

Supplemental Information:

Improving Open Circuit Potential in Hybrid P3HT:CdSe Bulk Heterojunction Solar Cells via Colloidal *tert*-Butylthiol Ligand Exchange

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Supplemental 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 8:1 (wt/wt) ratio of CdSe to P3HT and under identical processing conditions to the working devices. The P3HT:CdSe layer was floated off of the PEDOT:PSS layer in water and collected on a grid for imaging. No significant morphological differences were observed upon comparison of the three different CdSe samples. For each sample, it appeared that the 8:1 (wt/wt) CdSe:P3HT loading produced a uniform distribution of nanocrystals throughout the polymer matrix.

Atomic Force Microscopy (AFM). Plain-view AFM images of hybrid films on glass were obtained on a Digital Instruments Dimension 3100 Atomic Force Microscope using intermittent contact mode equipped with a Vista Probes Al coated Si tip with a force constant of 10 N m⁻¹ and a nominal tip radius of <10 nm.

Supplemental Figures

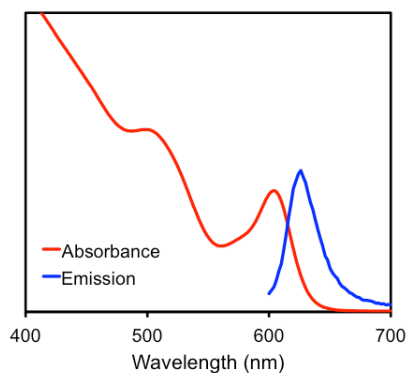


Figure S1. UV-vis absorption and PL emission spectra for a dispersion of CdSe(NL) in toluene. A 550 nm excitation wavelength was used for the PL acquisition.

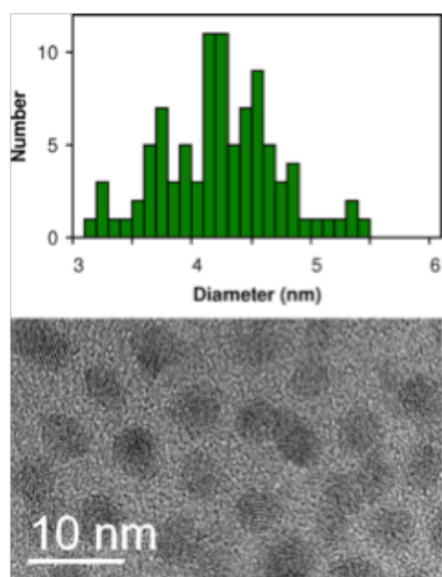


Figure S2. TEM image and corresponding particle size histogram for a typical batch of CdSe(NL) nanocrystals. Based on the statistical analysis of 93 nanocrystals, the average diameter was found to be 4.2 ± 0.5 nm, in agreement with the size determined from UV-vis analysis.

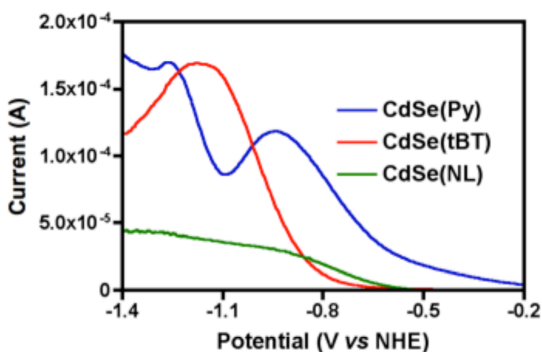


Figure S3. DPV of CdSe(NL), CdSe(Py), and CdSe(tBT) spun-cast on ITO collected at 10 mV s^{-1} using a Pt wire counter electrode and Ag-wire reference electrode in 0.10 M TBAP.

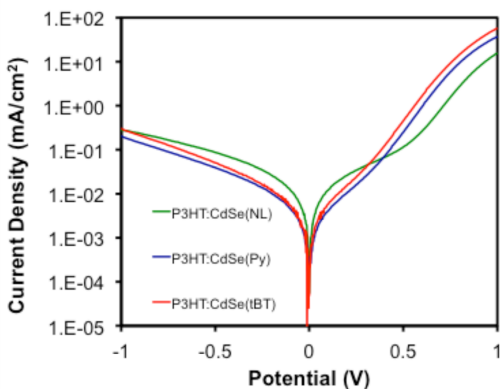


Figure S4. Dark I - V characteristics for P3HT:CdSe(NL), P3HT:CdSe(Py), and P3HT:CdSe(tBT) hybrid solar cells.

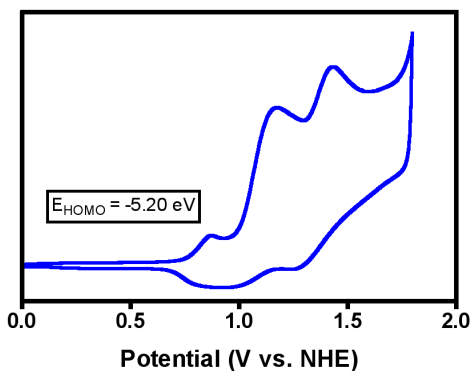


Figure S5. CV of P3HT spun-cast onto ITO obtained at a 20 mV s^{-1} scan rate using a Pt counter electrode and Ag wire reference electrode in acetonitrile with 0.1 M TBAP as the supporting electrolyte.

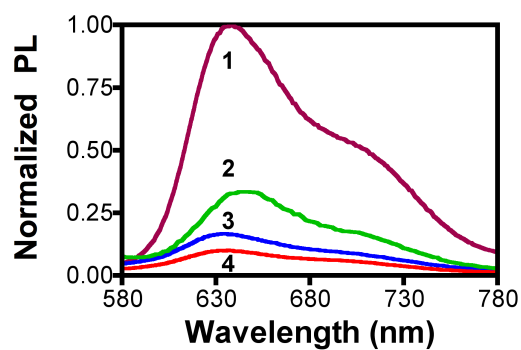


Figure S6. Steady-state PL spectra ($\lambda_{\text{ex}} = 550$ nm) for films of neat P3HT (**1**), P3HT:CdSe(NL) (**2**), P3HT:CdSe(Py) (**3**), and P3HT:CdSe(tBT) (**4**). All hybrid films were prepared using an 8:1 (wt/wt) ratio of CdSe to P3HT. Spectra were normalized to reflect the relative intensities compared to neat P3HT emission at 635 nm.

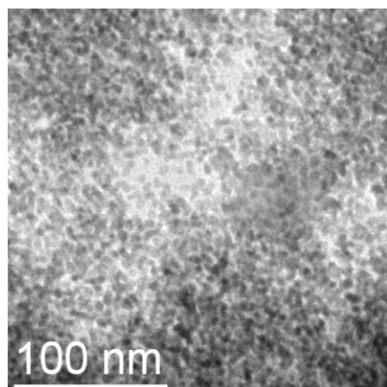


Figure S7a. TEM image of P3HT:CdSe(NL).

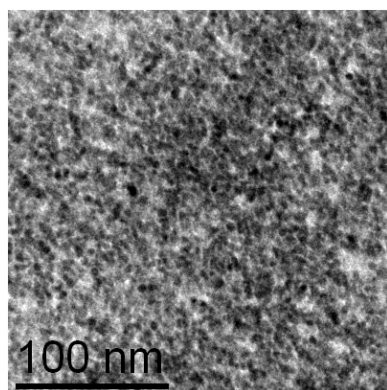


Figure S7b. TEM image of P3HT:CdSe(Py).

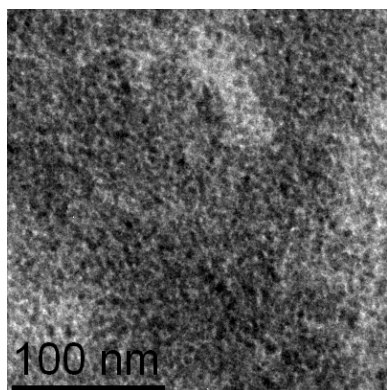


Figure S7c. TEM image of P3HT:CdSe(tBT).

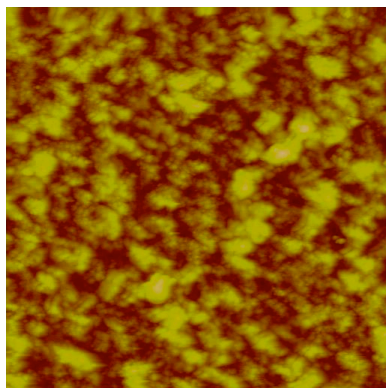


Figure S8a. AFM topological image of P3HT:CdSe(NL). Image was obtained using $5 \times 5 \mu\text{m}$ window with a 53 nm maximum vertical height and an rms roughness of 12 nm.

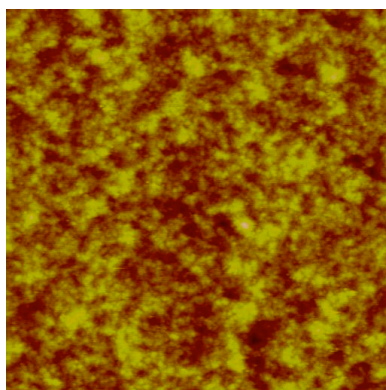


Figure S8b. AFM topological image of P3HT:CdSe(Py). Image was obtained using $5 \times 5 \mu\text{m}$ window with a 39 nm maximum vertical height and an rms roughness of 5 nm.

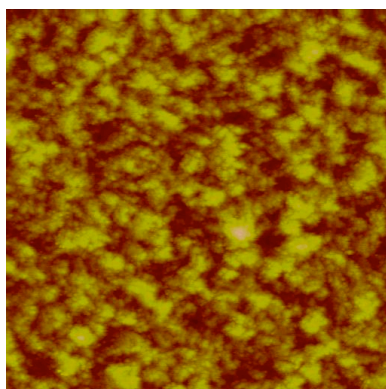


Figure S8c. AFM topological image of P3HT:CdSe(tBT). Image was obtained using $5 \times 5 \mu\text{m}$ window with a 43 nm maximum vertical height and an rms roughness of 10 nm.

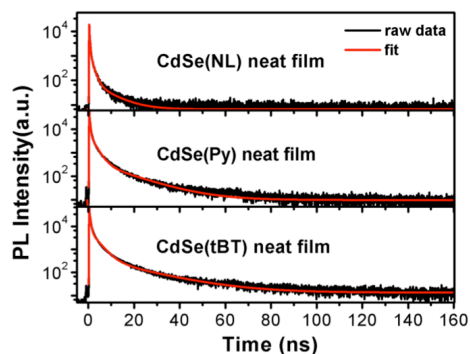


Figure S9. PL lifetime decay traces for films of neat CdSe films ($\lambda_{\text{ex}} = 400$ nm; $\lambda_{\text{em}} = 650$ nm). Data were fit with a sum of three exponential functions, and lifetimes were determined using a weighted average. Lifetimes of 1.4, 3.3, and 4.4 ns were measured for CdSe(NL), CdSe(Py) and CdSe(tBT), respectively. The fitting parameters are given in Table S2.

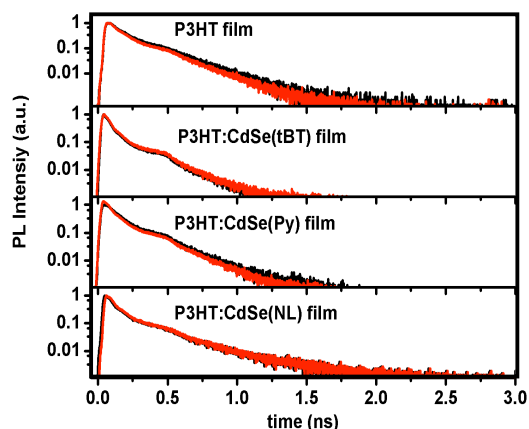


Figure S10. Normalized PL lifetime traces of the neat P3HT film and hybrid blends ($\lambda_{\text{ex}} = 550$ nm; $\lambda_{\text{em}} = 650$ nm) at two different excitation fluences, $3 \mu\text{J cm}^{-2}$ (black) and $6 \mu\text{J cm}^{-2}$ (red).

Supplemental Tables

Table S1. Fitting parameters for the PL lifetime measurements of hybrid films.

Hybrid Film	t_1 (ps)	a_1	t_2 (ps)	a_2
P3HT: CdSe(NL)	70	0.924	371	0.076
P3HT: CdSe(Py)	57	0.797	182	0.203
P3HT: CdSe(tBT)	30	0.839	156	0.162

Table S2. Fitting parameters for the PL lifetime measurements of neat CdSe films.

Acceptor	t_1 (ns)	a_1	t_2 (ns)	a_2	t_3 (ns)	a_3
CdSe(NL)	0.20	0.630	0.89	0.220	2.24	0.15
CdSe(Py)	0.31	0.517	1.24	0.314	4.82	0.169
CdSe(tBT)	0.45	0.493	1.29	0.351	6.60	0.156