Supporting information

Quantum Dot Donor-Polymer Acceptor Architecture for a FRET Enabled Solar Cell

Ramesh K. Kokal,[a,†], Sai Santosh Kumar Raavi,[b,†] Melepurath Deepa,[a,†,*]

[a]Department of Chemistry, [b]Department of Physics, [†]Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana (India)-502285

[*]Email: mdeepa@iith.ac.in Tel: +91-40-23016024, Fax: +91-40-23016003.

The XRD patterns of pristine- TiO_2, PCDTBT and CdS are shown in Figure S1. The XRD pattern of pristine TiO_2 shows peaks at d = 3.51, 2.42, 2.37, 1.88, 1.69, 1.66, 1.48 and 1.26 Å which correspond to the (101), (103), (004), (200), (105) (211), (204) and (215) planes of the tetragonal symmetry of body centered cubic lattice, in concurrence with the PDF (powder diffraction file) # 89-4921. The XRD pattern of CdS QDs grown on a glass plate by a SILAR process shows two broad low intensity peaks at $2\theta = 26.45^{o}$ (d = 3.37 Å) and at and $2\theta = 43.87^{o}$ (d = 2.06 Å) and these are assigned to the (111) and (220) reflections of the face centered cubic (fcc) lattice of CdS (PDF # 65-2887). The broadness of the peaks indicates the semi-crystalline nature of the CdS QDs. PCDTBT shows a few broad peaks.

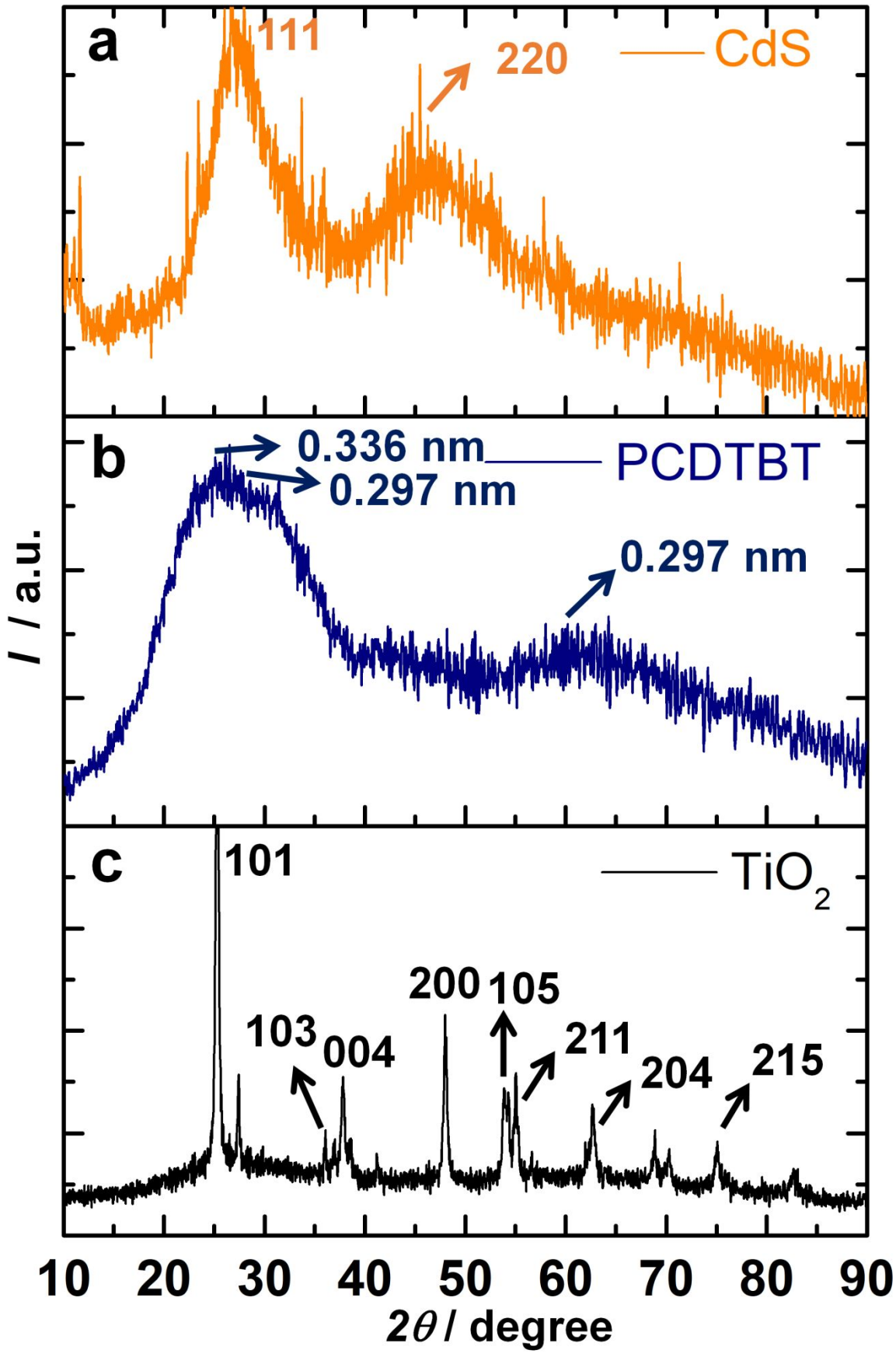

Figure S1 XRD patterns of (a) CdS QDs, (b) PCDTBT and (c) pristine TiO_2.

Mott-Schottky plots of PCDTBT

To affirm the electron conductivity capability of the PCDTBT polymer, Mott-Schottky plots were recorded in a 0.1 M KCl electrolyte with PCDTBT deposited on FTO electrode as the working electrode, Pt as a counter electrode and Ag/AgCl/KCl as a reference electrode. The Mott–Schottky plots ($1/C^2$ versus E), where C is the capacitance and E is the applied bias varied from -1 to + 1 V, are obtained for PCDTBT at two different frequencies of 1 Hz and 10 Hz shown in Figure S2. Positive slopes observed for the plots indicating n-type semiconducting with electrons as majority charge carriers.

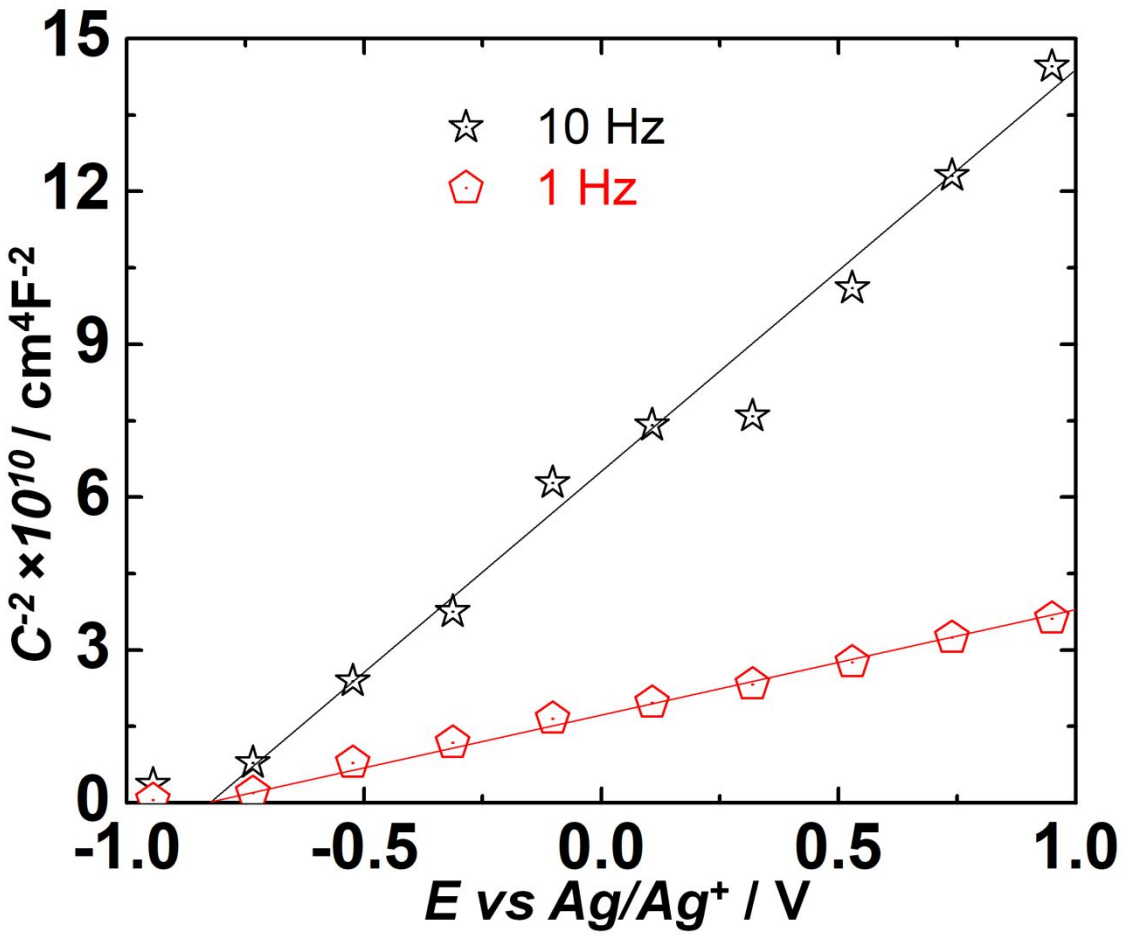

Figure S2 Mott-Schottky plots of a FTO/PCDTBT film, recorded in 0.1 M KCl in dark, with an Ag/AgCl/KCl as a reference electrode, and a Pt rod as the counter electrode.

Cyclic voltammetry

Cyclic voltammograms of pristine- TiO_2, CdS and PCDTBT films (as working electrodes), recorded in an aqueous 0.1 M KCl solution, with a Pt rod as the counter electrode and a Ag/AgCl/KCl as the reference electrode are shown in Figure S3. For pristine TiO_2 (Fig. S3a), a reduction peak was observed in the cathodic sweep at –0.67 V *versus* Ag/AgCl/KCl, and this E_{red} can be equated to the conduction band (CB) position of TiO_2. The electrode potential of the reference is +0.197 V. So, E_{red} (*versus* NHE (normal hydrogen electrode)) of TiO_2 = –0.58 V + 0.197 V = –0.383 V. The value of –0.383 V (*versus* NHE) in eV is given by: –4.5 eV (≅ 0 V *versus* NHE) – (–0.383 V) = –4.117 ≅ –4.12 eV. The position of the valence band (VB) of TiO_2 is determined by addition of the pre-determined optical band gap energy value to the CB energy, i.e., –4.12 eV + (–3.27 eV) = -7.39 ≅ -7.4 eV. For PCDTBT electrode (Figure S3b), a reduction peak were observed in the cathodic sweep at –1.12 V *versus* Ag/AgCl/KCl, and this E_{red} can be equated to the CB position of PCDTBT. So, E_{red} (*versus* NHE) of PCDTBT = –1.12 V + 0.197 V = –0.923 V. The value of –0.923 V (*versus* NHE) in eV is given by: –4.5 eV – (–0.923 V) = –3.577 ≅ –3.6 eV. By adding the optical E_g of PCDTBT to the CB energy level (–3.6 eV + (–1.85 eV)), the VB energy level is calculated to be at -5.45 eV. For CdS electrode (Figure S3c), a reduction peak was observed in the cathodic sweep at –0.783 V *versus* Ag/AgCl/KCl, and this E_{red} can be equated to the CB position of CdS. So, E_{red} (*versus* NHE) of CdS = –0.783 V + 0.197 V = –0.586 V. The value of –0.586 V (*versus* NHE) in eV is given by: –4.5 eV – (–0.586 V) = –3.914 ≅ –3.9 eV. By adding the optical E_g of CdS to the CB energy level (–3.9 eV + (–2.26 eV)), the VB energy level is calculated to be at -6.16 eV.

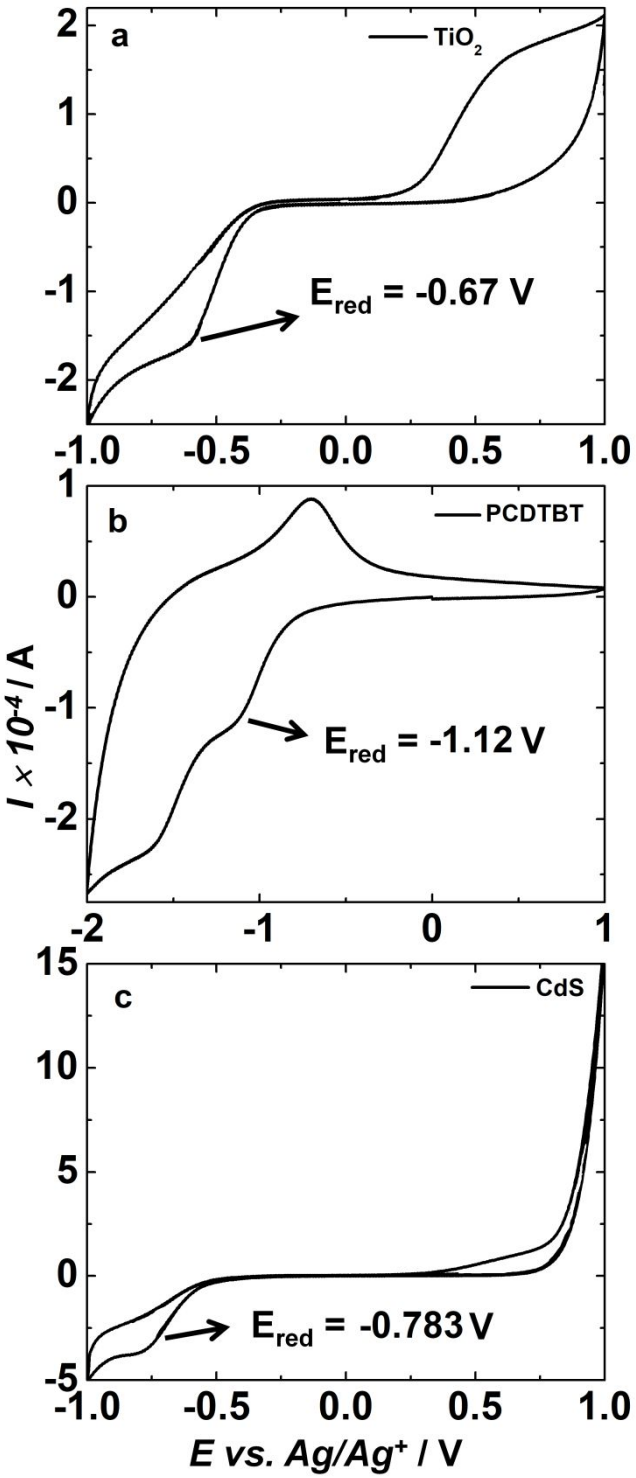

Figure S3 Cyclic voltammograms of (a) TiO_2, (b) PCDTBT, and (c) CdS serving as working

electrodes. All CV plots were recorded in a 0.1 M KCl solution as electrolyte, with a Pt sheet as the counter electrode and an Ag/AgCl/KCl as the reference electrode, at a scan rate of 10

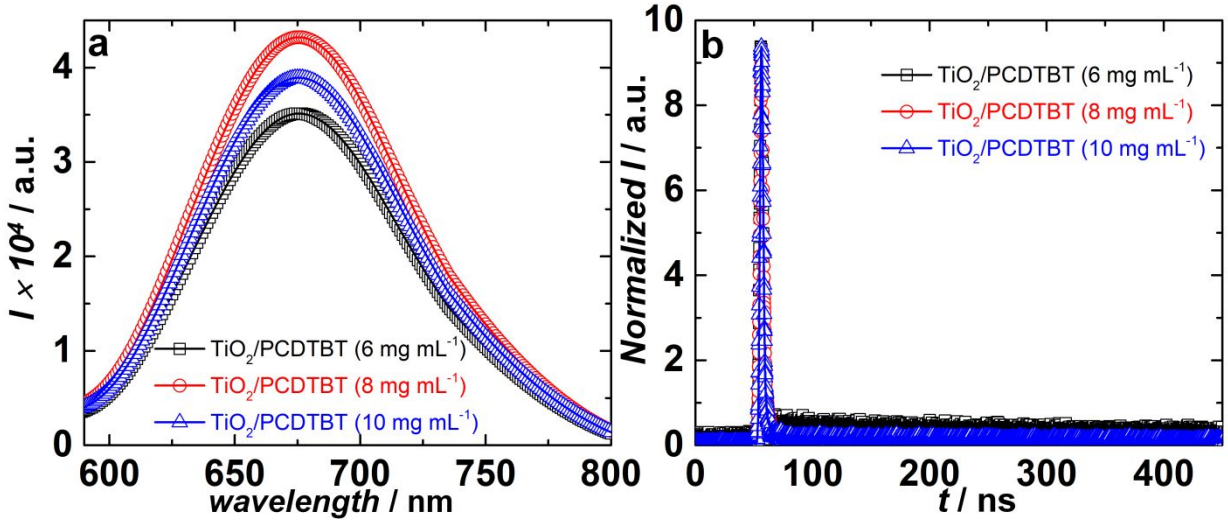

Figure S4 (a) Fluorescence spectra of TiO_2/PCDTBT at 6, 8 and 10 mg mL-1 concentrations of PCEDTBT recorded at λ_{ex} = 370 nm, and corresponding (b) Time resolved fluorescence decay traces recorded at λ_{ex} = 370 nm, and at λ_{em} = 660 nm wavelengths.

mV s-1.

Fluorescence quenching for TiO_2/PCDTBT films at 6, 8 and 10 mg mL^{-1} concentrations of PCDTBT was recorded λ_{ex} = 370 nm at shown in the Figure S4.

Table S1 Kinetic parameters of emission decay analysis of TiO_2/PCDTBT films at different concentrations of PCDTBT deduced from double exponential fits; the λ_{ex} was fixed at 370 nm and λ_{ex} = 660 nm.[a]

Concentration (mg mL^{-1})	B_1	τ_1 (ns)	B_2	τ_2 (ns)	$\langle\tau\rangle$ (ns)	χ^2
6	13.0	0.9	87	2.1	2.0	1
8	65.35	0.2	34.6	2.9	2.5	1
10	53.3	0.05	46.7	2.2	2.2	1

[a]B is the relative amplitude of each lifetime, τ_1 and τ_2 are the components of fluorescence lifetime and χ^2 denotes the fit quality.

Table S2 Kinetic parameters of emission decay analysis of photosensitizers deduced from double/single exponential fits; the λ_{ex} was fixed at 370 nm for all samples.[a]

Sample	λ_{em} (nm)	B_1	τ_1 (ns)	B_2	τ_2 (ns)	$<\tau>$ (ns)	χ^2
CdS	520	100	11.2	-	-	11.2	1
PCDTBT	660	100	6.2	-	-	6.2	0.98
TiO_2/CdS	520	29.0	0.3	71	5.15	5.0	1
TiO_2/PCDTBT	660	65.35	0.26	34.65	2.9	2.5	1
PCDTBT/CdS	520	35.0	0.01	65.0	1.5	1.5	1
	660	17.8	0.02	82.2	0.6	0.6	0.98
TiO_2/ PCDTBT/CdS	520	93.6	0.6	6.4	1.55	0.75	1
	660	36.2	0.02	63.8	0.5	0.5	1

[a]B is the relative amplitude of each lifetime, τ_1 and τ_2 are the components of fluorescence lifetime and χ^2 denotes the fit quality.

Table S3 Quantum yield data for CdS and reference.

Rhodamine 6G		CdS	
Absorbance	Area of Fluorescence	Absorbance	Area of Fluorescence
0.02	3911447	0.06	32929665
0.03	5826101	0.1	5666364
0.054	9597795	0.15	8293685
0.07	13379483	0.17	9159208

FRET calculations (Output file of the PHOTOCHEMCAD software)

Donor	: CdS
Acceptor	: PCDTBT
Refractive index	: 2
Orientation factor	: 0.66
Donor quantum yield	: 0.3
Acceptor ε (M^{-1} cm^{-1})	: 39330
Wavelength for ε	: 560
Low wavelength	: 460
High wavelength	: 650
J (M^{-1} cm^{3})	: 2.37×10^{-13}
Forster distance (nm)	: 3.67

Table S4 Solar cell parameters of cells by considering standard deviation using 0.1 M Na_2S and 0.1 M KCl as electrolyte, exposed cell area: 0.12 to 0.15 cm^2, under 1 sun illumination (AM 1.5G, 100 mW cm^{-2}) with the listed photoanodes; all cells with both C- fabric and C-dots/C-fabric assembly as the counter electrode.

Photoanode configuration	Counter Electrode	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	η (%)
TiO_2/PCDTBT	C-fabric	382	1.33	41.33	0.21
		381	1.4	41.25	0.22
		383	**1.43**	**42**	**0.23**
	C-dots/C-fabric	406	1.4	38.7	0.22
		405	1.43	40	0.23
		407	**1.45**	**40.7**	**0.24**
TiO_2/CdS	C-fabric	787	17.2	38	5.1
		786	17.1	38.1	5.12
		790	17.3	38	5.2
		789	17.3	38.6	5.27
		791	**17.4**	**38.5**	**5.3**
	C-dots/C-fabric	821	19	36	5.6
		819	19.1	36.6	5.72
		818	19	37.3	5.8
		820	19.1	37.7	5.91
		820	**19.23**	**38.1**	**6**
TiO_2/PCDTBT/CdS	C-fabric	852	20.14	36.1	6.2
		853	20.3	36.2	6.27
		856	20.35	36.7	6.3
		854	20.3	36.5	6.33
		857	**20.32**	**36.7**	**6.4**
	C-dots/C-fabric	873	25	33.1	7.22
		870	25.14	33.3	7.28
		868	25.25	33.4	7.32
		874	25.21	33.6	7.40

		877	**25.3**	**33.44**	**7.42**
TiO_2/CdS/PCDTBT	C-fabric	775	17.13	36.5	4.85
		774	17.2	36.5	4.86
		776	17	37.14	4.9
		775	17.21	37	4.93
		776	**17.25**	**37**	**4.95**
	C-dots/C-fabric	806	17.7	37.2	5.3
		802	17.3	38.4	5.33
		804	17.65	38.1	5.4
		805	17.5	38.8	5.47
		807	**17.8**	**38.3**	**5.5**

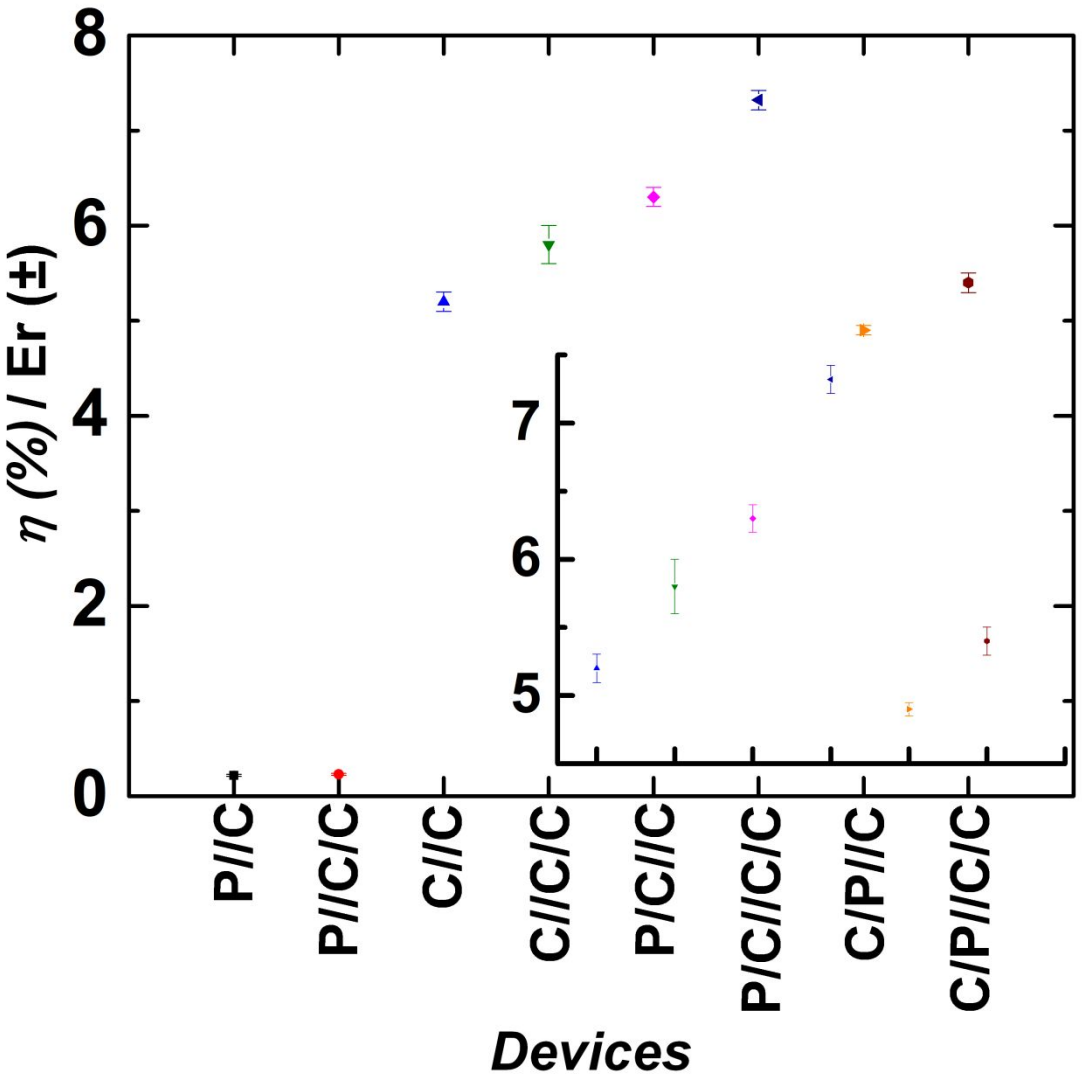

Figure S5 Error bar plots of QDSCs devices.

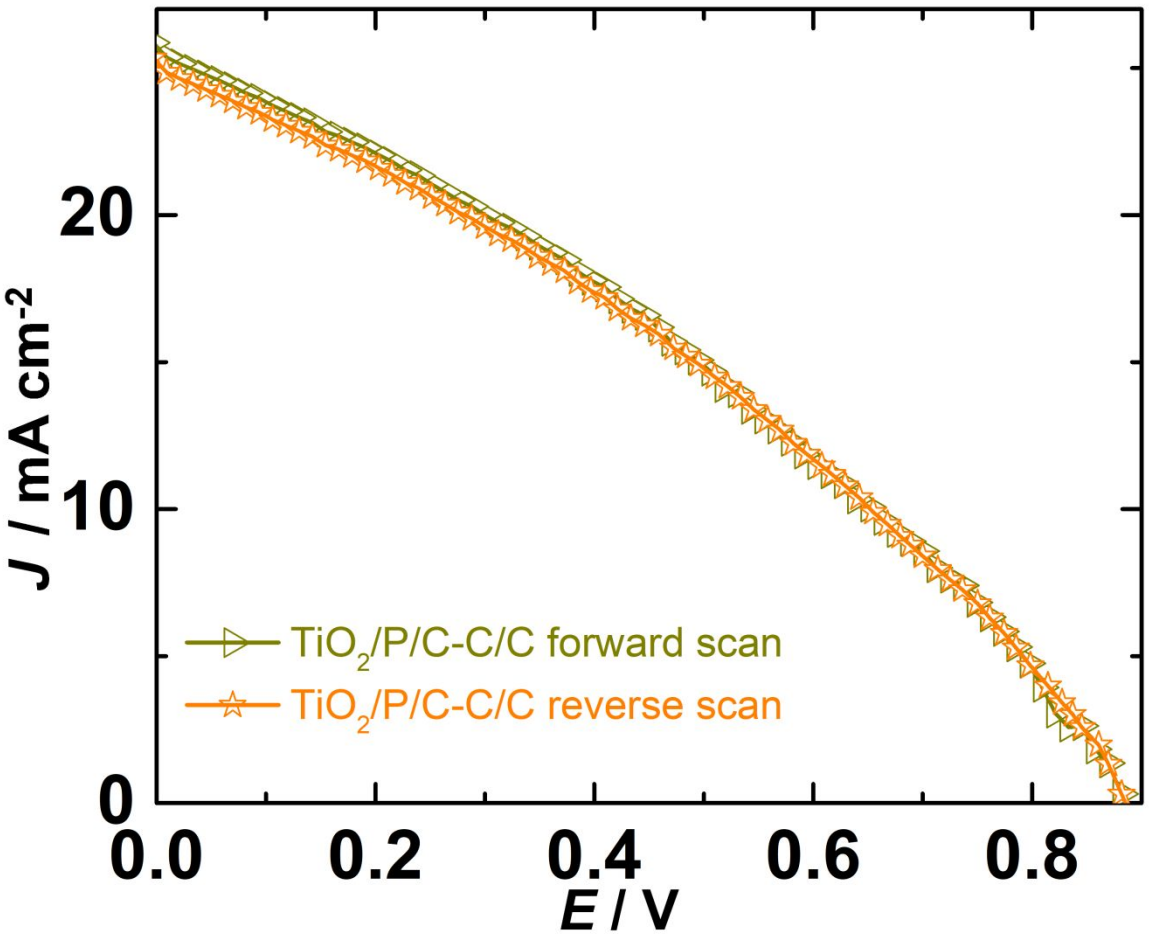

Figure S6 J-V characteristics of TiO_2/PCDTBT/CdS (P/C), and C-dots/C-fabric (C/C) CEs: C-dots/C-fabric (C/C) under 1 sun (100 mW cm^{-2}) illumination (AM 1.5G) in forward and reverse scan.

Table S5 Fitting parameters for EIS spectra of symmetric cells of CEs: C fabric and C-dots/C-fabric.

Cells	R_b (Ω cm^2)	R_{ct} (Ω cm^2)	R_{gb} (Ω cm^2)	C_{dl} (μF cm^{-2})	C_{gb} (mF cm^{-2})	Y_o (S $s^{1/2}$)
C-fabric//C-fabric	10	2.3	16	0.3	3.6	0.14
C-dots/C-fabric//C-dots/C-fabric	8	1.24	9.5	2.6	4.5	0.44