Modification of the FRET Rate in Quantum Dot Structures

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ABSTRACT

Förster resonant energy transfer (FRET) can be applied to create energy flow on the nano-scale for light-harvesting, colour conversion or sensing applications. The performance of such devices depends on the efficiency of the energy transfer process between the donors and acceptors. In order to achieve high FRET efficiencies, the FRET rate has to dominate over the other donor decay rates. The FRET rate depends on the donor-acceptor separation, the acceptor concentration and it has also been proposed that it can be strongly enhanced by localized surface plasmons supported by metal nanoparticles. The impact of these different parameters on the FRET rate in a CdTe quantum dot donor-acceptor bilayer structure is presented. The quantum dot structures, prepared by a layer-by-layer deposition technique, were characterized by steady-state photoluminescence (PL) and absorption spectroscopy as well as time-resolved PL measurements. The FRET rate of the different structures was determined from the time-resolved donor PL decays and its separation and concentration dependence was compared with FRET theory.

Keywords: Förster resonant energy transfer, nanocrystal quantum dots, localized surface plasmon resonances, colloidal gold nanoparticles, time-resolved emission decay

1. INTRODUCTION

Förster resonant energy transfer (FRET) is an energy transfer mechanism from a donor to an acceptor species by dipole-dipole interactions [1]. It has been suggested as the working mechanisms for applications such as nano-sensors, graded energy structures and light emitting devices [2]. The performance of these devices is strongly linked to the efficiency of the FRET process. The FRET efficiency, E_{FRET}, is determined by the rate of the FRET process, k_{FRET}, as well as the other donor decay rates, the radiative and non-radiates rates k_r and k_{nr}, as shown in equation (1).

$$E_{FRET} = \frac{k_{FRET}}{k_r + k_{nr} + k_{FRET}} \tag{1}$$

The rate of the FRET process between donor and acceptor layers [3], given in equation (2), can be expressed as a function of the acceptor concentration (c_{Acc}), the Förster radius (R_0), the donor reference lifetime in the absence of acceptors [$\tau_D = (k_r + k_{nr})^{-1}$], and the donor-acceptor separation (d):

$$k_{FRET} = \frac{c_{Acc} \cdot \pi \cdot R_0^6}{2 \cdot \tau_D \cdot d^4} \quad . \tag{2}$$

Due to their unique optical properties - such as tuneable emission wavelengths, high quantum yields and good photostability - colloidal quantum dots (QDs) offer many advantages for the use as donors and acceptors in FRET applications [4]. The relatively large diameter of the QDs leads however to donor-acceptor separation in QD FRET structures of a few nanometers, which is of the order magnitude of the Förster radius for these systems. As can be seen from equation (2) the FRET rate decreases strongly with increasing donor-acceptor separation. Therefore, the QD size limits the FRET rate and consequently also the FRET efficiency, which impacts on the performance and sensitivity of QD FRET devices. To increase the FRET rate, research has mainly focused on decreasing the donor-acceptor QD separation. By forming closely-packed QD layers by the Langmuir-Blodgett technique [5] or by self-assembling layers of negatively charged donor and positively charged acceptor QDs on top of each other [6], FRET rates as high as $(120 \, \text{ps})^{-1} = 8 \, \text{ps}^{-1}$ and $(50 \, \text{ps})^{-1} = 20 \, \text{ps}^{-1}$, respectively, were achieved.

Here, the distance dependence of the FRET rate in donor-acceptor QD bilayer structures as well as its acceptor concentration dependence will be discussed and compared with the theoretically expected trends calculated with equation (2). Furthermore, it will be shown that localized surface plasmons, supported by gold nanoparticles, can

enhance the FRET process, giving rise to high FRET rates for donor-acceptor separations at which no energy transfer would be normally expected.

2. Experimental Methods

Negatively charged CdTe nanocrystal QDs, stabilized by thioglycolic acid in aqueous solution [7], of two different sizes were used as donor (diameter 2.7 nm) and acceptor QDs (3.5 nm), respectively. The emission of the donor QDs is centred at 555 nm and that of the acceptor QDs at 620 nm in the monodispersed reference monolayers, as can be seen in Fig. 1(a).

Bilayer structures with monodispersed donor and acceptor QD layers separated by a polyelectrolyte spacer, with a thickness tuneable in 3 nm steps, were prepared by a layer-by-layer electrostatic self-assembly technique [8]. Details on the sample preparation can be found in Ref. [4]. To investigate the impact of localised surface plasmons on the FRET process, colloidal gold nanoparticles (NPs) with a diameter of approximately 5.5 nm, showing a surface plasmon resonance centred at 530 nm in the layer (as shown in Fig. 3(b)), were used. The gold NP layer was introduced between the donor and acceptor QD layers, including polyelectrolyte spacers with thicknesses of 12 and 3 nm to separate the gold NPs from the acceptor and donor QD layers respectively.

A double beam UV-Vis Recording Spectrometer (Shimadzu UV-2401 PC) was used to record the absorption spectra of the QD structures. The steady-state photoluminescence (PL) spectra were measured with a Perkin-Elmer LS 55 fluorescence spectrometer with an excitation wavelength of 400 nm. Time-resolved PL decays were recorded with a PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution. A LDH-480 laser head controlled by a PDL-800B driver (PicoQuant) provided picosecond pulses at 470 nm for excitation. Areas of 80 by 80 μm (150 by 150 pixels) were scanned during the measurements, with integration times of 4 ms per pixel and a repetition rate of 10 MHz. A broad band filter (FWHM: 70 ± 5 nm) centred at 500 nm was used to isolate the donor PL decay in the measurements of the reference and FRET structures.

3. Results and Discussion

In the following, firstly the influence of the distance of the FRET rate in a donor-acceptor bilayer structure (without gold NPs) will be discussed, followed by the analysis of its acceptor concentration dependence. Subsequently, the impact of a gold NP layer on the FRET process between the donor and acceptor QD layers will be presented.

3.1 Distance Dependence

In Fig. 1(a), the PL spectrum of a QD bilayer with a donor-acceptor separation $d \approx 3.6$ nm is shown, along with the spectra of donor and acceptor reference monolayers with similar donor / acceptor concentrations as in the bilayer structure. The absorption spectrum of the acceptor monolayer (right-hand axis) is also included. As can be seen the donor emission overlaps well with the acceptor absorption, which is a prerequisite for efficient FRET from the donor to the acceptor QDs. Based on the spectral overlap, a Förster radius $R_0 = 3.9$ nm was calculated, valid at the time of the distance dependence measurements. The energy transfer leads to a large donor emission quenching (92 %) and a large acceptor enhancement (145 %), as can be seen in the bilayer PL spectrum. Furthermore, the FRET rate $k_{FRET} = \tau_{DA}^{-1} - \tau_D^{-1} = 0.9$ ns^{-1} and efficiency $E_{FRET} = 1 - \tau_{DA}/\tau_D = 71\%$ were determined from the time-resolved donor PL decays shown in Fig. 1(b). The value of the FRET rate is lower than the highest values reported in literature, probably due to a larger donor-acceptor separation.
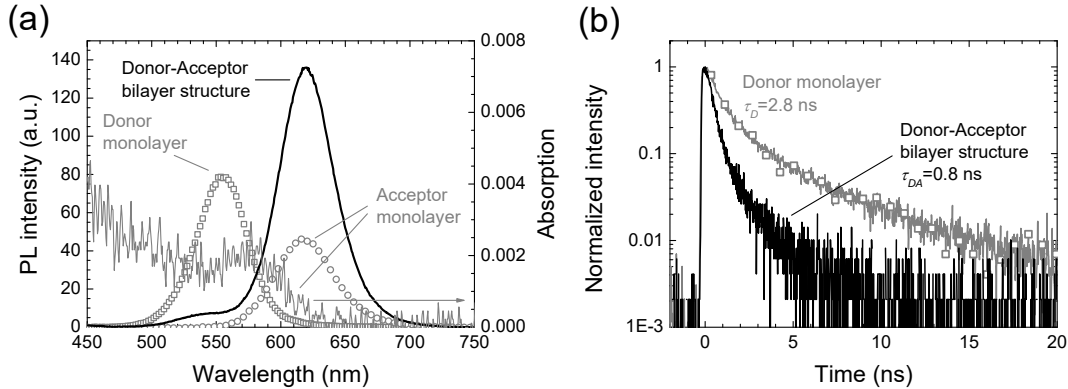

Figure 1. (a) Photoluminescence (PL) spectra (left-hand axis) of a donor-acceptor bilayer structure (black line) as well as a donor (open grey squares) and acceptor (open grey circles) reference monolayer. The absorption

From the donor lifetime decays of bilayer structures with different donor-acceptor separations, the FRET rates were determined as a function of the layer separation shown in Fig. 2(a). As can be seen the FRET rate decreases strongly from the above determined value of $k_{FRET} = 0.9$ ns^{-1} with increasing separation. In line with the report by Kim et al. [9], a good agreement of the experimentally determined distance dependence of the FRET rates is found with FRET theory, using $R_0 = 3.9$ nm in the calculation of k_{FRET} with equation (2).
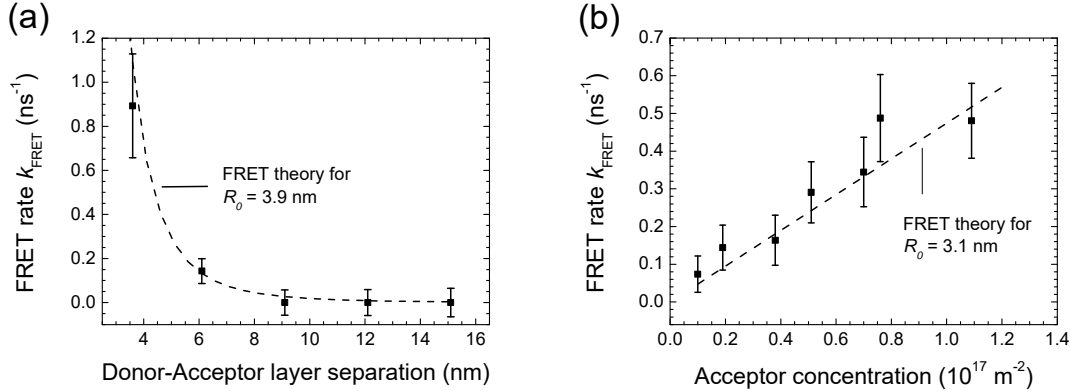

Figure 2. (a) Distance dependence of the FRET rate (k_{FRET}) determined for donor-acceptor QD bilayer structures. The dashed line represents the distance dependence of the FRET rate calculated with equation (2) based on FRET theory. (b) Acceptor concentration dependence of the FRET rate determined experimentally for QD bilayer structures with a donor-acceptor separation of 3.6 nm (solid squares) and calculated with equation (2) (dashed line).

3.2 Acceptor Concentration Dependence

Next, the acceptor concentration dependence of the FRET process was investigated [4]. At the time of the measurement the donor quantum yield had decreased, and consequently the Förster radius had reduced to $R_0 = 3.1$ nm. The FRET rates determined from the donor PL decays measured for donor-acceptor bilayer structures ($d \approx 3.6$ nm) with different acceptor concentrations are shown in Fig. 2(b). As can be seen the FRET rate increases with increasing acceptor concentration as expected from FRET theory, represented by the dashed line, calculated with equation (2). Due to the reduced R_0, the FRET rate is lower than the highest rate achieved for the smallest layer separation, $R_{ex} = 3.6$ nm, shown in Fig. 2(a). However, it can be seen that the rate increases by a factor 5, corresponding to an increase of the FRET efficiency from 12% to 49%, as the acceptor concentration increases from 0.1×10^{17} m^{-2} to 1.1×10^{17} m^{-2}.

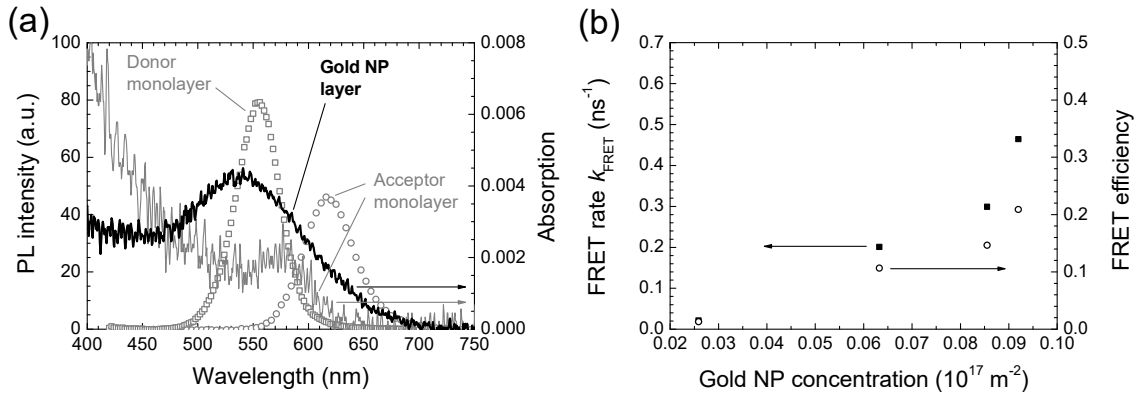### 3.3 Impact of Surface Plasmons on FRET

Figure 3. (a) Photoluminescence (PL) spectra (left-hand axis) of monodispersed donor (open grey squares) and acceptor monolayers (open grey circles), as shown in Fig. 1(a). Also shown are absorption spectra (right-hand

axis) of the acceptor monolayer (solid grey line, as in Fig. 1(a)) as well as of a gold nanoparticle (NP) layer (solid black line). (b) Gold NP concentration dependence of the surface plasmon enhanced FRET rate (k_{FRET}) (solid black squares, left-hand axis) as well as the FRET efficiency (open black circles, right-hand axis).

It has been proposed, that localised surface plasmons can enhance the FRET process between donors and acceptors [10]. To investigate this effect, gold NPs, with a surface plasmon resonance centred at 530 nm in the layer, were introduced as an intermediate layer between the acceptor and donor QD layers. In Figure 3(a) it can be seen that the surface plasmon resonance overlaps well with the donor emission and the acceptor absorption, which should allow for an efficient enhancement of the donor-acceptor FRET process. Due to the inclusion of the gold NPs and the thickness of the additional polyelectrolyte spacers, the donor-acceptor separation is increased to approximately $d \approx 23\,\mathrm{nm}$. Calculations with equations (1) and (2) show that no significant FRET rate ($k_{FRET} = 0.002\,\mathrm{ns}^{-1}$) or FRET efficiency ($E_{FRET} = 0.1\%$) is expected at this separation.

The FRET rates of four acceptor-gold-donor structures with different gold NP concentrations were determined from the donor PL decays. These FRET rates are shown as a function of the gold NP concentration in Fig. 3(b). As can be seen the FRET rate increases with increasing gold NP concentration up to a value of $k_{FRET} = 0.46\,\mathrm{ns}^{-1}$, corresponding to a rate enhancement by a factor of 230. The FRET efficiency, also shown in Fig. 3(b), increases to $E_{FRET} = 21\%$, showing a similar enhancement as for FRET rate.

4. Conclusion

In summary, we have shown that the FRET rate varies strongly with the donor-acceptor separation, the acceptor concentration as well as with the Förster radius, which is influenced by the spectral overlap as well as the donor quantum yield. Therefore, all these parameters represent important factors that can be tuned to increase the FRET rate and FRET efficiency. The good agreement of the experimentally determined distance and acceptor concentration dependence of the FRET rate with FRET theory lay a basis for the optimization of the performance and / or sensitivity of QD FRET devices. Additionally, it has been shown that gold nanoparticles included in a donor-acceptor bilayer structure can strongly enhance the FRET process. Due to this enhancement, high FRET rates and efficiencies can be achieved for donor-acceptor separations at which usually no energy transfer would be observed. Therefore, along with the optimization of the other, afore-mentioned parameters, surface plasmons represent a promising means to improve the performance of QD FRET devices.

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