Using cyanine dye J-aggregates as luminescence probe for nanostructured media

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Due to excitonic nature of electronic excitations in J-aggregates causing the unique spectral properties they successfully applied as luminescent probes in biology. In present report we demonstrate a possibility using J-aggregates as the probe for nanostructured materials basing on BIC J-aggregates. As the probing tool the exciton delocalization length has been used as well as the lifetime. It has been shown direct dependence of the exciton characteristics of the J-aggregates on the specific features of solid matrices such as nanoporous matrix and polymer films.

Keywords: J-aggregates, nanoporous matrix, polymer films.

Исследована возможность применения J-агрегатов в качестве зонда для наноструктурированных материалов на основе J-агрегатов красителя BIC. В качестве зондирующего инструмента использованы длина делокализации экситонов и время их жизни. Показана прямая зависимость экситонных характеристик J-агрегатов от особенностей твердотельных матриц, таких как нанопористая матрица и полимерная пленка. Благодаря экситонной природе электронных возбуждений J-агрегаты обладают уникальными спектральными свойствами, что делает их перспективными для применения в качестве люминесцентных зондов в биологии.

Використання J-агрегатів ціанінових барвників в якості люмінесцентних зондів для наноструктурних середовищ. *О.В. Сорокін, І.Ю. Ропакова, І.А. Боровой, І.І. Беспалова, С.Л. Єфимова*

Досліджено можливість використання J-агрегатів в якості зонда для наноструктурованих матеріалів на основі J-агрегатів барвника BIC. У якості зондуючого інструмента використано довжину делокалізації екситонів і час їх життя. Показано пряму залежність екситонних характеристик J-агрегатів від особливостей твердотільних матриць, таких як нанопориста матриця і полімерна плівка. Завдяки екситонній природі електронних збуджень J-агрегати мають унікальні спектральні властивості, що робить їх перспективними для застосування в якості люмінесцентних зондів у біології.

1. Introduction

In modern optics the most popular destinations are optoelectronics, photovoltaics, optical methods of recording and processing of information [1-3]. They are inseparably linked with the nanophotonics where a special role is played by organic fluorescent nanostructures, such as conjugated polymers and J-aggregates, due to their unique spectral properties, relative ease of manufacture and enormous opportunities of functional design [1-3]. The photophysical characteristics of J-aggregates, such as narrow absorption band, resonant fluorescence, giant third-order susceptibility, high oscillator strength etc., are dramatically differ-

ent from those of the individual molecules forming the aggregate [4-8]. Such optical properties of J-aggregates are explained by strong interaction between the molecules and their ordering within the aggregates resulting in delocalization of electronic excitations over certain molecules on the chain with Frenkel exciton formation [4-8]. As a result a red-shifted exciton band (J-band, the "face-to-tail" arrangement) appears thought depending on a molecular packing in the aggregate chain a blue-shifted exciton band (H-band, the "face-to-face" arrangement), or both J- and H-bands (the "herringbone" arrangement with two molecules in the chain unit resulting in Davydov-splitting [9]) can be also observed [4-6]. The special feature of J-aggregates is a close correlation between J-aggregate excitonic properties and structure that opens up possibilities for the manipulation of J-aggregate optical characteristics by changing the condition of nanocluster formation [4-8].

J-aggregates can be applied in many areas of science: in electronic engineering for preparing some elements for solar panels or for creation lighting devices of new generation, they also can be used for biomedical applications as luminescent nanoprobes or for photodynamic therapy [4-8,10]. The specific feature of J-aggregates is strong dependence of the spectral properties (e.g. J-band width and lifetime) on the exciton delocalization length which is typically much smaller comparing with aggregate physical size [4-8]. So, the exciton delocalization length could be applied to probe different media especially nanostructures ones first of all using simple linear absorption [11]. Of course, luminescence characteristics also important and provides additional information [4-8].

Unfortunately, J-aggregates could change their structure in different media, especially solid nanostructured materials like nanoporous matrices or polymer films [12-14]. However, recently we found that J-aggregates of BIC dye possess by spherical structure with diameter about 20 nm which is unusual for J-aggregates [5] and preserved in different nanostructured media [12,15]. BIC J-aggregates reveal single relatively narrow J-band and popular for different applications [4,5,12,15,16-19]. So the aim of present report is to compare the spectral properties of BIC J-aggregates in different nanostructured media and to make a conclusion if they could be used as the luminescent probes for these media.
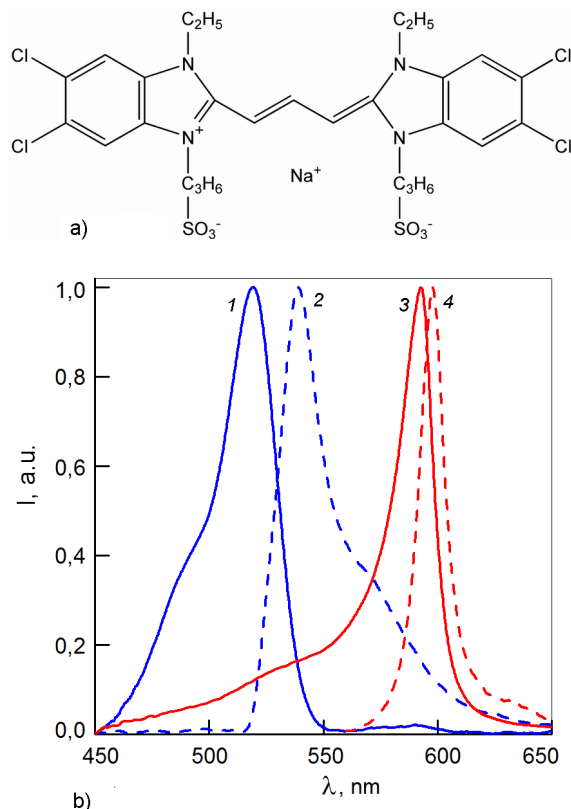

Fig. 1. a) Structural formula of BIC dye; b) absorption (*1,3*) and luminescence (*2,4*) spectra of BIC (C = 10^{-4} M) monomers in ethanol (*1,2*) and J-aggregates in water (*3,4*).

2. Experimental

BIC dye (1,1'-disulfopropyl-3,3'-diethyl-5,5',6,6'-tetrachlorobenzimidazolylcarbocyanine sodium salt) dye was synthesized by Dr. I.A. Borovoy with purity controlled by NMR and thin layer chromatography. J-aggregates were prepared by dye dilution in deionized water at definite concentration. Poly(vinyl alcohol) (PVA, Mw ~ 89000 – 98000 g/mol) and poly(diallyldimethylammonium chloride) (PDDA, average Mw < 100000 g/mol, solution 35 wt.% in H_2O) were purchased from Sigma Aldrich (USA) and used as-received.

To prepare spin-coated polymer films the dye was dissolved in PVA (4 wt.%) water solution at definite concentration. After that 75 μL of the obtained solution was spread on a glass substrate and rotated for 3 min. at 2000 rpm velocity using lab centrifuge with home-made substrate holder.

To prepare layered polymer films the spray layer-by-layer assembly method has been used [13,14]. For this purpose commercially available paintbrushe 80-897 (Miol,
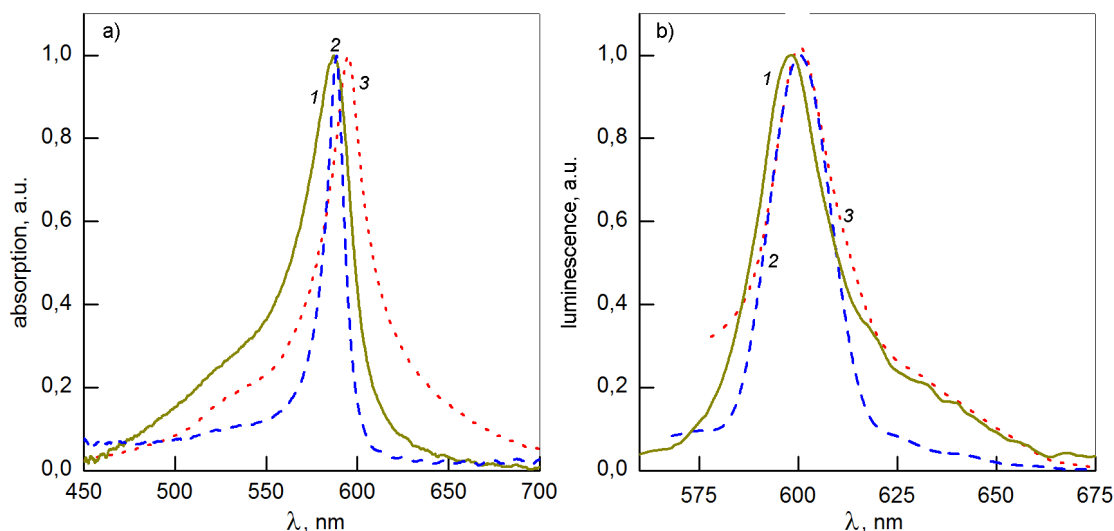
Fig. 2. Absorption (a) and luminescence (b) spectra of BIC J-aggregates in different solid matrices: *1* – LbL film, *2* – PVA spin-coated film and *3* – AAO matrix.

China) has been used. A substrate glass plate was preliminarily cleaned by hot (95 °C) piranha acid (H_2SO_4 + H_2O_2 = 2:1). Then, an aqueous PDDA solution (0.5 wt.%) was sprayed on the substrate for coating by a positively charged film. The BIC J-aggregates layer was deposited on the PDDA layer from the water solution. The J-aggregates layer was coated by PDDA layer to provide isolation from surrounded air. Each layer deposition was followed by rinsing sprayed distilled water.

Highly porous anodic aluminium oxide (AAO) matrices with the average pore diameter is 42±4 nm and the distance between their centres is 83±2 nm were synthesized by Dr. I.I. Bespalova according to procedure described in [20]. To embed J-aggregates into AAO matrix it was immersed in the J-aggregates water solutions for at least 24 hours that leads to intense uniform matrix coloration [12]. Then the surface of composite obtained was washed with alcohol to remove the dye excess [12].

Absorption spectra was registered using a microspectrometer USB4000 (OceanOptics, USA) supplied with an incandescent lamp. Fluorescence spectra were recorded using Lumina spectrofluorimeter (Thermo Scientific, USA). To decrease scattering influence front-face illumination geometry has been realized using solid sample holder and thin 2 mm quartz cuvette. Fluorescence decay spectra were registered 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. The solid sample holder was used to provide front face illumination. For decay curves analysis FluoFit software (PicoQuant, Germany) was used. Absolute fluorescence quantum yield was measured using a home-made integrating sphere (diameter of 100 mm), which provides a reflectance > 99% over the 300-1000 nm range. As an excitation source, a diode-pumped Nd^{3+}:YAG laser (λ_{exc} = 532 nm, 5 mW) was used.

3. Results and Discussion

Due to double sulfo-groups BIC dye possess by good solubility in water with simultaneous J-aggregate formation even at low concentrations [4-6,12,15]. The BIC monomer (in ethanol) has typical for cyanine dyes narrow absorption (λ_{max} = 519 nm) and fluorescence (λ_{max} = 539 nm) bands (Fig. 1b). J-aggregates formation leads to red-shifted much narrower J-band (λ_{max} = 592.5 nm and Δ_{FWHM} = 310 cm^{-1}) and near-resonant luminescent band (λ_{max} = 598 nm) appearing (Fig. 1b). The exciton delocalization length N_c could be found using equation [7]:

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

where Δv^{mon}_{FWHM} and Δv^{J}_{FWHM} are widths of the monomer and J-bands, respectively. Using = 785 cm^{-1} for the main electronic transition of the monomer band we obtain $N_c \sim 8$ monomers which is less than one for

PIC J-aggregates [13], but larger than one for amphi-PIC J-aggregates [8].

As the examples of nanotructures materials were chosen nanoporous AAO matrices (the average pore diameter is ~ 42 nm) previously used in our study [12], layered PDDA polymer film with the layer thickness ~ 1.5 nm [13,19] and spin-coated PVA film with typical thickness ~ 50 nm [21]. The spectral position of BIC J-band in all these solid matrices is nearly the same but its width and shape strongly different for all media (Fig. 2a) contrary to luminescence band (Fig. 2b). The most significant J-band shape changing with additional red-shift is observed for AAO matrix despite its pores have sufficient size for the J-aggregate embedding (Fig. 2a). The long-wavelength tail of BIC J-band in AAO takes a Lorentzian shape instead of typical Gaussian one indicating strong topological disorder [7,8].

The J-band widths for the main excitonic transitions in different media are: Δ^{PVA}_{FWHM} = 240 cm^{-1}, Δ^{PDDA}_{FWHM} = 665 cm^{-1} and Δ^{AAO}_{FWHM} = 730 cm^{-1} (with Lorentz approximation). Hence, the exciton delocalization length could be found using Eq.1 and taking into account the monomer and width in polymers $\Delta\nu^{pol}_{FWHM}$ = = 870 cm^{-1}: N_c^{PVA} ~ 18 monomers, N_c^{PDDA} ~ 2 monomers and N_c^{AAO} ~ 1-2 monomers. So, if for layered polymer film and AAO matrix the exciton delocalization length is a very small indicating strong static disorder, for PVA spin-coated film that is more than twice larger comparing with the water solution.

To understand the results obtained the luminescence decays should be also analyzed (Fig. 3). In the water the average lifetime (taking into account nonmonoexponential form of luminescence decay) is τ^{water} ~ 124 ps (for C_{BIC} = 10^{-3} M) [12]. Embedding the J-aggregates into AAO matrix lead to the lifetime decreasing to τ^{AAO} ~ 75 ps (Fig. 3) [12]. For both polymeric films used the BIC J-aggregates lifetime is even much less with τ^{PVA} ~ 35 ps and τ^{PDDA} < 20 ps (less than the setup resolution) (Fig. 3). So, taking into account the strong delocalization length increasing for the BIC J-aggregates in PVA film the coherence effects life exciton superradiance [7,17] could be supposed. Very uniform the J-aggregates distribution is assumed for PVA films with a small contact between single J-aggregates. Contrary, the very thin PDDA film cause the exciton delocalization length strong decreasing simultaneously with the lifetime. In that case disorder increasing
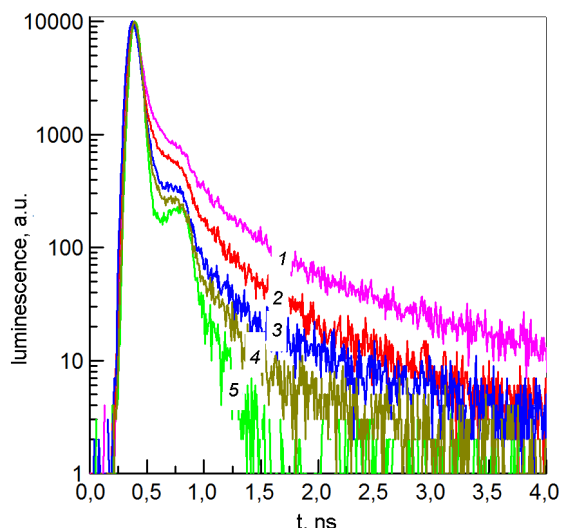

Fig. 3 Luminescence decay curves of BIC J-aggregates in different media: 1 – water (for comparison), 2 – AAO matrix, 3 – PVA spin-coated film, 4 – LbL film and 5 – IRF.

should be taking into account and some processes affected on the exciton dynamics like exciton self-trapping [8] should be considered. According with the AFM data obtained for similar system [19] there is strong contact between single J-aggregates. The nanoporous AAO matrix with rather large pores should be assumed as the most complicated host for BIC J-aggregates. Taking into account the influence of J-aggregate coagulation on their spectral properties [22] the BIC J-aggregate efficient accumulation could be supposed for this case. Defect local areas appeared at the boundaries of contacting single J-aggregates leads to the exciton strong localization [8] and the J-band transformation. However, contrary to the exciton self-trapping [8] such exciton localization on defects has much less influence on the exciton dynamics resulting in relatively small lifetime decreasing.

4. Conclusions

Spherical BIC J-aggregates have been used as luminescence probes for different solid matrices, namely nanoporous anodic aluminium oxide matrix, nanolayered polymer PDDA film and thin spin-coated polymer PVA film. The spectral properties of the J-aggregates are strongly different for all these nanostructured media, with main changes in the exciton delocalization lengths and the lifetimes. Taking into account specific excitonic properties of J-aggregates they could be sufficiently used as

the luminescence probes for nanostructured materials.

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