

Plasmon-activated Förster energy transfer in molecular systems

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To explain the experimentally observed effect of silver nanoparticles on the fluorescence of organic dyes and the nonradiative intermolecular transfer of electronic excitation energy in multilayer nanostructures, the previously proposed theoretical model of plasmon resonance in spherical nanoparticles of metals was used. The rates of radiative and nonradiative (FRET) processes in film structures with Ag nanoparticles were calculated for fluorescein and rhodamine B molecules, as well as for two-component systems fluorescein–nile red (NR) and rhodamine B–NR. A version of the model was used that takes into account the effect of NPs on FRET between molecules, the radiative decay of donor and acceptor molecules, and the energy transfer from the dye to plasmonic nanoparticles. The calculation of the U_{DA} rate for pairs with different energy transfer efficiency showed a greater increase in the U_{DA} parameter for the fluorescein–nile red pair than for the rhodamine B–nile red pair. Estimation of the fluorescence enhancement factor of donor and energy acceptor molecules and the rate of energy transfer from the dye to silver NPs showed their insignificant contribution to the formation of the resulting energy transfer efficiency enhancement in the presence of plasmonic NPs.

Keywords: energy transfer, silver nanoparticles, plasmon, model

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Introduction

Intermolecular non-radiative inductive resonance energy transfer (FRET) has found wide application in the field of biophysics and bioimaging [1,2], near-field optical microscopy [3] and photovoltaics [4–6]. It is also of interest in solving problems in which the efficient transfer of optical excitation at distances smaller than the wavelength is the key process.

At present, there are a fairly large number of articles devoted to the effect of metal nanoparticles (NPs) on the intermolecular non-radiative energy transfer in a donor-acceptor (DA) system. It is shown that the efficiency of energy transfer can be both increased and decreased and depends on the properties of the plasmon resonance of metal NPs, the mutual arrangement of the system components and the distance between the donor-acceptor pair and the metal NP, as well as on the spectral overlap between them [7–9]. In addition, the plasmon effect makes it possible to significantly increase the distances at which energy transfer occurs, as was shown in the articles [10–12].

For example, the authors of articles [13–15] have shown that plasmon-enhanced energy transfer between light-emitting molecules makes it possible to increase the luminescent characteristics of acceptor molecules or quantum dots. As was shown in articles [16–18], this phenomenon is being actively studied from the point of view of its use in metal-semiconductor hybrid nanostructures to

create new active materials for light-emitting diodes. In addition, the strong dependence of the efficiency and rate of FRET under conditions of dipole-dipole interaction with plasmonic nanostructures and resonant photonic cavities has a high potential for use in metamaterials and photonic crystals [19,20].

In a number of theoretical and experimental works, FRET has been studied at the level of individual molecules and particles, or for certain (so-called „model“) compounds [21,22]. However, for a wide class of compounds, this process is still poorly understood, and the number of articles devoted to the creation of model representations of plasmon-activated energy transfer between organic molecules is relatively small [23–26].

In this article, we use the theoretical model previously proposed in [23], which describes the effect of localized plasmon resonance of spherical metal NPs on the development of FRET, and test its modified version using a regularized molecular nanostructure as an example. For this, we used the experimental data published in the article [27], where the plasmon-enhanced Förster resonant energy transfer in donor-acceptor pairs with different energy transfer efficiencies was experimentally studied. Layered dye films interspersed with screening layers of stearic acid molecules using the Langmuir–Blodgett technology (LB technology) with an island distribution of silver NPs on the substrate surface were prepared for the study in [27]. The size of Ag NPs in films was 80–100 nm. It was shown that

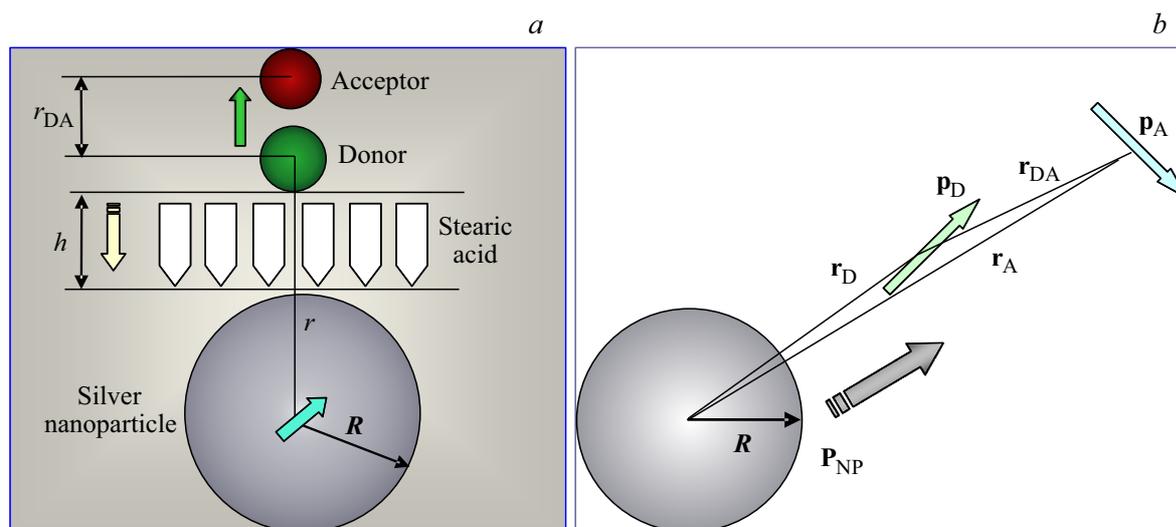


Figure 1. (a) A fragment of a layered nanostructure is a cluster of nearby particles: a plasmonic Ag NP, a part of a layer of stearic acid molecules, and a separate donor-acceptor pair of dye molecules. (b) Donor-acceptor pair of molecules near a spherical NP. The orientation of the molecular dipoles of the donor \mathbf{p}_D and acceptor \mathbf{p}_A near the metal NP is random.

the maximum plasmon effect on the fluorescence intensity of the dye film is observed at a distance of about 6 nm from the silver island film. The plasmonic increase in non-radiative energy transfer turned out to be greater for a pair with a low energy transfer efficiency in the absence of NPs. In this case, the energy transfer rate constant in the presence of NPs was almost 4 fold higher for the fluorescein–nile red (NR) pair compared to the rhodamine B–NR pair (NR as an acceptor). The highest increase in the energy transfer rate in a regular nanostructure with plasmonic components was registered in cases where monolayers of donor molecules were located at a distance of $h \sim 6$ nm from the surface of the silver island film.

Theoretical model

The proposed model takes into account only one of the spherical plasmonic NPs of an island metal film, which is closest to the selected molecular pair DA. The SEM images obtained in the article [27] indicate a rather isolated nature of individual NPs (islands). Therefore, in contrast to the models of articles [28–30], in which a continuous homogeneous metal layer was considered, in this case it is appropriate to identify only nearby particles into a separate cluster: a plasmon globule with radius R and one donor-acceptor molecular pair separated from it by several layers of stearic acid with thickness h (Fig. 1).

Decay of the electronically excited state of the S_1^D donor molecule is possible along one of three competing channels (Fig. 1):

1) radiative decay of $S_1^D \rightarrow \hbar\omega + S_0^D$ at rate of $w_{sp} = (\omega|r_D = h)$ with formation of a luminescence photon with energy $\hbar\omega$;

2) intermolecular non-radiative transfer of electronic excitation energy from donor to acceptor $S_1^D + S_0^A \rightarrow S_0^D + S_1^A$ at rate of $U_{DA}(\omega|r_{DA}, r_D, r_A)$, where r_{DA}, r_D, r_A — the distances between D and A molecules, as well as the distance from the NP center to the D and A molecule, respectively;

3) non-radiative transfer of electronic excitation energy at rate of $U(\omega|r_D)$ from a donor molecule to a metal NP $S_1^D \rightarrow S_0^D + \hbar\omega_{res}$, with formation of attenuating localized plasmon with energy of $\hbar\omega_{res}$ (direct quenching of the luminescence of a metal NP donor).

In the presence of a plasmonic NP in the near zone of the donor D and acceptor A molecules, the rates of all three decay channels change, i.e. become plasmon-dependent. Introduction of a homogeneous or composite NP into the nearest neighborhood of a molecule with a molecular dipole \mathbf{p} changes the local electromagnetic field at its location, which can be taken into account by introducing a common dipole moment $\mathbf{p}' = [\mathbf{I} + \vec{\mathbf{G}}(\mathbf{r})\vec{\alpha}(\omega)]\mathbf{p}$ of the system „NP–molecule“ containing the contribution of the polarized NP. Here \mathbf{I} — unit dyad, $\vec{\alpha}(\omega)$ — particle dipole polarizability tensor, $\vec{\mathbf{G}}(\mathbf{r})$ — dyadic Green's function,

$$\vec{\mathbf{G}}(\mathbf{r}) = r^{-3} \left[\frac{3(\mathbf{r} \otimes \mathbf{r})}{r^2} - \mathbf{I} \right],$$

of quasi-static field of a dipole source [23]. The dipole polarizability $\vec{\alpha}(\omega)$ of a particle is a second rank tensor if the shape of the particle is other than spherical (for example, ellipsoidal) and/or the conducting particle is in an external magnetic field [31,32], which forms the anisotropic properties of the electron plasma of the particle metal.

Then, the expression for the rate of spontaneous emission of a donor D molecule located near NP at a distance r from

its center can be written as follows [23]:

$$w_{sp}(\omega|\mathbf{r}) = \frac{4}{3} \frac{\omega^2}{\hbar c^2} \left[\mathbf{p}_D^2 + \mathbf{p}_D \left| \vec{\alpha}(\omega) \vec{\mathbf{G}}(\mathbf{r}) \right|^2 \mathbf{p}_D + 2 \operatorname{Re} \mathbf{p}_D \left(\vec{\alpha}(\omega) \vec{\mathbf{G}}(\mathbf{r}) \right) \mathbf{p}_D \right]. \quad (1)$$

In case of a spherical particle and in the absence of external magnetic field, the dipole polarizability tensor $\vec{\alpha}(\omega)$ of such a particle is reduced, $\vec{\alpha}(\omega) \rightarrow \alpha(\omega)$, to its scalar prototype $\alpha(\omega)$ [31]. The first term in (1) corresponds to the rate of radiative decay of the donor in the absence of NPs, the second one — to the contribution to the decay of the field reflected from NPs. The third term is the result of the interference of the two mentioned decay channels and can have any sign „+“ or „-“ depending on the phase relation between the decay rates. Based on (1), a computer calculation of the frequency dependences (spectra) of the radiative decay rate of the donor, as well as the dependence of this rate on the distance $r = |\mathbf{r}_D| = h + R$ between donor and NP. Even without performing such calculations, some preliminary conclusions can be drawn regarding the dependence of the transfer efficiency on the parameter h . Thus, the second term in (1) has the dependence $(h + R)^{-6}$, while the third, interference term — $(h + R)^{-3}$. Thus, at relatively large distances h the role of this term can become decisive. Moreover, as already noted, its sign can be anything.

The intensity $\mathbf{E}(\mathbf{r}_A)$ of the resulting field at the point where the acceptor is located, i.e. the field of the donor source and the reflected NP field, can be written in the form

$$\mathbf{E}(\mathbf{r}_A) = \vec{\mathbf{G}}(\mathbf{r}_{DA}) \mathbf{p}_D + \vec{\mathbf{G}}(\mathbf{r}_A) \vec{\alpha}(\omega) \vec{\mathbf{G}}(\mathbf{r}_D) \mathbf{p}_D.$$

Then, the rate $U_{DA} \sim (\mathbf{p}_D \mathbf{E}(\mathbf{r}_A))^2$ of non-radiative energy transfer to an acceptor molecule with transition dipole moment \mathbf{p}_A located at a point \mathbf{r}_A can be presented as

$$U_{DA}(\mathbf{r}_{DA}, \mathbf{r}_D, \mathbf{r}_A) \sim \left| \mathbf{p}_D \vec{\mathbf{G}}(\mathbf{r}_{DA}) \mathbf{p}_A \right|^2 + \left| \mathbf{p}_D \vec{\mathbf{G}}(\mathbf{r}_D) \vec{\alpha}(\omega) \vec{\mathbf{G}}(\mathbf{r}_A) \mathbf{p}_A \right|^2 + 2 \operatorname{Re} \left\{ \mathbf{p}_D \vec{\mathbf{G}}(\mathbf{r}_{DA}) \mathbf{p}_A \left[\mathbf{p}_D \vec{\mathbf{G}}(\mathbf{r}_D) \vec{\alpha}(\omega) \vec{\mathbf{G}}(\mathbf{r}_A) \mathbf{p}_A \right] \right\}. \quad (2)$$

Based on the structure of expression (2), we can conclude that the rate $U_{DA} \sim (\mathbf{p}_A \mathbf{E}(\mathbf{r}_A))^2$ depends on the distance $r = |\mathbf{r}_D| = h + R$. It has a character similar to the dependence $w_{sp}(|\mathbf{r}_D|)$. As for the rate of radiative decay, the third (interference) term in (2) is characterized by the dependence $w_{sp}^{(3)}(|\mathbf{r}_D|) \sim (h + R)^{-3}$.

Distance r_{DA} between molecules D and A in an arbitrary planar configuration of vectors \mathbf{p}_D and \mathbf{p}_A of the dipole moment and radius-vectors \mathbf{r}_D and \mathbf{r}_A of molecules are written in the general case as $r_{DA} = \sqrt{r_D^2 + r_A^2 - 2r_D r_A \cos \theta}$, and

when the molecules are aligned vertically to the plane of the layer (Fig. 1, b), the angle $\theta = 0$ and $r_{DA} = r_A - r_D$.

The resulting expression for FRET rate can be written as follows:

$$U(r_{DA}, r_D, r_A, \theta, \vartheta_D, \vartheta_A) = U_F(r_{DA}, \theta, \vartheta_D, \vartheta_A) + \frac{32\pi}{\hbar^2} \frac{p_D^2 p_A^2}{r_{DA}^6} \cos^2 \theta \left(\frac{r_{DA} R}{r_D r_A} \right)^3 \int \left[|\alpha'(\omega)|^2 \left(\frac{r_{DA} R}{r_D r_A} \right)^3 - \frac{(1 - 3f(\theta, \vartheta_D, \vartheta_A))}{2} \operatorname{Re}[\alpha'(\omega)] \right] G_D(\omega) G_A(\omega) d\omega, \quad (3)$$

where $G_D(\omega), G_A(\omega)$ — the Gaussian contours of the spectral bands of the luminescence of the donor and the absorption of the acceptor. The first term in (3) is the rate $U_F(r_{DA}, \theta, \vartheta_D, \vartheta_A)$ of energy transfer according to Förster:

$$U_F(r_{DA}, \theta, \vartheta_D, \vartheta_A) = \frac{2\pi}{\hbar^2} \frac{p_D^2 p_A^2}{r^6} \cos^2 \theta (1 - 3f(\theta, \vartheta_D, \vartheta_A))^2 \times \int G_D(\omega) G_A(\omega) d\omega,$$

$$U_F(r_{DA}, \theta, \vartheta_D, \vartheta_A) = \frac{U_0}{r_{DA}^6} \cos^2 \theta (1 - 3f(\theta, \vartheta_D, \vartheta_A))^2,$$

where the angular factor

$$f(\theta, \vartheta_D, \vartheta_A) = \frac{\cos \vartheta_D \cos \vartheta_A}{\cos \theta}$$

(ϑ_D, ϑ_A — angles between the direction of the dipole moments of transitions in the corresponding molecules D and A and the vector connecting the centers of gravity of the donor and acceptor molecules), $\alpha'(\omega)$ — specific polarizability of a spherical NP,

$$\alpha'(\omega) = \frac{\alpha(\omega)}{R^3} = \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}, \quad (4)$$

$\varepsilon_1(\omega)$ and ε_2 — dielectric permittivities at a frequency ω of metal NP (silver) and the environment.

In the configuration of Fig. 1, depending on the direction of the vectors of molecular dipoles aligned along the normal to the layer ($m = 0$ or $m = 1$), we obtain $f(0, 0, m\pi) = \pm 1$, $1 - 3f(0, 0, m\pi) = 1 \pm 3$, $U_F(r_{DA}, 0, 0, m\pi) = (1 \pm 3)^2 U_0 r_{DA}^{-6}$.

The effect of a metallic NP in the system under consideration is not limited to the enhancement of spontaneous transitions in a molecule. It is also necessary to take into account the non-radiative transfer of the electron excitation energy from the donor molecule to the NP plasmonic modes and the subsequent attenuation of these modes. The rate U of such a process in tensor form can be written as follows [25]:

$$U(\omega|\mathbf{r}) = (2\hbar)^{-1} V \operatorname{Im}[\mathbf{E}^*(\omega) \alpha'(\omega) \mathbf{E}(\omega)] = (2\hbar)^{-1} V \operatorname{Im}[\mathbf{p}_D \vec{\mathbf{G}}(\mathbf{r}) \alpha'(\omega) \vec{\mathbf{G}}(\mathbf{r}) \mathbf{p}_D]. \quad (5)$$

Here V — the volume of the nanoparticle.

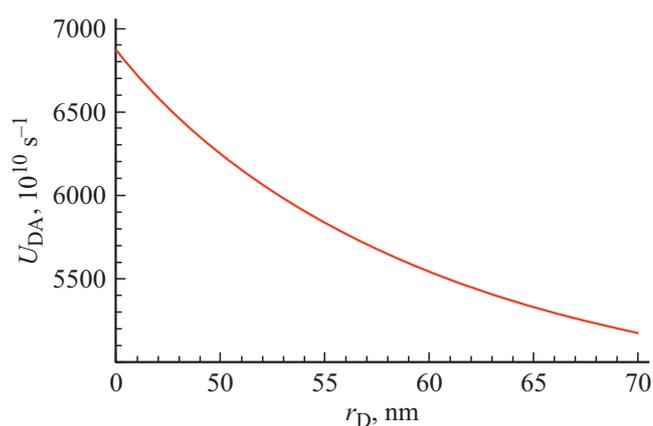


Figure 2. Distance dependences of the total rate of non-radiative energy transfer U_{DA} in the presence of Ag NP for a pair of fluorescein–NR.

Results and discussion

According to the proposed model, the energy transfer rates were calculated for the above pairs of molecules studied in [27]. In the calculation program, all three particles: two dye molecules and a metal NP were located along the same straight line, all angles in the accepted configuration were taken equal to zero. To determine the overlap integrals of the donor-acceptor pair, as well as with the plasmon spectrum of Ag NPs, the parameters of the spectra approximation by the Gaussian method were used. The distance between the donor and acceptor molecules was taken to be 1.2 nm for the fluorescein–NR pair and 2.2 nm for the rhodamine B–NR pair, which corresponds to the geometrical dimensions of the donor molecule, taking into account their van der Waals radii [33], evaluated when simulating by molecular mechanics methods AM⁺ in the HyperChem 8.0 package. The radius of Ag NPs was taken equal to 45 nm, and the distance between the center of the donor molecule and the surface of Ag NPs was 6 nm [27].

The distance dependence of the total energy transfer rate for DA pairs of fluorescein–NR (Fig. 2) and rhodamine B–NR is calculated. The plot along the abscissa shows the distance from the center of Ag NPs to the center of the donor molecule. It can be seen in Fig. 2 that an increase in the distance from the donor molecule to the plasmon particle leads to a power-law decrease in the energy transfer rate. A similar relationship was obtained for the rhodamine B–NR pair. The values U_{DA} are much larger for the fluorescein–NR pair. At a distance of ~ 6 nm, the values of the plasmon-enhanced energy transfer rate differ by a factor of 3.6 for the donor-acceptor pairs under study. An estimate of the energy transfer rate increase factor U_{DA}/U_F gave the values $5.9 \cdot 10^3$ and $29 \cdot 10^3$ for rhodamine B–NR and fluorescein–NR pairs, respectively. The dependences obtained correlate well with the data given in the article [27], where a greater increase in the energy

transfer efficiency is observed for pairs with lower FRET efficiency.

Dye	p, D	w_{sp}^0, s^{-1}	w_{sp}, s^{-1}	w_{sp}/w_{sp}^0	$U(\omega, r), \text{s}^{-1}$
Fluorescein	6.23	$0.8 \cdot 10^8$	$1.23 \cdot 10^9$	15.4	$0.08 \cdot 10^9$
Rhodamine B	9.78	$1.5 \cdot 10^8$	$2.1 \cdot 10^9$	14.0	$0.15 \cdot 10^9$
NK	12.06	$1.6 \cdot 10^8$	$2.0 \cdot 10^9$	12.5	$0.17 \cdot 10^9$

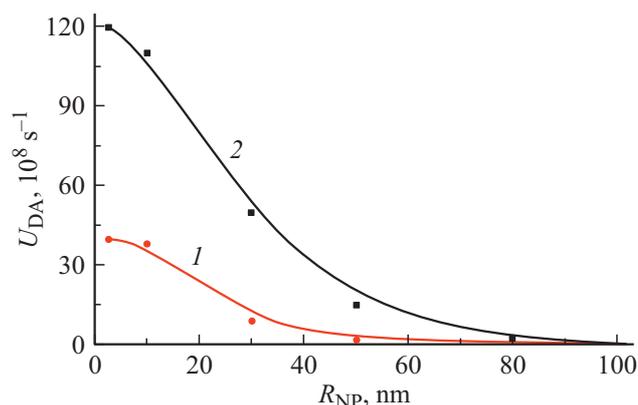


Figure 3. Dependence of the total energy transfer rate U_{DA} (1, 2) in the presence of Ag NPs of various radii for fluorescein–NR (1) and rhodamine B–NR pairs (2).

transfer efficiency is observed for pairs with lower FRET efficiency.

We also estimated the fluorescence enhancement coefficients of individual donor and energy acceptor molecules w_{sp} and the rate $U(\omega, r)$ of non-radiative energy transfer from the dye to silver NPs (table).

It can be seen in the table that the fluorescence enhancement factor is larger for the first energy donor (fluorescein), while the $U(\omega, r)$ values are larger for rhodamine B and NR. Perhaps, it is this circumstance that causes a smaller increase in the U_{DA} values when performing FRET between the last dyes. At the same time, the order of magnitude of the rates w_{sp} and $U(\omega, r)$ is much smaller than for U_{DA} , and, consequently, they make much less contribution to the overall enhancement of the energy transfer efficiency in the presence of plasmonic NPs.

In order to find the optimal conditions for increasing the efficiency of the process of energy transfer between organic dyes, we calculated the dependence of the total energy transfer rate U_{DA} on the Ag NP radius (Fig. 3). This is due to the fact that it was shown in the article [27] that after annealing of the deposited silver film, clusters of almost regular spherical silver particles with a radius of 80–100 nm are formed. Intermediate sections between them are occupied by NPs with a smaller radius equal to 20–40 nm.

For the donor and acceptor molecules under study, the energy transfer rate strongly depends on the radius of the plasmonic NPs. In this case, the dependence can be

described by a power function. It is characteristic that for NPs with a radius in the range from 2.5 to 10 nm, the energy transfer rate U_{DA} is practically independent of the NP size. An increase in the Ag NP radius to 30 nm leads to an almost twofold decrease in the plasmon-enhanced energy transfer rate. For the largest Ag NPs, the decrease of U_{DA} by 3 orders of magnitude for the fluorescein–NR pair and by 2 orders of magnitude for the rhodamine B–NR pair was obtained. Thus, a greater increase in FRET will be observed when Ag NPs of a smaller diameter are used.

For these donor-acceptor pairs, the angular dependences U_{DA} for the fluorescein–NR pair were also calculated. The angular dependence of the total energy transfer rate changes little with a change in the NP size, however, the coefficient of increase in this rate is greater for particles of a smaller radius.

Conclusion

Thus, the applicability of the theoretical model proposed in [23,25] for the effect of plasmon resonance of metal NPs on the non-radiative transfer of electronic excitation energy is shown to describe a number of processes developing in regular layered nanostructures [27]. The model modified for the experimental conditions [27] takes into account the effect of NPs on FRET, the radiative decay of donor and acceptor molecules, and the energy transfer from the dye to plasmonic NPs.

The calculation results obtained using the modified model show a good correlation with the experimental data [27]. In particular, the calculation of the U_{DA} rates in the presence of plasmonic NPs in the system for pairs of molecules with different energy transfer efficiency showed a greater increase in U_{DA} as a result of the action of the plasmonic catalyst for the fluorescein–NR pair. The coefficient of plasmon enhancement of the fluorescence of donor and acceptor molecules was also estimated by calculating the rate w_{sp} of spontaneous transitions and the rate of energy transfer from the dye to silver NPs $U(\omega, r)$. For the studied dyes, these rates turned out to be significantly lower than U_{DA} , which means that although these channels are sensitive to the plasmon effect, they make a minimal contribution to the overall increase in the efficiency of energy transfer in the presence of plasmonic NP. The calculation also showed that the effect of an increase in the FRET rate will increase when Ag NPs of a smaller diameter are used.

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Conflict of interest

The authors declare that they have no conflict of interest.

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