonant luminescence, giant oscillator strength, giant optical nonlinearities, etc. [7–9]. It is of interest that natural light harvesting complexes (LHC) providing an extremely fast and efficient energy transport of absorbed light to the photochemical reaction centers in plants and photosynthetic bacteria, are self-organized molecular aggregates with a circular structure, containing two rings of 8–18 molecules [12, 13]. Recently, it has been demonstrated that J-aggregates are the most promising objects to mimic LHC by artificial systems [6]. Thus, the study of an excitation energy transfer in J-aggregates is a problem of importance for numerous areas of nanotechnology that require an efficient energy delivery to a nano-scale reaction center.

There are numerous experimental works aimed at the study of exciton energy migration in J-aggregates [6, 14–32]. Two approaches are used to determinate the exciton transport characteristics. The first one is to consider the time parameters of exciton luminescence decay [14–17]. The second approach is a direct observation of the exciton energy transfer to an energy or electron acceptor which is imbedded into the J-aggregate and acts as a exciton trap [6, 18–31]. The data concerning the efficiency of exciton energy trapping differ significantly. For instance, 50 % quenching of the J-aggregate luminescence is reported at the ratio of 1 trap molecule to 250 molecules forming the J-aggregate [25, 30], whereas in [19] this ratio is reported to be 1:12000. It should be noted that the most of these researches were done on J-aggregates obtained in LB films [19, 20, 22, 24, 30], polymer layers [23, 29, 31] or even liposome surfaces [21]. J-aggregates obtained on such surfaces are supposed to possess more perfect 2D structure described by the brickstone lattice [7–9]. That can explain the high efficiency of the exciton transport reported in [19]. Really, if the exciton trap is located in other layer than the J-aggregate, the exciton migration efficiency is much less [19, 29, 30]. When J-aggregates are formed in solutions, their structure is very complicated and a lot of different conditions can effect the exciton migration therein [5, 6]. We can refer to three works only reporting the incorporation of an exciton trap into J-aggregates self-organized in solutions [6, 18, 32]. In [25–28], formation of J-aggregates of Cyanine Dye Pendant Polymer (CDP) in a solution is directed by a polymerization rather than self-assembling.

In this work, we report the observation of the exciton energy transfer in J-aggregates of cationic amphiphilic cyanine dye amphi-PIC (Fig. 1a) to two energy acceptors: a zwitterionic diindolenine derivative of squaraine dye (Sq-2Me) (Fig. 1b) and cationic amphiphilic cyanine dye 1,1'-dioc-tadecyl-3,3,3', 3'-tetramethylindodicarbocyanine perchlorate (DiD) (Fig. 1c). Both cyanine and squaraine dyes belong to the class of polymethine dyes and exhibit a sharp and intense electron absorption in the region from visible to near-IR, and sometimes show fluorescence emission properties [9, 33–35]. However, the intramolecular electron resonance in the cyanine π -conjugation system is extended from the heterocyclic component at one end to that at the other

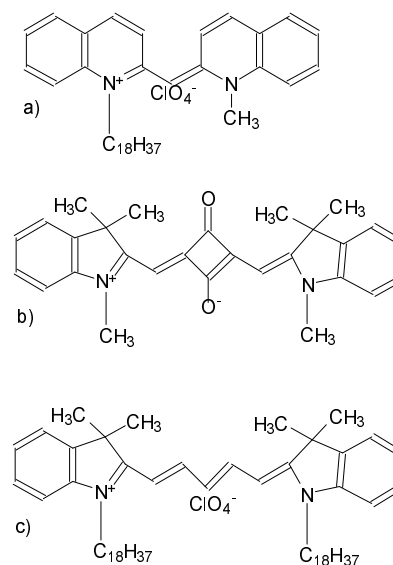


Fig. 1. Molecular structures of the dyes investigated: a) amphi-PIC, b) Sq-2Me, c) DiD.

end [33]. On the other hand, squaraine dyes consist of the central cyclobutene and the heterocycles at both ends, yielding an electron donor-acceptor-donor (D-A-D) charge transfer structure [34, 35]. Due to their structure, squaraines reveal hydrophobic properties [34, 35].

The dyes were obtained from the dye collection of Dr. I. A. Borovoy, the dye purity was controlled by thin layer chromatography. Sample solutions containing amphi-PIC J-aggregates with traps were prepared as follows. Sq-2Me or DiD and amphi-PIC were dissolved in dimethyl formamide (DMF) to form a mixture at a preset ratio, then doubly distilled water was added to obtain a binary solution DMF:water with 90 % water content. The prepared samples were stored for one hour to attain equilibrium. The concentration of amphi-PIC in all solutions was $5 \cdot 10^{-5}$ M. The luminescence spectra were recorded using a spectrofluorimeter based on two MDR-23 grating monochromators and a xenon lamp. One of the monochromators was used to select a required wavelength (FWHM ~ 0.5 nm), the other one collected the luminescence. In all experiments the excitation wavelength was 530 nm. For absorption spectra registration, the spectrofluorimeter was supplied with an incandescent lamp.

DiD was used as an exciton trap in amphi-PIC J-aggregates [18, 32], whereas Sq-2Me is a new dye which can be used as an effective energy trap. So it is interesting to compare spectral parameters of these two

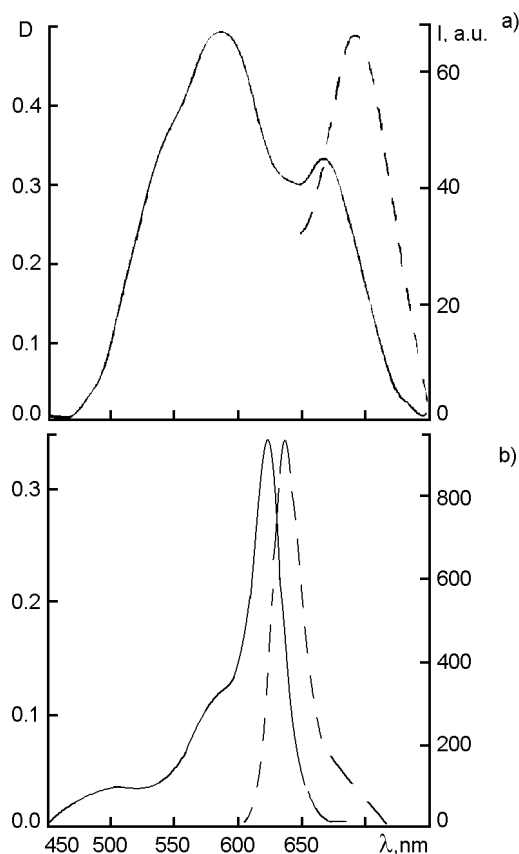


Fig. 2. Absorption (solid line) and luminescence (dashed line) spectra of DiD (10^{-5} M) (a) and Sq-2Me (10^{-5} M) (b) in a binary solution DMF:water (1:9).

dyes. Both dyes are well soluble in DMF and reveal quite narrow absorption and luminescence bands peaked at $\lambda_{abs} = 650$ nm and $\lambda_{lum} = 675$ nm for DiD and $\lambda_{abs} = 636$ nm and $\lambda_{lum} = 648$ nm for Sq-2Me. However, DiD and Sq-2Me reveal different spectral properties in a binary DMF:water solution, where amphi-PIC J-aggregates are formed. The absorption spectrum of DiD is strongly broadened and reveals two maxima ($\lambda_1 = 585$ nm and $\lambda_2 = 665$ nm) and its luminescence ($\lambda_{lum} = 690$ nm) is almost absent (Fig. 2a) that points to the formation of non-fluorescent aggregates (H-type [8, 9]). In contrast, Sq-2Me is well soluble in the binary solution, reveals quite narrow absorption and luminescence bands ($\lambda_{abs} = 623$ nm and $\lambda_{lum} = 637$ nm) and an intense emission (Fig. 2b). In solutions containing J-aggregates, an intense sensitized luminescence of both DiD and Sq-2Me was observed (Fig. 3). The luminescence excitation spectra of both dyes (not shown) exhibit bands which correspond to the J-aggregate absorp-

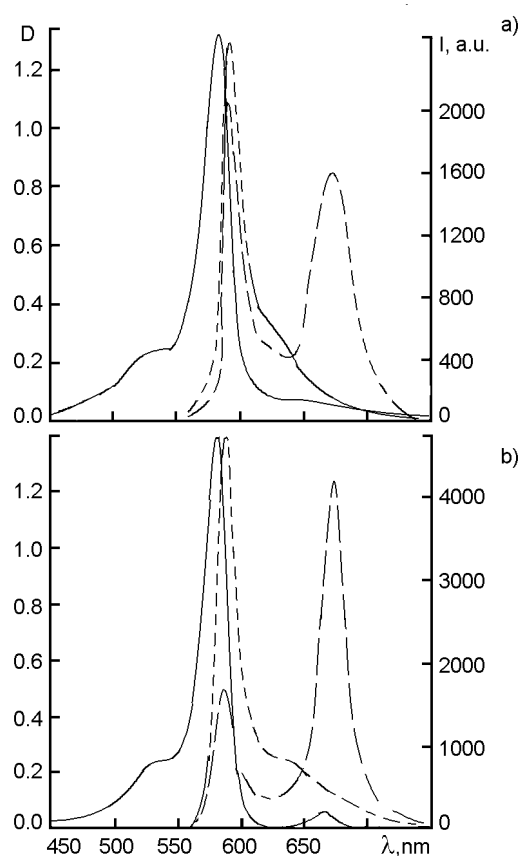


Fig. 3. Absorption (solid line) and luminescence (dashed line) spectra of amphi-PIC J-aggregates containing the traps (DiD (a) and Sq-2Me (b), amphi-PIC:trap = 20:1) in a binary solution DMF:water (1:9). Short dashed lines are luminescence spectra of amphi-PIC J-aggregates without the traps.

tion band (J-band) that is an evidence for the energy transfer [32]. Moreover, the spectral bands of both dyes in the presence of J-aggregates (Fig. 3) are shifted as compared to the aggregate-free solutions (Fig. 2). However, the character of the shift differs strongly for DiD and Sq-2Me. In the solution containing J-aggregates, the DiD absorption and luminescence bands ($\lambda_{abs} = 660$ nm and $\lambda_{lum} = 675$ nm) are similar to those in DMF, while in case of Sq-2Me, are strongly red-shifted ($\lambda_{abs} = 665$ nm and $\lambda_{lum} = 671$ nm) as compared to the DMF. At the same time, the luminescence intensity of Sq-2Me increases as compared to the binary DMF:water solution and the luminescence band becomes narrower ($\Delta\nu_{FWHM} = 490$ cm^{-1} instead of 700 cm^{-1}). The spectra (Fig. 3) show that in the solution there are no squaraine molecules not coupled with J-aggregates. That evidences a strong inter-

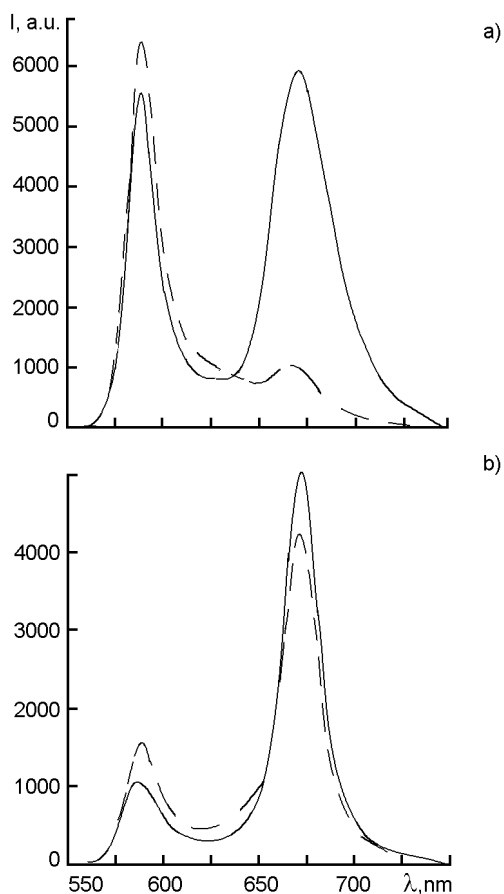


Fig. 4. Luminescence spectra of amphi-PIC J-aggregates with the traps (DiD (a) and Sq-2Me (b), amphi-PIC:trap = 20:1) in a binary solution DMF:water (1:9) at different preparation conditions: solid line, the traps are embedded to the J-aggregates at their formation; dashed line, the traps are embedded in the formed J-aggregates.

action between Sq-2Me and amphi-PIC J-aggregates. Such strong influence of the Sq-2Me-amphi-PIC J-aggregate interaction on Sq-2Me spectral properties could not be explained only by the solubilization effect. Our investigations show that when the dye is solubilized by cetyl pyridinium bromide micelles in the binary solution, its spectral properties are similar to that in DMF (not shown). A reasonable explanation of the significant long-wavelength shift of the Sq-2Me spectral bands is the interaction of the squaraine π -electron system with excitonic states of J-aggregates and the Sq-2Me electron density redistribution. Such redistribution is similar to the effect of extending Sq-2Me π -electron system and results in the long-wavelength shift of its spectral bands. Such unique effect of the Sq-2Me-J-aggre-

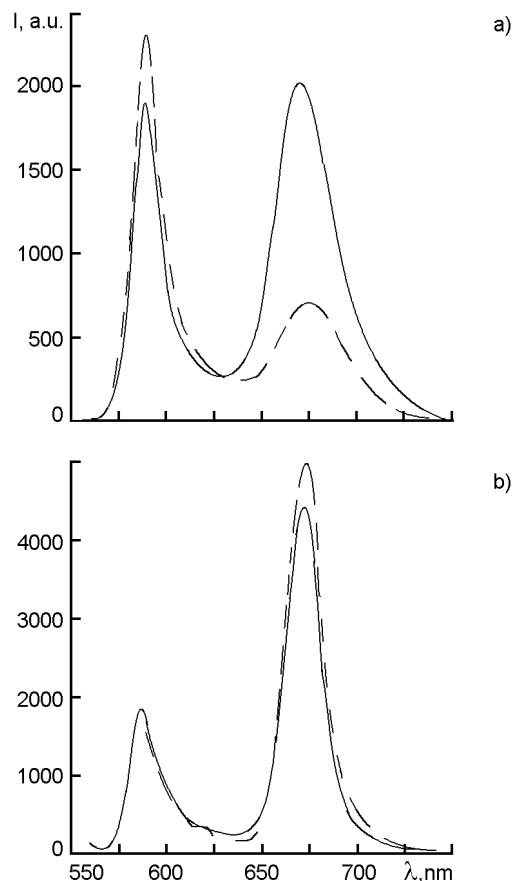


Fig. 5. Luminescence spectra of amphi-PIC J-aggregates with the traps (DiD (a) and Sq-2Me (b), amphi-PIC:trap = 20:1) in a binary solution DMF:water (1:9): solid line, the freshly prepared samples; dashed line, the samples after 2 day storage.

gate interaction on the squaraine spectral properties facilitates the Sq-2Me application as a specific trap for amphi-PIC J-aggregates.

Another advantage of Sq-2Me over DiD is that the J-aggregate luminescence is quenched much stronger by the Sq-2Me trap (Fig. 3). Both Sq-2Me and DiD possess hydrophobic properties which favor the dye interaction with J-aggregates. Nevertheless, in contrast to DiD, Sq-2Me does not have long hydrocarbon tails, so the dyes are incorporated into aggregates by different ways that affect the traps capability to exciton trapping.

To find out the interaction way of the traps with the J-aggregates, different methods of samples preparation were used. Both traps are well incorporated into aggregates at the moment of a sample preparation and, consequently, formation of J-aggregates (Fig. 4, solid lines). However, if the traps

are added to a solution containing J-aggregates, the degree of the trap coupling with J-aggregates was found to differ strongly depending on the trap type. Due to long alkyl tails (see Fig. 1), DiD is water-insoluble and practically does not interact with formed J-aggregates (Fig. 4a, dashed line), whereas Sq-2Me is well incorporated into J-aggregates (Fig. 4b, dashed line) and in this case the energy transfer efficiency is just slightly lower as compared to the case of the trap incorporation at the moment of J-aggregate formation (Fig. 4b, solid line).

It has been found that the storage of samples in darkness for 2 days affects the energy transfer efficiency to the traps DiD and Sq-2Me in different ways (Fig. 5). Efficiency of energy transfer to the DiD trap is revealed to be much lower (Fig. 5a, dashed line) as compared to the freshly prepared sample (Fig. 5a, solid line) that points to the DiD dye displacement out of J-aggregates. At the same time, the solution with Sq-2Me trap shows high stability and the energy transfer process becomes even more effective (Fig. 5b).

As it was shown in [36], the structure of amphi-PIC J-aggregates is a cylindrical packing of ring-like units. Another feature of amphi-PIC J-aggregates is changing their morphology as a result of J-aggregate size increasing in time [37]. We suggest that the DiD trap is incorporated between J-aggregate rings due to steric hindrance (two long alkyl tails, Fig. 1c). So the capability of DiD to trap excitons is not high (Fig. 3a). During the solution storage, coagulation of the aggregates results in the trap displacement to the defect regions that leads to a drop of the energy transfer efficiency (Fig. 5a). Unlike DiD, Sq-2Me is incorporated into the J-aggregate ring and during the sample storage does not displaced out of the J-aggregate. Thus, the capability of Sq-2Me to trap excitons is larger (Fig. 3b) as compared to DiD.

To conclude, two polymethine dyes DiD and Sq-2Me of different types (cyanine and squaraine, respectively) have been studied as exciton traps for amphi-PIC J-aggregates. Unlike DiD which was used as an exciton trap for amphi-PIC J-aggregates before, Sq-2Me is used for the first time. Both dyes are coupled with amphi-PIC J-aggregates and reveal sensitized luminescence as a result of exciton trapping. The experimental data obtained demonstrate the advantages of the squaraine dye (Sq-2Me) as compared to the cyanine one (DiD). The spectral

bands of Sq-2Me are significantly red-shifted due to a specific interaction with the J-aggregates. The solution with Sq-2Me trap has revealed high stability and the energy transfer process becomes even more effective in time as compared to the solutions with the DiD trap. That allows us to propose Sq-2Me as an exciton trap in exciton transport investigations that is very important for energy delivery nanosystems creation.

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Порівняння двох поліметинових барвників, що використані в якості екситонних пасток для J-агрегатів amphi-PIС

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Два поліметинових барвника (ціаніновий та сквариновий), які мають гідрофобні властивості, використано в якості екситонних пасток (акцепторів енергії) для J-агрегатів amphi-PIС. Встановлено, що обидва барвники взаємодіють з даними J-агрегатами та виявляють інтенсивну сенсibilізовану люмінесценцію. Проведено порівняння властивостей цих барвників як пасток для виявлення найбільш придатного для введення до J-агрегатів amphi-PIС. Виявлено, що сквариновий барвник має низку переваг у порівнянні з ціаніновим барвником. Цей барвник запропоновано для використання як найбільш ефективну екситонну пастку для дослідження екситонного транспорту в J-агрегатах.