

Electronic Supplementary Information

Novel Semi-Random and Alternating Co-Polymer Hybrid Solar Cells Utilizing CdSe Multipods as Versatile Acceptors

*Matthew J. Greaney,^a Jose Araujo,^a Beate Burkhart,^{a,b} Barry C. Thompson,^{a,b} and Richard L. Brutchey^{*a}*

^a Department of Chemistry and the Center for Energy Nanoscience, University of Southern California, Los Angeles, CA, 90089-0744, USA

^b Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA, 90089-1661, USA

CdSe Multipod Synthesis and Ligand Exchange.

CdO (0.512 g, 3.99 mmol), octylphosphonic acid (1.55 g, 8.00 mmol) and trioctylphosphine oxide (3.85 g, 9.97 mmol) were heated to 300 °C under a nitrogen atmosphere. Once the solution became transparent, it was cooled to 25 °C and allowed to age for 48 h. After aging, the solution was brought back to 300 °C and stirred for 1 h. A solution of selenium (0.632 g, 8.00 mmol) in tributylphosphine (2.05 g, 10.0 mmol) was cooled to 0 °C and then rapidly injected into the cadmium precursor solution. The temperature was lowered to 260 °C immediately after selenium injection, and stabilized at 250 °C. After 60 min, the reaction was quenched in a 25 °C oil bath, and 10 mL of toluene was injected to prevent solidification. The CdSe multipod product was purified by flocculation with isopropanol and redispersion in toluene (3×) to afford multipods coated with the insulating native ligands, CdSe(NL). CdSe(NL) multipods (200 mg) dispersed in 3 mL of toluene were added to 6 mL of pyridine and 2 mL of tBT. The suspension was kept in the dark at room temperature for 1 h, and then flocculated with pentane and isolated via centrifugation. This procedure was repeated five to six times to ensure complete ligand exchange.

Donor Polymers.

PCPDTBT (28.5 kDa, 1.9 PDI) and PCDTBT (3.0 PDI, 56 kDa) were purchased from 1-Material, Inc. (Quebec, Canada). P3HT (93% R.R., 52 kDa, 2.2 PDI) was purchased from Reike Metals. P3HTT-DPP was prepared as previously reported (*Macromolecules* **2011**, *44*, 5079-5084).

Device Fabrication.

Devices were fabricated and tested in air. Aluminum shot (Al; Alfa Aesar, 99.999%) was purchased and used as received. Patterned ITO-coated glass substrates (10 Ω cm⁻², Thin Film Devices, Inc.) were sequentially cleaned by sonication in tetrachloroethylene, acetone, and isopropanol followed by 30 min of UV-ozone treatment. A 40 nm layer of PEDOT:PSS (Baytron P VP AI 4083, filtered through a 0.45 μm PTFE syringe filter) was spun-cast onto the clean ITO and heated at 120 °C for 30 min under vacuum. Donor polymer solutions of 15 mg mL⁻¹ were prepared in 1,2-dichlorobenzene by dissolving under mild heating (40-50 °C) and filtering through a 0.45 μm PTFE syringe filter. The CdSe(tBT) multipods were probe sonicated in 1,2-dichlorobenzene for 30-45 min and

filtered through a 1 μm PTFE syringe filter. The polymer stock solutions were then mixed with the pre-filtered 1,2-dichlorobenzene dispersions of CdSe to final concentrations of 20:4, 21:3.4, 16:4, and 24:4 mg mL^{-1} with equivalent vol/vol ratios of 1:1, 1.3:1, 0.8:1, and 1.2:1 (assuming CdSe and polymer densities of 5.8 and 1.2 g cm^{-2} , respectively) for CdSe:P3HT, CdSe:P3HTT-DPP, CdSe:PCDTBT, and CdSe:PCPDTBT, respectively. Active layers were spun-cast in air onto annealed PEDOT:PSS layers (700 rpm, 60 s) and allowed to dry for 25-40 min in a dark nitrogen filled cabinet, forming films with thicknesses between 65-100 nm. Zinc oxide nanocrystals dispersed in ethanol (20 mg mL^{-1}) were spun-cast on top of the active layers (4000 rpm, 60 s) to produce a 20-25 nm layer, and then the device was immediately annealed at 160 $^{\circ}\text{C}$ for 10 min under flowing nitrogen. Finally, the devices were loaded into a high vacuum ($\sim 2 \mu\text{Torr}$) thermal deposition chamber (Angstrom Engineering) for deposition of 100-nm thick Al cathodes through a shadow mask at a rate of 2 \AA s^{-1} . Device active areas were 4.3 mm^2 .

Device Characterization.

Current-density dependence on applied test voltage measurements were performed under ambient conditions using a Keithley 2400 SourceMeter (sensitivity = 100 pA) in the dark and under ASTM G173-03 spectral mismatch corrected 1000 W m^{-2} white light illumination from an AM 1.5G filtered 450 W Xenon arc lamp (Newport Oriol). Chopped and filtered monochromatic light (250 Hz, 10 nm FWHM) from a Cornerstone 260 1/4 M double grating monochromator (Newport 74125) was used in conjunction with an EG&G 7220 lock-in amplifier to perform all spectral responsivity measurements. Reported device metrics were averaged over 12 individual pixels from at least three separate substrates.

Material Characterization.

Transmission Electron Microscopy (TEM). TEM images of hybrid films were obtained on a JEOL JEM-2100 microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CCD camera. Samples were prepared with the same (wt/wt) ratio of polymer to CdSe(tBT) and under identical processing conditions to the working devices. The polymer:CdSe(tBT) layer was floated off of the PEDOT:PSS layer in water and collected on a copper grid for imaging. No significant morphological differences were observed upon comparison of the four different polymer:CdSe(tBT) samples. For each sample, it appeared that a uniform distribution of nanocrystals throughout the polymer matrix was achieved.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were collected under nitrogen on a Jasco FT-IR 4100 from 4000-400 cm^{-1} by averaging over 64 scans with a resolution of 2 cm^{-1} . Semi-quantitative FT-IR was performed on CdSe(NL) and CdSe(tBT) to help gauge the efficiency of tBT ligand exchange. Nanocrystal samples were dried for 24 h under flowing nitrogen, and then quantitatively mixed into a KBr matrix containing an internal standard. Specifically, 7 mg of nanocrystals were mixed into KBr (200 mg) containing a $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$ (0.17 mg) internal standard, and ground with a mortar and pestle for at least 10 min. A small amount (20 mg) of each thoroughly mixed sample was pressed into a pellet and immediately analyzed. A similarly prepared

KBr blank was employed for the background run. The spectra were normalized to the absorbance at 2090 cm^{-1} corresponding the main C–H stretch of the internal standard.

UV-visible Absorption Spectroscopy (UV-vis). UV-vis spectra were acquired on a Shimadzu UV-1800 spectrophotometer, using borosilicate glass microscope slides as film substrates.

Thermogravimetric Analysis (TGA). TGA measurements were made on a TA Instruments TGA Q50 instrument, using sample sizes of 5-15 mg in an alumina crucible under a flowing nitrogen atmosphere heated at 10 °C min^{-1} . TGA samples were prepared by drying the colloid under flowing nitrogen at $80\text{-}100\text{ °C}$ for up to 90 min, and then lightly crushing them with a spatula.

Energy Dispersive X-ray (EDX) Spectroscopy. EDX spectra were acquired using an EDAX Apollo silicon-drift detector (model JSM 6490) mounted on a JEOL JSM-6610 SEM with an accelerating voltage of 15 kV. Amp time was $51.2\text{ }\mu\text{s}$, with count rate of $\sim 3400\text{-}3700\text{ cps}$ giving a dead time of $\sim 30\text{-}34\%$. Counts were acquired for 50 s live time. For each sample, data were obtained for five random areas of several tens to hundred of square microns each, and the mean value was taken.

Spectroscopic Ellipsometry. Film thicknesses were determined using a J.A. Woollam variable angle spectroscopic ellipsometer equipped with a 150 W Xe-arc lamp. Data were collected from 1000-1500 nm at 64° , 69° , and 74° angles incident to the sample and were fit with a Cauchy model, in which the index of refraction can be represented by a slowly varying function of wavelength with the form $n(\lambda) = B + C/\lambda^2$, where λ is given in μm . The thickness and B and C parameters were simultaneously fit using the Cauchy model, which is applicable to the optical data collected between 1000-1500 nm since the films do not have any measurable absorption in this spectral region. A summary of the fits for B, C, and the thickness are given in Table S1. Reported thicknesses were derived from at least three measurements per sample substrate. The sample thicknesses were found to vary between 10-20% across a single film, yet the values for B and C remained within the measured error. All samples were prepared analogously to optimized devices, but on Si wafers.

Table S1. Parameter fits for polymer:CdSe(tBT) films from spectroscopic ellipsometry.

Sample	B	C (μm^2)	thickness (nm)
P3HT:CdSe(tBT)	1.920 (± 0.009)	0.146 (± 0.010)	80-90
P3HTT-DPP:CdSe(tBT)	1.867 (± 0.008)	0.187 (± 0.006)	65-75
PCDTBT:CdSe(tBT)	1.937 (± 0.014)	0.168 (± 0.014)	75-85
PCPDTBT:CdSe(tBT)	1.898 (± 0.040)	0.164 (± 0.007)	90-100

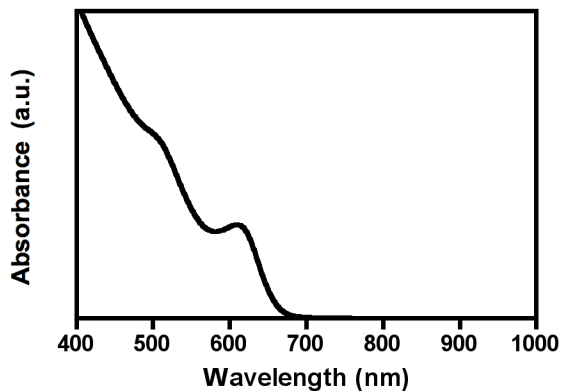


Figure S1. Optical absorption spectrum of CdSe(tBT) multipod thin film.

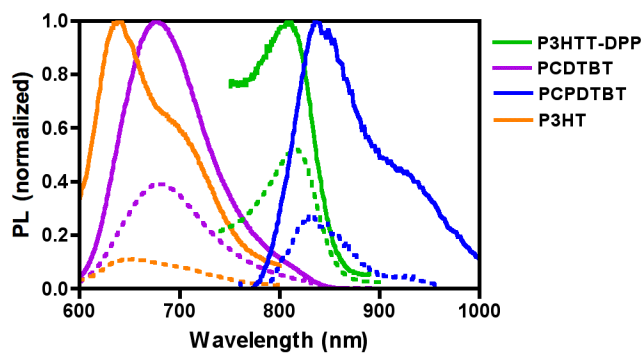


Figure S2. PL spectra for neat polymers (solid lines) versus hybrid blends with CdSe(tBT) multipods (dashed lines) made under identical conditions as the optimized devices. The data show significant PL quenching for each hybrid film compared to the neat polymers, suggesting the occurrence of energy or charge transfer. The figure legend gives the donor polymer in each hybrid blend.

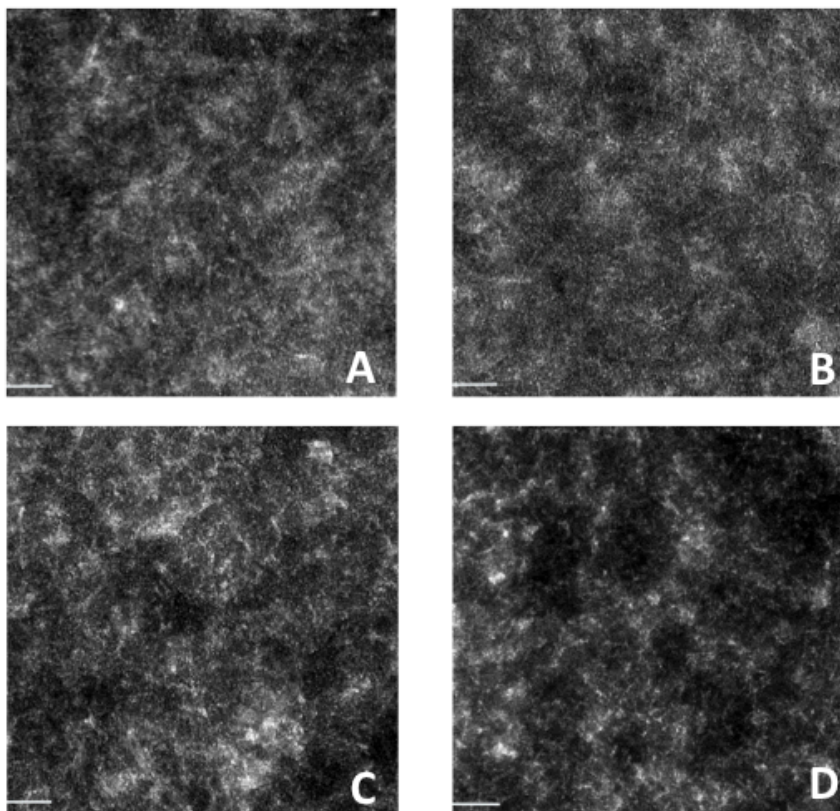


Figure S3. TEM micrographs of (a) P3HT:CdSe(tBT), (b) PCDTBT:CdSe(tBT), (c) P3HTT-DPP:CdSe(tBT), and (d) PCPDTBT:CdSe(tBT) hybrid films on copper TEM grids. The scale bars are 500 nm.

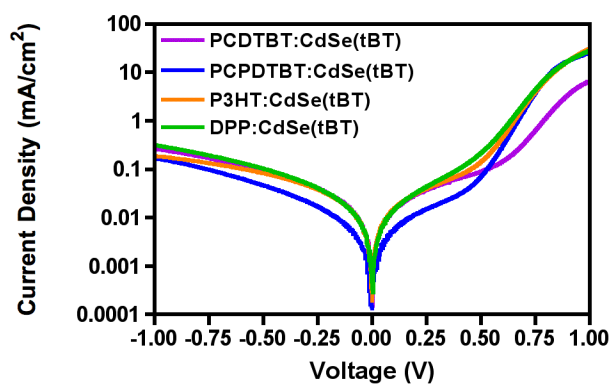


Figure S4. Semi-log plots for each of the four polymer:CdSe(tBT) devices studied demonstrating negligible differences in the reverse saturation currents.