Plasmon enhancement of thiacyanine J-aggregates luminescence in polymer films

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Formation of thiacyanine dye J-aggregates in layered polymer films has been studied. This process leads to the J-aggregates spectral bands widening as a result of static disorder increasing. To enhance the J-aggregate luminescence the effect of their interaction with plasmon resonances of silver nanoparticles has been used. It was found that about 4-fold luminescence enhancement for thiacyanine J-aggregates in the polymer films could be obtained at 15 nm distance from silver nanoparticles.

Keywords: J-aggregate, exciton, metal nanoparticle, plasmon resonance, luminescence enhancement.

Исследовано формирование J-агрегатов тиацианинового красителя в слоеных полимерных пленках. Этот процесс приводит к уширению спектральных полос J-агрегатов вследствие увеличения статического беспорядка. Для усиления люминесценции J-агрегатов использован эффект их взаимодействия с плазмонными резонансами серебряных наночастиц. Показано, что можно добиться максимального 4-кратного усиления люминесценции тиациановых J-агрегатов в полимерных пленках на расстоянии 15 нм от серебряных наночастиц.

Плазмонне посилення люмінесценції тіаціанінових J-агрегатів у полімерних плівках. М.В.Переверзєв, О.В.Сорокін, В.М.Лях, І.А.Боровой, С.Л.Єфімова.

Досліджено формування J-агрегатів тіаціанінового барвника у шаруватих полімерних плівках. Цей процес призводить до уширення спектральних смуг J-агрегатів внаслідок збільшення статичного безладу. Для посилення люмінесценції J-агрегатів використано ефект їх взаємодії з плазмонними резонансами срібних наночасток. Показано, що можна отримати максимальне 4-кратне посилення тіаціанінових J-агрегатів у полімерних плівках на відстані 15 нм від срібних наночасток.

1. Introduction

An effect of luminescence enhancement (LE) by metal nanoparticles (MNP) is a very intriguing and prominent phenomenon in modern photonics [1–4]. It could be explained by concentration of the electromagnetic field near MNP due to interaction of their localized surface plasmon resonances with an incident electric wave [1–4]. Placing luminescent species in the area of the electromagnetic field concentration one could significantly increase their luminescence quantum yield [3–6]. The LE is strongly dependent on the distance between the MNP and the luminescent species. If the distance is too small the luminescence could be quenched due to radiationless energy transfer or electron transfer [3–6]. On a large distance the field concentration effect
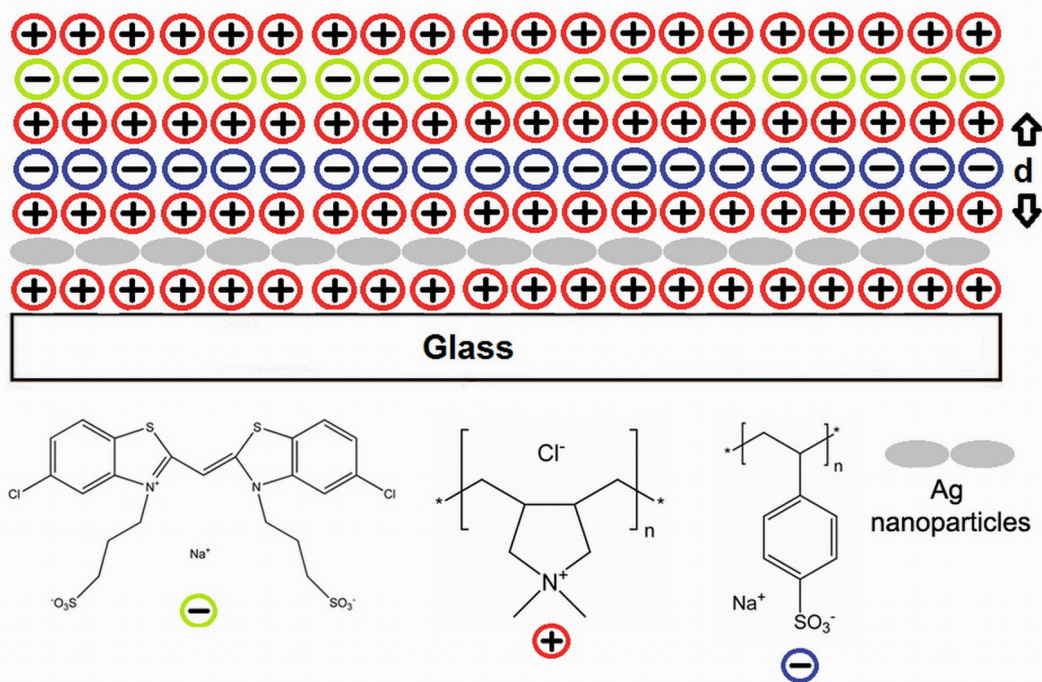
Fig. 1. Scheme of layered polymer film with structural formula of TC dye and the polyelectrolytes.

is disappeared and the luminescence remains unperturbed by MNP. So, to achieve the maximal LE the optimal distance should be found.

There are a lot of studies devoted to the LE of the different molecules (see [1−6] and references therein). However, there is few literature data concerning the LE by MNP in the case of delocalized excitation like excitons in such materials as quantum dots, conjugated polymers or molecular aggregates [7−10]. This inspired us to conduct analogous studies with molecular aggregates [11, 12]. Molecular aggregates or *J*-aggregates are clusters of non-covalently coupled luminophores such as cyanines, porphyrins, etc. with high ordering degree and strong interactions in molecular chains resulting in delocalization of electronic excitations and Frenkel excitons formation [13−16]. They attract great attention due to unique optical properties such as: narrow absorption band, high oscillator strength, giant third-order susceptibility, resonant fluorescence, etc. [13−16].

Using silver nanoparticles we obtained the 2-fold LE for thiacyanine (TC) *J*-aggregates in aqueous solution as the theory predicts 20-fold enhancement possibility [11]. Further, with gold nanoparticles we have achieved the 8-fold LE for pseudoisocyanine (PIC) *J*-aggregates in polymer films [12]. One of the reasons of a low success in the

first study was a small interaction area of MNP and the *J*-aggregates in the aqueous solution [11]. Thus the purpose of the present article is to test the LE by MNP for TC *J*-aggregates in polymer film.

2. Experimental

Thiacyanine dye (3,3′-disulfopropyl-5,5′-dichlorothiacyanine sodium salt, TC, Fig. 1) was synthesized by Dr.I.A. Borovoy. In order to prepare TC *J*-aggregates, the dye was dissolved 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. Anionic polyelectrolyte PSS (poly(sodium 4-styrenesulfonate), average $Mw \approx 70000$ g/mol, powder) and cationic polyelectrolyte PDDA (poly-(diallyldimethylammonium chloride), average $Mw < 100\ 000$ g/mol, 35 wt. % solution in water) were purchased from Sigma Aldrich (USA) and used as received. Silver nanoparticles were obtained using citrate method [17] from silver nitrate (Sigma Aldrich, USA) water solution. As a result, spherical nanoparticles were obtained with the average diameter of about 50 nm and the maximum of plasmonic resonance band at around 435 nm [11].

To prepare polymer films containing TC *J*-aggregates, the spray layer-by-layer assembly method [18] has been applied. For
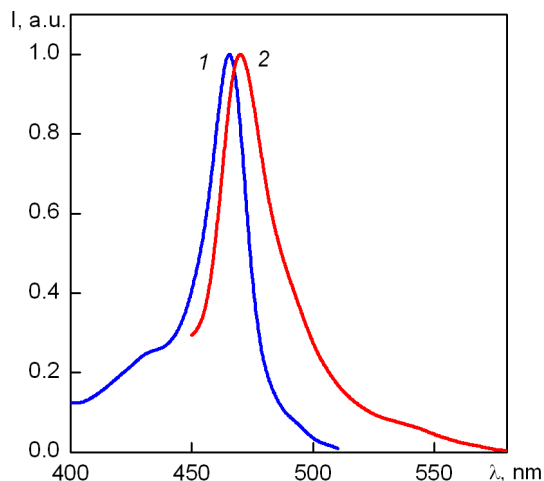
Fig. 2. Absorption (*1*) and luminescence (*2*, λ_{exc} = 430 nm) spectra of TC *J*-aggregates in the polymer film.

this purpose, commercially available paintbrush 80-897 (Miol, China) has been used. A substrate glass plate was preliminarily cleaned by hot (95°C) "piranha acid". Cleaning by the "piranha acid" results in a negatively charged surface of the glass. Then, an aqueous polycation PDDA solution (2 wt.%) was sprayed on the substrate for coating by a positively charged film (Fig. 1). As the MNPs are coated by a negatively charged citrate shell they were coated on the PDDA layer by spraying from the aqueous silver nanoparticles solution. Then a PDDA layer was deposited on the MNP layer with successive deposition of a negatively charged *J*-aggregate layer (Fig. 1). As TC dye is an anionic one (Fig. 1), such situation corresponds to the case of minimal distance between MNP and TC *J*-aggregates. To control the distance between MNP and the *J*-aggregates, the PSS layer was deposited upon PDDA one from an aqueous polyanion PSS solution (2 wt. %), thus PDDA and PSS layers were alternated. Each layer deposition was followed by rinsing sprayed distilled water. The outer layer was positively charged (PDDA) to provide effective interaction with negatively charged TC *J*-aggregates.

Absorption spectra were registered using a spectrophotometer Specord 200 (Analytik Jena, Germany). Fluorescence spectra were recorded with a fluorescence spectrometer Lumina (Thermo Scientific, USA) using a solid sample holder. Atomic force microscopy (AFM) images were obtained using a scanning probe microscope Solver P47H-PRO (NT-MDT, Russia) working in a con-

tact mode. AFM images were treated using free SPM data analysis software Gwyddion 2.39 (http://gwyddion.net).

3. Results and discussion

Recently, the influence of MNP on TC monomer luminescence in layered polymer film has been studied [19]. Maximal 4.5-fold LE of TC has been found at the average distance of about 20 nm between silver nanoparticles and the dye molecule. This value is larger comparing with the case of LE for TC *J*-aggregates in solution [11], however LE was observed on larger distance between the MNP and the luminescent species [19]. It should be noted, that the layer-by-layer assembly for polymer film preparation manifested itself as a reliable method to control the above discussed distance due to repeatable thickness of each polymer layer of about 1.5 nm [6, 11, 12, 18, 19].

Formation of TC *J*-aggregates in layered polymer film results in some spectral changes comparing with the case of TC *J*-aggregates in the aqueous solution [11]. Both absorption and luminescence spectra appeared to be red-shifted (λ_{abs}^{film} = 465 nm and λ_{lum}^{film} = 470 nm vs. λ_{abs}^{sol} = 461.5 nm and λ_{lum}^{sol} = 466 nm [11]) and widened (Δv_{abs}^{film} (FWHM) = 760 cm^{-1} and Δv_{lum}^{film} (FWHM)= 1260 cm^{-1} vs. Δv_{abs}^{sol}(FWHM) = 660 cm^{-1} and Δv_{lum}^{sol}(FWHM) = 575 cm^{-1} [11]) (Fig. 2). This could be regulated by two main factors: the *J*-aggregate structure change in the polymer film comparing to that in aqueous solution [13] and a static disorder increase due to local environment influence [12].

First of all we had to compare TC *J*-aggregate structure in aqueous solution and in the polymeric film. According to TEM data in the first case the TC *J*-aggregates reveal rod-like structure with the diameter of ~50 nm and length of ~500−700 nm [11]. To observe the *J*-aggregate structure in the polymer film the Atomic Force Microscopy (AFM) technique has been applied as the most suitable one (Fig. 3a). For this measurement the simplest case of polymer film was prepared containing only one PDDA layer on the glass substrate with TC *J*-aggregates deposited on it. According to AFM images in such case *J*-aggregates look like elongated islands with length of about 500−700 nm, thickness of about 150−200 nm and height of about 45 nm (Fig. 3b). Taking into account features of contact mode AFM measurement method, which causes some
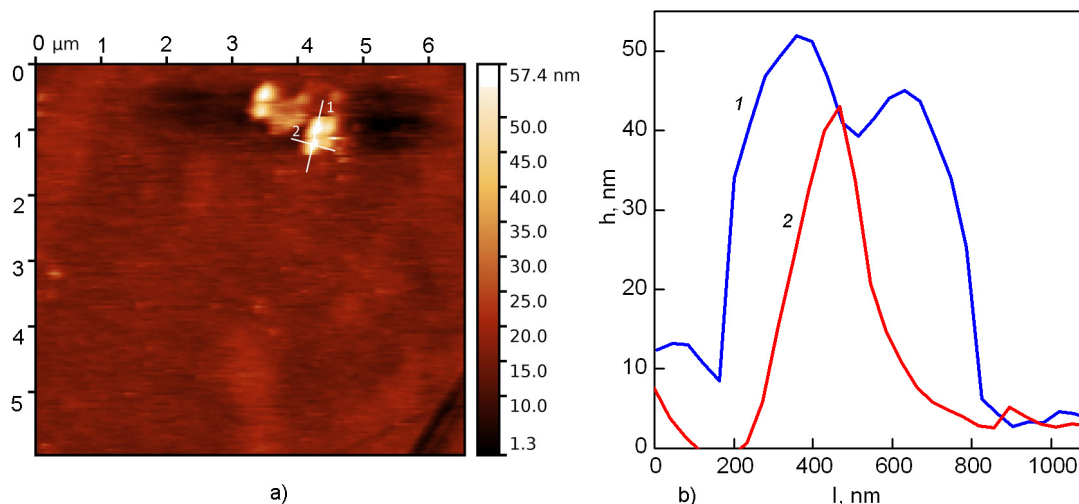
Fig. 3. a) AFM image of polymer film with TC *J*-aggregates, b) profiles of TC *J*-aggregate from the part (a) with the legend corresponding to the cutting lines *1* and *2*, respectively.
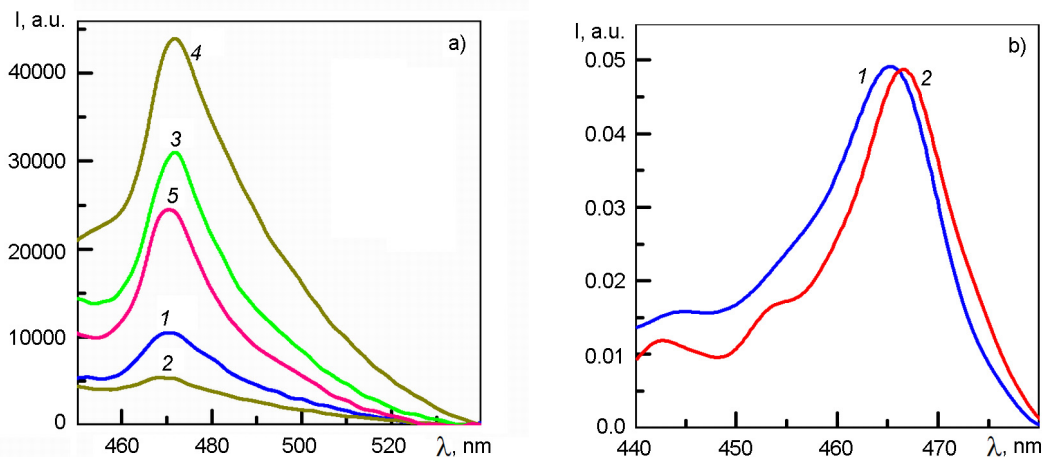

Fig. 4. Transformation of the TC *J*-aggregates optical properties under interaction with silver nanoparticles depending on the amount of the polymer layers between them: a) luminescence spectra (λ_{exc} = 430 nm): *1* — MNP are absent, *2* — 1 layer, *3* — 5 layers, *4* — 9 layers, *5* — 13 layers; b) absorption spectra: *1* — MNP are absent, *2* — 13 layers.

artifacts due to an interaction of the AFM tip with the sample [20], we assumed that TC *J*-aggregate structure has a minor change in polymeric film. So, main effect on the spectral properties should be caused by a more rigid local environment of the *J*-aggregate in polymer film comparing with that in aqueous solution leading to the static disorder increase.

It is well-known that static disorder increase in *J*-aggregates leads to different excitation localization effects causing the luminescence quantum yield decrease [12, 21]. Note that the LE by the MNP is probably the only way to solve this problem. To estimate the static disorder change we could use an exciton delocalization length [12]:

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

where Δv_{FWHM}^{mon} and Δv_{FWHM}^{J} are full widths at half maxima (FWHM) of monomer and *J*-aggregate absorption bands, respectively. Estimating Δv_{FWHM}^{mon} = 1485 cm^{-1} for the main electronic transition of the TC monomer band in the polymer film [19] we obtain N_c ~ 3–4 monomers that is lesser compared to the case of the aqueous solution [11]. The fact, that exciton delocalization length decreases together with the exciton band widening, proves our supposition concerning the static disorder decrease.

So, understanding the TC *J*-aggregates features in the polymer film we could estimate the MNP influence on the *J*-aggregate luminescence. It should be noted that the luminescence decay of TC *J*-aggregates appeared to be very fast with the lifetime less than 20 ps and, consequently, in the present work the lifetime analysis was not applied.

We prepared a series of the polymer films containing TC *J*-aggregates and silver nanoparticles with varied polymer layers thickness and analyzed the *J*-aggregate luminescence spectra (Fig. 4a). As both the *J*-aggregates and the nanoparticles are negatively charged ones odd polymer layer amount had to be placed between them. It is clearly seen that at the minimal distance between the MNP and the *J*-aggregates their luminescence is quenched. The increase of polymer spacer thickness leads to the luminescence growth with further fall, when the amount of spacing layers exceeds 9 (Fig. 4a). Such picture is typical to the luminescent species interaction with MNPs [3–6]. As in the case of PIC *J*-aggregates in polymer film [12], interaction of TC *J*-aggregates with silver nanoparticles in case of the optimal polymer spacer thickness (9 layers) leads to the red-shifting (λ^{MNP}_{lum} = 472 nm) and widening (Δv^{MNP}_{lum}(FWHM) = 1375 cm^{-1}) of the *J*-aggrregate luminescence band. This contradicts to the case of "TC *J*-aggregates-MNP" complexes in aqueous solution and is not interpreted still. However, analyzing the absorption band change (Fig. 4b) one could found that it appeared to be slightly red-shifted (λ^{MNP}_{abs} = 466.5 nm) and had lower intensity in accordance with the PIC *J*-aggregates case [12], its width revealed a strong narrowing down to Δv^{MNP}_{abs}(FWHM) = 580 cm^{-1} with the delocalization length growth up to N_c^{MNP} ~ 8 monomers in accordance to the TC *J*-aggregates solution case [11].

Further we plotted the LE graph (Fig. 5) as a ratio of the luminescence intensities measured in the band maximum in presence and absence of MNP versus the distance between TC *J*-aggregates and silver nanoparticles. The discussed distance was estimated as 3 nm thickness for each PDDA-PSS bilayer plus 2 nm thickness of the nanoparticles citrate shell [11, 12]. So, the best *J*-aggregates LE of about 4 times has been achieved at 15 nm distance between TC *J*-aggregates and silver nanoparticles. The obtained value is larger than that for TC *J*-aggregates in aqueous solution [11] and smaller than one obtained for PIC *J*-aggre-
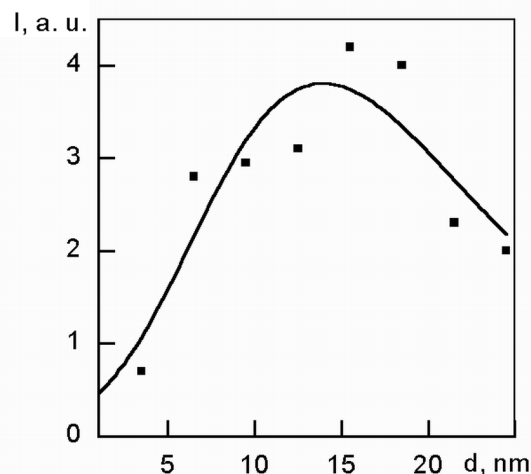

Fig. 5. Luminescence enhancement graph depending on the distance between TC *J*-aggregates and silver nanoparticles.

gates in layered polymer films [12], having the same order with that for TC monomers in the film [19]. So, further study had to be done to increase LE up to the theoretically predicted enhancement. It should be noted that the optimal distance between MNP and the *J*-aggregates for the maximal LE is similar for all *J*-aggregate cases under study but is smaller than that in the case of TC monomers.

4. Conclusions

Thiacyanine *J*-aggregates have been formed in the layered polymer films. Formation of TC *J*-aggregating in the films results in the both luminescence and absorption bands widening and red-shift. The main reason of this was explained as the static disorder decrease under the local environment influence.

To increase the *J*-aggregates luminescence the effect of the luminescence enhancement by interaction with plasmon resonances of metal nanoparticles has been used. For this purpose the effect of the polymer spacer between the *J*-aggregates and silver nanoparticles thickness on TC *J*-aggregate luminescence has been studied. It was found that maximal 4-fold TC *J*-aggregate luminescence enhancement in the polymer films could be achieved at 15 nm distance from 50 nm diameter silver nanoparticles. The resulted luminescence enhancement is 2 times larger comparing with that for TC *J*-aggregates in aqueous solution but 2 times smaller comparing with the case of pseudoisocyanine *J*-aggregates

in similar polymer films. The observed influence of metal nanoparticles onto the width of excitonic band is not understood to the end. The exciton-plasmon coupling in the multilayered dye-polymer-NP compositions will be the subject of our future investigations.

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