Forster Resonance Energy Transfer and Carbon dots Enhance Light Harvesting in a Solid-State Quantum Dot Solar Cell

Remya Narayanan,[a] Melepurath Deepa,[a,] Avanish Kumar Srivastava[b]*
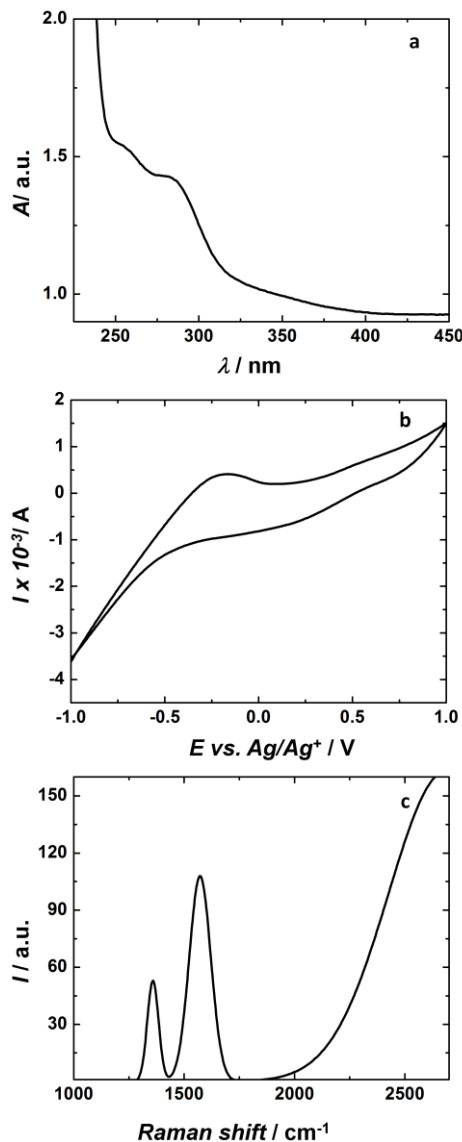
Characterization of C-dots:

Figure S1 (a) Absorption spectrum of the C-dots dispersed in the deionized water, (b) cyclic voltammogram of the C-dot solution with two platinum rods as the electrodes and Ag/AgCl/KCl as reference electrode and (c) Raman spectrum of an electrophoretically deposited C-dot film obtained at a laser excitation wavelength of 532 nm.

Determination of LUMO for C-dots:

The cyclic voltammogram of C-dots with Pt electrodes and recorded at a sweep rate of 20 mV s^{-1} is shown in Figure S1b. In the anodic sweep of the voltammogram, no distinct oxidation peak was observed, but in the reverse sweep, a broad reduction peak is observed at a potential (E_R) of –0.197 V (versus Ag/Ag$^+$). The potential of reference electrode (Ag/Ag$^+$) was +0.197 V (*versus* NHE). The reduction potential (*vs.* NHE) corresponds to the LUMO of the electroactive material.

Therefore, the reduction potential of C-dots (*vs.* NHE) will be: E_R = (–0.197+0.197) V = 0 V.

0 V (vs. NHE) corresponds to 4.5 eV (w.r.t. vacuum level). The LUMO of C-dots was therefore fixed at 4.5 eV in the energy band diagram shown in Figure 1.

The Raman spectrum of the C-dots in Figure S1c shows a G band at 1570 cm^{-1} and the 2D band was observed at 2650 cm^{-1}.
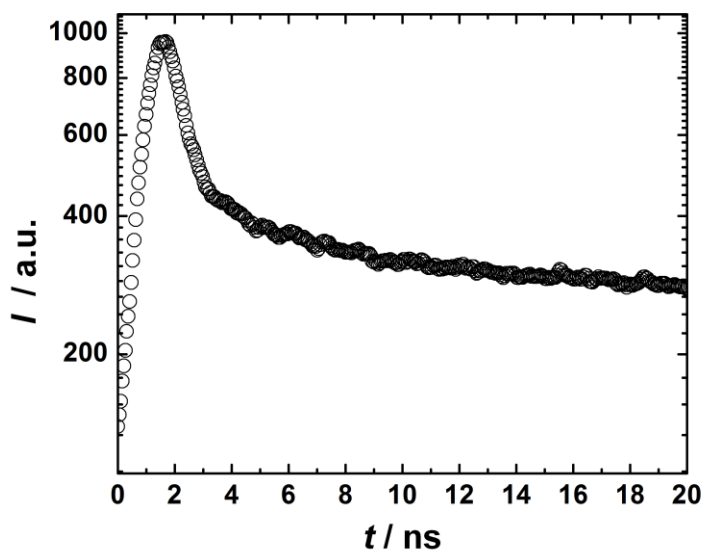
Lifetime of ZnS/CdS/ZnS/C-dot:

Figure S2 PL decay trace of ZnS/CdS/ZnS/C-dot (λ_{ex} = 370 nm and λ_{em} = 530 nm).

The fluorescence lifetime for the ZnS/CdS/ZnS/C-dots system at λ_{em} = 530 nm and λ_{ex} = 370 nm is shown in Figure S2; the average lifetime was 16 ns which is almost equivalent to the average

lifetime of the ZnS/CdS/ZnS system ($<\tau>$ = 15.9 ns), indicating that C-dots do not contribute significantly to the decay response of the ZnS/CdS/ZnS/C-dots/CuPc system (at λ_{em} = 530 nm).
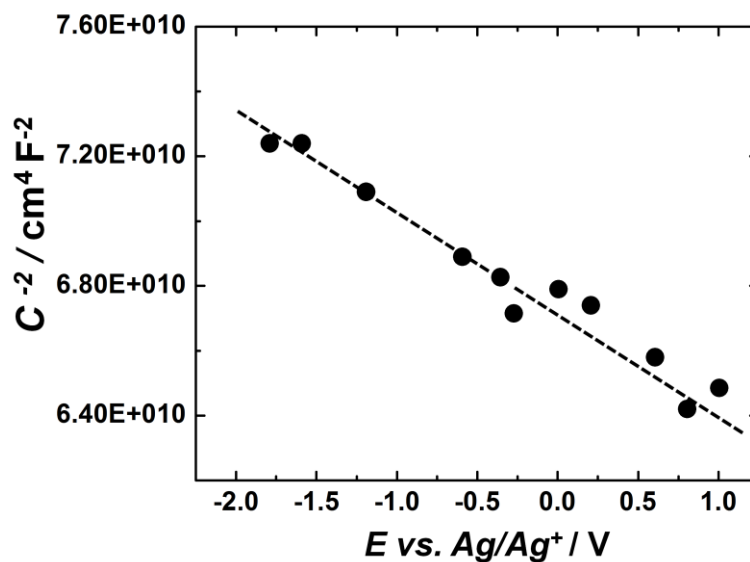
Possibility of hole transfer from C-dots to CuPc:

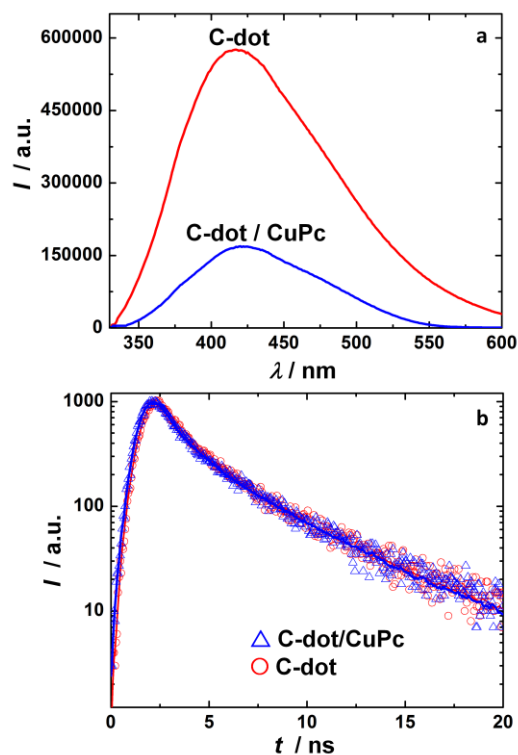**Figure S3** Mott-Schottky plot of a C-dot dispersion in water by employing two platinum rods as electrodes.

Figure S4 (a) Emission profiles of C-dots and C-dot/CuPc dispersions in water (at λ_{ex} = 370 nm) and (b) emission decay response of C-dots and C-dot/CuPc (at λ_{ex} = 370 nm and λ_{em} = 416 nm).

The p-type semiconducting behavior of C-dots was ascertained by recording a Mott-Schottky plot of the C-dot suspension with Pt rods as working and counter electrodes and Ag/Ag$^+$ as the reference electrode; at a constant frequency of 1000 Hz, over a dc potential range of –2 to +1 V (Figure S3). The negative slope of the $1/C^2$ *versus* potential indicates a p-type conduction behavior, thus suggesting that C-dots prepared by us are capable of conducting holes. Since hole transfer from CuPc to C-dot is energetically favorable, and the fact that C-dots do have the capability of conducting holes, holes, in principle can be transferred from CuPc to C-dots as both the materials are in direct contact. Pristine C-dots exhibit an emission peak at 416 nm (at λ_{ex} = 370 nm), but upon addition of the CuPc (0.03 mM, added in solid form to avoid the possibility of concentration quenching), we found that the fluorescence of C-dots was quenched (Figure S4). This quenching can be ascribed to (i) electron transfer from C-dots to CuPc and (ii) hole transfer from CuPc to C-dots. The corresponding average lifetimes also concur with the quenching: for pristine C-dots the electron lifetime is 2.13 ns and for the C-dots/CuPc system,

4

the lifetime reduced to 1.97 ns; again confirming charge transfer. However, it is difficult to distinguish electron transfer from hole transfer; but the p-type conduction profile of C-dots, the favorable conduction band offsets of C-dots and CuPc, do indicate hole transfer.

Determination of quantum yield of the donor (ZnS/CdS/ZnS):

The quantum yield for the donor ZnS/CdS/ZnS was determined by measuring the fluorescence and absorption of the donor at different concentrations at an excitation wavelength of 370 nm, and by comparing the same by measuring the fluorescence and absorption of a standard/reference Rhodamine 101. In this experiment Rhodamine 101 was dissolved in ethanol as a standard with a known quantum yield of 100 %.
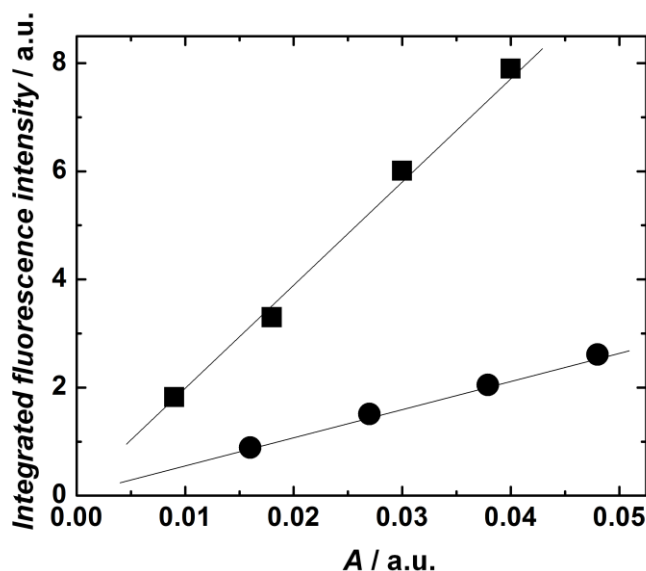

Figure S5 Integrated fluorescence intensity *versus* absorbance of donor: ZnS/CdS/ZnS QDs (●) and reference: Rhodamine 101 (■). The excitation wavelength was fixed at 370 nm for ZnS/CdS/ZnS and 367 nm for Rhodamine 101.

$$\phi_X = \phi_{ST}\,(\text{Grad}_X / \text{Grad}_{ST})\,(\eta^2{}_X / \eta^2{}_{ST}) \quad (1)$$

In equation (1), X and ST denote the test (or donor, ZnS/CdS/ZnS) and the standard or reference (Rhodamine 101) samples. ϕ, Grad and η respectively denote the quantum yield, slope of the integrated fluorescence intensity *versus* absorbance plots and the refractive index of the solvent.

By substituting the experimental values in equation (1), equation (2) is obtained. For the fluorescence or absorbance measurements, Rhodamine 101 was dissolved in ethanol and ZnS/CdS/ZnS was scratched out from the substrate and dispersed in the water.

$$\Phi_X = 100 \times (54/187) \, (1.33^2/\, 1.36^2) \qquad (2)$$

From equation (2), the quantum yield for ZnS/CdS/ZnS was calculated to be 0.28. This value was used for calculating Forster radius.

The following equation was used for determination of Forster radius.

$$R_o{}^6 = 9000 ln(10) k^2 Q_D J / 128 \pi^5 n^4 N_A \quad (3)$$

In the expression, n, the refractive index of the medium (the electrolyte containing CuPc), was determined by using the equation:

$$R = ((n_0 - n_1) \, / \, (n_0 + n_1))^2 \quad (4)$$

$$0.00034 = ((1.33 - n_1) \, / \, (1.33 + n_1))^2 \quad (5)$$

In the above equation, R is the integrated reflectivity of the CuPc/Na$_2$S solution over the 600-650 nm wavelength range and n_0 and n_1 are the refractive indices of water and CuPc/Na$_2$S solution respectively. Refractive index of water has been taken as 1.33.

Reason for applying only one layer of ZnS over CdS:

The HRTEM images (taken from two different regions) illustrating the distance between the donor and acceptor to be greater than 10 nm for a ZnS/CdS/ZnS/C-dot/CuPc assembly (with 2 layers of ZnS coated over CdS) are shown below. On increasing the number of ZnS layers to two, instead of one, we found that the actual distance of separation between the donor (CdS QDs) and the acceptor (CuPc) increased to more than 10 nm, which is outside the range within which FRET occurs (1-10 nm), so only one layer of ZnS was applied.
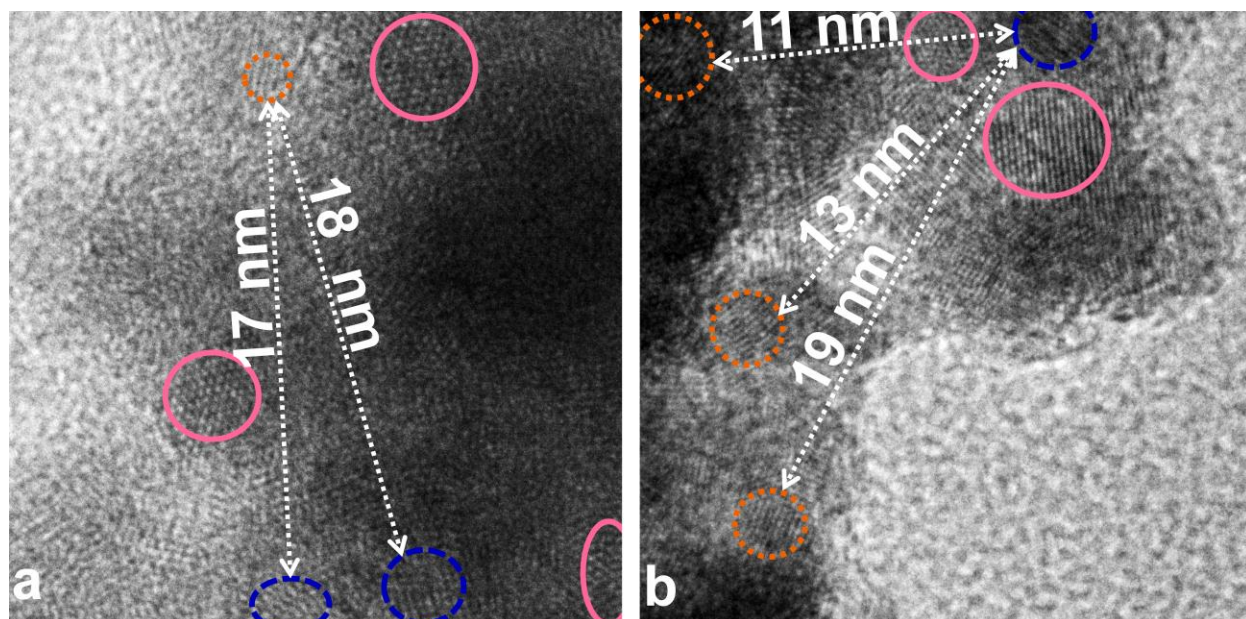
Figure S6 HRTEM images of ZnS/CdS/ZnS/C-dot/CuPc assembly, with two ZnS layers coated over CdS: the lattice fringes arising from CdS (••••), CuPc (----) and C-dots (—) are encpasulated in circles/ellipses. The dotted lines with arrowheads represent the distance (> 10 nm) between CdS QDs (donor) and CuPc (acceptor) molecules.
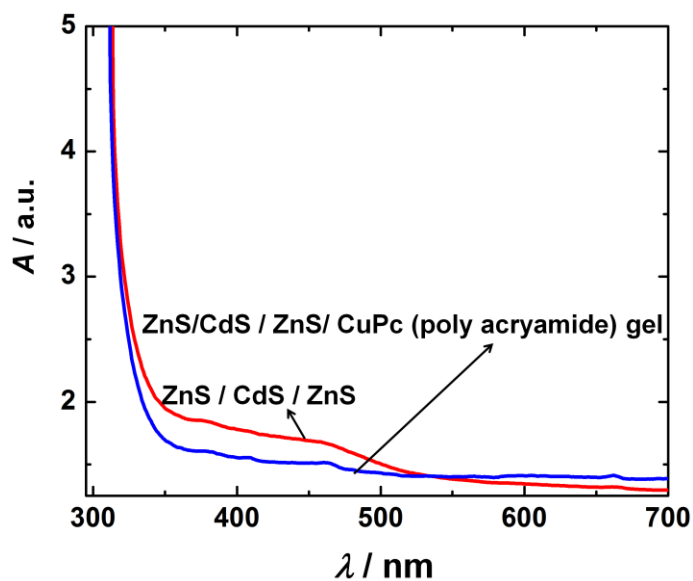

Figure S7 Absorption spectra of ZnS/CdS/ZnS and ZnS/CdS/ZnS with CuPc/Na_2S-poly(acrylamide) gel in the visible region.

It is evident from the spectra that the absorption of the ZnS/CdS/ZnS assembly is higher in the 350-525 nm range, relative to the same assembly with CuPc gel, thus indicating that ZnS/CdS/ZnS absorption contributes dominantly to photocurrent compared to the CuPc-(poly acrylamide) gel.

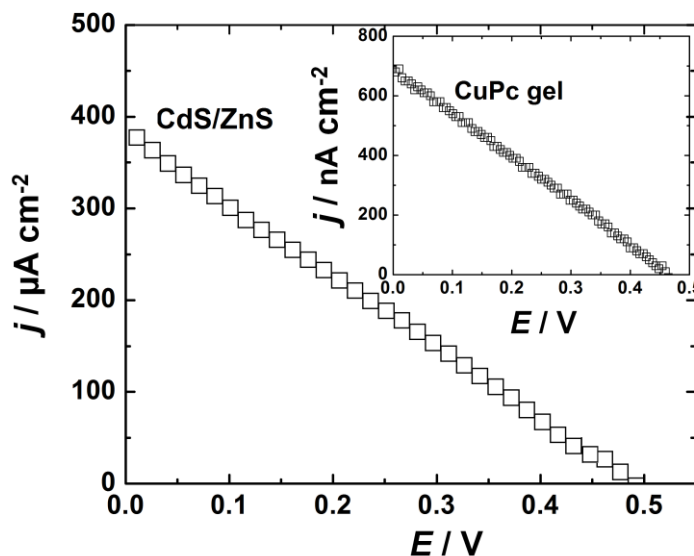**J-V characteristics of control cells:**

Figure S8 J-V characteristics of control cells with either donor or acceptor as photoanodes: FTO/CdS/ZnS/Na$_2$S gel/MWCNT and FTO/CuPc gel/MWCNT cell is shown in the inset.

Table S1 Solar cell parameters of cells ($\lambda > 300$ nm, 0.1 M Na$_2$S aqueous poly(acrylamide) based gel electrolyte with or without 0.03 mM CuPc, cell area: 1 cm^2, under 1 sun illumination (100 mW cm^{-2})) with the listed photoanodes; all cells with MWCNT/FTO as the counter electrode.

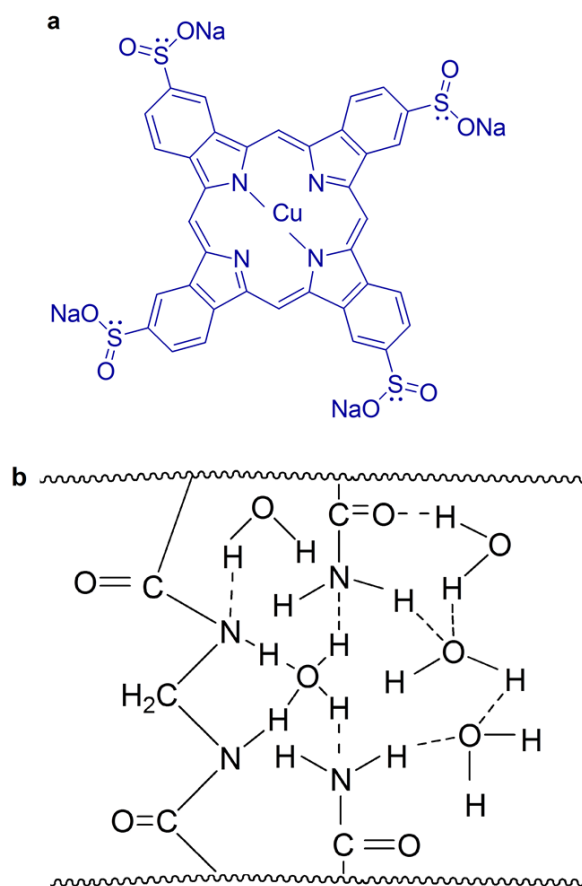| Electrode description	Voc (mV)	Jsc (µA cm^{-2})	FF	η (%)
FTO/CdS/ZnS	487	381	0.25	0.05
FTO/CuPc	467	687×10^{-3}	0.25	0.0001

Figure S9 Structure of (a) copper phthalocyanine-3,4',4",4'" tetrasulfonic acid tetrasodium salt and (b) the poly(acrylamide) based hydrogel, showing the role of the cross-linker and the formation of hydrogen bonds.