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DESIGN OF "CdTe QD-RH 101 DYE" FRET PAIR AS A NEW LIGHT HARVESTING SYSTEMS

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ABSTRACT:

Here we present Förster resonance energy transfer based light harvesting of aqueous colloidal CdTe quantum dots to Rhodamine 101 (Rh 101) dye molecules in water by using steady-state and time-resolved fluorescence spectroscopy. The light harvesting efficiency is tuned by varying the spectral overlap between the CdTe QD and Rh 101 dye. In our experiments, we observed a significant decrease in CdTe quantum dot's lifetime upon adding the Rh 101 dye and achieved upto 60% of energy transfer efficiency.

KEYWORDS : Förster resonance energy , light harvesting.

1. INTRODUCTION

Rising demand for energy soon will compel us to explore naturally clean alternate energy assets. Renewable energy such as solar radiation is perfect to meet the anticipated demand yet requires new activities to harvest incident photons with higher efficiency. In the search for a light absorbing material, it is now well established that semiconductor quantum dots (QDs) are very useful for enhancing the light harvesting process, as they can absorb light over a wide spectral window and they are able to transfer this absorbed energy to fluorescent dye molecules using FRET technique. In this perspective, we outlined inorganic-organic conjugate framework where CdTe QDs will assimilate the visible light as an antenna material, and subsequently transfer the excitons to Rh 101 dye as acceptor molecule nonradiatively [1-3].

2. EXPERIMENTAL SECTION

Hydrophilic COOH functionalized CdTe QDs of two different sizes (2.04 nm and 2.34 nm) were purchased from Plasmachem GmbH, Germany and Rh 101 dye from Lambdaphysik, Inc., Germany were used. Double-distilled water was used for further purification. The optical absorption spectra were obtained using 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 (TCSPC) system (ChronosBH with ps resolution) with Laser diode as source of excitation at 375 nm.

3. RESULTS AND DISCUSSION

The optical absorbance and emission of CdTe quantum dots and Rhodamine 101 dye are shown in Fig. 1. The emission spectra of CdTe QDs retain sharp peak at 515 and 543 nm when excited at 375 nm. The absorption spectrum of Rh 101 dye has a peak at 595 nm. This figure shows a significant overlap between the absorption spectrum of an acceptor and emission spectra of donors. Note that the acceptor dye Rh 101 does not show any absorption at 375 nm and therefore allows for exclusive excitation of donor and a clean photon induced energy transfer from donor-acceptor is possible.

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The overlap integral is defined as

$$J(\lambda) = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \qquad (1)$$

where $F_D(\lambda)$ is the normalized emission spectrum of donor (CdTe) and ε_A is the absorption coefficient of acceptor (Rh 101). Forster radius (R_0) and intermolecular distance (r) is calculated from

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

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

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 [4-7]. It is interesting to note that the overlap integral value increases with the changing size of the QD. The FRET spectra are shown in Fig. 2, increasing the concentration of acceptor (0 to $10\ \mu M$), leads to decrease in the intensity of the donor emission and a simultaneous enhancement of the acceptor emission at 595 nm. The fluorescence lifetime of two donors CdTe 520 and CdTe 540 are measured in the absence and presence of acceptor Rh 101 dye by single photon counting technique (TCSPC). The data was fitted in to tri-exponential with value close to unity. We observed a drastic reduction in the fluorescence lifetime of the CdTe 520 and 540 QDs from 19.8 ns to 15.1 ns and 20.4 ns to 8.21 ns, respectively. The Efficiency values are calculated using

for Steady-state $\qquad E = 1 - \dfrac{F_{DA}}{F_D} \qquad (4)$

for Time-resolved $\qquad E = 1 - \dfrac{\tau_{DA}}{\tau_D} \qquad (5)$

and are listed in Table 2.

We achieved up to 60% of energy transfer efficiency from CdTe QDs to Rh 101 dye molecule and confirm that CdTe QDs act as light harvesting antennae. Further, all FRET parameters are estimated and the impact of size of the QD on light harvesting efficiency is discussed.

Table 1: FRET Parameters

FRET System	$J(\lambda)$ ($M^{-1}cm^{-1}nm^4$) x10^{-13}	R_0 (nm)	r (nm)
CdTe 520 – Rh 101	0.54	3.85	5.23
CdTe 540 – Rh 101	1.22	4.67	5.4

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

FRET Pair	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	Average $\langle \tau \rangle$ ns	Efficiency* (%)	Efficiency# (%)
CdTe 520	0.42	3.38	18.9	0.01	0.08	0.91	17.5		
CdTe 520 – Rh 101	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 – Rh 101	0.45	2.04	8.42	0.19	0.45	0.36	4.01	29.2	34

* From Time-resolved measurements   # From Steady-state measurements
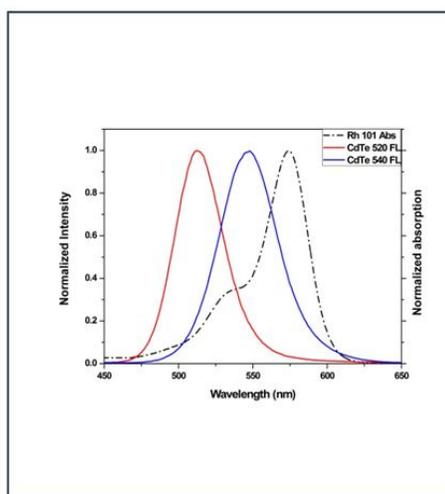
Figure 1. Normalized steady-state emission spectra of CdTe 520 nm and 540 nm QDs and absorption spectra Rh 101 dye.
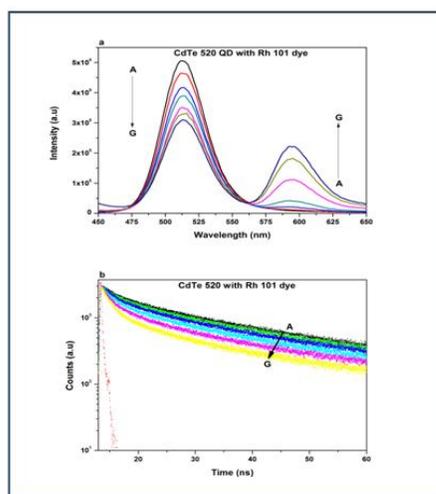
Figure 2 (a & b). Steady-state and time resolved spectra of CdTe 520 QD with Rh 101 dye. (A) QD alone, (B) 0.2x10⁻⁵M, (C) 0.4 x10⁻⁵M , (D) 0.6x10⁻⁵M, (E) 0.8x10⁻⁵M, (F) 1x10⁻⁵M, (G)1.2 x10⁻⁵M, excited at 375 nm.

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 Rh 101 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^{-1}s^{-1} and 1.72 x10^{13}M^{-1}s^{-1} respectively. The present study also demonstrates this system exhibits FRET and acts as very sensitive chemical sensor.

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