Supporting Information

Study of Diffusion Assisted Bimolecular Electron Transfer Reactions: CdSe/ZnS Core Shell Quantum Dot acts as an Efficient Electron Donor as well as Acceptor.

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Contents   **Page no.**

1. EXPERIMENTAL SECTION

Chemicals. *CdSe/ZnS QD*s (~4.4 nm and ~6 nm sizes), *N-methyl-aniline* (*NMA*), *2,4-dinitrotoluene (DNT)* and toluene were purchased from Sigma-Aldrich and used without further purification.

Instruments used. Steady state absorption and emission were recorded by using Perkin-Elmer lambda-750 spectrophotometer and Perkin-Elmer LS-55 fluorescence spectrometer respectively. Fluorescence lifetime measurements were performed by using a time-correlated single photon counting (TCSPC) setup (Edinburgh Instruments, model OB-920). All the samples were excited at 375 nm (IRF~80ps) by using a picoseconds diode laser and fluorescence emission was collected at magic angle (54.7^0) by an advanced PMT detector. A long-pass filter of 395 nm was used to avoid scattering from the sample and laser light. The lifetime data were analysed by F900 software provided with the instrument.

Fluorescence Correlation Spectroscopy (FCS) Measurements and Calculation of Diffusion Coefficients. Fluorescence correlation spectroscopy (*FCS*) experiments were performed by using a confocal microscope (Zeiss LSM 780). A diode laser of 405 nm has been used to excite the samples. FCS data was used for determination of translational diffusion coefficients (D_t) of *CdSe/ZnS* core shell *QD*s in toluene. Details of this technique, measurement procedure and instrumental setup are described elsewhere.[1] D_t of *QD480* and *QD560* were found to be *~1.72×10^{-6}* and *1.02×10^{-6} cm^2 sec^{-1}*, respectively. Since *NMA* and *DNT* are non fluorescent, we could not used *FCS* technique to determine the diffusion coefficients. The D_t values of *NMA* and *DNT* in toluene were calculated by using Stokes-Einstein equation using the sizes of the molecules obtained from DFT calculations. These D_t values were used as a fitting parameters within the SQCK model.

Sample Preparation. All the experiments were performed at room temperature (~25^0 C). We kept dilute quantum dot dispersions for several hours before measurement to ensure complete dissolution in toluene. No changes in spectral shape, *FWHM* or intensity of the *QD*s were noticed over a several hours of time. A clear and colorless solution of solid *DNT* was prepared in toluene. Liquid *NMA* was injected to the quantum dot solution with extreme care. Sample mixture was allowed to get equilibrated for 10 minutes before measurement.

2. CALCULATION OF BAND POSITIONS AND FREE ENERGY CHANGE

Chemical driving force for electron transfer reaction was calculated from the redox potential values of the reactant molecules. The reduction potential of electron acceptor molecule *DNT* and the oxidation potential of the electron donor molecule *NMA* were taken from the literature.[2-3] The valance and conduction band energies of the quantum dots were calculated from the band gap energy ($E_{cdse*}[1S_e,1S_h]$) of first exciton sate using equation S1. We used Brus's recipe to obtain redox potentials of a semiconductor nano-crystal from band gap energy.[4-5] According to this recipe, exciton energy of *QD** was calculated first by using the following equation.[4]

$$E_{CdSe*}[1S_e,1S_h] = E_g + \frac{h^2\pi^2}{2R^2 m_e^*} + \frac{h^2\pi^2}{2R^2 m_h^*} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R} \qquad (S1)$$

Where E_g is the bulk band gap, m_e^* and m_h^* are the effective masses of the electron and hole, respectively and *R* is the core radius of the *QD*. Bulk band gap (E_g) of *CdSe* was obtained from reported value (1.7 eV vs. *SCE*).[5] The *R* value was taken from the supplier's information. Values of the other parameters can be found within the refs 5 and 6. For *CdSe*; m_e^*=0.13 m_0, m_h^*=1.14 m_0 (m_0 is the rest mass of a free electron) and ε=5.8. The second and the third terms of equation S1 implies the confinement energies of electron and hole, respectively. The last term represents the electron hole columbic attraction energy for a *QD* of radius *R*. Using the above equation, we can calculate the energy of conductance band of an excited *QD* by adding the band gap energy of the *QD* with valance band energy. One can easily get oxidation and reduction potentials of *QD** from these energy levels. Now, utilising the oxidation (E_{ox}^0) and reduction (E_{red}^0) potential values of donor and acceptor, we calculated free energy changes associated with *QD-NMA* and *QD-DNT* couples using the linear equation, $\Delta G^0 = E_{ox}^0 - E_{red}^0$. Calculated ΔG^0 values along with the redox potentials have been tabulated in table 3 of the main manuscript.

Figure S1. Fitted auto correlation curves for *QD480* (blue) and *QDS560* (red) in toluene.
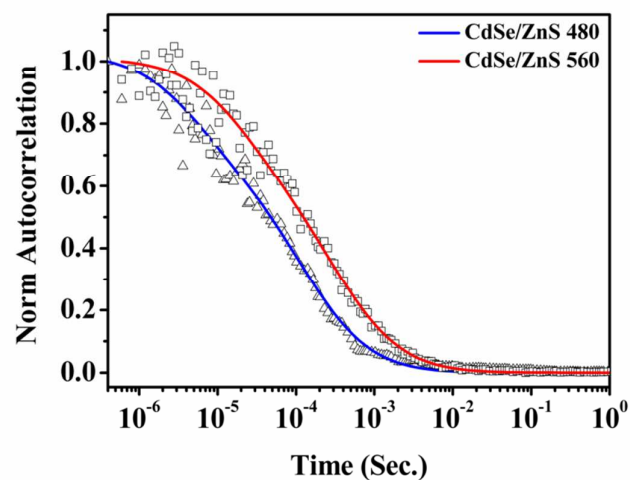

Figure S2. Steady state emission spectra of (A) *QD480* and (B) *QD560* in toluene at various *NMA* concentrations. Excitation wavelength = 375 nm.
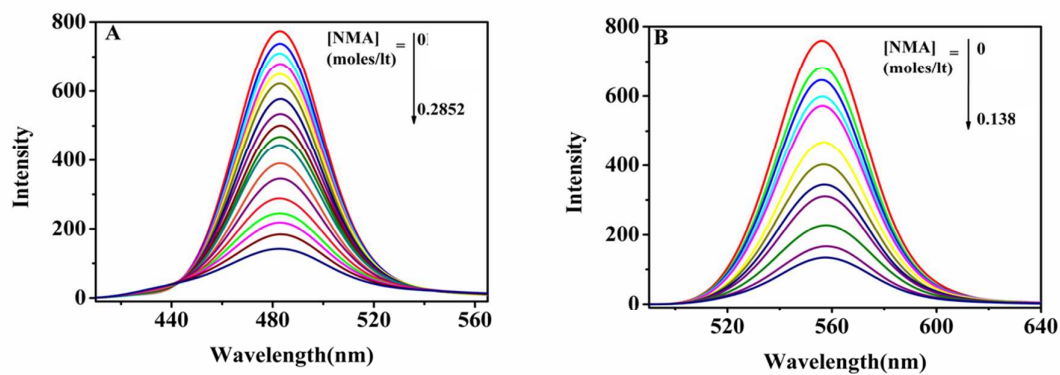
Figure S3. Fluorescence lifetime decay profile for (A) *QD480* and (B) *QD560* in *toluene* at various *NMA* concentrations. Excitation wavelength = 375 nm.
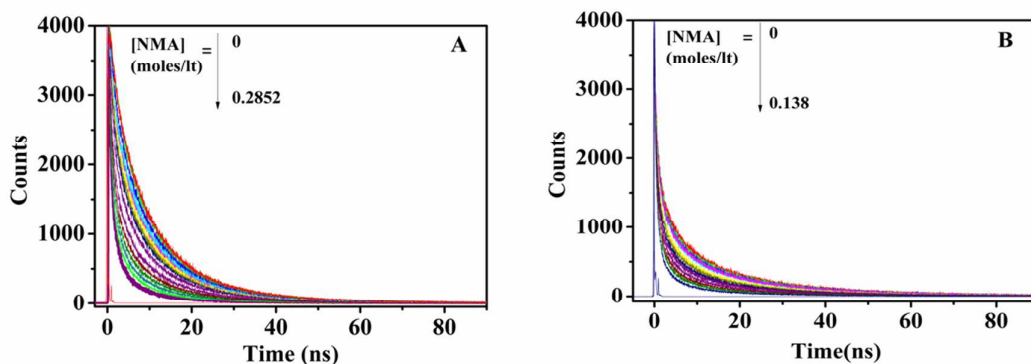

Figure S4.Steady state emission spectra of (A) *QD480* and (B) *QD560* in toluene at various *DNT* concentrations. Excitation wavelength = 375 nm
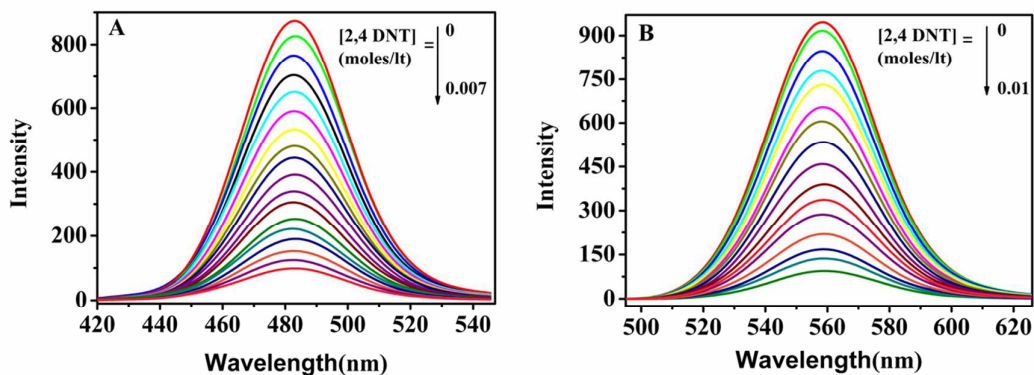

Figure S5. Fluorescence lifetime decay profile for (A) *QD480* and (B) *QD560* in *toluene* at various *DNT* concentrations. Excitation wavelength = 375 nm.
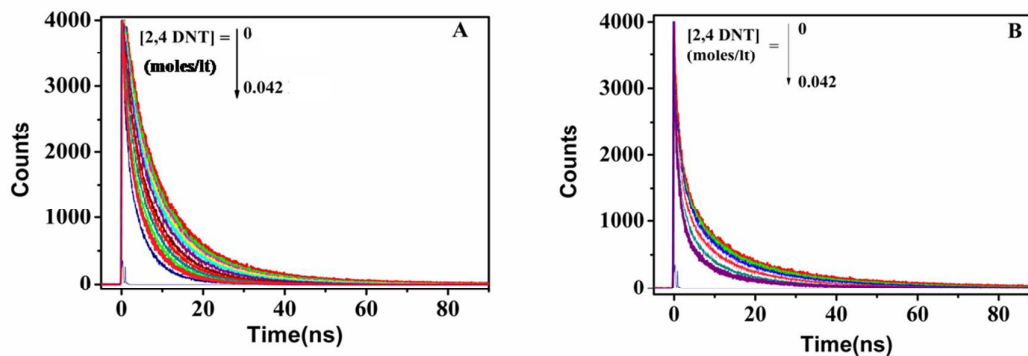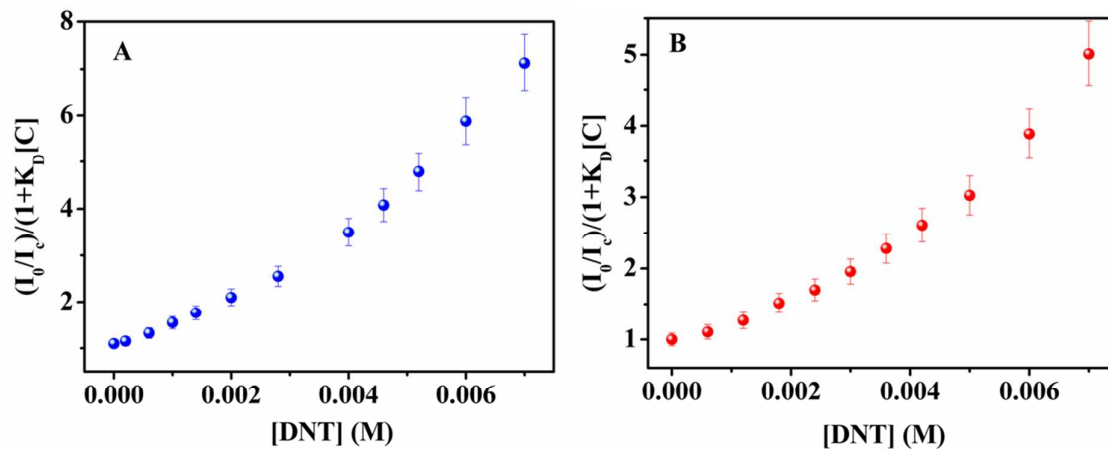
Figure S6. Plot of $(I_0/I_c)/(1+k_D[C])$ as a function of quencher concentration $[C]$ for (A) *QD480-DNT* pair and (B) *QD560-DNT* pair. A clear non linear behavior can be observed from these two plots. The bar represents the error limit within the data points.

4. References

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