

Forster Resonance Energy Transfer in a Hybrid System of CdTe Quantum dots-RhB

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Abstract. The forster resonance energy transfer (FRET) between different CdTe QDs and RhB were investigated by steady-state and femtosecond time-resolved photoluminescence spectra technique. Through the measurements on three different CdTe sample solutions, it was found that the FRET efficiency is proportional to the spectral overlap degree of CdTe QDs' emission and RhB's absorption. And the FRET efficiency was found to increase with the increase of the RhB's concentration, while the concentration increase to more than 4.5×10^{-5} mol/L, the transfer efficiency decreases. The FRET efficiency can reach to 32.6% when RhB concentration is 4.5×10^{-5} mol/L. With the wide use of FRET in biomolecular interaction analysis and cell physiology, the CdTe QDs-RhB hybrid systems could be a promising candidate for fluorescent probe and photodynamic therapy.

Introduction

Forster resonance energy transfer (FRET) is widely used for the detection of interactions between a directly excited emitter of fluorescence (donor) and a molecule of an energy acceptor [1-8]. The efficiency of FRET depends on several factors : (i) distance between the donor and the acceptor, (ii) overlap degree of the donor emission and the acceptor absorption spectra and (iii) relative orientation of the donor emission and the acceptor absorption transition dipole moments. Besides, FRET can be engineered in artificial structures in order to create light harvesting devices and highly efficient nanosensors [9-12].

Colloidal QDs have attracted great attentions for their unique optical properties [13-15], which are originated from the photoexcitation of the QDs and the electron transfer between valence-band and the conduction-band [16]. In addition, the unique size-tunable absorption and emission properties of nanoparticles are very beneficial for multi-color applications. Depending on the requirements, multiple color QDs can be excited by single-photon or two-photon excitation wavelength, [17].

In this study, the forster resonance energy transfer between CdTe QDs with different emission spectra and RhB solution were investigated by steady-state and femtosecond time-resolved photoluminescence spectra technique. Moreover, the influences of spectral overlap degree and RhB concentration on the FRET efficiency were discussed.

Experimental

The CdTe QDs used the reaction between Cd^{2+} and NaH₂Te solution in the presence of 3-mercaptopropionic acid as stabilizer according to the procedure in Ref. [18]. Three negatively charged CdTe quantum dots samples with different sizes, whose photoluminescence emission maxima at 522nm, 597nm, and 650nm, were used in this study. RhB was obtained from Sanaisi Company (Shanghai, China). CdTe-RhB complexes were prepared by adding appropriate amounts of RhB to 150 uL different CdTe QDs solutions. The deionized water was used as solvent for dissolving the RhB. Five samples with different RhB concentrations were prepared [19-20], which

were 5.5×10^{-6} mol/L (R1), 1.5×10^{-5} mol/L (R2), 2.8×10^{-5} mol/L (R3), 4.5×10^{-5} mol/L (R4), 6.0×10^{-5} mol/L (R5), respectively.

The optical absorption spectra and photoluminescence spectra for emission were measured by a double beam spectrometer (HITACHI U3310) and a fluorescence spectrometer (JASCO FP6500), respectively. Pulses of 130 fs duration at a wavelength of 800nm produced from a Ti:sapphire laser system are used as the two-photon excitation light source. Repetition rate of the laser pulse is 76MHz. The spectra are recorded by EM-CCD (Andor DU970P) through monochromator (Andor SR500).

Theory

FRET is a resonant dipole-dipole coupling interaction that transfers excitation energy from a donor fluorophore to an acceptor chromophore through space. The rate of energy transfer for an isolated single D-A pair separated by a distance r can be expressed by the Forster formalism [21-22]

$$k_{D-A} = \frac{B \times Q_D I}{\tau_D r^6} = \left(\frac{1}{\tau_D}\right) \times \left(\frac{R_0}{r}\right)^6 \quad (1)$$

where, Q_D is the quantum yield of the donor and τ_D is the excited-state lifetime of the donor; the constant B is a function of the refractive index of the medium n_D , Avogadro's number N_A , and a parameter κ_p that depends on the relative orientation of the donor and acceptor dipoles

$$B = \frac{[9000 \times (\ln 10)] \kappa_p^2}{128 \pi^5 n_D^4 N_A} \quad (2)$$

where, $\kappa_p^2 = 2/3$ for randomly oriented dipoles and varies between 0 and 4 for the cases of orthogonal and parallel dipoles, respectively. The overlap integral I , which is defined as

$$I = \int_0^\infty PL_{D-corr}(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda, \quad (3)$$

is a quantitative measure of the donor-acceptor spectral overlap over all wavelengths λ ; it is a function of the normalized donor emission spectrum (dimensionless property), PL_{D-corr} , and the acceptor absorption spectrum (expressed as an extinction coefficient), ε_A . The Forster radius R_0 , which is defined as

$$R_0 = (B Q_D I)^{1/6} = \left(\frac{9000 (\ln 10) \kappa_p^2 Q_D}{N_A 128 \pi^5 n_D^4}\right)^{1/6}. \quad (4)$$

The FRET efficiency, E , defined as

$$E = \frac{k_{D-A}}{k_{D-A} + \tau_D^{-1}} = \frac{R_0^6}{R_0^6 + r^6}, \quad (5)$$

accounts for the fraction of excitons that are transferred from the donor to the acceptor nonradiatively.

For FRET within the quasi-monodispersed QD assembly, where these QDs act as donors, the FRET efficiency can be estimated as

$$E = 1 - \frac{\tau_{DA}}{\tau_D}, \quad (6)$$

where, τ_D and τ_{DA} are the lifetime of the donor in the absence and presence of the acceptor. The

Forster theory treats the donor and acceptor as points in the interaction space, whereas the nanocrystals have finite size and are relatively large compared to the dye molecules [23].

Results and Discussion

We first carried out measurements on three different CdTe sample solutions to study the influence of the spectral overlap degree on the FRET efficiency. It should be noted that the effect of solvent have been removed from all the results. Fig. 1 shows the absorption spectrum of RhB dye which is located at 553 nm and emission spectra of QDs1, QDs2 and QDs3, which are located at 522, 597 and 650nm, respectively. It clearly indicates that the spectral overlap degree between the QD donors and RhB acceptor varies as a function of the emission location for each QD population.

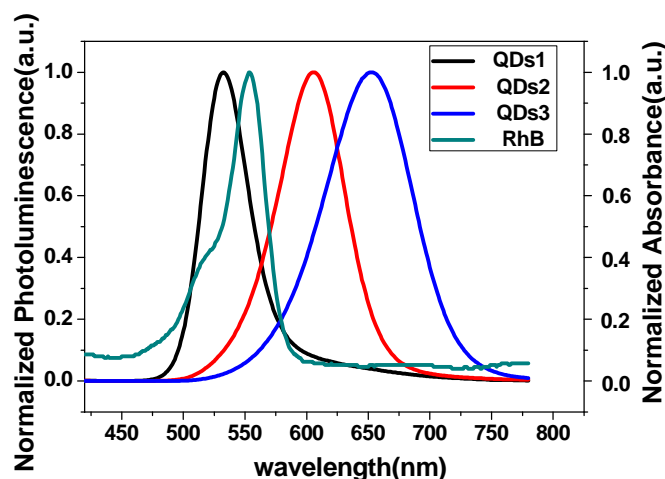


Fig. 1 Normalized absorption spectra of RhB and photoemission spectra of three CdTe QDs.

Table 1. Overlap Integrals and Calculated Forster Distances for QD-RhB Pairs.

donor-acceptor pair	overlap integral $I \times 10^{13} (cm^3 / M)$	Forster distance $R_0 (\text{\AA})$
QDs1-RhB	8.09	75.5
QDs2-RhB	3.59	61.4
QDs3-RhB	1.23	57.8

The overlap Integral of QD donor and RhB acceptor can be calculated by Eq. (3), which is shown in Table 1. It clearly shows that the overlap integral and Forster distance of QDs1-RhB are the largest, that of QDs2-RhB are middle, and that of QDs3-RhB are the smallest. Usually, the wider R_0 indicates the higher probability to realize the FRET in donor-acceptor pairs.

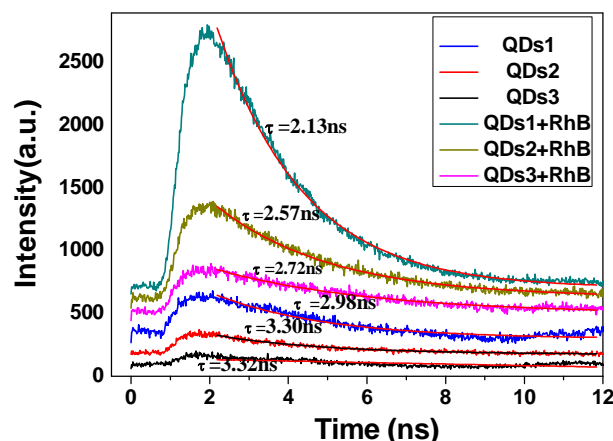


Fig. 2 The time-resolved fluorescence decays of different QDs and QDs-RhB.

The time-resolved fluorescence decays were obtained by exciting at 800 nm, the intensity decays for each QD and QDs-RhB hybrid system were shown in Fig. 2. The lifetime measurements of the donor in the absence (τ_D) and presence (τ_{DA}) of the acceptor can be obtained by single-exponential fitting of the decay curves. To further quantify the presence of FRET one can calculate the transfer efficiency E based on Eq. (6), which are shown in Table 2. It can be seen that the QDs1-RhB pair has the largest energy transfer efficiency, QDs3-RhB has the smallest one, and QDs2-RhB has the middle one, which has the same sequence with the spectral overlap Integral of QD donor and RhB acceptor.

Table 2. Fluorescence decay time and energy transfer efficiency.

	τ_D (ns)	τ_{DA} (ns)	E (%)
QDs1-RhB	2.98	2.13	28.5
QDs2-RhB	3.30	2.57	21.9
QDs3-RhB	3.32	2.72	18.0

Next, we study the influence of RhB concentrations solution to the rate of FRET efficiency. Fig. 3 (a) shows steady-state PL spectra of the QD-RhB complex upon incubation with an increasing amount of RhB. Sample R0 is CdTe only, in sample R1 to sample R5, the QD concentration remains the same but the amount of RhB increases. It can be seen that the QD intensity decrease with the increase of RhB concentration. The time-resolved fluorescence decays of samples R0-R5 are shown in Fig. 3 (b). The lifetimes of QDs can be obtained by fitting the PL decay curves with a single-exponential function, which are shown in Table 3. It clearly shows that the QDs lifetimes decrease with increasing the RhB concentration.

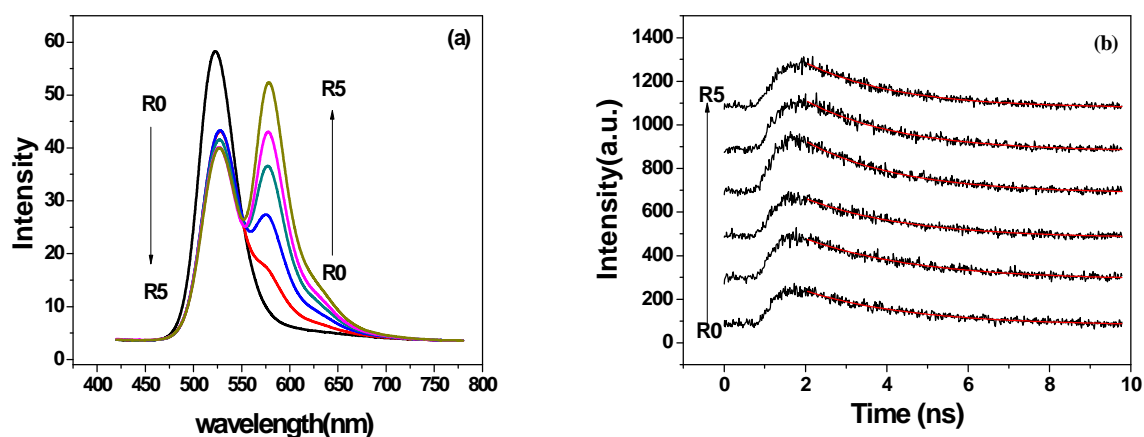


Fig. 3 (a) The concentration effect of RhB on FRET and (b) fluorescence decays of CdTe QDs1 (R0) and QD-RhB (R1-R5).

Table 3. Lifetimes of CdTe and CdTe/RhB.

	R0	R1	R2	R3	R4	R5
Average lifetimes(ns)	2.98	2.75	2.64	2.41	2.01	2.23
E (%)		7.7	11.4	19.1	32.6	25.2

Fig. 4 shows the effect of the RhB concentration on transfer efficiency. The FRET efficiency becomes stronger with the increase of RhB concentration from 5.5×10^{-6} mol/L to 4.5×10^{-5} mol/L. The phenomenon is because that the effective RhB molecules per QD increase along with the RhB solution's concentration increase, which leads to higher efficiency. However, when RhB

concentration is increased to be larger than 4.5×10^{-5} mol/L, the transfer efficiency begins to decrease with the increase of RhB concentration, which is due to the fixed QDs molecules that can form limited QD-RhB pairs. The FRET efficiency can reach to be about 32.6% when RhB concentration is 4.5×10^{-5} mol/L.

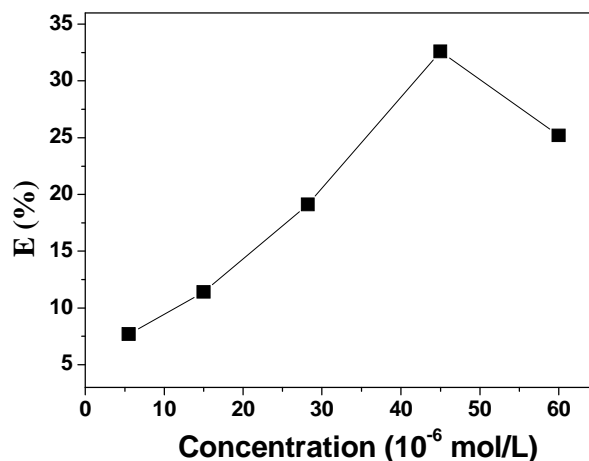


Fig. 4 Effect of the concentration of RhB on energy transfer efficiency.

Conclusion

In summary, it is possible to obtain efficient FRET in such a hybrid system even without chemical conjugation of the donor and the acceptor. The FRET efficiency is directly dependent on the degree of spectral overlap. In order to acquire a higher FRET efficiency, selecting material with high spectral overlap degree can't be avoided. And FRET efficiency become larger with an increase of RhB concentration, while the concentration increase to be larger than 4.5×10^{-5} mol/L, the transfer efficiency decreases. The FRET efficiency can reach to be about 32.6% when RhB concentration is 4.5×10^{-5} mol/L. In order to acquire a higher FRET efficiency, selecting material with high spectral overlap degree can't be avoided, appropriate concentration is important too. This study could be helpful to take advantage of the QD-RhB system in the application of fluorescent probe and photodynamic therapy.

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