

# Förster Resonant Energy Transfer in Quantum Dot Structures

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## ABSTRACT

Förster resonant energy transfer (FRET) has been investigated in two different quantum dot (QD) structures. Colloidal CdTe QDs of two different sizes act as energy donors and acceptors. They have been deposited in a mixed monolayer and a separate donor/acceptor layer structure. The optical properties of these structures have been analysed by steady-state absorption and photoluminescence (PL) spectroscopy, as well as time-resolved PL measurements. To characterize FRET in the mixed QD monolayer, a theory of FRET in two dimensions, taking into account exclusion zones around the donors, has been applied. This theory allows for the extraction of all important FRET parameters from time-resolved donor PL measurements only and also explains the acceptor concentration dependence of the FRET efficiency in the mixed QD layer. In a separate donor/acceptor layer structure the characteristic distance dependence of the FRET process has been demonstrated and the increase of the FRET efficiency with increasing acceptor concentration has been observed.

**Keywords:** Förster resonant energy transfer, CdTe quantum dots, optical spectroscopy, time-resolved photoluminescence, acceptor concentration dependence, distance dependence

## 1. INTRODUCTION

Förster resonant energy transfer (FRET) is a nano-scale mechanism mediated by dipole-dipole interactions [1]. Based on FRET, energy flow is created in light harvesting devices [2] and nano-sensors [3]. Semiconductor quantum dots (QDs) can be used as energy donors and/or acceptors in these structures. Due to their unique optical properties they offer several advantages over commonly used molecular dyes, such as spectrally tuneable emission, broad absorption and a higher photostability [4]. However, the larger size of the QDs as well as the inhomogeneous broadening of the QDs is not taken into account in most FRET theories, as these have been mainly developed for molecules [5]. It is important to study QD systems and to understand the influence of the QD properties on the FRET process, in order to optimize FRET structures for the applications mentioned above.

We present the data and analysis of FRET in two different QD structures, a mixed monolayer and a separate donor/acceptor layer structure. To characterize FRET in the mixed QD monolayer we apply a theory of FRET in two dimensions [6] which had been developed, and previously only used, for biological systems. We find very good agreement of this theory with the experimental time-resolved donor data [7] and consequently demonstrate that all important FRET parameters: the Förster radius, the FRET efficiency and rate, can be determined from the donor decays alone for the case of a mixed QD monolayer. The acceptor concentration dependence in this structure can also be explained within the theory [7]. In the separate layer structure FRET efficiencies similar to those in the mixed monolayer can be achieved. Additionally, the FRET distance dependence [8], as well as the increase of the FRET efficiency with increasing acceptor concentrations is shown for the separate donor/acceptor layer structure.

## 2. EXPERIMENTAL METHODS

Negatively charged CdTe quantum dots, stabilized by thioglycolic acid (TGA), with two different sizes were deposited in a mixed monolayer or in separate donor/acceptor layers on quartz substrates. QDs with a diameter of 1.9 nm, emitting at 524 nm, acted as energy donors and larger QDs with a diameter of 3.5 nm, emitting at 617 nm, were used as acceptors.

Both structures were prepared by a layer-by-layer deposition technique, based on the electrostatic assembly of charged particles [9]. To provide good adhesion of the QDs to the substrate they were deposited on top of several polyelectrolyte (PE) bi-layers, consisting of a negatively charged poly(sodium 4-styrene sulfonate) (PSS) and a positively charged poly(diallyldimethylammonium chloride) (PDDA) layer. The mixed QD monolayers were deposited on two bi-layers formed by immersion in PE solutions with a sodium chloride concentration of 0.5 M, resulting in a bi-layer thickness of approximately 7 nm. The separate donor/acceptor layer structure was prepared on top of four PE bi-layers, deposited from solutions containing 0.1 M sodium chloride, resulting in a bi-layer thickness of approximately 3 nm. The layer thickness was determined by X-ray diffraction measurements.

The pure QD layers were prepared by immersion in aqueous solutions containing either donor or acceptor QDs with micromolar concentrations. The mixed monolayers were deposited from solutions with varying acceptor:donor ratios. Further information on the deposition of pure and mixed QD monolayers with different concentration can be found elsewhere [7]. For the separate layer structure, the acceptor QD layer was deposited

first. This layer was then covered with PDDA and up to 3 PE bilayers (0.1 M sodium chloride concentration), before the donor QD layer was deposited.

The absorption spectra between 350 and 800 nm were measured with a double beam UV-Vis Recording Spectrometer (Shimadzu UV-2401 PC). Room temperature photoluminescence (PL) spectra were recorded with a Perkin-Elmer LS 55 fluorescence spectrometer. The excitation wavelength for the PL measurements was 400 nm. Time-resolved PL decays were recorded with a PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution. Excitation was provided by 470 nm picosecond pulses at a 10 MHz repetition rate from a LDH-480 laser head controlled by a PDL-800B driver (PicoQuant). The PL decays were measured over an area of  $80 \times 80 \mu\text{m}$  ( $150 \times 150$  pixels) with an integration time of 4 ms per pixel. Broad band-filters at 500 and 600 nm were used for the time-resolved PL measurements to distinguish between the donor and acceptor QD emission signals, respectively.

### 3. RESULTS AND DISCUSSION

The properties of the pure QD monolayers will be presented first. Then the FRET process in the mixed QD monolayers will be discussed, followed by the separate donor/acceptor layer structure.

#### 3.1 Pure Donor and Acceptor Monolayers

Figure 1 shows the absorption and PL spectra of pure donor (Fig. 1a) and acceptor QD monolayers (Fig. 1b). The concentration of the donors and acceptors in these films is  $(3.7 \text{ and } 1.1) \times 10^{17} \text{ m}^{-2}$ , respectively.

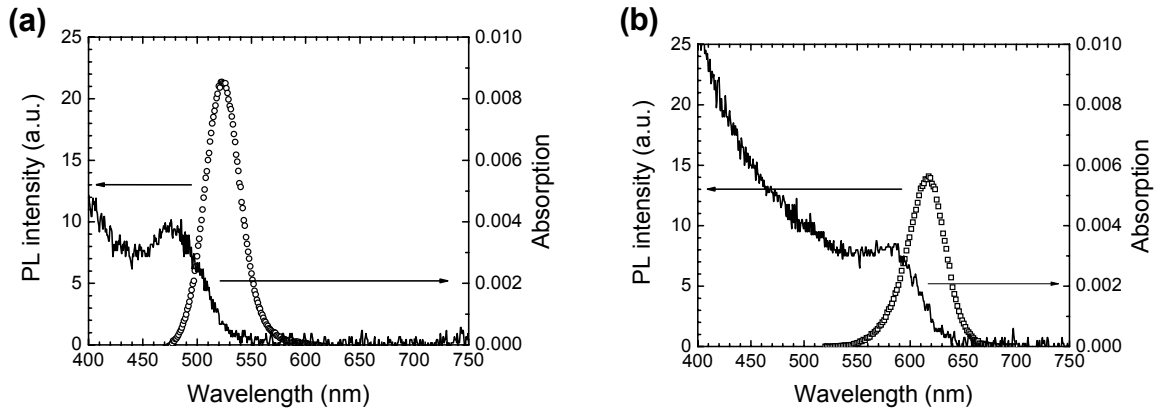


Figure 1. PL (symbols, left-hand axis) and absorption spectra (solid line, right-hand axis) of a donor (a) and acceptor monolayer (b).

The Förster radius  $R_0$  (equation 2), the donor-acceptor distance at which the FRET efficiency is 50%, can be calculated via the spectral overlap  $J$  (equation 1) of the area normalized donor PL spectrum  $I_D(\lambda)$  with the acceptor extinction spectrum  $\epsilon_A(\lambda)$ . The latter is obtained from the acceptor absorption spectrum via the Lambert-Beer Law [10].

$$J = \int_0^{\infty} I_D(\lambda) \cdot \epsilon_A(\lambda) \cdot \lambda^4 d\lambda \quad (1)$$

$$R_0 = 0.211 \cdot \left( \frac{\kappa^2 \cdot Q_D}{n^4} \cdot J \right)^{\frac{1}{6}} \quad (2)$$

For randomly oriented dipoles, as it is the case in the structures presented here, the orientation factor  $\kappa^2$  is  $2/3$ . The donor quantum yield  $Q_D$  in the monolayer is approximately  $4 \pm 2\%$  and the volume-weighted refractive index is  $n = 2.1 \pm 0.3$ , which takes into account the CdTe QD and its ligand shell.

From the spectra shown in Fig. 1, the Förster radius  $R_0$  is found to be  $3.3 \pm 2$  nm. Additionally, the closest separation  $R_{ex}$  between the donor and acceptor QD centres was calculated.  $R_{ex}$  depends on the size of the QDs and the thickness of the TGA ligand shell, which is approximately 0.5 nm [11]. Due to the QD size an exclusion zone with a radius of  $R_{ex} = 3.2 \pm 0.3$  nm is formed around the donors. As  $R_{ex}$  and  $R_0$  have similar values, the QD size has an important impact on the FRET process and thus limits the FRET efficiencies that can be achieved in QD structures because donors and acceptors cannot come very close.

#### 3.2 Mixed Donor and Acceptor Monolayer

Figure 2a shows the PL spectrum of a mixed QD monolayer with acceptor and donor concentrations of  $c_{don} = (2.5 \pm 0.2) \times 10^{17-2}$  and  $c_{acc} = (0.33 \pm 0.20) \times 10^{17} \text{ m}^{-2}$ , respectively. For comparison, the PL spectra

of the pure donor and acceptor monolayers with similar QD concentrations have also been included in Fig. 2a. It can be clearly seen that energy is transferred from donor to acceptor QDs, as the donor PL signal is quenched whereas the acceptor emission increases.

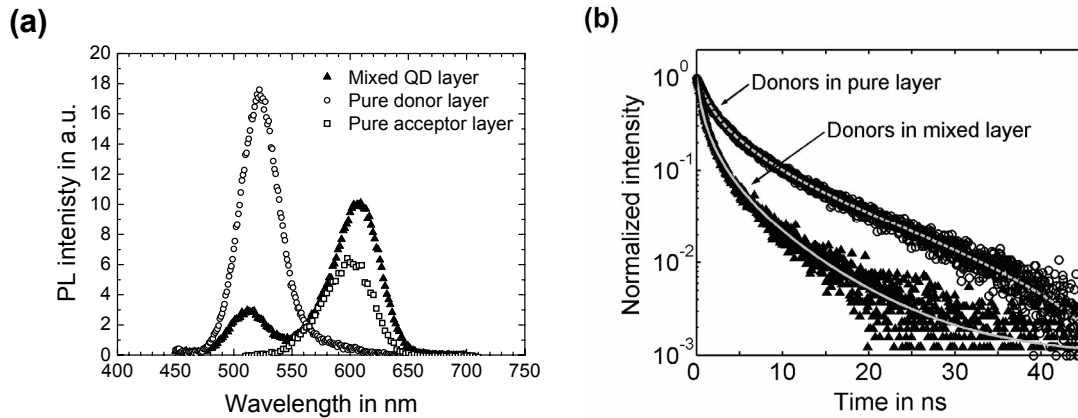


Figure 2. (a) PL spectra of a mixed donor-acceptor monolayer (triangles), as well as pure donor (rounds) and acceptor (squares) monolayers. (b) PL decays of donors in a pure monolayer (rounds) and in a mixed layer with acceptors (triangles). The fitting curves for both decays are shown as well (light grey lines).

Figure 2b shows the donor decay curves for the pure donor layer and the mixed layer. The average lifetime is reduced from  $\tau_D = 6.1$  ns to  $\tau_{DA} = 3.0$  ns in the presence of acceptors. This corresponds to a FRET efficiency  $E_{FRET} = 1 - \tau_D / \tau_{DA}$  of 51%. The decay curve for the pure donor monolayer is best reproduced by a three-exponential decay. To fit the donor decay in the mixed film a theory of FRET in two dimensions [6], which takes into account exclusion zones around the donors, was applied. The best fit for the donor decay in presence of the acceptors is shown as a solid line in Fig. 2b. Very good agreement between theory and data was achieved for the fitting parameters  $R_0 = 3.5 \pm 0.3$  nm,  $R_{ex} = 3.0 \pm 0.2$  nm and  $c_{acc} = (0.65 \pm 0.1) \times 10^{17}$  m<sup>-2</sup>. These values agree well with those obtained by the more common analysis as presented above, in which  $R_0$  is determined from the spectral overlap and  $E_{FRET}$  is determined independently from the donor PL decay as the donor-acceptor separation is not known. We have demonstrated that, by application of the theory of FRET in two dimensions, it is possible to extract all the QD FRET parameters from time-resolved donor PL measurements alone, avoiding the comparison of data taken with different measurement systems.

Samples with different acceptor:donor concentration ratios have been studied and excellent agreement of the donor decays with theory has been found for all samples. Moreover, the acceptor concentration dependence of the FRET efficiency can also be explained with this theory [7]. For a high acceptor concentration, FRET efficiencies of over 90% were reached. However, the acceptor enhancement is low in this case as the acceptor:donor ratio is too high to show a large impact of FRET on the acceptor luminescence. When decreasing the acceptor:donor ratio, the acceptor emission enhancement factor increases as more donors per acceptor are available to transfer energy. For a monolayer with 33 donors per acceptor a greater than ten-fold increase in acceptor emission was observed.

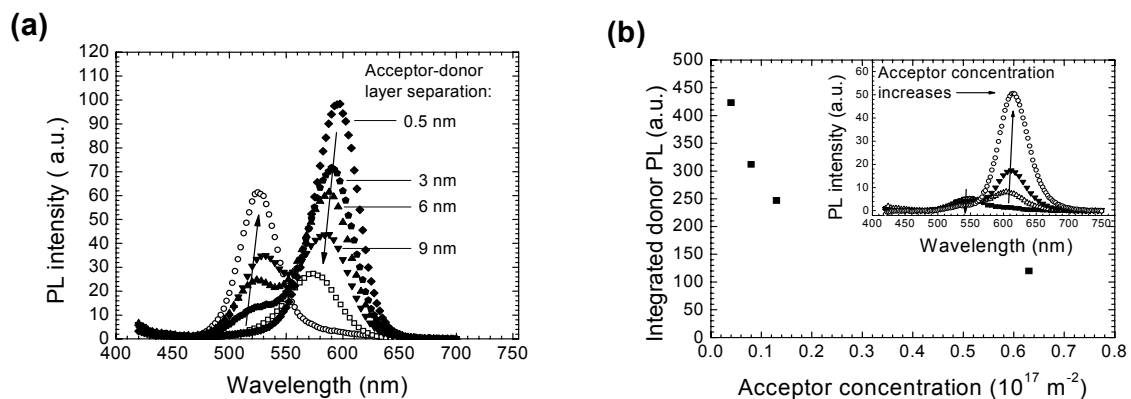


Figure 3. (a) PL spectra of a pure donor monolayer (empty rounds), pure acceptor monolayer (empty squares) and acceptor/donor layer structures for several layer separations (filled symbols). (b) Concentration dependence of the integrated donor PL intensity. The PL spectra of the according acceptor/donor layer structures are shown in the inset.

### 3.3 Separate Donor/Acceptor Layer Structure

In the separate donor/acceptor layer structure the distance dependence of the FRET process can be probed [8], and the QD concentrations can be varied independently, which is not possible in the mixed layer structure.

In Figure 3a PL spectra for samples with varying acceptor-donor layer separations are shown. The spectra for the pure donor and acceptor monolayers are also presented for comparison. For the closest layer separation (black diamonds), little donor emission is observed as energy is transferred to the acceptors with a FRET efficiency of 60%. The acceptor PL is enhanced by a factor of 2.3. This enhancement factor depends on the FRET efficiency and the acceptor:donor ratio, which is approximately 0.43 for the separate donor/acceptor layer structures presented here. More details on the distance dependence will be published elsewhere.

The PL spectra for samples with different acceptor concentrations are shown in the inset of Fig. 3b. With increasing acceptor concentration the donor PL signal decreases (Fig. 3b). As the concentration of the donors is kept constant, this is a clear indication of increasing FRET efficiency. With increasing acceptor concentration, more suitable acceptors can be found in the proximity of a single donor and therefore the probability of the donor transferring energy to a nearby acceptor increases.

## 4. CONCLUSIONS

FRET in two different structures has been analyzed. In a mixed QD monolayer, the time-resolved donor PL decay can be fitted with a theory of FRET in two dimensions that takes into account the QD size in form of exclusion zones. With this theory all important FRET parameters, such as the Förster radius and the FRET efficiency, can be determined from time-resolved measurements only. This is otherwise not possible as the acceptor-donor separation is not known in a mixed monolayer and therefore, complications that can arise when comparing data acquired with different measurement systems are avoided. Additionally, the dependence of FRET on the acceptor concentration can be explained within this theory.

In the separated acceptor/donor layer structure similar efficiencies to that in the mixed QD monolayer have been achieved for the closest layer separation. Furthermore, the distance dependence of the FRET process was investigated and an increase of the FRET efficiency with increasing acceptor concentration was observed.

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## REFERENCES

- [1] T. Förster: Zwischenmolekulare Energiewanderung und Fluoreszenz, *Annalen Der Physik*, vol. 2, pp. 55-57, 1948.
- [2] T. Franzl *et al.*: Exciton recycling in graded gap nanocrystal structures, *J. Nano Lett.*, vol. 4, pp. 1599-1603, Sept. 2004.
- [3] I. L. Medintz *et al.*: Self-assembled nanoscale biosensors based on quantum dot FRET donors, *Nat. Mater.*, vol. 2, pp. 630-638, Sept. 2003.
- [4] Alphantery *et al.*: Highly efficient Förster resonance energy transfer between CdTe nanocrystals and Rhodamine B in mixed solid films, *Chem. Phys. Lett.*, vol. 338, pp. 100-104, April 2004.
- [5] G. D. Scholes, D. L. Andrews: Resonance energy transfer and quantum dots, *Phys. Rev. B.*, vol. 72, pp 125331 – 1-8, Sept. 2005.
- [6] P. K. Wolber, B. S. Hudson: Analytic solution to the Förster energy-transfer problem in 2 dimensions, *Biophys. J.*, vol. 2, pp. 197-210, 1979.
- [7] M. Lunz *et al.*: Two-dimensional Förster resonant energy transfer in a mixed quantum dot monolayer: Experiment and theory, *J. Phys. Chem. C*, vol. 113, pp. 3084-3088, Feb. 2009.
- [8] D. Kim *et al.*: Experimental verification of Förster energy transfer between semiconductor quantum dots, *Phys. Rev. B*, vol. 78, pp. 153301 – 1-4, Oct. 2008.
- [9] G. Decher: Fuzzy Nanoassemblies: Toward layered polymeric multicomposites, *Science*, vol. 227, pp. 1232-1237, Aug. 1997.
- [10] W. W. Yu *et al.*: Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals, *Chem. Mater.*, vol. 15, pp. 2854-2860, Jul. 2003.
- [11] Z. Y. Tang *et al.*: Simple preparation strategy and one-dimensional energy transfer in CdTe nanoparticle chains, *J. Phys. Chem. B.*, vol. 108, pp. 6927-6931, Jun. 2004.