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Plasmon Controlled Exciton Fluorescence of Molecular Aggregates

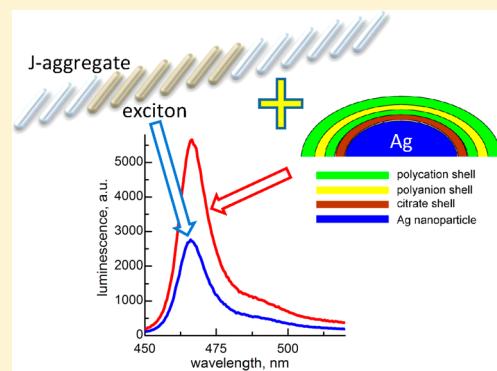
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Supporting Information

ABSTRACT: In the present work controlled plasmon enhanced fluorescence of thiacyanine dye J-aggregates in water solution has been demonstrated. To control a distance between J-aggregates and silver nanoparticles the latter have been covered by a polymer shell of variable thickness using the layer-by-layer assembly method. The best 2-fold fluorescence enhancement has been observed for the 16 nm thick polymer shell. Transmission electron microscopy (TEM) images have revealed an insufficient contact between J-aggregates and NPs that could be the main reason for the small fluorescence enhancement. Experimental results have been described using a model of two-level system affected by the local plasmon resonances field. According to the model more than 20-fold enhancement of J-aggregates fluorescence could be expected under optimal conditions. Besides, strong fluorescence enhancement dependence on an exciton coherence length has been predicted. According to it, significant fluorescence response should be observed for metal nanoparticles interacting J-aggregates with large exciton coherence length such as pseudoisocyanine J-aggregates and some others.



INTRODUCTION

In recent decades, the field of nanoplasmonics dealing with localized surface plasmon (LSP) resonances in noble metal nanoparticles has attracted a considerable interest.^{1–3} Strong enhancement of electromagnetic field near metal nanoparticles in combination with tunable large extinction in the visible and near-infrared region results in very attractive possibilities for manipulation by optical species properties such as the surface-enhanced Raman scattering (SERS)^{4,5} and plasmon-enhanced fluorescence (PEF).^{2,3,6,7} The latter appears to be strongly dependent on a distance between fluorescent species and metal surface because both radiative and nonradiative decay rates are influenced by LSP.^{1–3} As the nonradiative decay rate is usually caused by resonance energy transfer or electron transfer from fluorescent species to metal nanoparticles, it dominates on short distances and leads to strong fluorescence quenching. The distance increase can lead to more than 10-fold fluorescence enhancement due to the radiative decay rates enhancement.^{1–3}

The exciton–plasmon interaction in composites based on excitonic materials such as quantum dots,^{8,9} conjugated polymers¹⁰ or molecular aggregates^{11–19} could provide a much more interesting case study as compared to the plasmonic interaction with a localized excitation. For example, fluorescent molecular aggregates, the so-called J-aggregates, exhibit unique spectral properties such as narrow spectral bands, high extinction coefficients, and excellent nonlinear properties.^{20–22} The PEF phenomenon could be very useful in order to improve further the spectral characteristics of J-aggregates and to design novel optical materials and devices. J-

aggregate formation on metal nanoparticles leads to new hybrid electronic states appearing as a result of exciton–plasmon coupling.^{13–18} However, such composites are not fluorescent due to nonradiative processes predominance. Only few examples of fluorescent J-aggregate–metal nanoparticle composites with a fixed length spacer and nonoptimal fluorescence enhancement have been found in the literature.^{11,12} Hence, the full-scale manifestation of exciton–plasmon interaction in J-aggregate based composites needs to be studied carefully.

It this work, we demonstrate for the first time a possibility to control thiacyanine dye J-aggregates fluorescence via interaction with Ag nanoparticles modified by a polymer shell of a tunable size. Experimental results are described using a model of a two-level system affected by the LSP field. The obtained results could be used as a basis for development of novel hybrid nanomaterials, which are of interest in various applications.

EXPERIMENTAL SECTION

Thiacyanine dye (3,3'-disulfopropyl-5,5'-dichlorothiacyanine sodium salt, TC, Chart 1) was synthesized by Dr. I. A. Borovoy (Institute for Scintillation Materials of NAS of Ukraine) with purity controlled by NMR and thin layer chromatography. In order to prepare TC J-aggregates, the dye was dissolved in dimethyl formamide (DMF) to get a stock solution with a dye concentration of 10^{-3} M. Then doubly

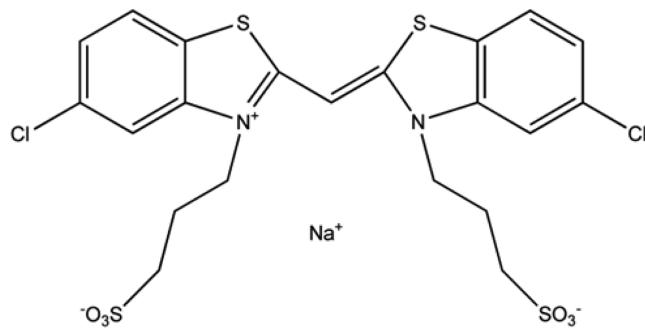
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Chart 1. Chemical Formula of TC Dye



distilled water was added to obtain a binary solution of DMF/water with 90% water content. Anionic polyelectrolyte PSS (poly(sodium 4-styrenesulfonate), average $M_w \approx 70\,000$ g/mol, powder) and cationic polyelectrolyte PDDA (poly(diallyldimethylammonium chloride), average $M_w < 100\,000$ g/mol, solution 35 wt % in H₂O) were purchased from Sigma Aldrich (USA) and used as received.

Silver nanoparticles were obtained using citrate ion reduction method²³ from silver nitrate water solution purchased from Sigma Aldrich (USA). As a result, spherical nanoparticles were obtained with the average diameter of about 50 nm and the maximum of plasmonic resonance at around 435 nm (see Supporting Information Figure S1).

To form a polymeric shell with varied thickness around nanoparticles, a layer-by-layer assembly method was used, which had been earlier adapted for colloidal solutions.^{8,12,24} Briefly, a silver nanoparticles water solution ($C = 0.09$ g/L) was mixed with a water solution of PDDA polycation (2 wt %) in ratio 5:1, then the mixture was ultrasonicated using an ultrasonic bath for about 3 min. After that the mixture was centrifuged at 3000 min⁻¹ for 10 min and washed with deionized water to remove a nonadsorbed polyelectrolyte. Then the procedure was repeated using PSS polyanion and PDDA again to create an alternative polycation/polyanion layered shell around silver nanoparticles. 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 and fluorescence excitation spectra were recorded with a fluorescence spectrometer Lumina (Thermo Scientific, USA) using a solid sample holder and a thin (3 mm) cuvette to avoid reabsorption. Transmission electron microscopy (TEM) images were obtained using a PEM-125K (Selmi, Ukraine) microscope.

RESULTS

Monomethine thiacyanine dye TC absorbs light in the blue spectral region with the main absorption band maximum at $\lambda_{\text{abs}} = 432$ nm in DMF (Figure 1, the blue dashed curve). Since it coincides with the Ag nanoparticles plasmon absorption maximum (see Supporting Information Figure S1), TC dye and its J-aggregates are good candidates to probe electron–plasmon (or exciton–plasmon) interaction.^{11–15} Because of the intramolecular rotational motions in TC dye, its fluorescence is weak with the quantum yield 0.008 according to ref 25. The fluorescence spectrum contains a wide emission band with the maximum $\lambda_{\text{lum}} = 485$ nm in DMF (Figure 1, the blue solid curve).

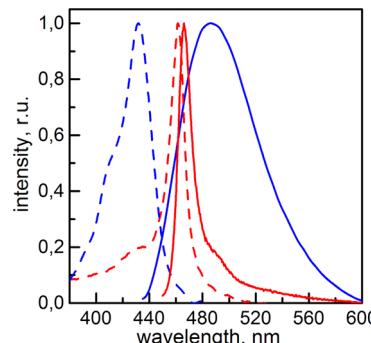


Figure 1. Absorption (dashed lines) and fluorescence (solid lines, $\lambda_{\text{exc}} = 430$ nm) of TC dye in DMF (monomers, blue lines) and in DMF/water = 1:9 solution (J-aggregates, red lines).

Water addition leads to J-aggregates formation and a red-shifted excitonic absorption band (J-band) appearing with the maximum at $\lambda_{\text{abs}}^{\text{J}} = 461.5$ nm together with a near-resonant fluorescence band with the maximum at $\lambda_{\text{lum}}^{\text{J}} = 466$ nm (Figure 1, red curves). The J-band is quite wide ($\Delta\nu_{\text{fwhm}} = 660$ cm⁻¹) as compared to typical J-band widths for most J-aggregate representatives.²⁶ However, it is narrower than the one ($\Delta\nu_{\text{fwhm}} = 959$ cm⁻¹) for TC J-aggregates formed in other conditions.²⁵ A large J-bandwidth indicates a small exciton coherence length as a result of significant static disorder.²⁶ Indeed, one could estimate the exciton coherence length N_c in J-aggregates using the following formula:²⁷

$$N_c = \frac{3(\Delta\nu_{\text{fwhm}}^{\text{mon}})^2}{2(\Delta\nu_{\text{fwhm}}^{\text{J}})^2} - 1 \quad (1)$$

where $\Delta\nu_{\text{fwhm}}^{\text{mon}}$ and $\Delta\nu_{\text{fwhm}}^{\text{J}}$ are full widths at half maxima (fwhm) of monomer and J-aggregate absorption bands, respectively. By estimating $\Delta\nu_{\text{fwhm}}^{\text{mon}} = 1220$ cm⁻¹ for the main electronic transition of the TC monomer band (Figure 1, the blue dashed curve), we obtain $N_c \approx 4$ monomers similarly to the case of strongly disordered amphi-PIC J-aggregates.^{26,27} It should be noted that the fluorescence decay curve of TC J-aggregates appeared to be very short with the lifetime less than 20 ps, and consequently, it could not be correctly resolved with our lifetime instrument (see Supporting Information Figure S2). Hence, in the present work the lifetime changes have not been analyzed.

In order to understand spectral features of TC J-aggregates interaction with silver nanoparticles, the information concerning aggregate structure is very important. In an aqueous electrolyte solution, TC J-aggregates revealed a large string formation²⁸ similarly to J-aggregates of PIC²⁹ or TDLC derivatives.³⁰ In contrast, under our preparation conditions TC J-aggregates form small strings with the diameter ~10 nm and length ~50 nm (Figure 2a), which are organized in bundled structures similarly to the PIC²⁹ or TDLC family³⁰ J-aggregates but much shorter in length. After several hours rod-like J-aggregates with the diameter ~50 nm and length ~500–700 nm (Figure 2b) were found. It should be noted that the observed string-to-rod transformation should not be associated with the one revealed for TC²⁸ and PIC³¹ J-aggregates earlier. The latter is related to the significant structure transformation with a new type of aggregate formation. In our case, we believe that the reorganization of small aggregates into larger ones occurs similarly to the case reported in refs 32 and 33.

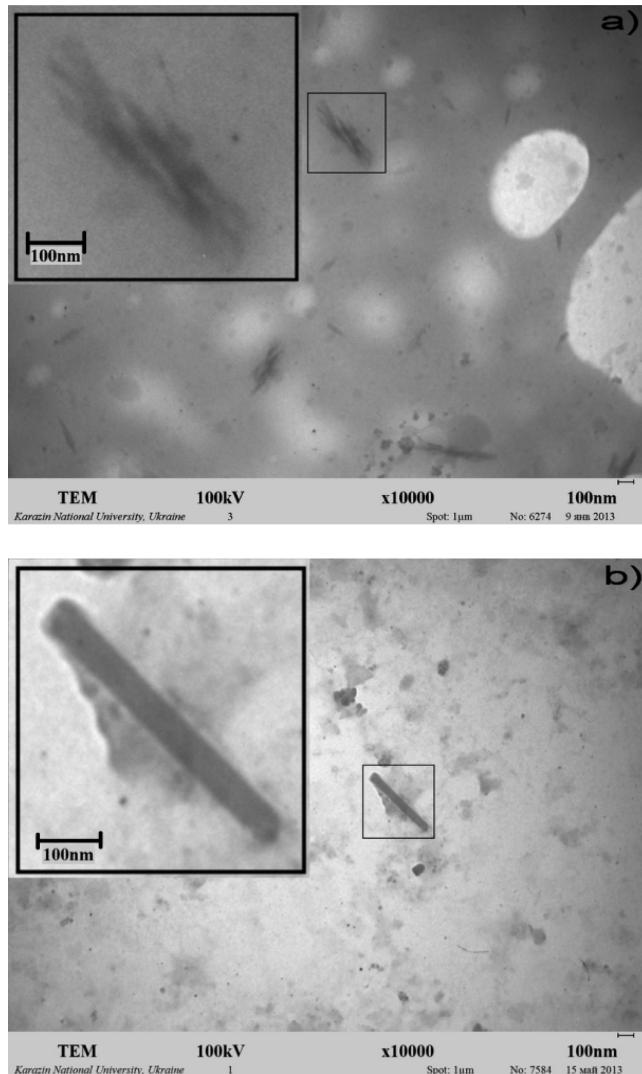


Figure 2. TEM images of TC J-aggregates: (a) freshly prepared and (b) several hours after preparation.

To achieve the highest PEF efficiency, the distance between metal nanoparticles (NP) and fluorescent species should be controlled. A survey of existing literature has shown that the most appropriate way to achieve this goal is a method of oppositely charged polyelectrolyte layer alternation known as layer-by-layer (L-b-L) assembly.^{8,12,24,34} Initially this method was used for PEF control in thin films formed on a glass substrate³⁴ and then it was successfully applied for the fluorescence enhancement of colloidal quantum dots.⁸ Recently, the L-b-L assembly method was used to form a spacer of variable thickness around gold nanorods, which interact with J-aggregates of several cyanine dyes.¹² Note, only the spacer thickness effect on absorption spectra has been examined in this study. So, we apply the L-b-L technique to obtain silver nanoparticles with polymer shells of tunable size (Figure 3). According to the data from available literature, the thickness of the polymer layer in the L-b-L assembly is about 1.5–2 nm.^{8,24} This was proved for our case using TEM images of silver nanoparticle based composite (Figure 3b). Indeed, the three-layered composite schematically shown in Figure 3a revealed an approximately 7 nm thick shell around Ag NP

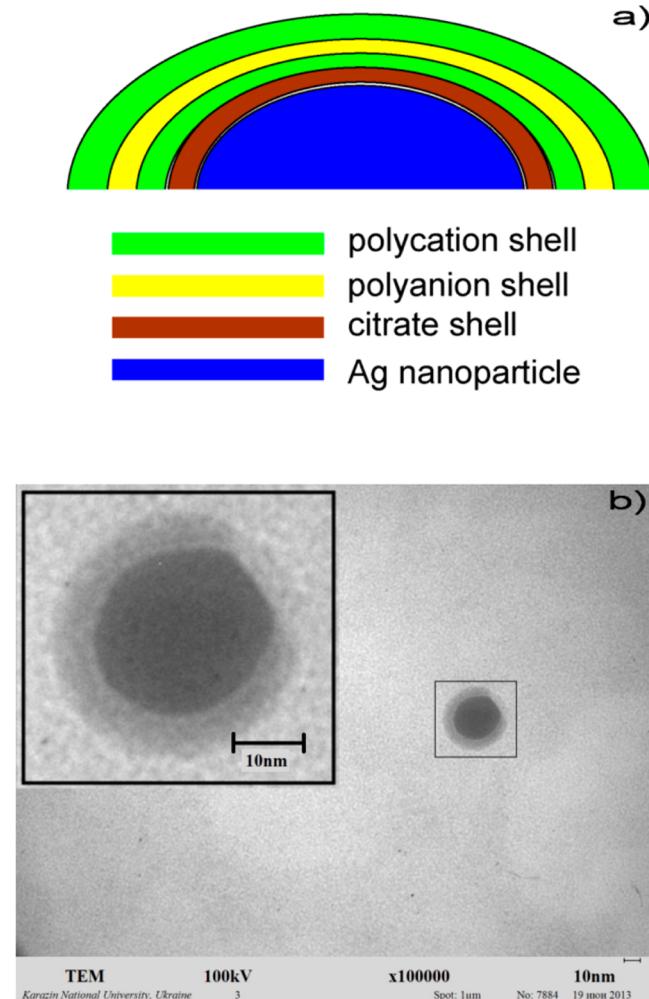


Figure 3. Model (a) and TEM images (b) of an Ag nanoparticle with a polymeric shell. For the TEM image an ammonium molybdate contrasting agent was used.

(Figure 3b). With the citrate coating thickness of about 2 nm, this results in about 1.5 nm polyelectrolyte layer thickness.

We prepared metal-based nanoparticles with the Ag core and a polymer shell consisting of a varied number of polyelectrolyte layers with an increment of about 3 nm (two layers) and the PDDA outer layers. Then the NPs were mixed with TC J-aggregates and absorption and fluorescence spectra were recorded (Figure 4).

One can easily observe the metal-based NPs influence both absorption and fluorescence spectra of J-aggregates. NP shell thickness increases up to 9 polymer layers (which corresponds to about 16 nm of the whole shell thickness) results in the bands intensity increase followed by the intensity decrease with further shell thickness growth (Figure 4). The intensity change in absorption spectra of the J-band is not so large, with the maximum intensity increase of about 13% only for the J-aggregates interacting with 9 polymer layers containing NPs as compared to the TC J-aggregates themselves (Figure 4a). It should be noted that the interaction of TC J-aggregates with the NPs leads to the J-band narrowing down to $\Delta\nu_{\text{fwhm}}^{\text{NP}} = 575 \text{ cm}^{-1}$. This suggests a static disorder decrease and hence the exciton coherence length increase ($N_c \approx 6$ monomers according to eq 1). In the case of the smallest distance between the Ag core and J-aggregates (i.e., for NPs with a single

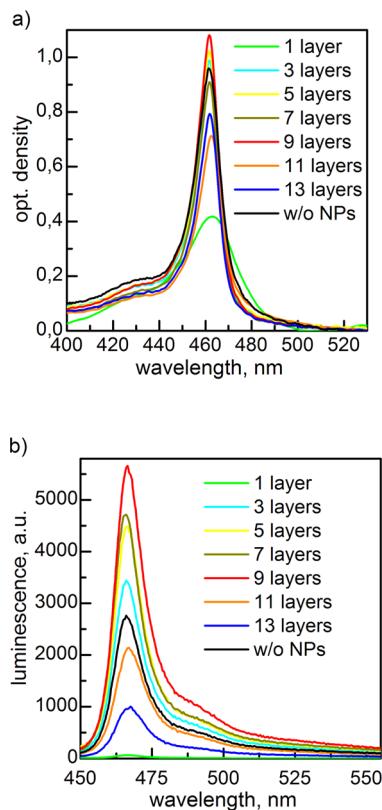


Figure 4. (a) Absorption and (b) fluorescence ($\lambda_{\text{exc}} = 430$ nm) spectra of DMF/water solutions containing TC J-aggregates and Ag-based nanoparticles with varied thickness of the shell. For comparison, TC J-aggregate data without NPs are presented.

polymer layer), the J-band becomes wide and slightly red-shifted (Figure 4a). The significant spectral change could be associated with the strong exciton-plasmon coupling.^{11–15}

In the fluorescence spectra much more dramatic intensity changes could be observed (Figure 4b). For single polymer layered NPs full fluorescence quenching was observed in agreement with the previously reported results.^{13–18} An increase of the shell thickness leads to the successive emission intensity growth of up to 2-fold enhancement in the case of the 9 polymer layered NP case as compared to the J-aggregates themselves. A further shell thickness increase results in fluorescence quenching (Figure 4b). The TC J-aggregates interaction with NPs produces some spectral narrowing (from $\Delta\nu_{\text{fwhm}} = 575 \text{ cm}^{-1}$ in a nanoparticles-free solution to $\Delta\nu_{\text{fwhm}} = 565 \text{ cm}^{-1}$ in solutions with 1 to 9 polymer layered NPs), which is small as compared to the absorption band narrowing. For 11 and 13 polymer layered NPs a small red-shift with some band widening up to 595 cm^{-1} was observed in the fluorescence spectra (Figure 4b). All the spectral transformations observed could be undoubtedly associated with the distance controlled exciton–plasmon interaction.

It is interesting to study how spherical nanoparticles interact with prolonged TC J-aggregates. In refs 11–13, a spherical TC J-aggregate layer formation over Ag NPs was assumed. However, in those cases J-aggregates do not exist in solutions without nanoparticles and the latter seem to be aggregation centers.^{11–14} On the contrary, in our case TC J-aggregates exist in solutions without nanoparticles and more complex morphology of interacting species could be assumed. Indeed,

TEM images showed that NPs stuck to J-aggregate rods due to the Coulombic attraction (Figure 5).

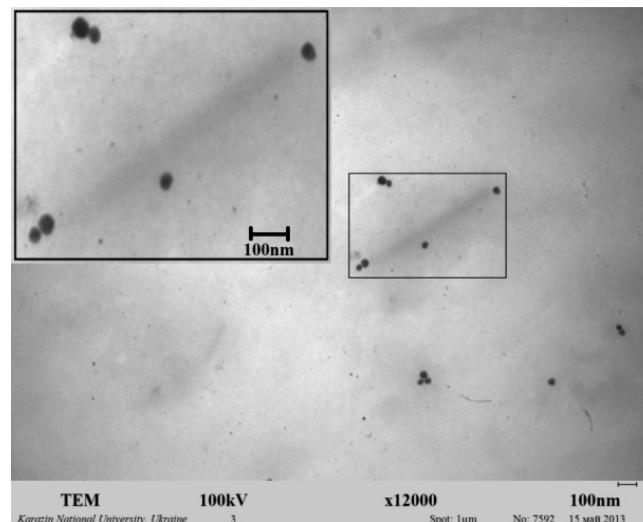


Figure 5. TEM image of DMF/water solution containing Ag-based NPs and TC J-aggregates.

Our estimates suggest the ratio of 1 silver NP per 1 small J-aggregate string in initial conditions, which corresponds to several NPs per 1 J-aggregate rod that is proved by TEM imaging (Figure 6). It is clear that the obtained structure is not

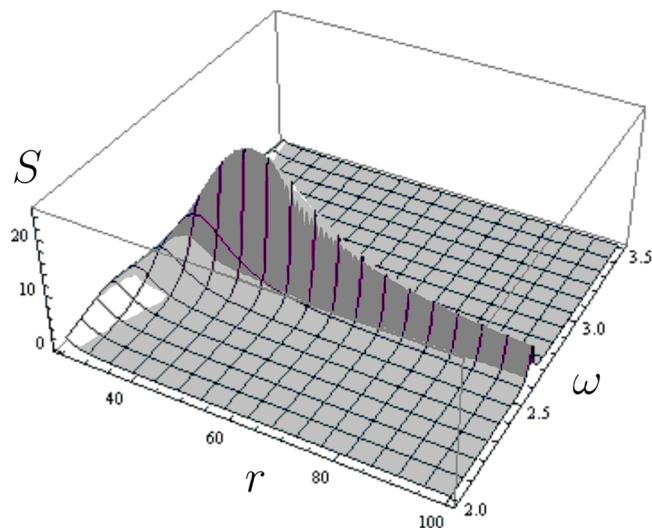


Figure 6. Dependence of the spectral density S vs ω (eV) and r (nm).

optimal for the most effective PEF. However, experiment with single polymer layered NPs shows essentially full fluorescence quenching, which suggests a very strong exciton–plasmon coupling despite imperfect NPs–J-aggregates contact. A possible explanation is an effective exciton migration over TC J-aggregate rods, but it should be proved experimentally.

DISCUSSION

In a contrast with the 5–10-fold PEF usually reported in the literature,^{1–3,6–8} we observed only 2-fold J-aggregate fluorescence enhancement by the silver core NPs. It could be assigned to the imperfect contact between J-aggregates and NPs

(Figure 5). However, it is very useful to describe theoretically the prepared system for further clarification of the experimental results.

Several models such as quasistatic^{6,34–36} and dynamic³⁷ approximations, multilayered medium,⁶ or three-layered sphere model³⁶ were used without success. Taking into account that a two-level system (TLS) model was successfully used to describe J-aggregates behaviors,⁶ our system could be described exploiting a similar approximation.

Let us describe a model of the J-aggregates fluorescence interaction with silver nanoparticles using fluorescence excitation by an incident light wave with the electric field

$$E(t) = E_0 \cos(\omega t) = \frac{1}{2} E_0 \exp(-i\omega t) + c.c. \quad (2)$$

where E_0 is an amplitude and ω is a carrying frequency. In the middle field and slow envelope approximations, the field acting on the J-aggregates is given by the formula

$$E_J = E_0 + A_{NP} N_p(r) \mu_0 b(t) \quad (3)$$

where $B = 1/2be xp(-i\omega t) + c.c.$ is a boson mode describing plasmon excitation in nanoparticles. N_p is the density of the NP. The coefficient $A(r)$ describes the field of an oscillating dipole at distance r and has the form:³

$$A_{NP}(r) = \frac{(k_0 r_0)^3}{\epsilon_h} \left[\frac{3(e \cdot e_d) - 1}{(k_0 r)^3} - i \frac{3(e \cdot e_d) - 1}{(k_0 r)^2} - \frac{(e \cdot e_d) - 1}{k_0 r} \right] e^{ik_0 r} \quad (4)$$

where $\epsilon_h = 1.75$ is the dielectric susceptibility of the host matter, $k_0 = \omega(\epsilon_h)^{1/2}/c$ is the wave vector of the electromagnetic field, and e_d is the unit vector, which is parallel to the dipole of the nanoparticle. μ_0 and r_0 are the effective dipole momentum and radius of the nanoparticle, respectively.

To estimate the dipole μ_0 we have used results of refs 38 and 39. In the dipole approximation we derive that

$$\mu_0 \approx \left(\frac{4r_0^3 \pi^3 \epsilon_h \hbar \omega_p}{9\sqrt{3}} \right)^{1/2} \quad (5)$$

where ω_p is the plasmon frequency. Estimating the dipole moment, we found $\mu_0 = 10^{-14}$ cgs for $r_0 = 15$ nm.

In what follows, we use a linear approximation to semiclassical description of the plasmon dynamics. Dynamics of the boson is governed by the equation

$$\partial_t p_n + (i\omega_n + \gamma_n) p_n = i \frac{\mu_0 \tilde{E}}{\hbar} \quad (6)$$

where \tilde{E} is the amplitude of the middle field acting on the nanoparticle

$$\tilde{E} = E_0 + A_j(r) P_j \quad (7)$$

where $P_j = 4\pi p_j d_j N_j N_c + c.c.$, p_j is the polarization of the exciton transition of the J-aggregate of dyes, N_j is the J-aggregates density. The number of domains N_c is determined by the space of the exciton localization, i.e., it is the coherence length of the excitons. The coefficient A_j could be described by eq 4.

The Bloch equations for the two-level exciton transition are as follows

$$\partial_t p_j + (i\omega_j + \gamma_j) p_j = i \frac{dE_j}{\hbar} n \quad (8)$$

$$\partial_t n + \gamma_p(n - n_0) = \frac{i}{\hbar} (dE_j p_j - d^* E_j^* p_j^*) \quad (9)$$

where γ_j^{-1} and γ_p^{-1} are the relaxation times.

We neglect the change of the levels population $n \approx n_0 = \text{const}$. Then after applying the Fourier transform to eqs 6 and 8 we obtain

$$\tilde{p}_j = \frac{n_0 E_0 \left[\frac{d_2}{2\hbar} + Q_j \frac{\mu_0}{2\hbar(\omega_p - \omega - i\gamma_p)} \right]}{(\omega_j - \omega - i\gamma_j) - n_0 \frac{Q_j Q_p}{\omega_p - \omega - i\gamma_p}} \quad (10)$$

$$\tilde{p}_p = \frac{\frac{\mu_0 E_0}{2\hbar} + Q_p \tilde{p}_j}{\omega_p - \omega - i\gamma_p} \quad (11)$$

where \tilde{p}_j and \tilde{p}_p are the respective Fourier transforms of p_j and p_p , and

$$Q_j(\omega, r) \approx \frac{A_j(r) \mu_0 d N_p}{\hbar}, \quad Q_p(\omega, r) \approx \frac{A_{NP}(r) \mu_0 d N_j}{\hbar} \quad (12)$$

The middle polarization of the system is $P = v_j \tilde{p}_j + v_p \tilde{p}_p$, where v_j and v_p are the relative volumes of J-aggregates and NPs, respectively. The spectral density of fluorescence $S(\omega, r)$ is proportional to $|P(\omega, r)|^2$. It could be shown that for small losses $\gamma_j \approx 0.001$ eV and $\gamma_p \approx 0.01$ eV the maximum of the $S(\omega, r)$ is shifting to the red region of the spectrum as r decreases. For larger losses $\gamma_p \approx 0.1$ eV this shift is small.

Let us estimate the radius r_m (the distance between a NP's center and a J-aggregate) corresponding to the maximum of $S(\omega, r)$ for a fixed ω near the exciton resonance using eq 10:

$$r_m^6 \approx r_0^6 \frac{\mu_0^2 d^2 N_p N_j N_c^2}{\hbar^2 \gamma_j \omega_p} \quad (13)$$

For our experimental data it could be assumed that

$$r_m \approx f r_0 N_c^{1/3} \quad (14)$$

where $f \approx 1$ is a dimensionless coefficient and N_c could be determined using eq 1.

In Figure 6 the dependence of $S(\omega, r)$ on different radii of the NPs core is shown. We use the following parameters $\omega_p = 2.84$ eV, $\omega_j = 2.636$ eV, $N_c = 3$; $\gamma_j = 0.011/\text{NR}$; $\gamma_p = 0.66$ eV; $d = 12 \times 10^{-18}$ SGSE, $N_p = 6 \times 10^{22} \text{ cm}^{-3}$, $N_j = 10^{14} \text{ cm}^{-3}$, and $r_0 = 25$ nm. The numbers of J-aggregates and NPs are approximately equal.

From Figure 6, good correlation with the experimental data could be observed concerning the distance dependence of fluorescence enhancement. Indeed, the maximum of PEF on the Figure 6 is corresponded to $r^{\text{theor}} = 45$ nm, while in the experiment $r^{\text{exp}} = 41$ nm has been found (Figure 4). It should be noted that more than 20-fold fluorescence enhancement could be expected under optimal conditions according to our theoretical model. There are two main reasons this could be responsible for significant discrepancy between experimental and theoretical results. The first one is the small contact between NPs and J-aggregates (Figure 5). The second one is a

difference between the exciton transition maximum ($\omega_t = 2.636$ eV) and the plasmon resonance maximum ($\omega_p = 2.84$ eV).

The exciton delocalization in J-aggregates seems to be one of the most important features. The delocalization is related to the energy transfer along the molecular structure. It is of particular interest to study the effect of delocalization on the spectral characteristics of the J-aggregates–nanoparticles system. In Figure 7 the spectral density $S(\omega_p r)$ is depicted for several values of N_c .

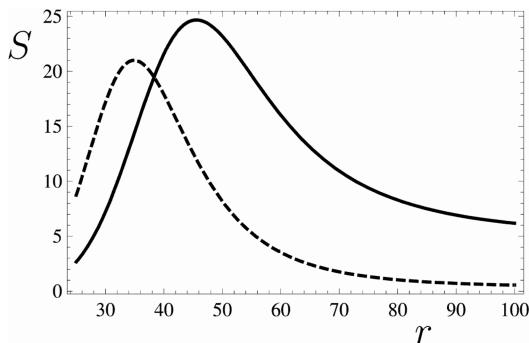


Figure 7. Dependence $S(\omega_p r)$ vs r (nm) for $N_c = 3$ and 6 shown by dashed and solid lines, respectively.

It is clear that the exciton coherence length growth leads to an increase of the fluorescence spectral density and a shift of its maximum toward longer distance between J-aggregates and NPs (Figure 7). Such PEF dependence on the exciton coherence length is a very interesting result, that needs to be experimentally confirmed for J-aggregates with large coherence lengths, e.g., such as pseudoisocyanine dye J-aggregates.

CONCLUSIONS

For the first time J-aggregate fluorescence varying through the distance controlled interaction with metal nanoparticles has been demonstrated. Maximal 2-fold plasmon enhancement of the fluorescence has been found at the distance of about 16 nm between metal nanoparticle surface and J-aggregates, which corresponds to the distance of about 41 nm from an NP's center to a J-aggregate. Plasmon influence on the J-aggregate fluorescence has been analyzed using a two-level system in the local plasmon field approximation. The model gives good correlation with the experimental results and predicts more than 20-fold enhancement of J-aggregates fluorescence and strong fluorescence enhancement dependence on the exciton coherence length. It could be used in further studies of the exciton–plasmon interaction in J-aggregate–metal nanoparticles systems.

ASSOCIATED CONTENT

Supporting Information

TEM image and absorption spectrum for silver nanoparticles are provided. Also, fluorescence decays curves for TC J-aggregates and monomers are shown. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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