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Research Article

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Plasmon-enhanced Förster energy transfer in Langmuir-Blodgett films based on organic dyes

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Abstract: The effect of plasmon resonance of silver island films (SIF) on the interlayer Förster resonance energy transfer (FRET) between xanthene and oxazine dye molecules was studied. It has been shown that the enhancement of FRET can be controlled by changing in the distance between the donor-acceptor system and the SIF. The maximum increase in energy transfer efficiency (E_{ET}) by a factor of 2.6 was recorded at a distance of 6 nm from the SIF. The assumption was made that an increase in E_{ET} can be associated with both the direct appearance of a plasmon-enhanced rate constant of energy transfer and an increase in the quantum yield of the energy donor in direct contact with the SIF. The results can serve as a basis for studying of photoinduced processes in hybrid materials such as "organic dye-plasmon nanoparticles", to increase the photosensitivity of solar cells in the visible region of the spectrum, and for the studying of photobiological processes, as well as to create materials with desired properties, sensors and light energy converters.

Keywords: electronic excitation energy transfer, silver island films, nanoscale films, plasmons, distance dependence

1 Introduction

The phenomenon of intermolecular electronic excitation energy transfer is one of the key processes in the transformation of absorbed light into other types of energy and underlies in many important photophysical and photochemical processes [1, 2]. Energy transfer can be realized via the exchange or inductive-resonance mechanism depending on the type of interaction of the reacting particles [3, 4].

Currently, interest in inductive-resonant energy transfer (or FRET) is not weakened due to its promising for dye-sensitized solar cells [5, 6], as well as for studying the morphology of metal nanoparticles in solutions and the process of their formation [7, 8]. In the ref. [9, 10] it was shown the using of the FRET for studying of photo-induced electron transfer process between organic molecules, which is very important for photovoltaic devices. In addition, this type of energy transfer can be used to identify the localization and interaction of proteins within cells [11], conformational changes in DNA [12] and etc.

Plasmon-enhanced energy transfer between light-emitting molecules allows increasing of the luminescent characteristics of acceptor molecules [13, 14]. As it was shown in ref. [15, 16], this phenomenon was being actively studied for its application in hybrid metal-semiconductor nanostructures to create new active materials for light-emitting diodes (LEDs).

In ref. [17] was shown that efficiency of energy transfer from donor to acceptor can be increased in the presence of Au-Ag metal nanostructures. In this case donor and acceptor fluorophores were embedded in the mesostructure shell of silica, which is uniformly covers core-shell structure on the basis of Au-Ag. A comparison of the scattering and fluorescence spectra recorded for hybrid nanostructures with different localized plasmon resonance (LPR) frequencies suggests that the energy transfer efficiency can be controlled by the LPR. When the peak of the plasmon resonance overlaps with the peak of the donor emission, the energy transfer channel is turned off. When the LPR maximum was shifted to the longer wavelength and localized between the peak of the donor's emission and the acceptor's absorption peak or to the right of the acceptor's emission peak, the energy transfer channel can be activated. This experimental result confirmed the results of a theoretical study of the energy transfer near a solid particle. Authors of ref. [18, 19] have shown that the efficiency of energy transfer and its enhancement coefficient strongly depend not only on the shape and size of particles, but also on the relative orientation of the dipole moments of

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the donor and acceptor, their location relative to this particle.

For a better understanding of the effect of plasmon resonance of metallic nanostructures on the energy transfer efficiency, more detailed studies with the possibility of changing in the parameters of the plasmon effect are necessary. For an experimental study of the effect of the distance between plasmonic nanoparticles and organic luminophores, the Langmuir-Blodgett (LB) technology can be used. This method allows to obtain systems with predictable distance between the reagents and their mutual orientation [20].

This paper presents the results of a study of the effect of plasmon resonance of silver island films on the interlayer FRET between xanthene and oxazine dye molecules. It is shown that the effect of FRET enhancement can be controlled by changing in the distance between the donor-acceptor system and the SIF.

2 Experiment

The amphiphilic derivative of Rhodamine B (HERB) was chosen as the energy donor, and the amphiphilic Nile Red (NR) was used as an energy acceptor. The dyes were obtained in Organic Intermediates and Dyes Institute (NIOPIK, Russia).

Silver island films (SIF) were deposited on glass substrates by thermal vacuum deposition. $AgNO_3$ salt (Sigma Aldrich, ≥ 99.999%) was used for deposition. The thickness of the deposited films was equal to 5–8 nm. The thermal annealing of the SIF was carried out in a muffle furnace for 10 minutes at a temperature of 240°C. The morphology and structure of the films were examined using a MIRA 3LMU (Tescan) scanning electron microscope (SEM).

As was shown by SEM studies (Figure 1), clusters of silver particles of almost regular spherical shape with a radius from 120 to 140 nm were formed in the film after annealing. The space between them was occupied by nanoparticles with a smaller radius of 15 – 20 nm. They cover the greater part of the surface under study.

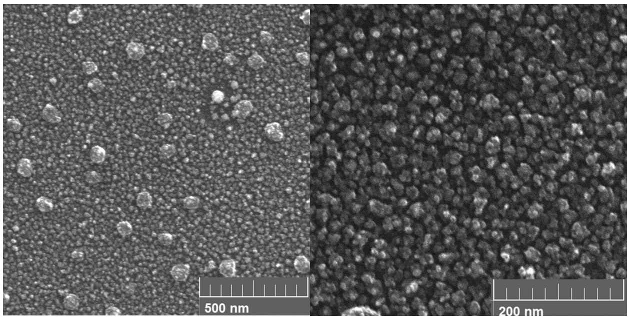


Figure 1: SEM images of SIF after annealing at 240°C

Then, the obtained Ag films were covered by the energy donor films. After that donor films was covered by acceptor films. Before deposition separately donor or acceptor solutions were mixed with amphiphilic polyampholyte (poly (N, N-diallyl-N-octadecylamine-alt-maleic acid) in appointed concentrations [21]. The concentration of donor molecules in the film was equal to 20 mol% relative to the amphiphilic polyampholyte, the concentration of NR was changed from 5 to 20 mol%. Dye films were deposited by using of Langmuir-Blodgett (LB) technology on a KSV Nima bath. Monolayers were transferred by vertical dipping according to Z type transfer (transfer during the upward stroke only) at surface pressure of 30 mN/m. The film thickness of donor or acceptor was equal to 5 monolayers of the dye. The distance from the SIF to dye LB film was changed with using of monolayers of stearic acid (SA, molecule length ~ 2 nm). The number of SA monolayers between SIF and dye films was changed and was equal to 1, 3, or 5 layers. The solvents and SA for LB films were A.C.S. grade and purchased from Sigma Aldrich.

The absorption and fluorescence spectra of the LB films were measured on Cary and Eclipse spectrometers (Agilent) correspondingly. The fluorescence lifetimes of the donor and acceptor in the films were recorded with the time correlated single photon counting system (TCSPC, Becker&Hickl) at λ_{ex} = 488 nm. The efficiency of energy transfer was estimated by the Förster formula.

3 Results and its discussion

The normalized absorption spectra of SIF and LB films of the donor and acceptor are shown on the Figure 2. It can be seen, that the bands of dyes and SIF overlap with each other, which is a necessary condition for the implementation of the plasmon effect. The absorption spectra of the acceptor and the fluorescence of the energy donor are almost completely superimposed on each other, which means that the efficiency of energy transfer in the chosen pair is expected to be high [22, 23].

The absorption and fluorescence spectra of HERB or NR dye LB films were measured for the studying of plasmon effect on pure donor and acceptor films. The data obtained are shown in Figure 3 and Table 1.

As can be seen from the figure, there is an increase by 15% was registered for the luminescence intensity of the dye in the direct contact of HERB with silver film. Fur-

Table 1: Spectral-luminescent parameters of LB films of pure dyes at different distances to the SIF

Sample	Amount layers of SA	λ_{absmax}, nm	$\Delta\lambda_{abs1/2}$, nm	λ_{flmax}, nm	$\Delta\lambda_{fl1/2}$, nm	I, a.u.	τ, ns
HERB	Pure	552	25	580	37	2.236	1.8
SIF+SA+ HERB	0	552	25	580	36	2.513	1.6
	1	552	25	580	35	2.542	1.4
	3	552	25	580	35	2.937	1.0
	5	552	25	580	35	2.425	1.6
NR	Pure	557	50	615	30	0.28	1.3
SIF + SA +NR	0	557	51	616	30	0.262	1.3
	1	557	51	616	30	0.274	1.0
	3	557	51	616	32	0.333	0.85
	5	557	50	616	30	0.288	0.9

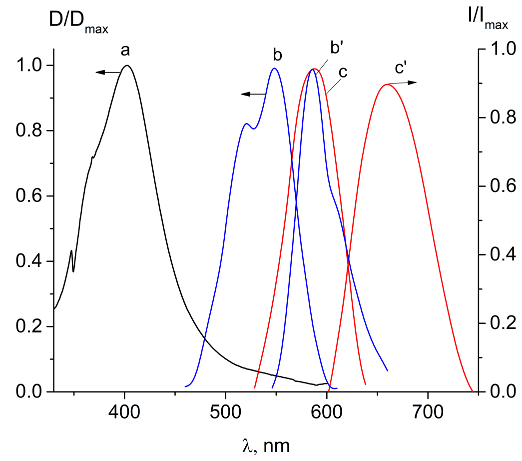
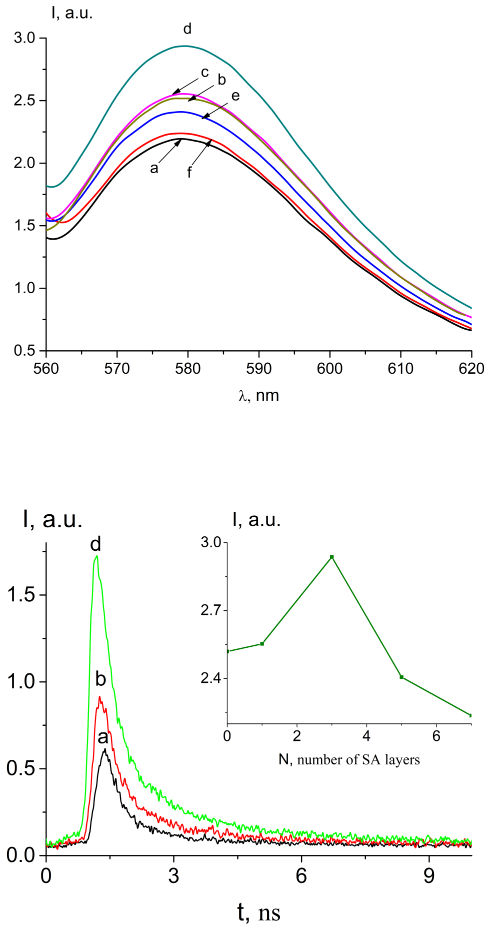


Figure 2: Absorption (a – c) and fluorescence (b′, c′) spectra of SIF (a), HERB (b, b′) and NR (c, c′)

ther growth in the fluorescence intensity was obtained when distance between the silver films and HERB was increased. The maximum increase in emission, almost 25%, was recorded at a distance from the dye to the SIF of ~6 nm, which is equal to three monolayers of fatty acid. Subsequent increase in the distance leads to a decrease in the intensity of the dye fluorescence to almost the original value (Table 3).

Spectral-kinetic measurements (Figure 3(2)) have shown that the fluorescence lifetime of the dye also decreases and repeats the dependency of changes in the fluorescence intensity of HERB in the presence of silver. Thus, the maximum decrease in the τ value (by 80%) was also recorded when the distance from the LB film of HERB to the silver was 6 nm. Similar results were obtained for NR films.



(1)

(2)

Figure 3: Fluorescence spectra (1) and kinetics (2) of HERB at different distances to SIF, stearic acid layers: a – pure dye; b – direct contact with the SIF; c – 1; d – 3; e – 5; f – 7. On the inset – distance dependence of the fluorescence intensity of the HERB at different distances from the SIF. On the abscissa – the number of SA layers

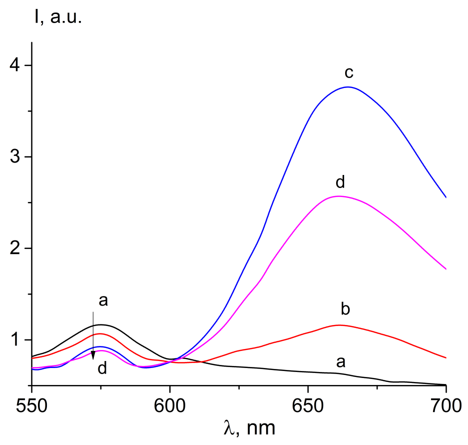


Figure 4: Fluorescence spectra (λ_{ex} = 490 nm) of the donor (a) and donor-acceptor films (b – d) at various acceptor concentration of acceptor, mol%: b – 5; c – 10; d – 20

In the FRET study, donor-acceptor films were excited in the absorption band of the energy donor (λ_{ex} = 488 nm).

An increase in the concentration of NR in LB films leads to the strong quenching of HERB fluorescence. When the neat acceptor films were excited by wavelength with λ_{ex} = 488 nm, no noticeable fluorescence was detected. Therefore, this long-wavelength emission should be attributed to the sensitized fluorescence of the acceptor molecules, which appear as a result of energy transfer from singlet-excited energy donor molecules to acceptor molecules in the ground state. Energy transfer in this case is carried out according to the scheme [23]:

$$S_1^D + S_0^A \rightarrow S_0^D + S_1^A \rightarrow S_0^D + S_0^A + h\nu_{fl} \qquad (1)$$

The observed quenching of the acceptor fluorescence in LB films is associated with the concentration effect [24, 25]. Since spectral changes in the absorption and fluorescence spectra of the NR films were not observed, it can be assumed that quenching of the dye fluorescence occurs as a result of the reabsorption of photons, emitted by the dye, by neighboring molecules.

The kinetic measurements of donor fluorescence decay also confirm interlayer energy transfer between LB films of HERB and NR. The measured fluorescence lifetimes (τ_{fl}) of the donor and sensitized fluorescence of the acceptor, as well as the energy transfer efficiency (E_{ET}) are presented in Table 2. The value of E_{ET} was estimated from the expression [24]:

$$E_{ET} = 1 - \frac{\tau_D}{\tau_{0D}} \qquad (2)$$

Since the highest energy transfer efficiency was observed when the NR concentration was equal to 10 mol%, further we used this concentration to study the plasmon effect on the FRET.

Table 2: Lifetimes of the fluorescence of the donor (λ_{reg} = 555 nm) and the acceptor (λ_{reg} = 655 nm) when excited in the absorption band of the donor.

Acceptor concentration, mol%	E_{ET}	τ_{fl}, ns λ = 542 nm	 λ = 655 nm
0	-	1.8	-
5	0.28	1.3	1.2
10	0.36	1.15	1.0
20	0.32	1.22	0.9

Table 3: The lifetime of the fluorescence of the energy donor in the presence of an acceptor and SIF

Sample	τ, ns	E_{ET}
Donor	1.8	-
Donor +SIF	1.6	-
Donor +SA+ SIF	1.0	-
Donor + acceptor	1.15	0.36
Donor + acceptor + SIF	0.82	0.50
Donor + acceptor +SA+ SIF	0.75	0.58

Spectral-kinetic measurements of donor-acceptor films on the SIF have shown that the efficiency of energy transfer was growing in the presence of Ag (Table 3). At the same time, when the donor-acceptor film was removed from the SIF at 6 nm, the energy transfer efficiency was also increases.

Thus, it has been shown that the efficiency of the FRET can be increased in the presence of SIF. At the same time, an increase in E_{ET} can be result of two factors. The first of these is associated with an increase in the number of donor molecules in the S_1-state in the presence of an SIF, which was also suggested by the authors of [14, 15, 26]. It can be assumed that in this case the effect of the SIF on the acceptor films is practically non-existent, since they are separated from the silver film by 3 monolayers of SA and 5 monolayers of donor.

A second possible factor is a direct influence of the LPR on the energy transfer rate. As it was shown in ref. [19, 27] the energy transfer rate constant k_{ET} can be estimated from the data on the energy transfer efficiency E_{ET} and the fluorescence lifetime of donor τ_{0D}. The estimation has shown that in the studied donor-acceptor pair k_{ET} is equal to $2.1 \cdot 10^8$ s^{-1}. In the direct contact with the SIF, the k_{ET} value was increased to $3.5 \cdot 10^8$ s^{-1}; when the donor-acceptor system was separated by 6 nm from the SIF, the energy transfer rate increased in 2.6 times compared to the initial value and was equal to $5.5 \cdot 10^8$ s^{-1}.

4 Conclusion

The influence of the distance between the films of dye and silver on the plasmon-enhanced fluorescence was studied. It was shown that an increase in the luminescence intensity of the dye can be registered in the case of direct contact of the dye film with silver nanoparticles. The maximum increase in the fluorescence intensity of both HERB and NR was recorded at a distance from the dye to the SIF of ~6 nm. A further increase in the distance leads to a decrease in the fluorescence intensity of the dye to almost the original value. The observed changes are associated with an increase in the rate of electronic transitions in dye molecules that are in the near field of metal NPs with excited plasmons, which is confirmed by a decrease in the fluorescence lifetime in this case.

Studies of the effect of silver nanoparticles on FRET showed that the efficiency of energy transfer can be increased in 1.6 times. In this case, the increase in E_{ET} can be associated with both the direct influence of the plasmon effect on the energy transfer rate constant and the increase in the fluorescence quantum yield of the energy donor due to the plasmon effect of the SIF. This confirms the findings of ref. [28, 29], where it was shown that the plasmon effect on FRET can include increase in the excitation rate due to local electromagnetic field, an increase in the of radiative decay rate through the coupling of a surface plasmon with emission, and the quenching resulting from nonradiative energy transfer from the chromophore to metal substrate.

The results can serve as a basis for studying of photoinduced processes in hybrid materials such as organic dye-plasmon nanoparticles, to increase the photosensitivity of solar cells in the visible region of the spectrum, for the studying of photobiological processes associated with the collection and delivery of light energy to reaction centers, as well as to create materials with given properties, sensors and transducers of light energy.

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