

# Influence of Intra-Ensemble Energy Transfer on the Properties of Nanocrystal Quantum Dot Structures and Devices

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## ABSTRACT

The impact of intra-ensemble Förster resonant energy transfer (FRET) on the optical properties of monodispersed quantum dot (QD) monolayers and a donor/acceptor FRET bilayer structure are presented. The QD structures are characterized by steady-state absorption and photoluminescence (PL) spectroscopy as well as time-resolved PL measurements. The optical properties of the monodispersed monolayers, such as peak emission wavelength and PL decays, are strongly influenced by FRET from smaller to larger QDs within the ensemble. Comparing several QD samples, the spectral overlap of the QD ensemble and the QD concentration were identified as parameters that allow for tuning of FRET in monodispersed QD structures.

For the donor/acceptor QD bilayer structure an unexpected decrease of the FRET efficiency between donor and acceptor layers is observed with increasing donor QD concentration. The concentration-dependent donor lifetime and a constant donor-acceptor FRET rate can explain this decrease within the FRET rate model. Even though the donor-acceptor FRET rate is donor-concentration independent – as expected from theory – its competition with donor-donor energy transfer leads to a concentration dependence of the FRET efficiency from donors to acceptors. This shows that intra-ensemble FRET can have an important impact on device performance.

**Keywords:** Förster resonant energy transfer, colloidal quantum dots, photoluminescence spectroscopy, time-resolved emission decay, inhomogeneous broadening, spectral overlap.

## 1. INTRODUCTION

Due to their unique optical properties semiconductor colloidal nanocrystals or quantum dots (QDs) have attracted a lot of interest in fundamental and applied research during the last decades. They show broad absorption bands and narrow, tuneable emission lines that make them ideal components for sensing devices or photovoltaics [1]. Most solid state QD devices contain QD layers that interact with other components of the structures as, for example, in graded energy structures [2], photovoltaic devices [3] and sensors [4]. In closely packed, monodispersed nanocrystal QD structures energy transfer between QDs can occur based on the overlap of emitting and absorbing states of QDs with different sizes, which is due to the inhomogeneous broadening of the QD ensemble and the Stokes shift between QD absorption and emission peak. This intra-ensemble energy transfer has been observed in QD solids [5, 6] and layers [7] for CdSe as well as PbS QDs, that have been suggested for applications in the visible and infrared wavelength region respectively. It is important to investigate energy transfer within monodispersed QD structures more closely in order to identify ways to control intra-ensemble energy transfer other than by temperature tuning [6].

Here we analyse the intra-ensemble energy transfer in monodispersed CdTe QD monolayers in detail for one QD sample and show that it is dominated by the Förster resonant energy transfer (FRET) mechanism [8]. Then, the properties of QD monolayers prepared from eleven different green-emitting CdTe QDs are compared at one concentration. The QD concentration and the self-overlap of the spectral features of the QD ensemble both influence the intra-ensemble process significantly [9]. As an example, a donor/acceptor QD bilayer structure is investigated to highlight the impact of intra-donor ensemble FRET on the FRET efficiency in this structure and therefore, in more general terms, on the performance of QD based devices.

## 2. EXPERIMENTAL METHODS

Negatively charged CdTe quantum dots (QDs), stabilized by thioglycolic acid in aqueous solution [10], were deposited into layer structures. A Layer-by-layer electrostatic assembly technique [11] was used to prepare structures with monodispersed QD monolayers only or with donor and acceptor QD layers separated by a poly(diallyldimethylammonium chloride) spacer layer. The QD layers were deposited by immersion in a micromolar QD solution and the QD concentration in the layers was changed by varying the immersion time. Further details about the sample preparation can be found elsewhere [9, 12].

The absorption spectra of the QD structures were measured using a double beam UV-Vis Recording Spectrometer (Shimadzu UV-2401 PC). The steady-state photoluminescence (PL) spectra were recorded with a Perkin-Elmer LS 55 fluorescence spectrometer using an excitation wavelength of 400 nm. A PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution was used to measure the time-

resolved PL decays of the QD structures. Picosecond pulses at 470 nm were provided by a LDH-480 laser head controlled by a PDL-800B driver (PicoQuant). The measurements were carried out over areas of 80 by 80  $\mu\text{m}$  (150 by 150 pixels) with integration times of 4 ms per pixel and repetition rates of 10 or 5 MHz, depending on the length of the decay. Broad band filters (FWHM:  $70 \pm 5$  nm) centred at 500 nm, 550 nm and 600 nm were used to measure the decays in different spectral regions of the QD ensemble emission.

### 3. RESULTS AND DISCUSSION

First, the concentration dependencies of the optical properties and the FRET process in a monodispersed monolayer are presented in detail for a sample with QDs of a mean diameter of 2.2 nm, and a peak emission wavelength of 532 nm in solution, see Fig. 1a. In the FRET bilayer structure discussed in the second part, these QDs act as donors. The acceptor QDs, used in the bilayer structure, have a diameter of 3.5 nm and emit at 610 nm in solution.

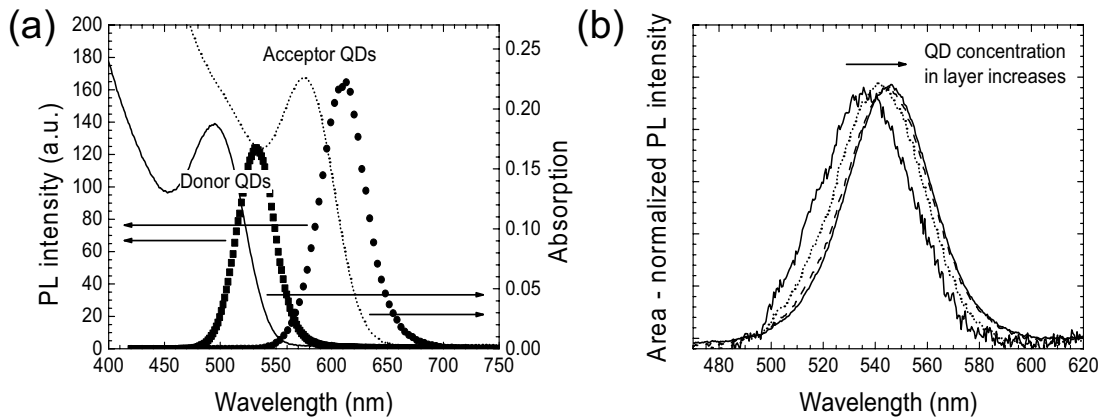


Figure 1. (a) Absorption (lines) and photoluminescence (PL) (symbols) spectra of donor (solid line, squares) and acceptor QDs (dotted line, circles) in solution. (b) Area-normalized PL spectra of monodispersed donor QD monolayers for different concentrations.

#### 3.1 Monodispersed Quantum Dot Monolayers

In the monodispersed donor QD layers a red-shift of the peak emission wavelength with respect to that in solution is observed. For monolayers with donor QD concentrations ranging from  $0.7$  to  $3.6 \times 10^{17} \text{ m}^{-2}$  the PL peak shifts from 536 to 545 nm with increasing concentration (see Fig. 1b). This peak shift is associated with energy transfer between smaller and larger QDs, emitting on the blue and red side of the ensemble emission spectrum respectively. The energy transfer occurs because of the overlap of emitting and absorbing states of the QD ensemble due to the inhomogeneous broadening and Stokes shift [5, 7]. The peak shift in closely packed QD layers has to be taken into account in the design of solid-state devices if matching the emission peak with other spectral properties of these structures is required for optimization. This is for example important for FRET-based sensors with QD donors and dye acceptors [4], as some dyes have quite narrow absorption bands.

In order to further investigate the nature of the energy transfer leading to the peak shift, time-resolved PL measurements have been carried out on all donor monolayer samples. Figure 2a shows a selection of three PL decays recorded on the blue side of the emission spectrum of donor QD monolayers with different concentrations. With increasing donor QD concentration  $c_{\text{Don}}$  – corresponding to a decreasing QD separation – a shortening of the decays is observed. This indicates that energy is transferred from the smaller QDs emitting on the blue side to larger QDs by the FRET mechanism [9]. The decrease of the corresponding lifetimes  $\tau_{\text{blue}}$ , obtained from a two-exponential fit of the PL decays, with increasing concentration  $c_{\text{Don}}$  can be fitted by the theory of FRET in two dimensions [13], that has already been applied to characterize FRET in mixed donor-acceptor monolayers [12]. Using the initial lifetime  $\tau_{\text{blue}}^0 = 7.8$  ns, extracted from the fit with theory, the FRET efficiency  $E_{\text{FRET}} = 1 - \tau_{\text{blue}}(c_{\text{Don}})/\tau_{\text{blue}}^0$  in the monodispersed donor monolayers can be calculated as a function of the donor concentration  $c_{\text{Don}}$ . This efficiency, shown in the inset of Fig. 2a, reaches values of over 50% at high donor concentrations where closely packed QD layers are formed. In the inset of Fig. 2a, the theoretically calculated trend for the FRET efficiency in a two dimensions structure is also presented and it explains well the increasing FRET efficiency with donor QD concentration. Details about the fitting can be found elsewhere [9]. This shows that the process causing the concentration dependence of the optical properties in monodispersed QD structures, such as the peak emission wavelength and the PL lifetime, is dominated by FRET. In particular, changes in QD lifetime can have an important impact on the dynamics of QD devices as the intra-ensemble FRET might dominate over the other processes when it becomes very fast; an example is going to be discussed below.

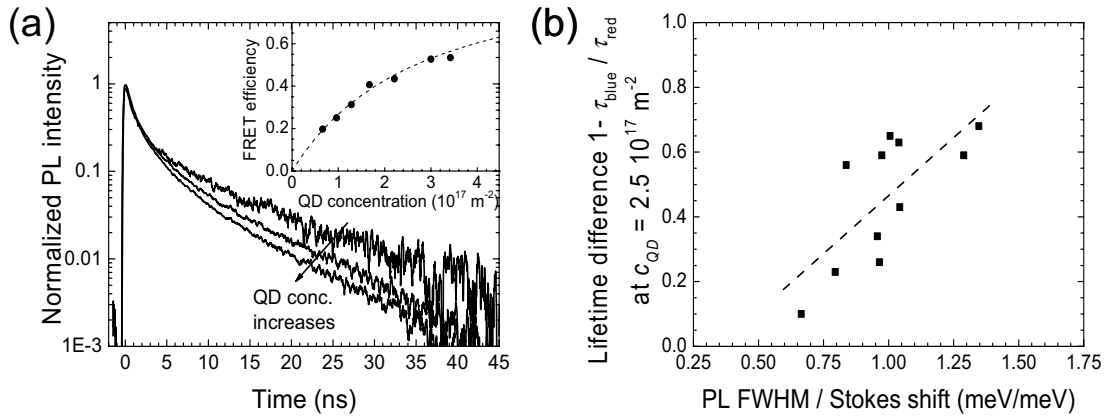


Figure 2. (a) Time-resolved PL decays on the blue side of the ensemble emission spectrum for donor monolayers with varying QD concentration. The inset shows the FRET efficiency calculated from the lifetime decrease (circles) and the trend expected from theory (line) as a function of the donor QD concentration. (b) Dependence of the lifetime difference on the blue and red side of the QD ensemble emission spectrum for monodispersed monolayers of eleven QD samples on their PL FWHM and Stokes shift ratios in solution.

Eleven different green-emitting CdTe QD samples have been investigated. To evaluate the impact of FRET in the monodispersed monolayers at one concentration  $c_{\text{QD}}$  the lifetime difference  $1 - \tau_{\text{blue}}(c_{\text{QD}}) / \tau_{\text{red}}(c_{\text{QD}})$  was determined at  $c_{\text{QD}} = 2.5 \cdot 10^{17} \text{ m}^{-2}$  for all samples. The values are shown in Fig. 2b as a function of the ratio of the PL peak FWHM and Stokes shift in the QD solutions. As the ratio decreases, corresponding to a reduced overlap of the ensemble PL and absorption spectra, the difference of the lifetimes recorded on the blue and red side of the QD ensemble emission spectrum decreases. This confirms that FRET within a QD ensemble is facilitated by a strong spectral overlap caused by a large inhomogeneous broadening and a small Stokes shift.

### 3.2 Donor/Acceptor Quantum Dot Bilayer Structure

As an example for how intra-ensemble FRET, discussed above, can impact on device performance, FRET between donor and acceptor layers in a donor/acceptor bilayer structure has been investigated. Figure 3a shows the PL spectra of a bilayer structure with a donor-acceptor QD separation of 3.4 nm and donor and acceptor concentrations of 1.4 and  $0.23 \cdot 10^{17} \text{ m}^{-2}$  respectively. The donor emission in the bilayer structure is quenched and the acceptor emission enhanced, confirming that energy is transferred from the donor to the acceptor layer.

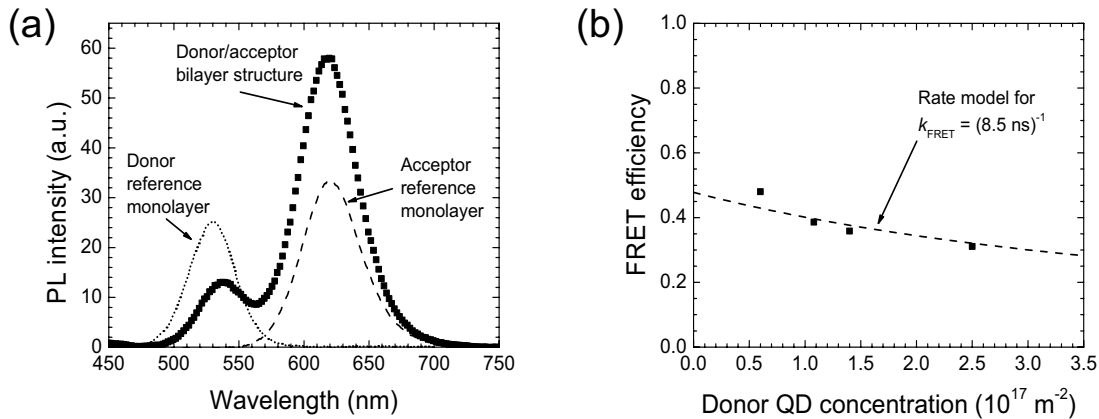


Figure 3. (a) PL spectra of a donor/acceptor bilayer structure with a QD separation of 3.4 nm (squares) and reference spectra for donor and acceptor monolayers at similar concentrations (dotted and dashed line). (b) Dependence of the FRET efficiency in the bilayer structure on the donor QD concentration (squares). A fit of the FRET efficiency based on a rate model including a constant FRET rate (dashed line) is also shown.

The FRET efficiency has been calculated from the donor lifetime decrease on the blue side of the donor ensemble emission for different donor concentrations while keeping donor-acceptor separation and acceptor concentration constant. The acceptor concentration dependence of FRET in similar QD bilayer structures has been previously reported [14]. As can be seen in Fig. 3b the measured FRET efficiency decreases with increasing donor concentration. From theory, developed for homogeneous donor and acceptor ensembles, a donor-concentration independent FRET process is expected. Here, the donor-donor intra-ensemble energy transfer represents another donor de-excitation mechanism that has to be taken into account. This system can be

described using a FRET rate model and a calculation of the FRET efficiency  $E_{\text{FRET}}$  based on the donor-concentration dependent donor lifetime and a constant FRET rate  $k_{\text{FRET}}$ :  $E_{\text{FRET}} = k_{\text{FRET}} / (\tau_{\text{blue}} (c_{\text{Don}})^{-1} + k_{\text{FRET}})$ . The competition between the donor-donor and donor-acceptor FRET introduces a concentration dependence of the donor-acceptor FRET efficiency that can be well explained within the rate model for  $k_{\text{FRET}} = (8.5 \text{ ns})^{-1}$  (dashed line in Fig. 3b). Due to the concentration dependence of the donor-acceptor FRET efficiency arising from donor-donor energy transfer,  $k_{\text{FRET}}$  is a better parameter to characterize the donor-acceptor FRET process than the FRET efficiency. However, it has to be kept in mind that due to the competition with donor intra-ensemble energy transfer, the probability for donor-acceptor FRET to occur can be reduced at high donor concentrations independent of a change in  $k_{\text{FRET}}$ .

#### 4. CONCLUSIONS

We have shown that energy transfer from smaller to larger QDs within a QD ensemble introduces a concentration dependence of the optical properties in monodispersed QD structures. The dominant mechanism mediating the energy transfer is FRET and this intra-ensemble FRET in monodispersed QD structures can be tuned by controlling the QD concentrations or selecting QDs with a particular spectral overlap in solution.

The competition between donor intra-ensemble FRET and donor-acceptor FRET in a donor/acceptor bilayer structure gives rise to a donor concentration dependence of the measured FRET efficiency. The decrease of the FRET efficiency with increasing donor concentration can be explained using a rate equation model and it was found that, as expected from theory, the actual donor-acceptor FRET rate is independent of the donor concentration. The impact of intra-ensemble FRET on device performance, such as the FRET efficiency in the example presented here, has to be taken into account. It can be reduced by preparing structures with low QD concentrations or by careful selection of the spectral properties of the QDs, however, this is usually at the expense of the quantum yield which represents an important trade-off.

#### ACKNOWLEDGEMENTS

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