

Förster resonance energy transfer in mixed-size CdTe quantum dots with optimized donor-acceptor concentration ratio

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ABSTRACT

The dynamics of Förster resonance energy transfer (FRET) in mixed-size water-soluble CdTe quantum dots (QDs) are studied by using photoluminescence (PL) and time-resolved PL spectroscopy. When donor concentration is increased, an enhancement of both the FRET and quantum efficiency in the mixed-size CdTe QDs films can be observed. Increasing donor concentration significantly quenches the emission intensity and lifetime in donor QDs and enhances that in acceptor QDs. However, as D/A ratios exceed 6, the emission intensity and the lifetime of acceptor QDs start to decline, reflecting a decreasing in both quantum and FRET efficiency due to a markedly declining availability of acceptor QDs.

Keywords: semiconductor quantum dots, nanocrystals, II-VI semiconductors, cadmium compounds, tellurides, energy transfer, nonradiative transitions, photoluminescence, time-resolved spectra, radiative lifetimes

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1. INTRODUCTION

Förster resonance energy transfer (FRET)^{1,2} between colloidal quantum dots (QDs) or semiconductor nanocrystals has received considerable attention in recent years owing to an increasing development of more efficient FRET-based sensors.³⁻⁷ FRET is a non-radiative dipole–dipole coupling mechanism governed to a large extent by the spectral overlap between the emission spectrum of small dots (donors) and the absorption spectrum of large dots (acceptors), as well as by the spatial distance between donors and acceptors. The spectral overlap between colloidal QDs can be controlled by the size while the distance between the donor and the acceptor is determined by surface capping and by the method used to assemble and to connect the QDs. On account of the sensitive spatial and spectral dependence of FRET, efforts to enhance the FRET efficiency have been focused on structures with reduced inter-dots separation and improved spectral overlap of the donor emission and acceptor absorption spectra. However, the influence of donor-acceptor (D/A) concentration ratios on FRET process has seldom been addressed. The availability of donor QDs per acceptor QD, which can be tuned by varying the ratios, markedly influences the probability of direct FRET between nearest-neighbor QDs. Kagan *et al.* demonstrated the electronic energy transfer in CdSe QDs solid films mixed with 82% donors and 18% acceptors.⁸ Mayilo *et al.* found that the PL intensity of acceptor QDs in CdTe clusters is increased via FRET with an increasing amount of donor QDs.⁹ Nizamoglu *et al.* observed an increase of quantum efficiency in CdSe QDs using FRET when the donor QDs concentration is about 2.4 times that of the acceptor QDs.¹⁰ In this paper, we systematically study the FRET process and efficiency in mixed-size CdTe QDs films as a function of D/A concentration ratios (from 1 to 9) by means of photoluminescence (PL) and time-resolved PL (TRPL) spectroscopy. The aim of this work is to study thoroughly the dependence of FRET on D/A concentration ratios, which is important for further biological and optoelectronic applications.

2. EXPERIMENTS

Monodisperse CdTe QDs were synthesized in an aqueous solution as described elsewhere.¹¹ The water-soluble

CdTe QDs used in this study were surface capped with mercaptopropionic acid (MPA). MPA-capped CdTe QDs with diameters of 3.4 and 5.1 nm, as estimated from the sizing curve of ref. 11, function as donors and acceptors, respectively. For mixed-size samples 33, 99, 165, 198, 231, 264, and 297 nmol of donor QDs and 33 nmol of acceptor QDs were mixed in 3 mL of deionized water. The D/A molar or molar concentration ratios varied as 1, 3, 5, 6, 7, 8, and 9, corresponding to an incremental increase in the amount of donors in the mixtures. Samples of the only donors and acceptors were also prepared as references. Prior to the formation of closely packed CdTe QDs films, mono-dispersive and mixed-size QDs were separately dropped cast onto a clean glass slide. Following solvent evaporation, QDs deposited on glass substrates and formed densely packed films. Room-temperature absorption spectra were recorded in air using a Cary 50 spectrometer (Varian). PL and TRPL were excited by a 200 ps pulsed laser diode (405 nm/2.5 MHz) at room temperature. The PL and TRPL signals were dispersed using an iHR550 single-grating 0.55 m spectrometer and detected, respectively, using a LN₂-cooled charge-coupled device and a high-speed photomultiplier tube. The decay traces were recorded using a time-correlated single photon counting approach (Time-Harp, PicoQuant).

3. RESULTS AND DISCUSSION

Figure 1(a) shows the absorption and the PL spectra of the only donor (3.4 nm) and only acceptor (5.1 nm) CdTe QDs in an aqueous solution at room temperature. The only donor and only acceptor QDs provide red and near-infrared emissions centered at around 615 and 720 nm, respectively. The emission spectrum of only donors and the absorption spectrum of only acceptors indicate sufficient spectral overlapping. Figure 1(b) presents the PL spectra of the only donor, only acceptor, and mixed-size (D/A = 1) CdTe QDs in closely packed films. Clearly, the PL peak energy for the films exhibits an energy redshift as compared with that in aqueous solution. The energy redshift in mono-dispersive CdTe QDs films can be ascribed to energy transfer between proximal QDs due to its size distribution.¹² We found that the magnitude of energy redshift depends enormously on the PL linewidth (QD size dispersion) of the mono-dispersive QDs samples.

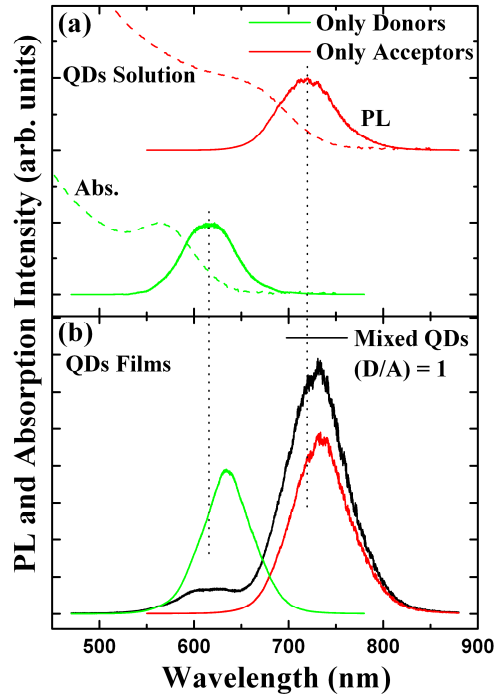


Figure 1: (a) Absorption and PL spectra of only donor (3.4 nm) and only acceptor (5.1 nm) CdTe QDs in aqueous solution. (b) PL spectra of only donor, only acceptor, and mixed-size ($D/A = 1$) QDs films.

As can be seen in Fig. 1(b), the PL intensity of donor QDs in the densely packed CdTe QDs film ($D/A = 1$) decreases whereas that of acceptor QDs enhances with respect to the emissions intensity of only donors and only acceptors. The integrated PL intensity of acceptors in the mixed film ($D/A = 1$) is increased by about 1.5 times that of its initial value of the only acceptors film. Above results provide evidence of nonradiative energy transfer from donor to acceptor QDs.

Figure 2(a) displays the dependence of PL spectra for CdTe QDs films on D/A concentration ratios. Increasing the ratio from 1 to 6 significantly enhances the PL intensity of acceptors. This is because the availability of additional donor QDs per acceptor rises. However, the PL intensity of donor QDs in the mixed film strongly reduces when compared with that of only donors. The integrated PL intensity of acceptors in the mixed film ($D/A = 6$) is about 7.5 times higher than

that of only acceptors film. For comparison, Fig. 2(b) shows the PL spectra of mixed-size CdTe QDs in water for various D/A concentration ratios. In contrast with mixed-size CdTe QDs films, the emission intensity of donors in mixed-size QDs solutions monotonically increases with an increasing donor concentration. This phenomenon is attributed to that the inter-dot distances between donors and acceptors in mixed QDs solutions exceed the Förster critical distance (< 10 nm). Consequently, the FRET process between donors and acceptors in mixed QDs solution can be neglected. The above observations imply that the quantum efficiency of acceptor QDs in mixed films can be easily controlled by tuning the D/A concentration ratios.

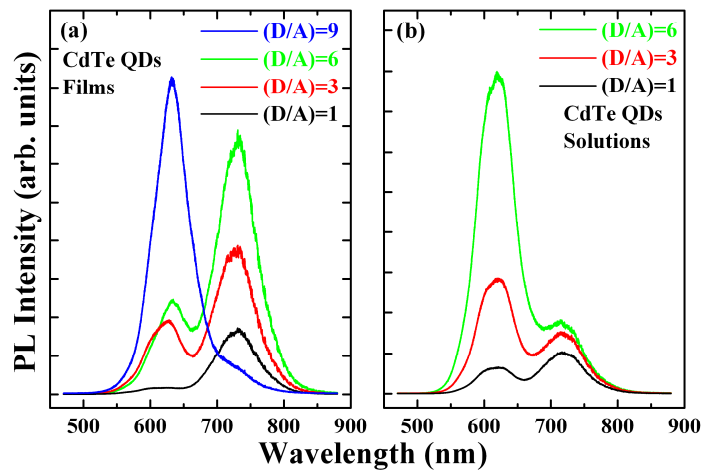


Figure 2: PL spectra of mixed-size CdTe QDs (a) films ($D/A = 1, 3, 6,$ and 9) and (b) solutions ($D/A = 1, 3,$ and 6).

To verify the dependence of FRET on D/A concentration ratios, we perform the TRPL measurements. Figure 3 and Fig. 4 display the TRPL spectra for mixed-size CdTe QDs films of various D/A concentration ratios monitored at the donor and acceptor peak emission, respectively. Increasing the ratio to nearly 6 decreases the PL lifetime of donors in the mixed film (τ_{DM}) and increases that of acceptors in the mixed film (τ_{AM}). Furthermore, the lifetime curves of acceptors in the mixed films ($D/A = 3$ and 6), shown in the inset of Fig. 4, exhibit prolonged excitation during the initial few nanoseconds. The phenomenon becomes even more pronounced upon recording of the long-wavelength emissions and

can be attributed to the feeding effect from the trapped excitations.¹³ However, further increasing the amount of donor QDs ($D/A > 6$), τ_{DM} increases along with a decreasing τ_{AM} . Additionally, as compared with Fig. 2(a), the emission intensity of acceptors starts to decline and that of donors starts to increase when the ratio exceeds 6. These phenomena imply the quenching of FRET efficiency, which could be attributed to the decreasing amount of available acceptor QDs per donor. In other words, donor QDs dominate the FRET process and the entire PL spectrum from the mixed films, as shown in Fig. 2(a) ($D/A = 9$).

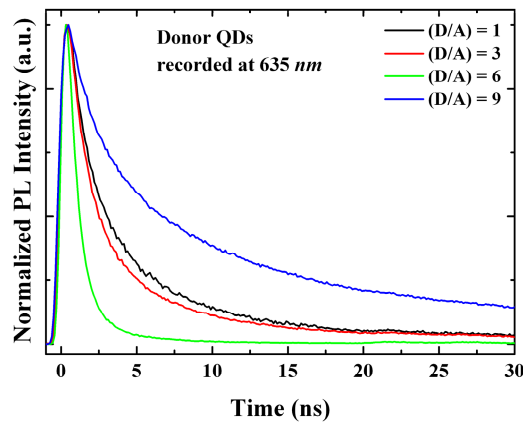


Figure 3: TRPL spectra of mixed-size CdTe QDs films with various D/A ratios monitored at the donor peak emission (635 nm).

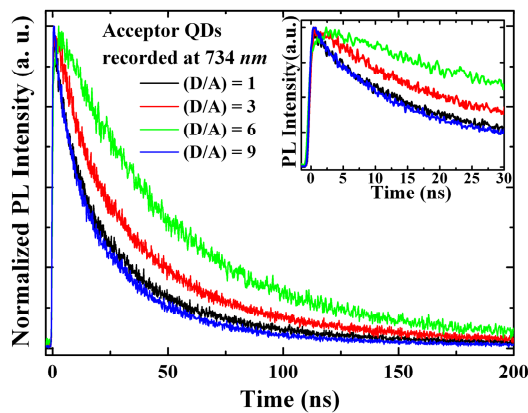


Figure 4: TRPL spectra of mixed-size CdTe QDs films with various D/A ratios monitored at the acceptor peak emission (734 nm).

Figure 5 summarizes the dependence of τ_{DM} as a function of D/A ratios. When the ratio exceeds 9, τ_{DM} in the mixed films returns to that of only donor QDs film ($\tau_D \sim 11.3$ ns). The kink in the inset reflects a situation in which the time constant changes maximally around D/A = 6, in which each acceptor QD is surrounded on average by six donor QDs. The above experimental findings along with the PL results (Fig. 2) provide strong evidence of FRET; however, the radiative energy transfer via photon reabsorption, which does not quench the lifetime from donor QDs, can be ruled out.

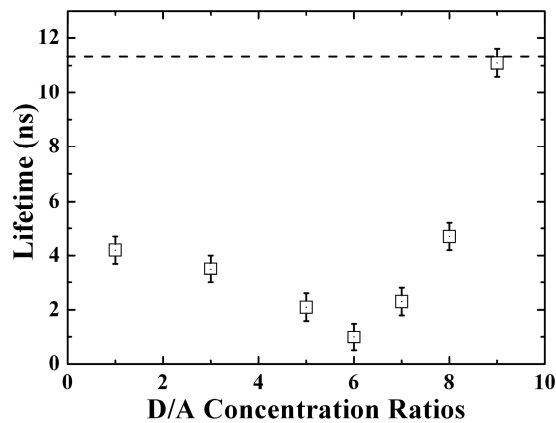


Figure 5: PL lifetime (monitored at 635 nm) of donor QDs in the mixed film as a function of D/A concentration ratios. The dashed line denotes the lifetime of only donor QDs film.

The dynamics of energy transfer can be further depicted by the TRPL image and the temporal evolution of PL spectra for mixed-size CdTe QDs film (D/A = 6). In Fig. 6, within the initial few nanoseconds after excitation, donor emissions dominate the PL spectrum. The emission intensity of donors is about five times higher than that of acceptors. As time passes, the emission intensity of donors (acceptors) sharply falls (enhances). Additionally, the PL maximum of the mixed QDs shifts dramatically towards the acceptor emission. Beyond 10.0 ns, the emission from acceptors dominates the entire spectrum (as shown in the inset of Fig. 6), revealing the suppression of an additional energy transfer. Figure 7 shows true-color luminescence images of the pure donors, pure acceptors, and mixed-size CdTe QDs (D/A = 6) in solutions and films. The images of pure donor (acceptor) QDs in both solution and film exhibit light red (dark red).

The image of the mixed-size QDs solution presents the color very close to pure donor QDs solution (light red). However, the image of the mixed-size QDs film displays almost the same color (dark red) with the pure acceptors. It verifies that the mixed-size CdTe QDs ($D/A = 6$) with reduced inter-dot distance in solid film results in more efficient FRET between donors and acceptors.

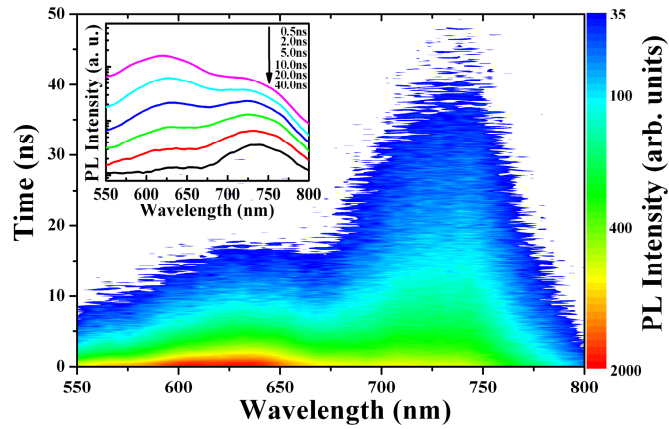


Figure 6: TRPL image of mixed-size CdTe QDs film ($D/A = 6$). The inset shows the temporal evolution of PL spectra.

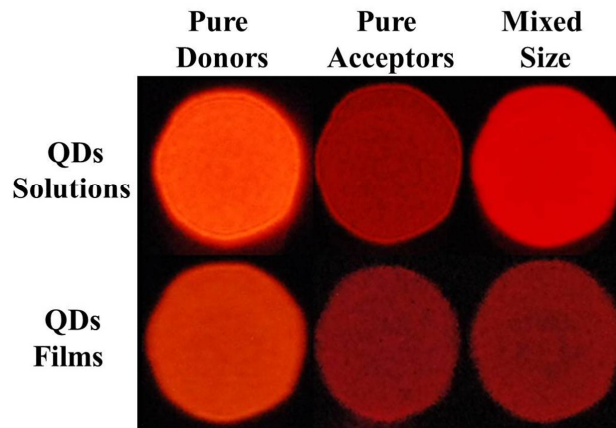


Figure 7: True-color luminescence images of the pure donors, pure acceptors, and mixed-size CdTe QDs ($D/A = 6$) in solutions and films.

Further quantitative analysis is performed by computing the FRET efficiency based on the TRPL measurements by using the following equation:¹⁴

$$\eta_{FRET} = 1 - \tau_{DM} / \tau_D . \quad (1)$$

This time-resolved method (Eq. 1) is a straightforward approach of determining the transfer rate constant, transfer efficiency, and donor–acceptor distance, when using the PL lifetime of donors in the absence and presence of acceptors. Increasing the ratio from 1 to 6, the FRET efficiency is enhanced from 63 to 91 %. Efficiency, as estimated from the relative integrated PL intensity, provides similar results.

4. CONCLUSIONS

In summary, this study investigated FRET in mixed-size CdTe QDs films as a function of D/A concentration ratios. Increasing the amount of donors initially increases the emission intensity of acceptors, followed by a monotonical decline. When the ratio approaches 6, FRET efficiency reaches 91 % and the emission intensity of acceptors in the mixed film is around 7.5 times higher than that of only acceptors film. The enhancement of both the quantum efficiency and FRET efficiency of mixed-size CdTe QDs films is crucial for hybrid organic/inorganic semiconductor nanostructures and for realizing efficient FRET-based sensors and light emitting devices.

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REFERENCES

- [1] Förster, T., "Zwischenmolekulare energiewanderung und fluoreszenz", *Ann. Phys.* **437**, 55 (1948).
- [2] Rogach, A. L., Klar, T. A., Lupton, J. M., Meijerink, A., and Feldmann, J., "Energy transfer with semiconductor nanocrystals", *J. Mater. Chem.* **19**, 1208 (2009).
- [3] Medintz, I. L., Clapp, A. R., Mattoussi, H., Goldman, E. R., Fisher, B., and Mauro, J. M., "Self-assembled nanoscale biosensors based on quantum dot FRET donors", *Nature Mater.* **2**, 630 (2003).
- [4] Zhang, C. Y., Yeh, H. C., Kuroki, M. T., and Wang, T. H., "Single-quantum-dot-based DNA nanosensor", *Nature Mater.* **4**, 826 (2005).
- [5] Medintz, I. L., Clapp, A. R., Brunel, F. M., Tiefenbrunn, T., Uyeda, H. T., Chang, E. L., Deschamps, J. R., Dawson, P. E., and Mattoussi, H., "Proteolytic activity monitored by fluorescence resonance energy transfer through quantum-dot-peptide conjugates", *Nature Mater.* **5**, 581 (2006).
- [6] Medintz, I. L. and Mattoussi, H., "Quantum dot-based resonance energy transfer and its growing application in biology", *Phys. Chem. Chem. Phys.* **11**, 17 (2009).
- [7] Jiang, G., Susha, A. S., Lutich, A. A., Stefani, F. D., Feldmann, J., and Rogach, A. L., "Cascaded FRET in conjugated Polymer/Quantum Dot/Dye-Labeled DNA complexes for DNA hybridization detection", *ACS Nano* **3**, 4127 (2009).
- [8] Kagan, C. R., Murray, C. B., Nirmal, M., and Bawendi, M. G., "Electronic energy transfer in CdSe quantum dot solids", *Phys. Rev. Lett.* **76**, 1517 (1996).
- [9] Mayilo, S., Hilhorst, J., Susha, A. S., Höhl, C., Franzl, T., Klar, T. A., Rogach, A. L., and Feldmann, J., "Energy transfer in solution-based clusters of CdTe nanocrystals electrostatically bound by calcium ions", *J. Phys. Chem. C* **112**, 14589 (2008).
- [10] Nizamoglu, S., Akin, O., and Demir, H. V., "Quantum efficiency enhancement in nanocrystals using nonradiative energy transfer with optimized donor-acceptor ratio for hybrid LEDs", *Appl. Phys. Lett.* **94**, 243107 (2009).

- [11] Rogach, A. L., Franzl, T., Klar, T. A., Feldmann, J., Gaponik, N., Lesnyak, V., Shavel, A., Eychmüller, A., Rakovich, Y. P., and Donegan, J. F., "Aqueous synthesis of thiol-capped CdTe nanocrystals: State-of-the Art", *J. Phys. Chem. C* **111**, 14628 (2007).
- [12] Crooker, S. A., Hollingsworth, J. A., Tretiak, S., and Klimov, V. I., "Spectrally resolved dynamics of energy transfer in quantum-dot assemblies: Towards engineered energy flows in artificial materials", *Phys. Rev. Lett.* **89**, 186802 (2002).
- [13] Franzl, T., Klar, T. A., Schietinger, S., Rogach, A. L., and Feldmann, J., "Exciton recycling in graded gap nanocrystal structures", *Nano Lett.* **4**, 1599 (2004).
- [14] Valeur, B., [Molecular Fluorescence: Principles and Applications], Wiley-VCH, New York, (2002).