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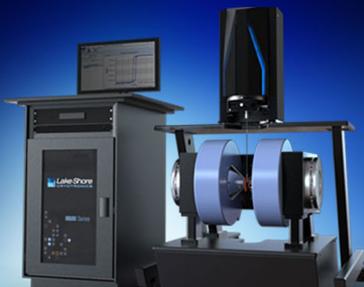
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Highly efficient nonradiative energy transfer using charged CdSe/ZnS nanocrystals for light-harvesting in solution

Evren Mutluğün,^{a)} Sedat Nizamoğlu, and Hilmi Volkan Demir^{b)}

Department of Physics; Department of Electrical and Electronics Engineering; and Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent University, Ankara TR-06800, Turkey

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We propose and demonstrate highly efficient nonradiative Förster resonance energy transfer (FRET) facilitated by the use of positively charged CdSe/ZnS core-shell nanocrystals (NCs) for light-harvesting in solution. With rhodamine B dye molecules used as the acceptors, our time-resolved photoluminescence measurements show substantial lifetime modifications of these amine-functionalized NC donors from 18.16 to 1.88 ns with FRET efficiencies $>90\%$ in solution. These strong modifications allow for light-harvesting beyond the absorption spectral range of the acceptor dye molecules. © 2009 American Institute of Physics. [DOI: 10.1063/1.3182798]

Organic dyes are widely used in biolabeling as staining molecules,^{1–3} thanks to their high efficiency and stability. They are also used in optoelectronics (e.g., dye-based lasers).^{4–6} However, these dye molecules are intrinsically limited in their optical absorption spectral ranges in general. For example, rhodamine B (RhB), which is one of the most commonly used dyes, suffers from a characteristically narrow absorption spectrum, typically 450–600 nm. Beyond this limited range, it is impossible for RhB to be optically excited efficiently. In various applications, this severely limits the possible spectral range for optically pumping these dyes. For instance, in bioimaging, this prevents the use of dyes in spectral multiplexing, where multiple agents of different colors are used to label different biological targets to be simultaneously excited by a single optical pump.⁷ To address these problems, we propose and demonstrate optical excitation of RhB dye molecules in solution based on strong nonradiative Förster resonance energy transfer (FRET), enabled with the use of light-harvesting, positively charged CdSe/ZnS core-shell quantum dot nanocrystals (NCs) at optical pump wavelengths well below the characteristic absorption spectral range of RhB. This effectively extends the absorption spectral range of RhB acceptor dye molecules in the presence of CdSe/ZnS donor quantum dots toward shorter wavelengths.

In literature, CdTe based quantum dots as donors, together with various dyes used as acceptors, have been reported to demonstrate FRET.^{8–10} Furthermore, CdSe/ZnS quantum dot donors have previously been used for energy transfer to various protein based acceptors.^{11–13} Additionally, FRET using CdS dots have been investigated.^{14,15} In these studies, it has been found that FRET efficiencies are typically not high (below 60%) in solution. CdTe and CdSe/ZnS dots of different sizes have further been studied for energy transfer in film.^{16,17} Recently, Mayilo *et al.*¹⁸ discussed the use of Ca²⁺ binding to enhance FRET between different sized CdTe NCs in solution. These reports have thus far shown different flavors of semiconductor NCs employed for energy transfer to fluorescent molecules. However, the use of electrostatic

interaction between charged quantum dots and dye molecules in solution for the enhancement of FRET has not been investigated to date. To this end, the control and tuning of FRET efficiencies and lifetime modifications have also not been studied for electrostatically interacting light-harvesting quantum dot-dye pairs thus far.

In this letter, using positively charged amine-functionalized CdSe/ZnS quantum dots, we present highly efficient FRET-based light-harvesting for RhB dye molecules in solution beyond their absorption range, with their FRET efficiencies and lifetime modifications carefully tuned and precisely controlled with quantum dot dye concentrations. For this purpose, we choose the emission wavelength of our CdSe/ZnS quantum dot donors (around 541 nm) to match well with the absorption range of RhB dye acceptors, while these donor quantum dots provide a very broad absorption band extending toward short wavelengths (with an absorption band edge of 520 nm).

We find out that the pH of acceptor RhB dyes in aqueous solutions becomes slightly acidic (varying from 6.7 to 6.2) as the concentration of RhB is increased (in the micrometer range for our experiments). Relying on this observation, to help the donor and acceptor molecules find each other and thus get in close proximity in the solution, especially at lower concentrations, we employ amine-functionalized NCs that are positively charged. These NCs electrostatically interact with the RhB acceptor molecules that are slightly negatively charged in the acidic solution. We experimentally demonstrate significant lifetime modifications of these NCs from 18.16 to 1.88 ns with FRET efficiencies $>90\%$ in solution. By repeating the same experiments using neutral non-functionalized CdSe/ZnS NCs, we show the effect of donor NC charge on the efficiency of FRET as a function of the acceptor to donor (A/D) concentration ratio.

Figure 1(a) presents the time-resolved photoluminescence (TRPL) of amine-functionalized CdSe/ZnS NC donors (AF/NC-Ds) together with RhB acceptors (RhB-As) at the donor emission wavelength (541 nm), parameterized with respect to the varied A/D concentration ratio (shown in the figure legend). In this set of experiments, as both the donor NCs and the acceptor dyes are water soluble, the acceptor molecules are carefully added to the initially prepared aque-

^{a)}Electronic mail: evren@fen.bilkent.edu.tr.

^{b)}Electronic mail: volkan@bilkent.edu.tr. Tel.: [+90](312) 290-1021. FAX: [+90](312) 290-1015.

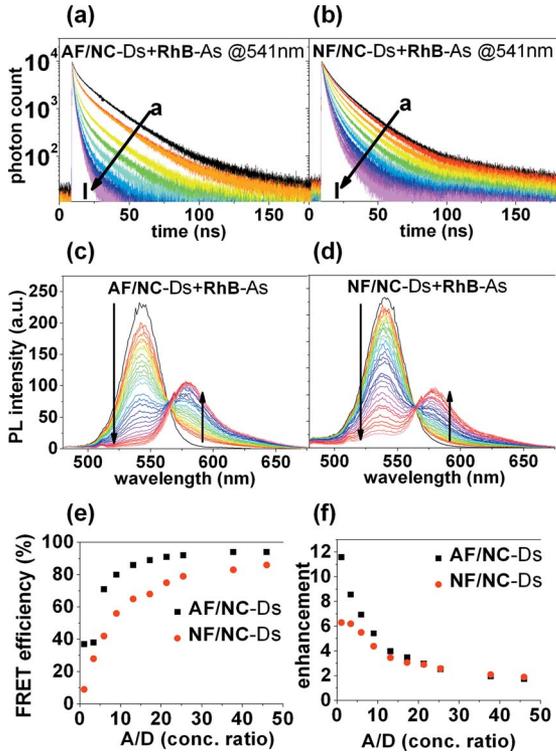


FIG. 1. (Color online) (a) TRPL of AF/NC-Ds together with RhB acceptors (RhB-As) at the donor emission wavelength (at 541 nm) and (b) TRPL of NF/NC-Ds together with RhB acceptors (RhB-As) at 541 nm. SSPL of (c) AF/NC-Ds+RhB-As and (d) NF/NC-Ds+RhB-As. All of the TRPL and SSPL measurements are presented as parameterized with respect to the varied concentration ratios of A/D. (e) FRET efficiency levels (extracted from TRPL) and (f) enhancement factor of acceptor emission with respect to the case of acceptors alone (with no donors), both as a function of A/D ratios.

ous donor solution in controlled increments. These TRPL measurements are taken at room temperature with PicoQuant 200 Flu Time time-resolved spectroscopy system using an excitation laser source at a pump wavelength of 375 nm. The photon decay lifetimes are calculated by the software package of PicoQuant (FluoFit) using exponential fittings with χ^2 error close to unity. In these TRPL experiments, we observe that the intensity weighted lifetime τ_i of AF/NC-Ds is de-

creased from 18.16 to 1.88 ns as the concentration of RhB acceptors (thus, the A/D ratio) is increased. These significant modifications observed in the donor photon lifetimes are attributed to the nonradiative energy transfer enhancing in increments from the donor molecules to the acceptor molecules with the incrementally increasing A/D ratio.

Figure 1(b) depicts the decay curves of the same TRPL experiments of Fig. 1(a) at the same A/D ratios, the only difference being the use of nonfunctionalized CdSe/ZnS NC donors (NF/NC-Ds) in the solution. In this set of TRPL experiments, we observe the same trend of modifications in emission kinetics of the donor NCs similar to the previous set. As a result of FRET, the donor photon lifetime is decreased in the presence of acceptors. Here, it is important to note that ZnS shells that surround CdSe cores and serve as a potential barrier in our NC structure provides full electronic isolation and prevents tunneling of the confined electron and hole wave functions. Therefore, this modification observed in emission kinetics cannot be due to Dexter-type charge transfer.

We also investigate the steady-state photoluminescence (SSPL) of RhB dyes in the presence of amine-functionalized CdSe/ZnS nanocrystals (AF/NC-Ds+RhB-As) and of non-functionalized CdSe/ZnS nanocrystals (NF/NC-Ds+RhB-As) as a function of A/D ratio, using Cary 100 Fluorometer at a fixed excitation wavelength of 375 nm, the same as that of the excitation source used in TRPL experiments. For each type of NCs, these SSPL experiments are carried over a set of 31 samples with varying A/D ratios. For (AF/NC-Ds+RhB-As) and (NF/NC-Ds+RhB-As), Figs. 1(c) and 1(d) show the respective evolution of the photoluminescence spectra of the donor and acceptor molecules changing their A/D concentration ratio in solution. As a result of FRET, we observe that the donor emission is quenched and the acceptor emission is enhanced incrementally as the A/D concentration ratio is increased.

Table I summarizes the results of the time-resolved spectroscopy analyses including the donor photon lifetimes along with their χ^2 error and the FRET efficiencies calculated from TRPL. Table I also presents the experimentally measured quantum yields of our amine-functionalized and nonfunc-

TABLE I. List of quantum yields, Förster radii, average decay lifetimes and their χ^2 error limits at the donor emission wavelength, and FRET efficiencies, all for different concentration ratios of A/D when using AF/NC-Ds and NF/NC-Ds.

Label	Concentration ratio A/D	Using amine-functionalized donors				Using nonfunctionalized donors		
		Quantum yield 29.5%		Förster radius 5.6 nm	Quantum yield 33.0%		Förster radius 5.6 nm	
		τ_i	χ^2		τ_i	χ^2		
a	0.00	18.16	1.09	...	16.65	1.08	...	
b	1.03	15.79	1.15	37	15.83	1.08	9	
c	3.34	15.44	1.14	38	13.97	1.15	28	
d	5.90	11.49	1.22	71	12.29	1.22	42	
e	8.98	8.94	1.24	80	10.45	1.26	56	
f	13.09	6.32	1.31	86	8.67	1.28	65	
g	17.20	3.99	1.27	89	7.88	1.31	68	
h	21.30	2.87	1.26	91	6.47	1.38	75	
i	25.41	2.51	1.25	92	5.88	1.39	79	
j	29.52	2.13	1.23	93	5.13	1.26	79	
k	37.73	1.94	1.14	94	4.52	1.32	83	
l	45.94	1.88	1.20	94	3.82	1.32	86	

tionalized CdSe/ZnS quantum dots in solution as well as the theoretically calculated Förster radii of these quantum dot donors for RhB acceptors. Here, the Förster radius, R_0 , the distance at which FRET efficiency is halved, is calculated using Eq. (1), where κ is the dipole orientation factor, (taken to be $2/3$ for random orientation), n is the refractive index of the media, Q_D is the quantum yield of the donor, and $J(\lambda)$ is the overlap integral of the donor emission and the acceptor absorption.¹⁹ The FRET efficiency level is calculated from TRPL using Eq. (2), where τ_{DA} is the amplitude weighted lifetime of donors in the presence of acceptors, while τ_D is that in the absence of acceptors.¹⁹ The quantum yield of AF/NC-Ds is measured to be 29.5% whereas that of NF/NC-Ds is found to be 33.0%. Both of them have a calculated Förster radius of ca. 5.6 nm.

$$R_0 = 0.021[\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6} \text{ (in nm)}, \quad (1)$$

$$\eta_{\text{FRET}} = 1 - \frac{\tau_{DA}}{\tau_D}. \quad (2)$$

The analysis of TRPL experiments shows that the efficiency level of FRET from the NC donors to the dye acceptors is increased from 37% to 94% when using positively charged amine-functionalized NCs and from 9% to 86% when using neutral nonfunctionalized NCs, as the A/D concentration ratio is increased, as presented in Table I and depicted in Fig. 1(e). This shows the same trend of increasing FRET efficiency level with the increased A/D. In Fig. 1(e), we observe that the amine-functionalized donors converge to a higher level of FRET efficiency faster than the nonfunctionalized donors do. These analyses suggest that AF/NC-Ds tend to exhibit higher efficiency (>90%) in light-harvesting for RhB-As than NF/NC-Ds (although NF/NC-Ds have a slightly higher quantum yield). This enhanced performance of AF/NC-Ds in light-harvesting is attributed to the electrostatic interaction between AF/NC-Ds and RhB-As in solution that possibly keeps them in closer proximity. The Brownian motion of the donor and acceptor molecules in the aqueous medium is also considered to affect FRET in solution at room temperature to some extent, especially for the case of NF/NC-Ds; it is otherwise less likely for these to be in close proximity to the acceptor molecules in the solution, given their low concentration levels. Also, in the case of using AF/NC-Ds, the screening effects are considered to partially prevent close electrostatic interaction and thus reduce FRET to some extent. Yet, with all other factors in play, we find out that the net effect of the charge of the donor NCs is toward improving FRET to the acceptor RhB.

To verify the enhanced emission of the acceptor molecules at the specified pump wavelength (375 nm), we perform SSPL measurement of RhB in the absence of the donor NCs, using exactly the same set of RhB concentrations as in the previous experiments. Figure 1(f) shows the enhancement factor calculated for the acceptor dye emission in the presence of AF/NC-Ds or NF/NC-Ds with respect to the case of the acceptor dyes alone. The enhancement factor is found to be larger for AF/NC-Ds than NF/NC-Ds at low A/D concentrations, which is once again attributed to the electrostatic interactions in the case of (AF/NC-Ds+RhB-As). As the ac-

ceptor amount in solution is increased, the enhancement decreases (despite increasing FRET efficiency) because the donor-acceptor system is evolving toward the case where there are effectively fewer and fewer donor molecules per acceptor molecule, thus converging toward the case of the dyes alone. On the other hand, increasing the overall emission of the acceptor molecules is not feasible at reduced A/D levels since the total emission intensity of the acceptors is low in diluted solutions. Given this trade-off, we find out that there is a good operating point for the A/D concentration ratio (around 10) in the case of AF/NC-Ds where a relatively high total emission can be obtained from the acceptor dyes with a good enhancement factor of >4. Far beyond this point, adding more and more acceptor molecules into the solution provides a diminishing enhancement of the acceptor emissions.

In conclusion, we have observed and reported highly efficient FRET-based light-harvesting of positively charged CdSe/ZnS core-shell NCs to RhB dye molecules in solution by utilizing the electrostatic interaction between them. This proof-of-concept demonstration has led to light-harvesting with FRET efficiency levels of >90%. This approach holds great promise for use in various dye-based biological and optoelectronic applications.

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