FRET in Self-Assembled CdTe Quantum Dot Nanoclusters

Clare Higgins[1], Manuela Lunz[1], A. Louise Bradley[1*],
Valerie A. Gerard[2], Stephen Byrne[2], Yurii K. Gun'ko[2]

[1]*Semiconductor Photonics Group, School Of Physics, Trinity College Dublin, Dublin 2, Ireland*

[2] *School Of Chemistry, Trinity College Dublin, Dublin 2, Ireland*

*Tel: +353-1- 8963595, Fax: +353-1-6711759, e-mail: bradlel@tcd.ie

ABSTRACT

Colloidal CdTe quantum dots (QDs) with oppositely charged ligand shells were used to form quantum dot nanoclusters in solution. The signatures of Forster non-radiative energy transfer in the photoluminescence and time-resolved photoluminescence data indicates that the electrostatic attraction draws the QDs into close proximity forming nanoclusters. The smaller QDs act as donors and the larger QDs act as acceptors within the cluster and a FRET efficiency of 45% has been recorded. Both the time-resolved and spectral PL data show a strong donor concentration dependence. The acceptor photoluminescence enhancement and FRET efficiency can be tuned by adjusting the donor:acceptor ratio.

Keywords: Förster resonant energy transfer (FRET); colloidal CdTe quantum dots; optical spectroscopy; time-resolved photoluminescence.

1. INTRODUCTION

Förster resonant energy transfer (FRET) is an energy transport mechanism that occurs on the nanoscale via dipole-dipole interactions [1]. Recently there has been increased interest in composite nano-assemblies for use in bio-sensing and light harvesting applications [2, 3]. These structures employ FRET to generate energy flow from an energy donor to an energy acceptor. Due to their unique optical properties, such as tuneable emission wavelength and high quantum yields [4], colloidal semiconductor Quantum Dots (QDs) are of particular interest as energy donors and acceptors for FRET nano-assemblies. FRET between donor and acceptor QDs has previously been investigated in various layered structures. It has been shown that the FRET efficiency and the acceptor enhancement can be tuned by varying the donor: acceptor ratio in randomly mixed donor – acceptor QD monolayers [5]. Nanoscale clusters provide the opportunity to investigate FRET on the single acceptor scale. Previously FRET has been observed in nanoclusters of electrostatically bonded oppositely charged CdSe QDs [6]. FRET has also been studied between two electrostatically bonded CdTe QDs (ratio 1:1) [7].

Here, we present the spectral properties and photoluminescence (PL) lifetime data for mixed solutions of oppositely charged colloidal CdTe QDs for a range of donor to acceptor concentration ratios. The data shows evidence for FRET from the donors to acceptors, consistent with the formation of donor-acceptor nanoclusters. The results will be discussed in terms of the influence of the donor: acceptor ratio on the FRET signatures observed in steady-state and time-resolved PL measurements

2. EXPERIMENTAL TECHNIQUES

The oppositely charged QDs, of two different sizes, were mixed in aqueous solutions. The negatively charged thioglycolic acid stabilized CdTe QDs (TGA-QD), with a diameter of 2.4 nm and an emission peak at 535 nm, act as the energy donor. The quantum yield of the TGA-QD in solution is 12%. The positively charged cysteamine stabilized CdTe QDs (cys-QD) with a diameter of 3.5 nm emit at 600 nm and act as the energy acceptor. The quantum yield of the TGA-QD in solution is 17%. Dilute QD solutions were prepared and subsequently mixed to achieve TGA-QD concentrations ranging from $2.6{\times}10^{-7}$ M to $41.6{\times}10^{-7}$ M. The concentration of the acceptor cys-QD was maintained at $4.9{\times}10^{-7}$ M throughout.

A Cary 50 UV-Vis spectrometer was used to record the absorption spectra. Room temperature photoluminescence (PL) spectra were obtained for an excitation wavelength of 400 nm, using a Perkin-Elmer LS 55 fluorescence spectrometer. Time-resolved PL decays were measured with a PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution. Excitation at 470 nm was provided in picosecond pulses. The decays were recorded with a 5 MHz repetition rate and measured over an area of 80×80 μm (150×150 pixels) with an integration time of 4 ms per pixel. Broadband filters at 500 and 650 nm were used to measure the time-resolved emission signals of the donor and acceptor QDs, respectively.

3. RESULTS

The properties of the pure QD solutions are presented first, followed by characterisation of the mixed QD solutions of varying donor:acceptor QD ratios. Figure 1 shows the absorption and photoluminescence (PL) spectra of the pure donor and pure acceptor CdTe QD in aqueous solutions. The concentrations of the pure donor and pure acceptor QD solutions are $c_{Don} = 3.9{\times}10^{-6}$ M and $c_{Acc} = 1.6{\times}10^{-6}$ M. This QD combination was selected

because the PL emission spectrum of the pure donor QDs and the high energy side of the absorption band of the pure acceptor QDs exhibit a suitable overlap to allow for energy transfer. From the spectral data the Förster critical radius (R_0) is calculated to be 4.6 nm.
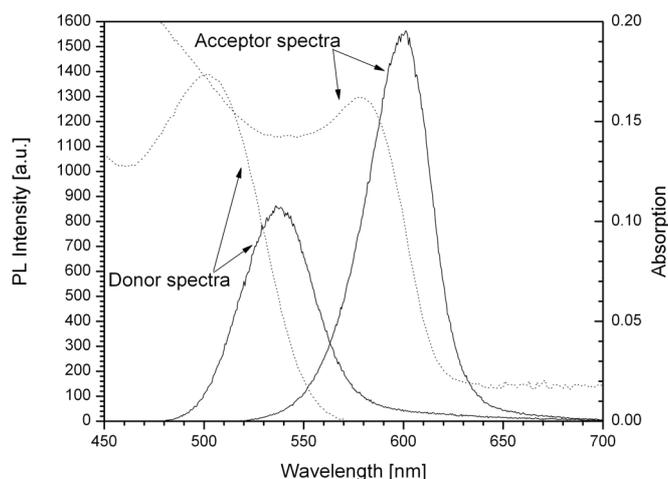

Figure 1. Photoluminescence (solid line, left-hand axis) and absorption (dotted line, right-hand axis) spectra of the pure donor TGA-QD and the pure acceptor cys-QD in aqueous solutions.

The spectra of a pure donor TGA-QD solution (dotted line) at a concentration of 21.1×10^{-7} M, a pure acceptor cys-QD solution (dashed line) at a concentration of 4.9×10^{-7} M and a mixed solution (solid line) for the same concentrations of QD are presented in Fig. 2. It can be clearly seen that the donor emission is quenched and that the acceptor emission is enhanced by 20% (as calculated from the integrated photoluminescence data presented later). While quenching of the donor emission and enhancement of the acceptor emission is a typical signature of energy transfer, reduction in the donor lifetime in the mixed solution, shown in the inset of Fig. 2, proves that energy is transferred via the Forster non-radiative energy transfer mechanism. The lifetime shown in the inset, reduces from 19.2 to 0.5 ns in the mixed solution, corresponding to a FRET efficiency of 45%. The observation of energy transfer via FRET indicates the donor and acceptor QD are in close proximity. The oppositely charged QDs achieve this proximity as they are drawn together by electrostatic attraction to form closely packed nanoclusters. As such the FRET evidence indicates the successful formation of electrostatically bound nanoclusters.
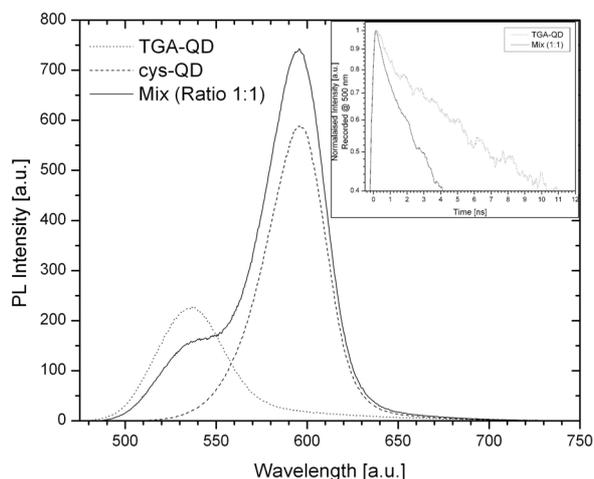

Figure 2. FRET in mixed solutions of oppositely charged quantum dots. Photoluminescence (PL) spectra of pure donor (TGA-QD), pure acceptor (cys-QD) and a mixed solution, of ratio 1:1 (dotted, dashed and solid line, respectively). Inset: PL decay curves of pure TGA-QD and mixed solution of ratio 1:1 (dotted line and solid line, respectively) recorded at 500 nm.

The efficiency of the quenching process is given by the term $Q = (I_{Dref} - I_{Mix})/I_{Dref}$, where I_{Dref} and I_{Mix} are the integrated donor PL intensities in the pure and the mixed solutions, respectively. In Fig. 3 the efficiency of the quenching of donor PL in the mixed solutions with reference to pure donor solutions at the same concentrations is presented as a function of the donor:acceptor ratio. For low donor concentrations, there is significant donor PL quenching in the mixed solutions. At these low donor concentrations, there is a relatively high probability that a donor QD will come close enough to an acceptor QD to allow for non-radiative energy transfer. In this regime,

quenching efficiencies greater than 50% are found for donor:acceptor ratios less than 1:1. With increasing donor concentration, an ever increasing proportion of the acceptor QD population will have bonded with one or more donor QDs. As the donor concentration continues to increase, the probability that the additional donor QDs will achieve the required proximity to an acceptor QD necessary for FRET begins to decrease. Consideration of the relative diameters of the donor and acceptor QDs indicates that no more than 8 donors can achieve a donor-acceptor separation comparable to the Forster radius in a cluster formed using a single acceptor. However it is more likely that the size of the cluster will be limited by the electrostatic charge of the ligand shells and this is supported by the experimental observations. The experimental data in Figure 3 shows the efficiency of donor PL quenching is decreasing with increasing donor concentration. The fact that the quenching efficiency begins decreases before the expected donor:acceptor ratio of 8 has been reached, shows that the charge states of the QDs are influencing the cluster formation. The electrostatic charge is insufficient to bind all of the 8 donors to the acceptor. For donor:acceptor ratios of greater than 4:1 the quenching efficiency decreases to less than 30%.

The efficiency of the enhancement process is given by the term $E = (I_{Mix} - I_{Aref})/I_{Aref}$, where I_{Aref} and I_{Mix} are the integrated acceptor PL intensities in the pure and the mixed solutions, respectively. As can be seen in Fig. 3 at low donor concentrations, little acceptor enhancement is observed since the acceptor population is predominantly composed of free acceptor QD. For donor:acceptor ratios of less than 1:1, the enhancement efficiency is less than 5%. As the donor concentration increases the proportion of the acceptor QD population in a nanocluster increases, with a greater than 20% enhancement of the acceptor PL evident for the highest donor concentration.
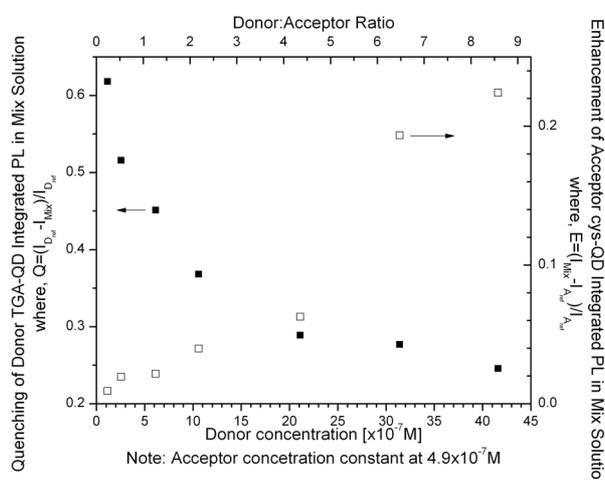

Figure 3. Left-hand axis: Quenching efficiency (Q) of the donor TGA-QD photoluminescence (PL) as a function of donor QD concentration. Right-hand axis: Enhancement efficiency (E) of the acceptor cys-QD PL of as a function of donor QD concentration. The acceptor QD concentration was maintained constant at 4.9×10^{-7} M throughout. I_{Dref}, I_{Aref} and I_{Mix} are the integrated intensities of pure TGA-QD solutions, pure cys-QD solutions and the mixed solutions, respectively. The corresponding number of donor QDs per acceptor QD is given on the top axis.

The time-resolved photoluminescence (PL) measurements of a pure donor TGA-QD solution and several mixed solutions are shown in Fig. 4. The decrease in the donor QD lifetime varies with the donor QD concentration. At low donor QD concentrations, the donor QD PL lifetime decreases from the reference value of 19.2 to 10.5 ns in the mixed solution, as mentioned above. At increased donor:acceptor ratios of 2:1 (solid triangles) and 4:1 (solid diamonds), the PL lifetime is reduced further to 9.5 ns. Further increasing the donor concentration and the corresponding donor:acceptor ratio causes the PL lifetime to return to the relatively longer value of 10.5 ns. The observed drop in donor QD lifetime at a particular donor:acceptor ratio, followed by a relative recovery has been previously reported by Lin *et al.* [8]. For ratios of 1:1 or less we can expect a dominance of nanoclusters formed from a single donor and single acceptor. As the ratio increases there is increased probability of more than one donor attaching to an acceptor, which brings the donors into proximity with each other and facilitates donor-donor interactions, which can result in a further decrease of the donor lifetime. However, the observed effects are small and will be further examined in another study to identify the process. As discussed above, as the donor concentration is further increased the cluster size is not expected to increase due to electrostatic considerations and measured donor lifetime will increase reflecting the increased proportion of unbounded donors. The lifetime data suggests that nanoclusters of 4 to 5 donors per acceptor are formed by the negatively charged TGA-QDs and positively charged cys-QDs. No such donor-donor interaction as a function of increasing donor concentration is observed in the pure donor QD solution since both the dilute nature of the solution and the negative charge of the ligand shell serve to keep the donor QDs suitably separated.
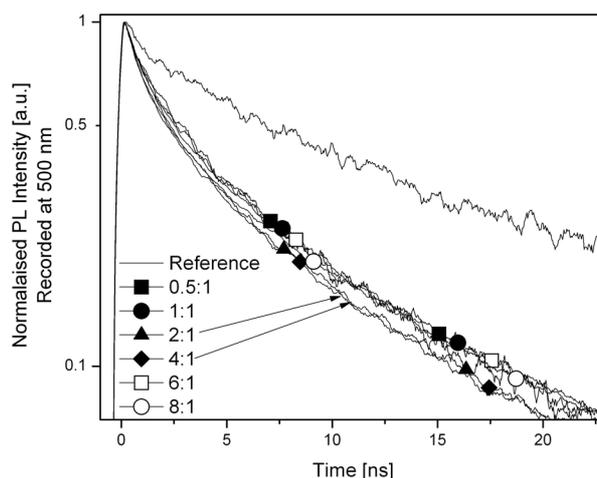
Figure 4. Time resolved photoluminescence measurements of the donor QDs in a pure solution (solid black line) and in mixed solutions (symbols).

4. CONCLUSIONS

In this study we have looked at preassembling CdTe QDs nanoclusters in aqueous systems. Spectral and time-resolved PL measurements show evidence for energy transfer via FRET providing insight into the formation of nanoclusters of the oppositely changed CdTe QDs. A FRET efficiency of 45% has been recorded. A donor concentration dependence of the donor lifetime and FRET efficiency in the mixed QD solution has been observed which may indicate the maximum size of the clusters being formed. Additionally, it has been shown that for these solution based clusters, it is possible to tune the acceptor enhancement by varying the donor: acceptor ratio, as has been reported for a mixed donor: acceptor monolayer [5]. In the same manner, it is also possible to tune the FRET efficiency by further decreasing the donor:acceptor ratio as required for a given application. Nanoclusters can be pre-assembled in solution at the selected donor:acceptor ratio prior to casting into structures tailored for applications such as solar-cell concentrators or biological sensors to optimise performance. A comparison of structures formed with random donor:acceptor distributions and those formed with preassembled clusters will evaluate the improvement of the FRET process due to the favourable geometrical design in the preassembled structure.

ACKNOWLEDGEMENTS

REFERENCES

[1] T. Förster: Self-assembled nanoscale biosensors based on quantum dot FRET donors, *Annalen der Physik,*, vol. 2, pp. 55, 1948.

[2] I.L. Medintz *et al*.: Self-assembled nanoscale biosensors based on quantum dot FRET donors, *Nat. Mater.*, vol. 2, pp. 630-638, 2003.

[3] T. Franzl *et al*.: Exciton recycling in graded gap nanocrystal structures, *Nano. Lett.*, vol. 4, pp. 1599-1603, 2004.

[4] E. Alphandery *et al*.: Highly efficient Förster resonance energy transfer between CdTe nanocrystals and Rhodamine B in mixed solid films, *Chem. Phys. Lett.*, vol. 388, pp. 100-104, 2004

[5] 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.

[6] R. Wargnier *et al*.: Energy transfer in aqueous solutions of oppositely charged CdSe/ZnS core/shell quantum dots and in quantum dot-nanogold assemblies, *Nano. Lett.*, vol. 4,. pp. 451-457, 2004.

[7] R. Osovsky *et al*.: Electrostatic and Covalent Interactions in CdTe Nanocrystalline assemblies, *J. Phys. Chem. B*, vol. 109,. pp. 20244-20250, 2005.

[8] Y. C. Lin *et al*.: Effect of donor-acceptor concentration ratios on nonradiative energy transfer in closely packed CdTe quantum dots, *Appl. Phys. Lett.*, vol. 95, pp. 1331123-3, 2009.