Supporting Information

Competition between Energy and Electron Transfer from CdSe QDs to Adsorbed Rhodamine B

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Absorption spectra of samples used for determining energy transfer efficiency

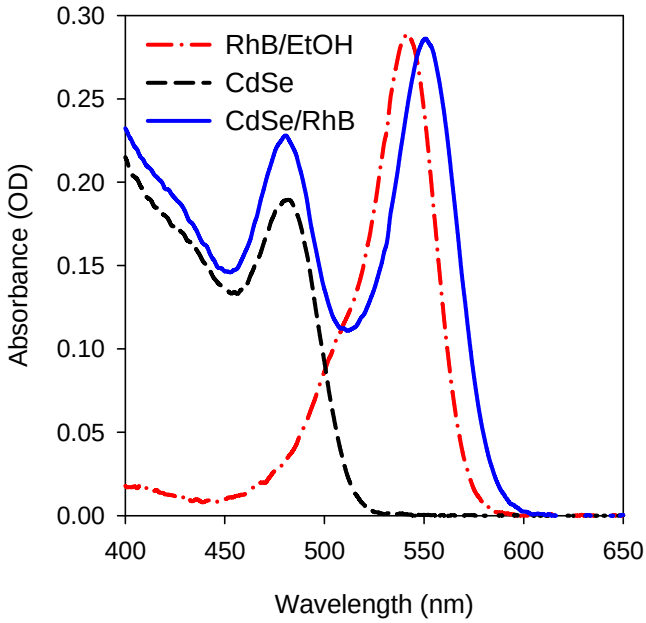

Figure S1: UV/VIS absorption spectra of CdSe in heptane (dashed black line), CdSe/RhB in heptane (Sample R6, solid blue line) and RhB in ethanol (red dash-dot line). CdSe/RhB has the same concentration of QDs as the sample of CdSe only and has the same concentration of RhB as the sample of RhB only. The corresponding emission spectra are shown in Figure 5.

Determination of quantum yield of CdSe480 QD in heptane

By comparing with a standard dye (Coumarin 343 in ethanol), the quantum yield of CdSe QD (Φ_{QD}) was calculated using equation S1:

$$\Phi_{QD} = \frac{I_{QD}}{I_{C343}} \times \frac{A_{C343}}{A_{QD}} \times \frac{n^2{}_{Heptane}}{n^2{}_{EtOH}} \times \Phi_{C343} \qquad \text{(S1)}$$

where the subscript QD denotes CdSe QD, and subscript C343 denotes Coumarin 343. I is the integrated emission intensity. A is the absorbance at the excitation wavelength (400 nm). $n_{heptane}$=1.387 and n_{EtOH}=1.361 are the solvent refractive indices for heptane and ethanol, respectively. Φ_{C343}= 63%[2] is the quantum yield of the Coumarin 343. Finally, Φ_{QD} can be determined to be 10%. The QD emission contains both 1S exciton (78%) and trap state (22%) contributions.

Determination of quantum yields of RhB in ethanol and on CdSe (in heptane).

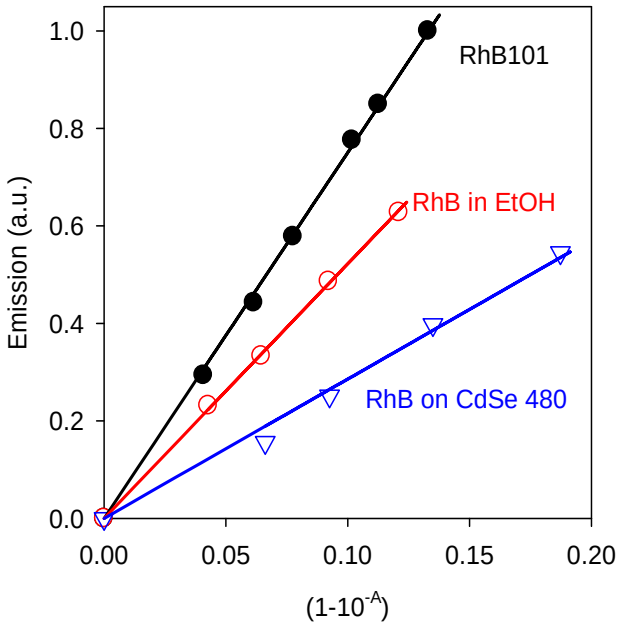

Figure S2: Relative emission intensity of RhB in ethanol (open circles) and RhB attached on CdSe in heptane (triangles) and RhB101 (filled circles) as a function of absorbed excitation photons at 550 nm. The emission intensity was obtained by the integrated area of fluorescence spectrum, the relative number of absorbed photon was calculated by ($1-10^{-A}$) where A is the sample absorbance at 550 nm. The solid lines are linear fits to the

data, whose slope determines the relative quantum yield. Assuming 100% quantum yield in the standard sample (RhB101), the quantum yields of RhB in ethanol and RhB/CdSe were found to be 68% and 38%, respectively.

Energy Transfer Rate

Since the fluorescence quenching shown in Figure 1 monitors the 1S exciton decay, only the fluorescence resonance energy transfer from 1S exciton is calculated here. The energy transfer rate k_{EnT} is described by the Förster rate equation[3]:

$$k_{EnT} = \frac{1}{\tau^0{}_{QD}} \times \left(\frac{R_0}{r} \right)^6 \qquad (S_2)$$

where $\tau^0{}_{QD}$ is the lifetime of donor (1S excitons in CdSe QD) in the absence of the acceptor (RhB), r is the donor-acceptor distance. R_0 is the Förster radius, which can be determined from spectroscopic data, given by:

$$R_0 = 0.2108 \left(\frac{\kappa^2 \Phi_{QD}}{n^4} \times J \right)^{1/6} \qquad (S_3)$$

where κ^2 (2/3) is the orientational factor, Φ_{QD} (0.078) is the quantum yield of CdSe exciton emission in the absence of RhB, and n (1.387) is the refractive index. J ($M^{-1}cm^{-1}nm^4$) is an overlap integral that quantifies the spectral overlap between the donor's emission and the acceptor's absorption. It can be calculated from the following equation:

$$J = \frac{\int d\lambda I_{QD}(\lambda)\varepsilon_{RhB}(\lambda)\lambda^4}{\int d\lambda I_{QD}(\lambda)} \qquad (S_4)$$

where I_{QD} is CdSe emission intensity and ε_{RhB} ($M^{-1}cm^{-1}$) is the RhB molar absorptivity.

The energy transfer efficiency (η) can be estimated by equation:

$$\eta = \frac{k_{EnT}}{\left(\tau^0{}_{QD}\right)^{-1} + k_1} \qquad (S_5)$$

where k_1 is the total exciton quenching rate (by energy and electron transfer) in the 1:1 CdSe/RhB complex and $\tau^0{}_{QD}$ is the exciton lifetime in QD without RhB.

UV/VIS spectra of samples used for k_{EnT} determination are shown in Figure S1. Figure S3 displays normalized CdSe emission, RhB (on QD) absorption and the resulting overlap, $J(\lambda)$. The J integral is calculated to be 1.6×10^{15} $M^{-1}cm^{-1}nm^4$ for this FRET pair by integrating the overlap spectrum $J(\lambda)$ in Figure S3. These values lead to a calculated R_0 value of 3.53 nm according to equation (S4).

In this study, we assume the donor-acceptor distance (r) to be in the range of 1.93 nm (the radius of QD) to 2.37 nm (radius of QD plus half the size of the RhB). With an average lifetime of free QD τ^0 of 12.2 ns, The estimated FRET rate (k_{ent}) for the 1:1 CdSe/RhB complex falls in the range of 0.9×10^9 to 3.1×10^9 s^{-1} according to equation S2. As described in the main text, the average total exciton quenching rate for the 1:1 complex (k_t) is 1.0×10^{10} s^{-1}. Using equation S5, the energy transfer efficiency can be estimated to be in the range of 9 – 31%, consistent with the measured value.

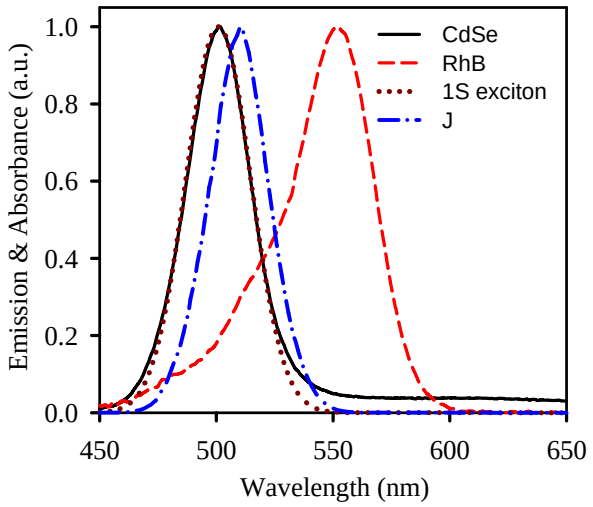

Figure S3: Normalized spectra of CdSe QD total emission (solid black line) and 1S exciton emission (dotted brown line), RhB absorption (dashed red line) and the resulting overlap spectrum $J(\lambda)$(blue dashed-dot line).

Risetime in RhB emission

To confirm that the RhB emission is mainly due to energy transfer, we have also measured the rise time of the RhB emission in sample R6 (from 580 to 610 nm, after 400nm excitation). The rise time should be instrument response limited if the emission is due to direct excitation of RhB. On the other hand, if the emission results from energy transfer from QD, its rise time should be the same as the decay time of QD emission. As shown in Figure S4, the rise time of RhB emission is slower than that of CdSe. CdSe emission is instrument response time limited. The risetime of RhB emission is similar to

the decay time CdSe emission, confirming that emission of RhB is indeed a result of energy transfer from CdSe.

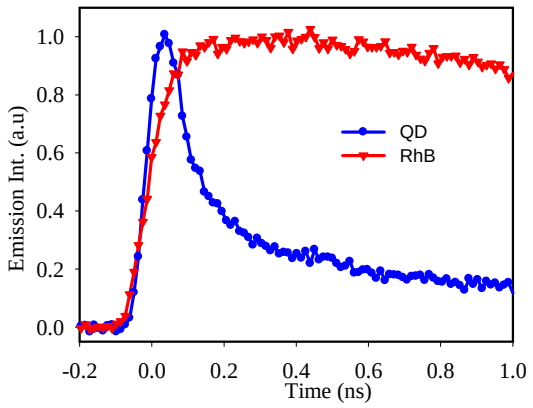

Figure S4. A comparison of rise times of RhB and CdSe emission in CdSe/RhB (sample R6, spectrum shown in Figure S1).

References

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