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Spectroscopic Signature of Semiconductor QDs: FRET Between CdTe QDs and Cresyl Violet Dye

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Abstract— Quantum dots (QDs), highly luminescent semiconductor nanocrystals, have found extensive applications in different fields, ranging from optoelectronic to bio-imaging. In present paper we report evidence of efficient Förster resonance energy transfer between CdTe QDs (donors) of varying sizes and cresyl violet dye (acceptor). The FRET efficiency of the systems was investigated as function of spectral overlap between donor emission and acceptor absorption spectra as well as size of the QDs. In steady-state measurement, upon increasing concentration of acceptor, donor fluorescence intensity starts decreasing simultaneous enhancement in acceptor along with fluorescence at 620 nm, which confirms the resonance energy transfer between CdTe QDs to Cresyl Violet dye. Further, this is confirmed by time-resolved measurements, shortening of lifetime of CdTe QD (donor) in the presence of cresyl violet (acceptor) confirms that clear photo induced energy transfer is occurring from present QD to dye system. FRET parameters such as spectral overlap $J(\lambda)$, Förster distance (R_0) and transfer efficiency (E) determined by steady-state and time-resolved fluorescence measurements. Dynamic quenching is also observed in the present FRET system and bimolecular quenching rate constants (k_q) are determined from Stern-Volmer plot.

Keywords-Quantum dot, Spectarl overlap, Forster distance, Transfer efficiency

1. INTRODUCTION

FRET, the acronym for fluorescence (Forster) resonance energy transfer is a near field dipole-dipole interaction that involves the radiationless energy transfer from an excited molecule (donor) to a proximal resonant molecule in a relaxed state (acceptor). Due to its sensitivity in the nanometer range (typically below 10 nm) and its practicability in spectroscopic measurements, FRET has been widely applied in the studies of biomolecular conformations and dynamics. The transfer of energy manifests in a reduction in the donor fluorescence intensity, the excited state lifetime and a simultaneous increase in the acceptor emission intensity. A pair of molecules, wherein FRET occurs in such a manner, is often referred to as donor- acceptor pair; and the efficiency of the FRET process depends on the separation between the donor and acceptor [1, 2]. Here water soluble CdTe nanocrystals of different size are used as energy donors due to the large absorption band, high photoluminescence (PL), quantum yield (QY), resistance to photobleaching, and size tunable PL spectra covering the region from blue to red. The potential applications are in the areas of luminescence tagging, imaging, medical diagnostics, multiplexing, and most recently as biosensors [3].

2. MATERIALS AND METHODS

The QDs CdTe 520 and 540 with diameter 2.04 nm and 2.34 nm were purchased from Plasmachem GmbH,

Germany and cresyl violet dye from Lambdaphysik, Inc. and used as received. To prepare the stock solutions a known amount of the NCs was dissolved in a desired volume of double distilled de-ionized water and cresyl violet (CV) dye used as acceptor. The optical absorption spectra were obtained with Uv-Vis spectrophotometer (Hitachi, U-2800) and photoluminescence (PL) spectra were recorded using spectrofluorometer (Horiba Floromax-4). Time resolved measurements were performed with time correlated single photon counting (ChronosBH with (TCSPC) system picosecond resolution) with Laser diode as source of excitation at 375 nm. By monitoring the fluorescence lifetime of quantum dots in the presence and absence of the dye, important information can be obtained on molecular interactions. Fluorescence lifetime is more precise parameter as it is concentration independent [4].

3. RESULTS AND DISCUSSION

With a view to develop FRET chemical and biosensors based on semiconductor QDs, two sets of QDs of sizes 520 and 540 nm are chosen as donors in the present study with CV dye as acceptor molecule. Each molar concentration was studied in free solution under steady state condition. The optical absorbance and emission of CdTe quantum dots and cresyl violet dye are shown in Fig.1. The emission spectra of CdTe QDs retain sharp peak at 520 and 540 nm when excited at 375 nm. The absorption spectrum of CV dye has a peak at 583 nm. From the Fig.1 it is clear that there is a significant overlap between the absorption spectrum of an acceptor and emission spectra of donors. Note that the acceptor dye CV

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does not show any absorption at 375 nm and therefore allows for excusive excitation of donor and a clean photon induced energy transfer from donor-acceptor occurs.



Fig. 1: Normalized steady-state emission spectra of CdTe 520 and 540 nm QDs and absorption spectra CV dye

The overlap integral is defined as

$$J(\lambda) = \int_{0}^{\infty} F_{D}(\lambda) \varepsilon_{A}(\lambda) \lambda^{4} d\lambda$$
 (1)

where $F_D(\lambda)$ is the normalized emission spectrum of donor (CdTe) and ε_A is the absorption coefficient of acceptor (CV). Forster radius (R_0) and intermolecular distance (r) is calculated from

$$R_0 = \left[8.8 \times 10^{23} k^2 n^{-4} \varphi_D J \right]^{1/6}$$
 (2)

$$r = R_0 (1/E - 1)^{1/6}$$
(3)

where k is orientation factor, n is refractive index, φ_D Quntum yield of donor, J is overlap integral, E is efficiency of the FRET pair. Steady state FRET parameters are listed in Table 1. Here emission properties of QDs were tuned by varying the size of the QD. By changing the size, emission property of QD is shifted to redder region [5]. It is interesting to note that the overlap integral value increases with the changing size of the QD.

Table 1: FRET Parameters

FRET System	$J(\lambda)$ ($M^{-1}cm^{-1}nm^{4}$) x10 ⁻¹³	R ₀ (nm)	r (nm)
CdTe 520 - CV	0.54	3.85	5.23
CdTe 540 - CV	1.22	4.67	5.4

The FRET spectra are shown in Fig 2. Increasing the concentration of acceptor (0 to $10 \,\mu\text{M}$), leads to decrease in the intensity of the donor emission and a simultaneous enhancement of the acceptor emission at 620 nm. The absorption of the CV dye at 375 nm is negligible and direct excitation of acceptor is ruled out. The fluorescence lifetime of two donors CdTe 520 and CdTe 540 are measured in the absence and presence of acceptor CV dye by single photon counting technique (TCSPC). The data was fitted in to tri-exponential with χ^2 value close to unity. Here we noticed that the lifetime of the donor is decreasing with increasing concentration of the acceptor. This clearly indicates that the excitation energy of donor is transferred to the unexcited acceptor (Fig.3) molecules via non radiative resonance energy transfer (RET) [6, 7]. The efficiency of FRET pair is calculated by equation 4 and 5. The Efficiency values are calculated using

For Steady-state

$$E = 1 - \frac{F_{DA}}{F_D} \tag{4}$$

For Time-resolved

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \tag{5}$$

and are listed in Table 2.



Fig. 2: (a) and (b) steady-state emission spectra of series of CdTe 520 and 540 QDs with CV dye (A) QD alone, (B) $0.2x10^{-6}$ M, (C) $0.4 x10^{-6}$ M, (D) $0.6x10^{-6}$ M, (E) $0.8x10^{-6}$ M, (F) $1x10^{-6}$ M, (G) $0.2 x10^{-5}$ M, excited at 375 nm. The enhanced emission at 621 nm corresponds to the CV dye resulting from energy transfer from the QDs.



Fig. 3: (a) and (b) Log scale plot of time-resolved PL traces for CdTe 520 and CdTe 540 with and without CV dye



Fig. 4: (a) & (b) Steady state stern-volmer plot of F_0/F vs. Concentration of Quencher, (c) & (d) Time resolved sternvolmer plot of τ_0/τ vs. Concentration of Quencher

The rate of quenching of donor emission is illustrated by the decrease in average lifetime. It reveals that transfer efficiency will depend on the size of the particle and spectral overlap between donor and acceptor [7, 8]. Quenching of donor emission as function of varying concentration of acceptor is expected and is described by the well known Stern-Volmer Equation [9].

$$\frac{F_0}{F} = 1 + K_q \tau_0[Q] = 1 + K_{sv}[Q] = \frac{\tau_0}{\tau}$$
(6)

where F_0 and F are the PL intensity in the absence and presence of quencher, respectively, [Q] is the

concentration of quencher, K_{sv} is the stern-volmer quenching constant, and τ_0 and τ are the lifetime in the absence and presence of quencher, respectively. Since this quenching is an additional rate process which depopulates the excited state; the above equation illustrates the important characteristics of quenching which is evident in decrease in fluorescence intensity and lifetime. A linear stern-volmer plot of F_0/F v/s quencher concentration (Q) and τ_0/τ versus quencher concentration (Q) is shown Fig. 4. If the quenching mechanism is dynamic, due to collision between fluorophore and the quencher,

FRET Pair	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_{1}	A_{2}	A_3	$\begin{array}{c} Average \\ \langle \tau \rangle ns \end{array}$	Efficiency [*] (%)	Efficiency [#] (%)
CdTe 520	0.42	3.38	18.9	0.01	0.08	0.91	17.5		
CdTe 520 - CV	0.35	3.24	18.2	0.04	0.17	0.79	15.1	13.7	26
CdTe 540	0.61	2.76	10	0.14	0.42	0.44	5.67		
CdTe 540 - CV	0.45	2.04	8.42	0.19	0.45	0.36	4.01	29.2	34

Table 2: Transfer efficiency from steady-state and time-resolved measurements

* From Time-resolved measurements

From Steady-state measurements

then $K_{sv} = K_q \tau_0$ where K_q is bimolecular quenching constant and τ_0 luminescence lifetime of fluorophore in the absence of quencher. By linear fitting of the data, the slope of plot, K_{sv} was found to be 0.029 x 10⁶ M⁻¹ and 0.097 x 10⁶ M⁻¹ in for CdTe 520-CV and CdTe 540-CV system, respectively. The estimated rate constant (K_q) values are 0.16x 10¹³ and 1.72 x10¹³ M⁻¹s⁻¹ for QD1-CV and QD2-CV system, respectively from time resolved stern-volmer plot. A decrease in fluorescence lifetimes of the QDs is equivalent to F₀/F.

4. CONCLUSION

In this study, we have explored the energy transfer between two sizes of CdTe QDs (2.04nm and 2.34nm) as donor and CV dye as acceptor. The results clearly illustrate the dependence of FRET efficiency on spectral overlap and size of the QDs. FRET parameters Forster distance (R_0), Spectral overlap (J), Energy transfer efficiency (E) are calculated from both steady state and time resolved measurements. The bimolecular quenching rate constants for the two systems are calculated by Stern-Volmer plot and are given by 0.165x 10^{13} M⁻¹s⁻¹ and 1.72 x 10^{13} M⁻¹s⁻¹ respectively. The present study also demonstrates this system exhibits FRET and acts as very sensitive chemical sensor.

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