Supporting Information

Cascading Electron and Hole Transfer Dynamics in CdS/CdTe Core-Shell Sensitized Bromo-Pyrogallol Red (Br-PGR): Slow Charge Recombination in Type II Regime

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A) High resolution Transmission Electron Microscope (HRTEM) Measurements:

SI Figure 1 (A) and (B) show the 2 nm scale bar HRTEM image of CdS and CdS/CdTe core/shell while SI Figure 1 (C) and (D) show the 1 nm scale bar resolution image respectively.
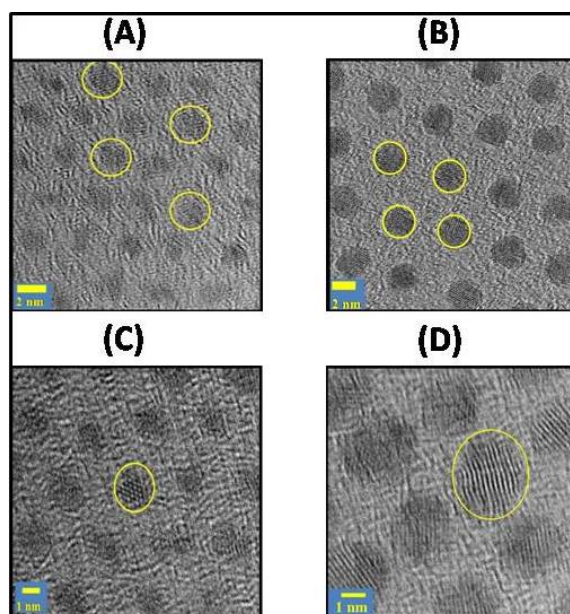
SI Figure 1: (A), (B) High Resolusion Transmission Electron Microscopic (HRTEM) images of CdS QD and CdS/CdTe core/shell respectively (scale bar 2 nm). **(C), (D)** HRTEM images of CdS QD and CdS/CdTe core/shell showing lattice frienge respectively (scale bar 1 nm).

B) Measurement of Emission Quantum Yield:

To determine emission quantum yield for all the QD materials we have used the equation below.

$$\phi_i = \phi_r \frac{I_i}{I_r} \frac{OD_r}{OD_i} \frac{\eta_i^2}{\eta_r^2}$$

where "ϕ" is the quantum yield, "I" is the integrated area of the emission intensity, "OD" is the optical density at excited wavelength, and "η" is the refractive index of the solvent. The subscript "i" and "r" refer to the quantum dot and reference sample respectively. In the present investigation we have used rhodamine 6G dye molecule as reference to determine the emission quantum yield for both the samples. In our experiment the sample and reference are excited at the same wavelength, and we used same solvent so that the ratio of the square of the refractive index becomes unit. So the equation can be simplified as

$$\phi_i = \phi_r \frac{I_i}{I_r} \frac{OD_r}{OD_i}$$

Following the above equation the emission quantum was determeined to be 36% for CdS and 2.9% for CdS/CdTe core-shell respectively.

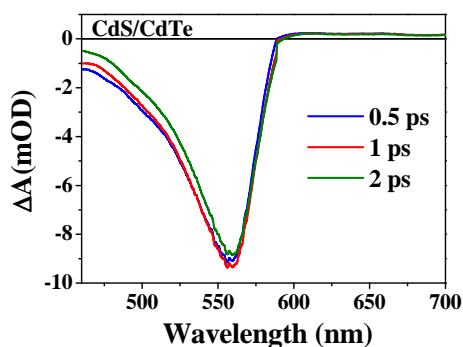## C) Ultrafast transient absorption Studies of CdS Quantum Dot:

SI Figure 2 shows the transient absorption spectra of photo-excited CdS QDs in different time delay after exciting the samples at 400 nm. The transient absorption spectra shows negative absorption band below 480 nm which can be attributed bleach due to excitonic absorption.
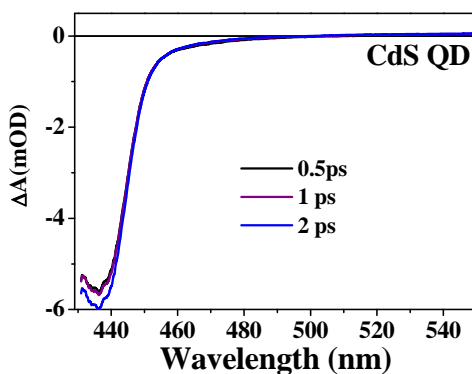
SI Figure 2: Transient absorption spectra of 1 μM CdS QD in chloroform at different time delay after excitation at 400 nm laser light.

## D) Ultrafast transient absorption Studies of type II CdS/CdTe core/shell:

SI Figure 3 shows the transient absorption spectrum of photo-excited CdS/CdTe core-shell in different time delay after 400 nm laser excitation. The transient spectra consist a broad bleach below 590 nm which matches with the excitonic absorption band of type II core-shell. A broad low intensity positive absorption was observed beyond 600 nm, which can be attributed to charge carrier absorption.

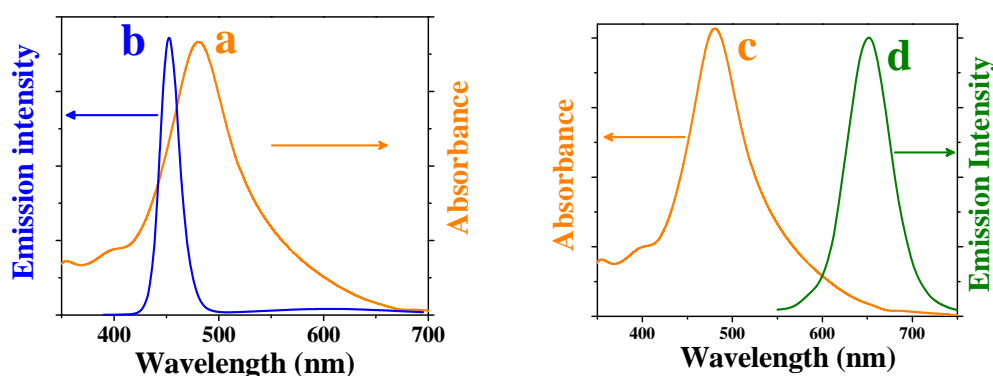**SI Figure 3:** Transient absorption spectra of CdS/CdTe) in chloroform solution at different time delays

E) Ultrafast transient absorption Studies of bromo-pyrogallol red (Br-PGR):

Solubility of Br-PGR is too low in chloroform to perform transient absorption measurements after exciting at 400 nm laser light. We have chosen ethyl acetate as solvent in which solubility of Br-PGR is good enough to do ultrafast transient measurements. SI Figure 4 shows the transient absorption spectra of Br-PGR at different time delay which shows a negative absorption band from 500-600 nm regions and a broad positive absorption band in 600-750 nm regions. The negative absorption (bleach) appears due to the ground state optical absorption the molecules can be attributed as first excited state (S_1) absorption. The positive absorption can be attributed as induced absorption of the dye molecule at higher excited state.
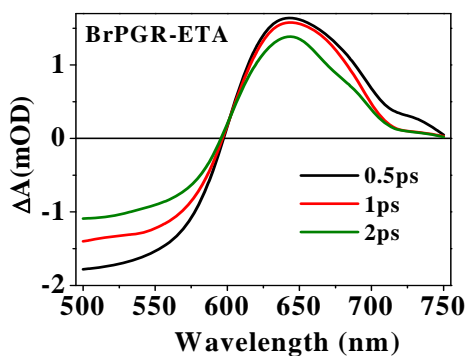
SI Figure 4: Transient absorption spectra of 0.5mM Br-PGR in Ethyl acetate solution at different time delays. Inset: kinetic decay trace at 550 nm after excitation with 400 nm laser light.

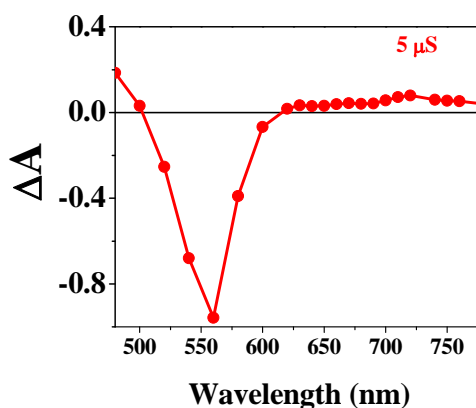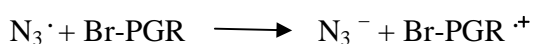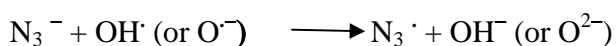## F) Steady state absorption of Br-PGR and emission of CdS QD and CdS/CdTe core-shell
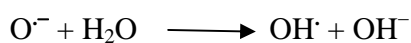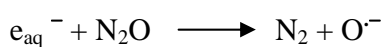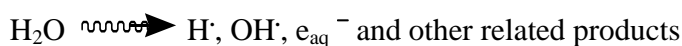

SI Figure 5::Left panel: (a) Optical absorption of BrPGR and (b) emission spectra of CdS QD.**:Right panel**: (c) Optical absorption of BrPGR and (d) emission spectra CdS/CdTe core/shell QD in chloroform solution.

To check whether energy transfer can take place between photo excited QDs and Br-PGR steady state absorption of Br-PGR and steady state emission spectra of CdS QD and CdS/CdTe core-shell has been recorded and shown in SI Figure 5. To realize energy transfer it's very important to have overlap between QD luminescence and Br-PGR absorbance. It is clear from the SI Figure 5 that energy transfer can not take place between CdS/CdTe core-shell and Br-PGR pair as there is no overlap between optical absorption of Br-PGR and emission spectra of CdS/CdTe core-shell. However there is some overlap between CdS QD luminescence and Br-PGR absorbance. So there is some possibility of energy transfer process between photo-excited CdS QD and BrPGR. Now on transferring energy from CdS QD to Br-PGR we should be able to see the emission from Br-PGR. However we did not see any emission from Br-PGR. Still we can not rule out energy transfer process between CdS QD and Br-PGR.

G) Transient absorption spectrum of cation radical of bromo-pyrogallol red (Br-PGR) (uncorrected)

To record the transient absorption spectrum of the cation radical for bromo-pyrogallol red (Br-PGR), one electron oxidation reaction has been carried out in aqueous solution (acetonitrile: water, 1:99) bubbled with N_2O and in the presence of N_3^- ion. SI Figure 6 shows the transient absorption spectrum (uncorrected) of the cation radical of Br-PGR dye. Br-PGR is oxidized to the corresponding cation radical by irradiation with the electron pulse. The presence of hydroxyl or azide radical allows the dye to undergo one-electron oxidation i.e. loss of an electron. The reactions are given below:

$$H_2O \rightsquigarrow H^{\cdot}, OH^{\cdot}, e_{aq}^{-} \text{ and other related products}$$

$$e_{aq}^{-} + N_2O \longrightarrow N_2 + O^{\cdot-}$$

$$O^{\cdot-} + H_2O \longrightarrow OH^{\cdot} + OH^{-}$$

$$N_3^{-} + OH^{\cdot} \text{ (or } O^{\cdot-}) \longrightarrow N_3^{\cdot} + OH^{-} \text{ (or } O^{2-})$$

$$N_3^{\cdot} + Br\text{-}PGR \longrightarrow N_3^{-} + Br\text{-}PGR^{\cdot+}$$

SI Figure 6: Transient absorption spectrum (uncorrected) of the cation radical of Br-PGR obtained from one electron oxidation in pulse radiolysis study.