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Förster resonance energy transfer from colloidal quantum dots to xanthene dye in polymer film

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Abstract. In the work, a system with effective (up to 90%) Förster resonance energy transfer is implemented. The system includes thin gelatin films with embedded CdTe quantum dots (donors) and rose bengal xanthene dye (acceptor). The energy transfer mechanism revealed to be possible due to the high local concentration of fluorophores as well as careful selection of donor and acceptor spectral characteristics. The energy transfer was confirmed by the quenching of the donor photoluminescence in both steady-state and time-resolved measurements. The Stern-Volmer formalism and the Förster theory were used to estimate the constants and efficiency of energy transfer. It was shown that the photoluminescence spectrum of the system can be driven by changing the ratio of the donor-to-acceptor concentration.

Keywords: Förster Resonance Energy Transfer, FRET, colloidal quantum dots, nanocrystals, polymer film

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Резонансный перенос энергии Фёрстера от коллоидных квантовых точек к ксантеновому красителю в полимерной пленке

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Аннотация. В работе реализована система с эффективной (до 90%) резонансной передачей энергии Фёрстера. Система для реализации механизма переноса энергии состояла из тонких желатиновых пленок, с внедренными квантовыми точками CdTe и ксантеновым красителем бенгальский розовым, в качестве донора и акцептора энергии соответственно. Механизм переноса энергии оказался возможным благодаря высокой локальной концентрации флуорофоров в составе полимерной пленки, а также тщательному подбору спектральных характеристик донора и акцептора. Перенос энергии был подтвержден тушением и уменьшением времени жизни фотолюминесценции донора, используя методы стационарной и разрешенной во времени спектроскопии. Для оценки констант и эффективности переноса энергии использовались формализм Штерна-Фольмера и теория Фёрстера. Было показано, что спектром фотолюминесценции системы можно управлять, изменяя стехиометрию донорно-акцепторной пары.

Ключевые слова: Фёрстеровский перенос энергии, коллоидные квантовые точки, нанокристаллы, полимерные пленки

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Introduction

Creation of light sources with adjustable spectral properties is of high interest in medicine [1], sensing [2], design of optoelectronic devices [3], lasers, photocatalysis and photopatterning [4]. Usually layers of several fluorophores are used to obtain a complex spectrum. In this case, it is necessary to simultaneously efficiently excite all components, which taking into account their different spectral properties is not always realizable.

One of the ways to obtain a complex spectrum in a wide spectral region is the implementation of the mechanism of nonradiative transfer of electronic excitation energy in a system of two fluorophores which is also called Förster Resonance Energy Transfer (FRET) [5]. This requires short-wavelength excitation of the donor, which partially transfers its energy to a longer-wavelength acceptor.

The efficiency of energy transfer depends on the degree of overlap between the photoluminescence spectra (PL) of the donor and absorption of the acceptor, the relative orientation of the dipole moments of transitions, and the distance between molecules [5]. Therefore, the key point for the implementation of this mechanism is the careful selection of the donor-acceptor pair and matrix.

The aim of the work was to create a luminophore in the form of a polymer film doped with semiconductor quantum dots (CdTe QDs) and xanthene dye (rose bengal). The photochemically stable QDs (donor) has a wide intense absorption spectrum from UV to the middle of the visible range and the acceptor has the ability to luminesce in the red region. The absorption, steady-state and time-resolved spectroscopy methods were used to determine the efficiency of spectral conversion. The results were interpreted using the Stern-Volmer formalism and the Förster theory.

Materials and Methods

The water dispersible semiconductor quantum dots CdTe (CdTe QDs stabilized with thioglycolic acid were supplied by PlazmaChem with a photoluminescence wavelength of 550 ± 5 nm and a size of 2.6 nm. Rose bengal (RB) (4,5,6,7-Tetrachloro-2′,4′,5′,7′-tetraiodofluorescein disodium salt) were supplied by Sigma-Aldrich. The stock solutions of CdTe QDs and rose bengal were 10^{-4} и 10^{-3} M respectively. Photographic gelatin type B were supplied by Vekton. All chemicals were used as delivered.

Polymer films formation

The gelatin solution (1% wt.) in which quantum dots and dye were added was used to prepare polymer films. The concentration of quantum dots in the mixture was constant and equal to 8.2 μM. The dye concentration was varied in the range of 1—67 μM. Then the solutions were mixed on a magnetic stirrer and applied by dropping onto glass substrates. The samples were left for a day at room temperature as a result films without visible defects were obtained.

The absorption and fluorescence measurements

The absorption spectra were recorded on a Lambda 35 (Perkin Elmer) spectrophotometer. The fluorescence spectra were measured on a Fluorolog 3–22 spectrofluorimeter (Horiba Scientific, USA) with excitation wavelength 453 nm. The spectra were corrected for the spectral sensitivity of the detector and the reabsorption effect.

The time-resolved measurements were performed using the DeltaHub timing module (Horiba, USA) upon excitation by a NanoLED N-453 pulsed laser diode with a maximum of 453 nm and pulse duration of < 1.3 ns. The intensity decays were detected at the wavelengths corresponding to the maxima of the fluorescence spectra and described by a sum of three exponents using deconvolution analysis by the DAS6 software (Horiba Scientific, USA). χ^2 statistical criteria was applied. Average lifetime was calculated taking the amplitude contribution of the components into account.

The L-geometry was used for measurements of aqueous solutions of dyes and quantum dots dispersed in water using standard quartz cuvettes with a cross section of 1×1 cm. The front-face geometry was used for measurements of polymer films doped with fluorophores. All measurements were carried out at room temperature.

The analysis of changes in the photoluminescence spectrum depending on the stoichiometry of the fluorophores

Estimation of the change in the gravity center of the spectrum (*GC*) which takes into account both changes in the position of the maximum and the shape of the contour was carried out to analyze the change in the PL spectrum [6]:

$$GC = \frac{\sum_i^j I(\lambda)\lambda}{\sum_i^j I(\lambda)}, \tag{1}$$

where *GC* – gravity center, $I(\lambda)$ – intensity at the corresponding wavelength λ, i and j – initial and final wavelengths, respectively.

FRET model

According to the theory of Förster [5] the rate constant k_{ET} is determined by equation:

$$k_{\mathrm{ET}}(r) = \frac{1}{\tau_{\mathrm{D}}}\left(\frac{R_0}{r}\right)^6, \tag{2}$$

where τ_D is the average lifetime of the donor, r is the distance between donor and acceptor, R_0 is the Förster distance (the distance at which the energy transfer efficiency is 50%) and determined by:

$$R_0 = \left(\frac{9000 \ln 10}{128\pi^5 n^4 N}\kappa^2\,\Phi_{\mathrm{D}}\,J\right)^{1/6}, \tag{3}$$

where κ^2 is the dipole orientation factor, Φ_D is the PL quantum yield of donor, n is refractive index of medium, N is Avogadro's number, J – spectral overlap between donor fluorescence and acceptor absorption and determined as follow:

$$J = \int I_{\mathrm{D}}(\tilde{\nu})\varepsilon_{\mathrm{A}}(\tilde{\nu})\tilde{\nu}^{-4}d\tilde{\nu} \Big/ \int I_{\mathrm{D}}(\tilde{\nu})d\tilde{\nu}, \tag{4}$$

where $I_{\mathrm{D}}(\tilde{\nu})$ is the intensity of the donor PL, $\varepsilon_{\mathrm{A}}(\tilde{\nu})$ is the molar extinction coefficient of the acceptor.

The transfer efficiency (E) which is only a function of actual (r) and Förster distance (R_0):

$$E = \frac{1}{1 + (r/R_0)^6}. \tag{5}$$

The experimental transfer efficiency obtained by:

$$E = 1 - \frac{I_{\mathrm{DA}}}{I_{\mathrm{D}}} \text{ or } E = 1 - \frac{\tau_{\mathrm{DA}}}{\tau_{\mathrm{D}}}, \tag{6}$$

where I_D and I_{DA} is PL intensity, τ_D and τ_{DA} is average lifetime in absence (D) and presence (DA) of acceptor, respectively.

Results and Discussion

Fig. 1 shows the absorption and photoluminescence spectra of quantum dots and rose bengal dye embedded in a gelatin film.

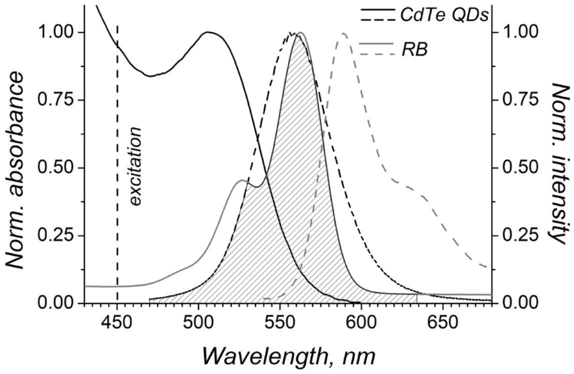

Fig. 1. Absorption and PL spectra of CdTe QDs (donor) and rose bengal (acceptor) in gelatin film

It is necessary to achieve a high degree of overlap between the photoluminescence spectrum of the donor and the absorption spectrum of the acceptor in order to implement energy transfer.

The spectral overlap and the Förster distance were obtained using **equations 3** and **4** which are $4.94 \cdot 10^{-13}$ M^{-1} cm^{-3} and 4.5 нм, respectively. The orientation factor κ^2 was chosen as for the case of static donor-acceptor orientations which do not change during the lifetime of the excited state. In this case $\kappa^2 = 0.476$ [6]. The PL quantum yield of quantum dots in a polymer film was 20% and was estimated by the relative method.

Also, an important parameter for the implementation of energy transfer is the achievement of a high local concentration of fluorophores which cannot be achieved in aqueous solutions. The estimation of the local concentration for the implementation of energy transfer was carried out according to the equation:

$$C_0 = 3000 / 4\pi N R_0^3. \tag{7}$$

Based on the equation and the found value of the Förster distance, the local concentration turned out to be $4.4 \cdot 10^{-3}$ M. The concentration of quantum dots in polymer films was $7.6 \cdot 10^{-3}$ M and the dye varied in the range $(1–62) \times 10^{-3}$ M which gives confirmationthe implementation of energy transfer in this system.

Experimental confirmation of energy transfer was recorded using stationary and time-resolved measurements (Fig. 2). A wavelength of 560 nm was chosen for recording donor PL quenching which corresponded to the maximum photoluminescence of CdTe quantum dots. It can be seen that with an increase in the dye concentration in the composition of the polymer film simultaneous quenching and a decrease in the PL lifetime occur which is evidence of energy transfer in the donor-acceptor system.

The energy transfer characteristics can be obtained on the basis of the Stern-Volmer quenching formalism. The quenching of PL intensity and decrease lifetime of donor as a function of acceptor concentration is describe by Stern-Volmer equation [7]:

$$\frac{I_{\mathrm{DA}}}{I_{\mathrm{D}}} = \frac{\tau_{\mathrm{DA}}}{\tau_{\mathrm{D}}} = 1 + K_{SV}[RB] = 1 + k_q \tau_{\mathrm{D}}[RB], \tag{8}$$

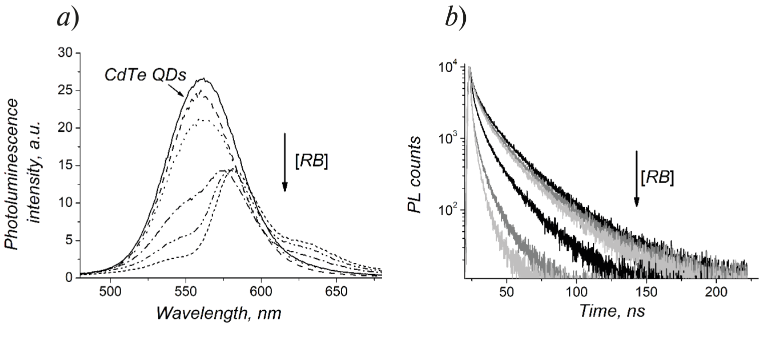

Fig. 2. The fluorescence steady-state spectra (*a*); time-resolved decays of CdTe QDs in gelatin films with increasing of the rose bengal concentration (*b*)

where K_{SV} – the Stern-Volmer quenching constant, k_q – bimolecular quenching constant, [RB] – concentration of dye.

The linear Stern-Volmer plots of I_{DA}/I_D and τ_{DA}/τ_D verses dye concentration is shown in (Fig. 3, *a*).

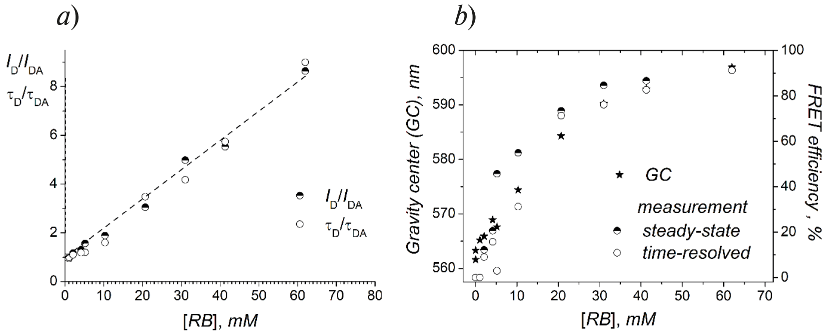

Fig. 3. The Stern-Volmer plots of I_{DA}/I_D and τ_{DA}/τ_D vs. concentration of dye (*a*). The gravity center and FRET efficiency vs. concentration of dye (*b*)

The Stern-Volmer constants are 118.4±0.2 M^{-1} and 119.8±0.3 M^{-1} for steady-state and time-resolved measurements, respectively. The energy transfer rate constants k_{ET} were estimated as (0.09–5.4)×10^8 and (0.09–5.5)×10^8 s^{-1} for steady-state and time-resolved measurements, respectively.

Figure 3, *b* shows the energy transfer efficiency obtained from steady-state and time-resolved measurements as a function of dye concentration as well as the change in the gravity center of the spectrum. The energy transfer efficiency reached 90%. It can be seen that an increase in the dye concentration leads to a change in the PL spectrum and an increase in the efficiency of energy transfer. It can be seen that after a concentration of about 40 mM there is no change in the FRET efficiency. The range of change in the gravity center for the donor-acceptor pair CdTe-rose bengal was 35 nm. Thus, by selecting and varying the ratio of fluorophores it is possible to tune the PL wavelength which can be used for a wide range of application where it is necessary to tune the PL spectrum.

Conclusion

We examined polymer films with embedded QDs (donor) and rose bengal dye (acceptor) with spectral properties that ensure efficient transfer of electronic excitation energy. The donor is able to efficiently convert energy in the near UV and visible range and photochemically stable. The tuning of PL spectrum was adjusted by the donor-acceptor concentration ratio. The FRET efficiency up to 90% and red shift in the emission spectrum of the system of 35 nm occurred with increasing acceptor concentration. The maximum effect was achieved at an acceptor concentration more than 40 mM. The presented approaches and objects are promising for the creation of low-cost systems with tunable spectra.

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