

## Influence of pseudoisocyanine J-aggregate agglomeration on the optical properties

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In the present letter, we have report the changing optical properties of pseudoisocyanine J-aggregates formed in electrolyte aqueous solution under agglomeration. The more pronounced changes occur in the case of the luminescence characteristics, which reveal about 30% improvement. The main reason has been supposed to be avoiding of the exciton trapping by local defects due to the inter-aggregate excitonic excitations energy transfer within the agglomerate.

**Keywords:** J-aggregate, agglomerate, luminescence, exciton, pseudoisocyanine.

Исследовано изменение оптических свойств J-агрегатов псевдоизоцианина, сформированных в электролитном водном растворе, при их агломерации. Показано, что наибольшие изменения происходят в случае люминесцентных характеристик, которые выявляют приблизительно 30% улучшение. Выдвинуто предположение, что главной причиной этого является избежание захвата экситонов локальными дефектами вследствие переноса энергии экситонных возбуждений между агрегатами в агломератах.

**Вплив агломерації J-агрегатів псевдоізоціаніну на їх оптичні властивості.**  
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Досліджено зміну оптичних властивостей J-агрегатів псевдоізоціаніну, сформованих у електролітному водному розчині, при їх агломерації. Показано, що найбільші зміни відбуваються у випадку люмінесцентних характеристик, які виявляють приблизно 30% покращення. Висунуто припущення, що головною причиною цього є уникнення захвату екситонів локальними дефектами внаслідок перенесення енергії екситонних збуджень між агрегатами в агломератах.

### **1. Introduction**

Highly ordered luminescent aggregates of organic dyes called J-aggregates are a prominent example of supramolecular systems [1-9]. Typically, dye aggregation is undesirable process leading to dye luminescence quenching due to an excitation energy transfer over identical molecules in the agglomerate (so-called homo-FRET) and an enhancement of non-radiative energy loss [10]. However, in the case of J-aggregates, the dye molecules form ordered molecular chains and due to translational symmetry

the electronic excitation delocalizes over segments of the molecular chains leading to molecular excitons (Frenkel excitons) occurrence [1-9]. As a result, J-aggregates demonstrate a number of unique spectral properties, which are distinctly different from those of the individual molecules constituting the aggregate: very narrow as for organics spectral lines (down to tens of  $\text{cm}^{-1}$  at low temperatures), near-resonant luminescence, large extinction coefficients (up to  $10^6 \text{ cm}^{-1}\cdot\text{M}^{-1}$ ), giant third-order optical nonlinearities (up to  $10^{-5}$  esu), exciton superradiance, energy migration up to micron distances, etc. [1-9]. Thus

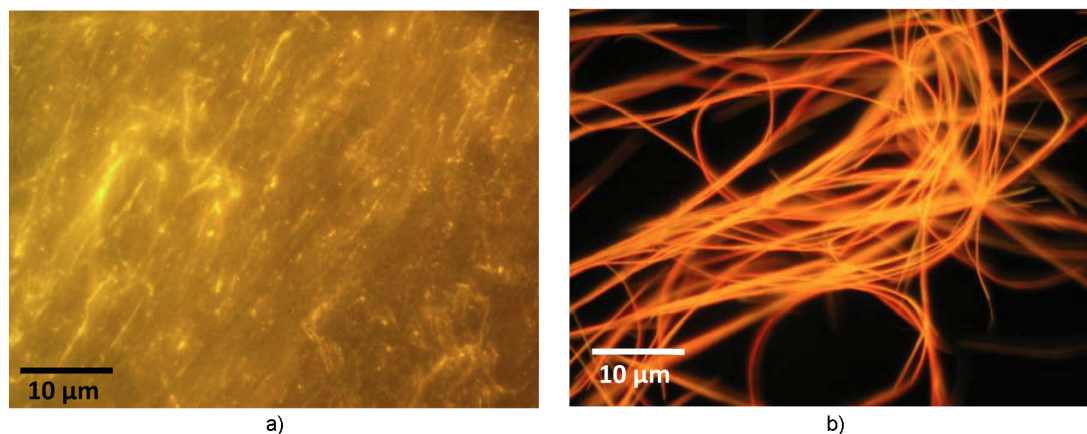


Fig. 1. Luminescent images of PIC J-aggregates: a) immediately after preparation, b) 1 day after preparation.

they attract a great attention both as an interesting low dimensional system for a fundamental study of the excitonic dynamics and as a perspective material for various applications [1-9].

The well-known phenomenon for J-aggregates is their further agglomeration especially in the presence of aggregation facilitating additives like salts, bases and so on [11-15]. For example, well-studied pseudoisocyanine (PIC) J-aggregates have fiber-like morphology with individual aggregate diameter 2.3 nm [16], but in electrolyte aqueous solutions they agglomerate into much larger "bundles" [11,14,17]. Different derivatives of 5,5',6,6'-tetrachlorobenzimidacarbocyanine (TDC) dye also forms bundles of the fiber-like individual aggregates which in their turn could have the tubular structure [18-21].

However, the influence of J-aggregate agglomeration on the optical properties is not clearly understood and need to be studied. For example, in the case of amphi-PIC J-aggregates broadening the luminescence band with simultaneous decreasing the luminescence decay time under agglomeration was observed [13]. It was ascribed to effective luminescence quenching by the local traps appeared on the contact sites between individual J-aggregates [13]. For C8S3 J-aggregates (one of TDC derivatives) much more efficient exciton migration were found in the case of aggregate bundles (average exciton migration length of several hundreds of nanometers) comparing with individual aggregates (average exciton migration length of 140 nm) [22]. The later pointing to efficient energy transfer between individual aggregates within the agglomerate [22].

In the present letter, we have reported the optical changes for PIC J-aggregates in electrolyte aqueous solution under their agglomeration.

## 2. Experimental

Pseudoisocyanine dye (1,1'-diethyl-2,2'-cyanine iodide, PIC) was purchased in Sigma Aldrich (USA) and used without further purification. Sample solutions were prepared by dissolving PIC (0.5 mM) in an aqueous NaCl (0.2 M) solution under moderate heating ( $< 80$  °C). Then the solutions were cooled down to room temperature. For microscopic investigations, a drop of the sample solution was placed between a glass slide and a cover slip.

Absorption spectra were registered using a microspectrometer USB4000 (OceanOptics, USA) supplied with an incandescent lamp. Luminescence images and spectra were recorded using the luminescent microscope MIKMED-2 var.11 (LOMO, Russia) coupled both with Mpixels microscope digital camera DCM510 (Oplenic Optronics, USA) and microspectrometer USB4000 (OceanOptics, USA) via a home-made fiber-optic adapter attached to the 20<sup>X</sup> eyepiece. Spectral output of the microspectrometer USB4000 was calibrated using calibrated tungsten halogen lamp HL-2000-CAL (OceanOptics, USA). Luminescence was excited at 450-480 nm and collected in the 560-700 nm spectral range. Absolute quantum yield of photoluminescence for all solutions was measured using a home-made integrating sphere (diameter of 100 mm), which provides a reflectance  $> 99\%$  over the 400-1000 nm range. As an excitation source, a Ar-laser (ModuLaser, USA) line ( $\lambda = 514$  nm) was used. The abso-

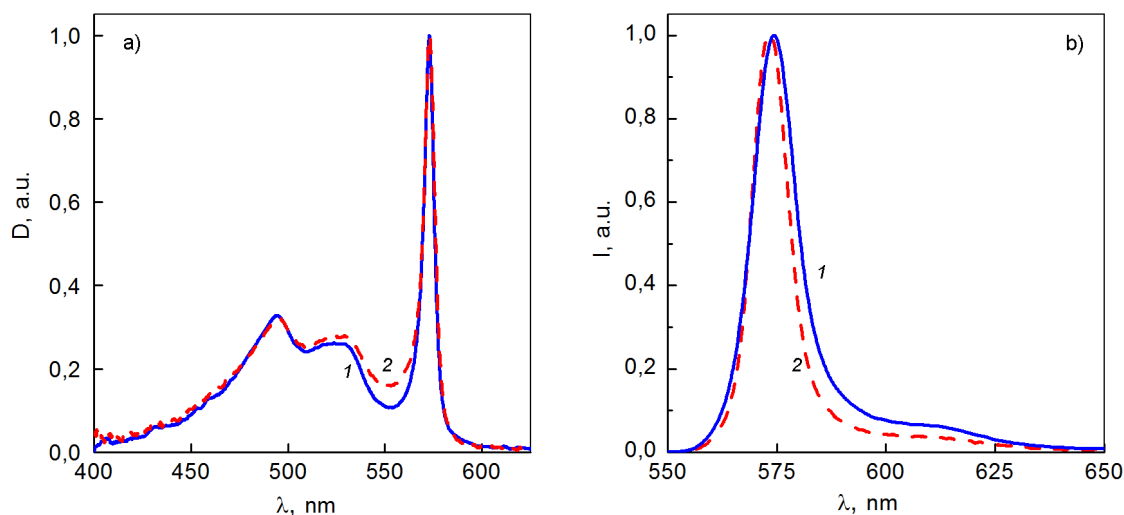


Fig. 2. Absorption (a) and luminescence (b) spectra of PIC J-aggregates: 1 – immediately after preparation, 2 – 1 day after preparation.

lute quantum yield was calculated using the two measurement method [23] taking into account self-absorption correction of luminescence spectrum [24] due to a very small Stokes shift characteristic for J-aggregates. The experimental setup was adjusted and tested on standard dyes such as rhodamine 6G (in ethanol,  $C = 10^{-5}$  M,  $Q_{lit} = 0.9435$ ) resulting in  $\pm 5\%$  accuracy which is typical for such type of setup [23]. Luminescence decay spectra were registered using FluoTime 200 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. The solid sample holder was used to provide front face illumination. For decay curves analysis FluoFit software (PicoQuant, Germany) was used.

### 3. Results and Discussion

As it was mentioned above, in electrolyte aqueous solutions PIC J-aggregates thin fibers agglomerate into large bundles [11,14,17]. However, this process is not instantaneous and to get the solution with the predominant large bundles takes about 24 h [14]. Indeed, the freshly prepared solution of PIC J-aggregates reveals bulky luminescent "cloud" [14] with mainly small fibers distinguished (Fig. 1a). This situation is correspondent to the initial stage of bundles formation so J-aggregates mainly present in form of individual fibers or small bundles which size couldn't be resolved by optical microscopy [11,14]. In 1 day after prepara-

tion (Fig. 1b), the PIC J-aggregate solution reveals mainly large fibers with diameters up to 1  $\mu\text{m}$  and lengths up to hundreds of microns, which undoubtedly are large bundles [11,14].

Large bundles formation leads to PIC J-aggregates optical properties modification, especially luminescent ones (Figs. 2 and 3). Contrary to previously reported observation [14] absorption spectrum reveals minor changes, although the excitonic bathochromic band (J-band) slightly broaden from  $\Delta v_{FWHM}^{fresh} \sim 185 \text{ cm}^{-1}$  to  $\Delta v_{FWHM}^{bundles} \sim 220 \text{ cm}^{-1}$  (Fig. 2a). As it well-known, J-aggregate excitonic band width is dependent on the exciton delocalization length  $N_c$ , which is a number of coherently coupled monomers and could be estimated as [7]:

$$N_c = \frac{3 \cdot (\Delta v_{FWHM}^{mon})^2}{2 \cdot (\Delta v_{FWHM}^J)^2} - 1, \quad (1)$$

where  $\Delta v_{FWHM}^{mon}$  and  $\Delta v_{FWHM}^J$  are full widths at half maximum of the monomer and J-bands, respectively. Using  $\Delta v_{FWHM}^{mon} = 990 \text{ cm}^{-1}$  for main electronic transition of PIC monomers in the solution at low concentration [25,26] we obtain  $N_c^{fresh} \sim 44$  and  $N_c^{bundles} \sim 30$ , respectively. The exciton delocalization length decreasing could be assigned with the static disorder decreasing in J-aggregate agglomerates [27].

Contrary to J-band slight widening luminescence band of PIC J-aggregates became narrower and slightly blue-shifted for bundles (Fig. 2b). Such transformation is ac-

accompanied by luminescence decay time increasing from  $\tau^{fresh} \sim 1$  ns to  $\tau^{bundles} \sim 1.4$  ns (Fig. 3) and luminescence quantum yield increasing from  $\eta^{fresh} \sim 0.25$  to  $\eta^{bundles} \sim 0.38$ . Such changes are opposite to those observed for amphi-PIC J-aggregate agglomeration [13]. The PIC J-aggregate luminescence characteristics enhancement could be understood taking into account large-scale exciton migration in J-aggregate agglomerates with inter-aggregate energy transfer found for C8S3 J-aggregates [22]. As PIC J-aggregates have similar fiber-like morphology with bundle formation we could suppose similar effective exciton migration which is impossible for much smaller amphi-PIC J-aggregates [13]. Due to the inter-aggregate excitonic excitations energy transfer within the agglomerate and quite large the exciton delocalization length leading to smaller exciton-phonon coupling [28], excitons in PIC J-aggregate bundles could avoid the trapping by stronger static disorder and inter-aggregate boundary induced defects. These defects supposed to be responsible for amphi-PIC J-aggregates luminescence properties degradation at the agglomeration [13].

Moreover, the strong photobleaching for PIC J-aggregates in solutions is well-known [14]. It has been found [14] that photobleaching expanded from separated sites of PIC fibers, possibly defected ones. We found that photobleaching is much more pronounced in the case of freshly prepared samples, possibly leading to worse luminescence characteristics. Indeed, successive measurement of luminescent decays in the same sample site results in monotonic luminescence decay curve shortening. We could suppose that the J-aggregate agglomeration leads to increasing photostability, particularly, again, due to less efficient trapping excitons by the defect sites.

It should be mentioned that further morphology transformation into the crystallites [14] which begin to develop after 1 week of PIC J-aggregates preparation leads to significant degradation of their optical properties. As an example, the luminescence decay became a very short ( $\tau^{week} \sim 0.13$  ns) with the luminescence quantum yield decreasing to  $\eta^{week} \sim 0.12$  (Fig. 3).

#### 4. Conclusions

The large agglomerates formation of PIC J-aggregates in electrolyte solutions leads to their luminescent characteristics enhancement despite the static disorder in-

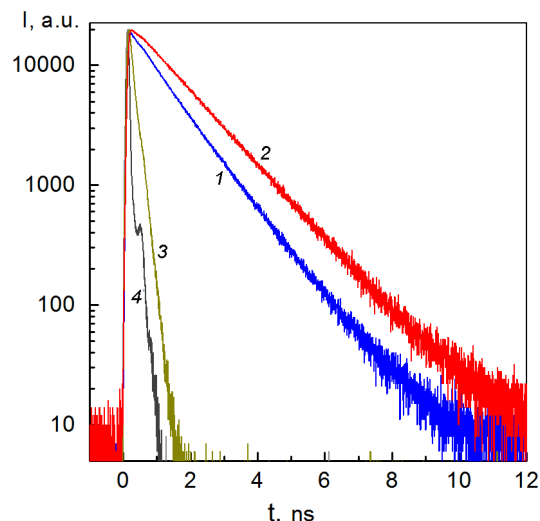


Fig. 3. Luminescence decay curves of PIC J-aggregates: 1 – immediately after preparation, 2 – 1 day after preparation, 3 – 1 week after preparation, 4 – IRF.

creasing. The main reasons for that supposed to be effective inter-aggregate excitonic excitations energy transfer, which increases the exciton migration efficiency, and increased J-aggregate photostability within the agglomerates. So, for PIC J-aggregate exploiting rather 1 day aged solution should be used instead the freshly prepared one. However, overlong aging should be prevented to avoid the J-aggregate optical properties degradation.

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