

Supporting Information for:

**Poly(3-Hexylthiophene)-CdSe Quantum Dot Bulk Heterojunction
Solar Cells: The Influence of the Functional End-Group of the
Polymer**

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Experimental

Materials. All reactions were conducted under prepurified nitrogen, using oven-dried glassware. All glassware was assembled while hot and cooled under nitrogen. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. All solvents were freshly distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl.

Structural analysis of synthesized polymers was performed by using ^1H NMR and MALDI-TOF-MS spectroscopy. MALDI-TOF-MS measurements were performed on a Voyager-DE STR Biospectrometry workstation by Biosystems, using terthiophene as a matrix. Measurements were performed in linear mode. ^1H NMR spectra were recorded on a 500 MHz Varian spectrometer, using deuterated chloroform as a solvent. TMS was used as reference.

Molecular weight of the polymers was determined by gel permeation chromatography (GPC) on a Viscotek separations module apparatus with tetrahydrofuran as the eluent (flow rate 1 mL/min, 35 °C). Calibration based on polystyrene standards was applied for determination of molecular weights.

Synthesis of H/Br-terminated poly(3-hexylthiophene) was performed as previously described.¹ The polymerization degree ($\text{DP}_n=60$) was estimated from ^1H NMR by integrating the methylene protons of the hexyl side chain *vs* the terminal methylene protons, as previously shown.¹

^1H NMR (500 MHz, CDCl_3): δ_{H} 0.9 (t, $J = 7$ Hz, 3H), 1.35-1.43 (m, 6H), 1.69 (t, $J = 7$ Hz, 2H), 2.80 (t, $J = 7$ Hz, 2H), 7.46 (s, 1H), GPC: $M_n = 12900$; PDI = 1.15

Synthesis of Br/allyl-terminated poly(3-hexylthiophene). A dry 100 mL three-neck flask was flushed with nitrogen and charged with 2,5-dibromo-3-hexylthiophene (9.8 g, 30 mmol) and anhydrous THF (20 mL). A 2M solution of *t*-butyl magnesium chloride (15 mL, 30 mmol) in diethyl ether (Et₂O) was added *via* a syringe, and the reaction mixture was stirred at room temperature for 2hrs. After 2 hrs a sample was collected for GC-MS analysis. The monomer conversion determined by GC-MS was 98%. Anhydrous THF (280 mL) was added to the reaction flask, followed by the addition of Ni(dppp)Cl₂ (0.135 g, 0.26 mmol). The polymerization was allowed to proceed for 10 min at room temperature followed by the addition of a 1M solution of allyl magnesium bromide (3 mL, 3 mmol). The reaction mixture was stirred for 5 min followed by quenching in methanol. The polymer was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by ¹H NMR and MALDI-TOF MS. The polymerization degree (DP_n=60) was estimated from ¹H NMR by integrating the methylene protons of the hexyl side chain *vs* the allyl protons.

¹H NMR (500 MHz, CDCl₃): δ_H 0.9 (t, *J* = 7 Hz, 3H), 1.35-1.43 (m, 6H), 1.69 (t, *J* = 7 Hz, 2H), 2.80 (t, *J* = 7 Hz, 2H), 3.49 (d, *J* = 7 Hz, 2H), 5.11 (m, 2H), 5.98 (m, 1H) 7.46 (s, 1H), GPC: M_n = 12200; PDI = 1.15

Synthesis of bromo/hydroxypropyl-terminated poly(3-hexylthiophene). Allyl-terminated P3HT (3g, 0.30 mmol, DP_n(NMR) = 60) was dissolved in anhydrous THF (100 mL) under nitrogen. To this reaction mixture, a 0.5 M solution of 9-BBN (4 mL, 2 mmol) in anhydrous THF was added via a syringe. The reaction mixture was stirred for 12 h at 40°C, at which point a 6M solution of NaOH (2 mL) was added to the reaction flask. The reaction mixture was stirred for additional 15 min at 40°C. The reaction mixture was allowed to cool to RT followed by slow

addition of a 33% aqueous solution of hydrogen peroxide (2 mL), and the reaction was heated at 40°C for 12 h. The hydroxypropyl-terminated P3HT was isolated by precipitation in methanol. The polymer was filtered and purified by a Soxhlet extraction with methanol. Polymer was characterized by ^1H NMR and MALDI-TOF MS.

^1H NMR (500 MHz, CDCl_3): δ_{H} 0.9 (t, $J = 7$ Hz, 3H), 1.35-1.43 (m, 6H), 1.69 (t, $J = 7$ Hz, 2H), 1.95 (p, $J = 7$ Hz, 2H), 2.80 (t, $J = 7$ Hz, 2H), 3.75 (t, $J = 7$ Hz, 2H), 7.46 (s, 1H), GPC: $M_n = 12700$; PDI = 1.16

Synthesis of bromo/propylthioacetyl-terminated poly(3-hexylthiophene). A 100 mL three-neck flask was placed in a dry ice bath at -30°C and charged with 10 mL anhydrous THF, 0.39 g triphenylphosphine (1.5 mmol), and 0.29 mL diisopropyl azodicarboxylate (DIAD) (1.5 mmol). A pale yellow precipitate, corresponding to the DIAD- PPh_3 adduct formed within 30 minutes. At this point the reaction flask was removed from the dry ice bath and allowed to warm to room temperature. A solution of 1.5 g (0.15 mmol) of hydroxypropyl-terminated P3HT in 30 mL anhydrous THF and 0.1 mL thioacetic acid (1.5 mmol) were added drop-wise to the DIAD- PPh_3 adduct. The reaction mixture was stirred for 8 hrs at 40 °C, followed by precipitation of polymer in methanol. The polymer was filtered and purified by sequential Soxhlet extractions with methanol, hexane, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by ^1H NMR and MALDI-TOF MS.

^1H NMR (500 MHz, CDCl_3): δ_{H} 0.9 (t, $J = 7\text{Hz}$, 3H), 1.35-1.43 (m, 6H), 1.69 (t, $J = 7\text{Hz}$, 2H), 1.95 (p, $J = 7\text{Hz}$, 2H), 2.35 (s, 3H), 2.80 (t, $J = 7\text{Hz}$, 2H), 2.95 (t, $J = 7\text{Hz}$, 2H), 7.46 (s, 1H), GPC: $M_n = 12700$; PDI = 1.16

Synthesis of H/propylthiol-terminated poly(3-hexylthiophene). Propylthioacetyl-terminated P3HT (1.5 g, 0.15 mmol) was dissolved in anhydrous THF (100 mL) under nitrogen. To this

reaction mixture, 1 mL of 0.5 M solution of lithium aluminium hydride was added via a syringe. The reaction mixture was stirred for 4 h at 40 °C, followed by precipitation in methanol/HCl mixture. The polymer was filtered and purified by sequential Soxhlet extractions with methanol, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by ^1H NMR and MALDI-TOF MS.

^1H NMR (500 MHz, CDCl_3): δ_{H} 0.9 (t, $J = 7\text{Hz}$, 3H), 1.35-1.43 (m, 6H), 1.69 (t, $J = 7\text{Hz}$, 2H), 1.95 (p, $J = 7\text{Hz}$, 2H), 2.6 ppm (m, 4H), 2.80 (t, $J = 7\text{Hz}$, 2H), 2.88 (t, $J = 7\text{Hz}$, 2H), 7.46 (s, 1H),
GPC: $M_n = 12700$; PDI = 1.16

Synthesis of CdSe quantum dots. Nearly monodispersed CdSe quantum dots have been synthesized using a previously reported procedure, with slight modifications. Cadmium oxide (1 mmol) was mixed with myristic acid (4 mmol) and heated under an inert atmosphere. The optically clear solution was cooled down under room temperature until a white solid formed. Equivalent amounts of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) was added to this complex and reheated to 320°C. Selenium (5 mmol) was mixed with tributylphosphine (2 mL) in glove box. This selenium shot was quickly injected into cadmium complex in the presence of ligands. Once the desired size was reached they were quenched in dry toluene and precipitated with methanol. This precipitate was collected by centrifugation and washed three more times with methanol.

Pyridine treatment of CdSe quantum dots. TOPO modified CdSe quantum dots were diluted in dry pyridine and refluxed under N_2 atmosphere. The particles were precipitated with excess hexane and dissolved in pyridine. This process was repeated six times. The particles were stored in neat pyridine. The ligand exchange reaction was monitored by ^1H NMR, following the

replacement of TOPO with pyridine. The yield of ligand exchange reaction was $\sim 70\%$ as determined from ^1H NMR.

Preparation of the devices. ITO/glass coupons were patterned using standard lithographic techniques. The coupons were cleaned with deionized water, acetone and isopropanol successively by sonication for 5 minutes each, and then ashed for 10 minutes in oxygen plasma. Immediately after the cleaning, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin coated (3000 min^{-1} , 60 seconds) followed by annealing at 150°C for 30 minutes under nitrogen, resulting in a film thickness of $\sim 40\text{ nm}$. The CdSe/polymer blend was prepared in dichlorobenzene/pyridine mixture (95/5, v/v) with the ratio of 5 to 1. This blend was spin-casted (500 min^{-1} , 40 seconds) and annealed at 150°C for 30 minutes. For direct annealed (DA) samples the coupon went directly from the spin chuck to the hot plate. For “slow-evaporation” (SE) samples, the wet film was first placed in a covered Petri dish for 90 seconds, after which the lid was removed, the SE film dried to a purplish color within approximately one minute, and then it was annealed. Cathode consisting of calcium (25nm) and silver (75nm) was thermally evaporated through a shadow mask to define solar cell active area at a rate of $0.2\text{-}0.6\text{ \AA/s}$. The coupons were encapsulated with epoxy resin (Addison) and cured under UV-light for 15 min before IV testing.

Curent-voltage testing. IV testing was carried out using a Keithley 2400 interfaced with LabView software. The solar simulator used was an ORIEL (model # 67005) equipped with Xenon lamp; the intensity of the light was calibrated to 100 mW cm^{-2} with a Si-photodiode purchased from PV measurements Inc (PV 242) and calibrated by NERL in Colorado.

AFM Images were recorded using a VEECO Dimension SPM. All the images were taken on solar cell coupons.

TEM images were recorded using a JOEL JEM 2100 F microscope. The samples were deposited on copper TEM grids coated with thin carbon films by dip coating. Samples were deposited from dichlorobenzene/pyridine mixtures (95:5) and dried before imaging.

Spectral Characterization of the Polymers

^1H NMR spectra of synthesized polymers

^1H NMR Spectrum of Br/allyl-terminated P3HT is shown in Figure S1.

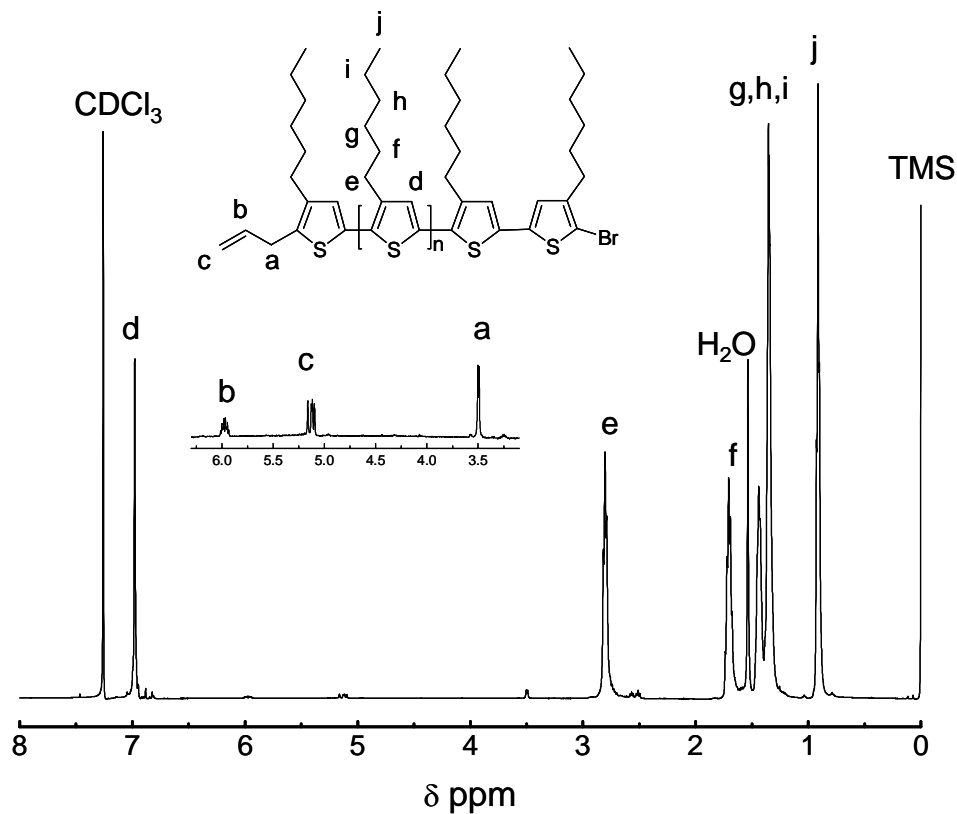


Figure S1. ^1H NMR spectrum (500 MHz, CDCl_3) of allyl-terminated regioregular poly(3-hexylthiophene)

The degree of polymerization was determined by the ratio of the integrals of *e* protons to *a* protons ($DP_n = 60$).

The conversion of the hydroxypropyl-terminated P3HT to propylthioacetyl-terminated P3HT was monitored by ^1H NMR spectroscopy. (Figure S2)

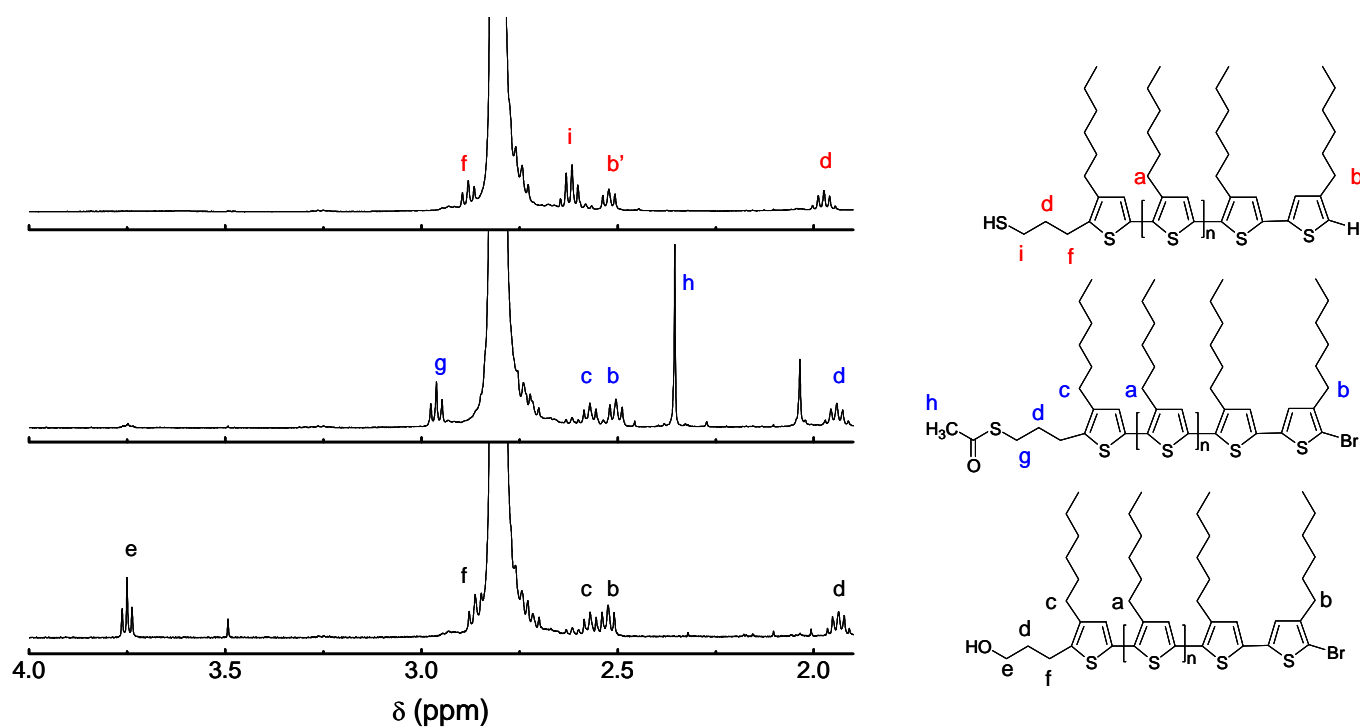


Figure S2. ^1H NMR spectra (expansion in the 1.9 - 4 ppm region) of Br/hydroxypropyl terminated (bottom), Br/propylthioacetyl- terminated P3HT (middle) and H/propylthiol-terminated P3HT (top)

MALDI-TOF MS spectra of synthesized polymers

MALDI-TOF MS spectrum of allyl-terminated P3HT is shown in Figure S3 and indicated the presence of H/allyl and Br/allyl end- groups. Less than 5% H/Br end-groups are present in the polymer.

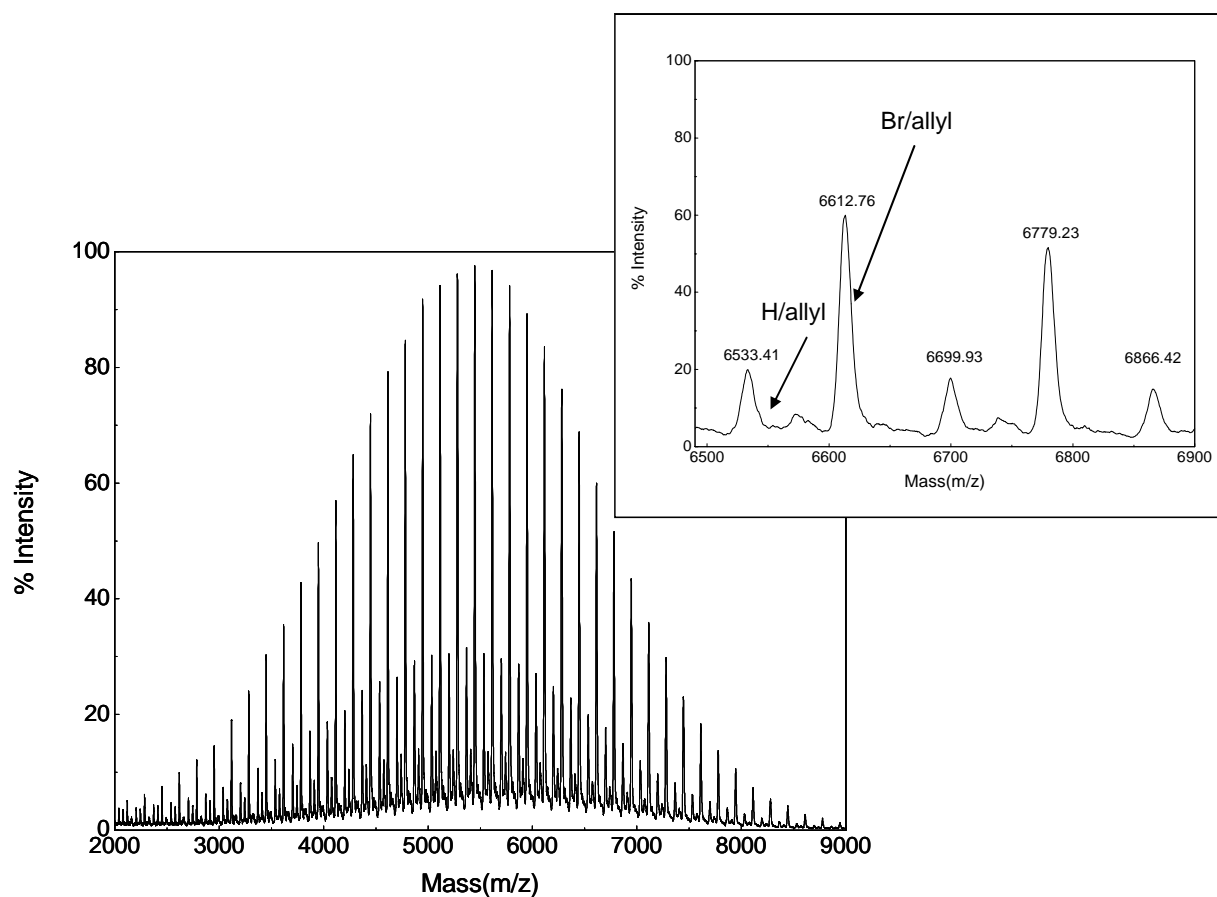


Figure S3. MALDI-TOF MS spectrum of Br/allyl-terminated poly(3-hexylthiophene)

MALDI-TOF MS spectrum of hydroxypropyl-terminated P3HT is shown in Figure S4 and indicated the presence of H/hydroxypropyl and Br/hydroxypropyl end- groups.

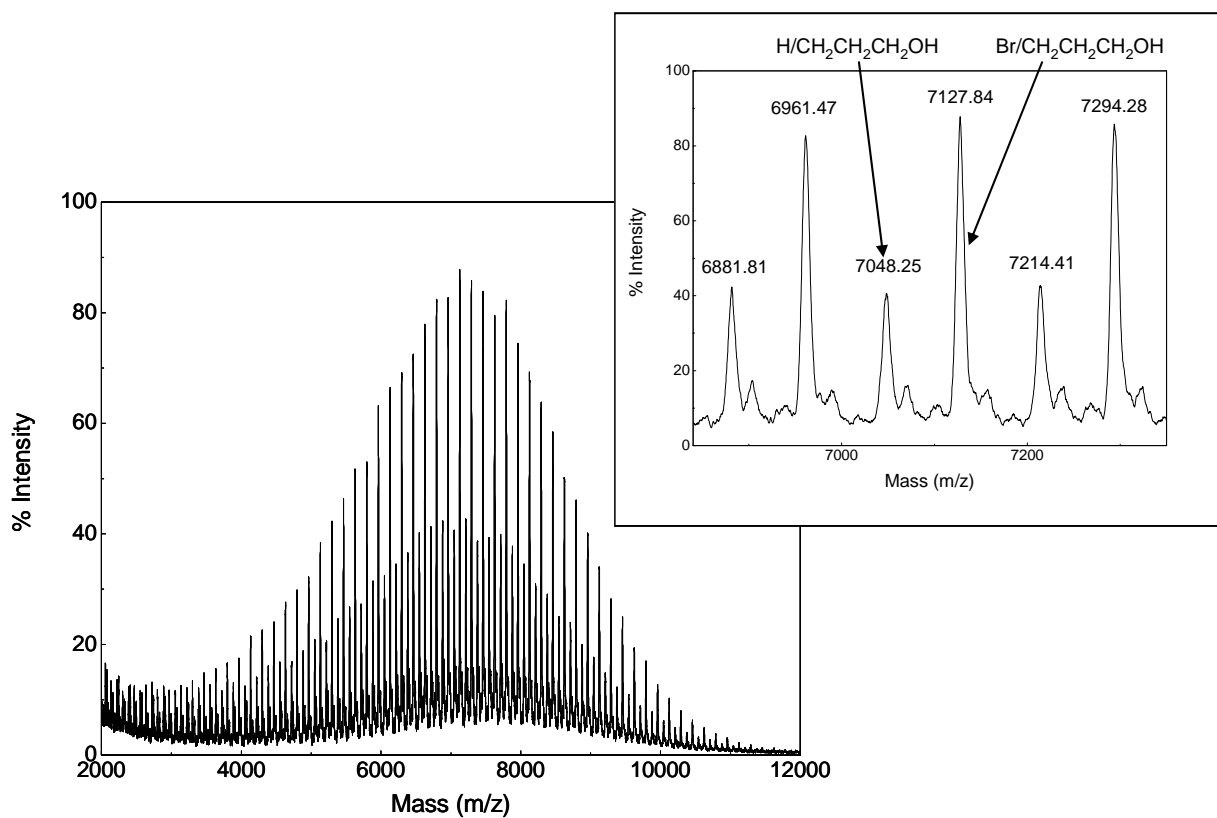


Figure S4. MALDI-TOF MS spectrum of hydroxypropyl- terminated poly(3-hexylthiophene)

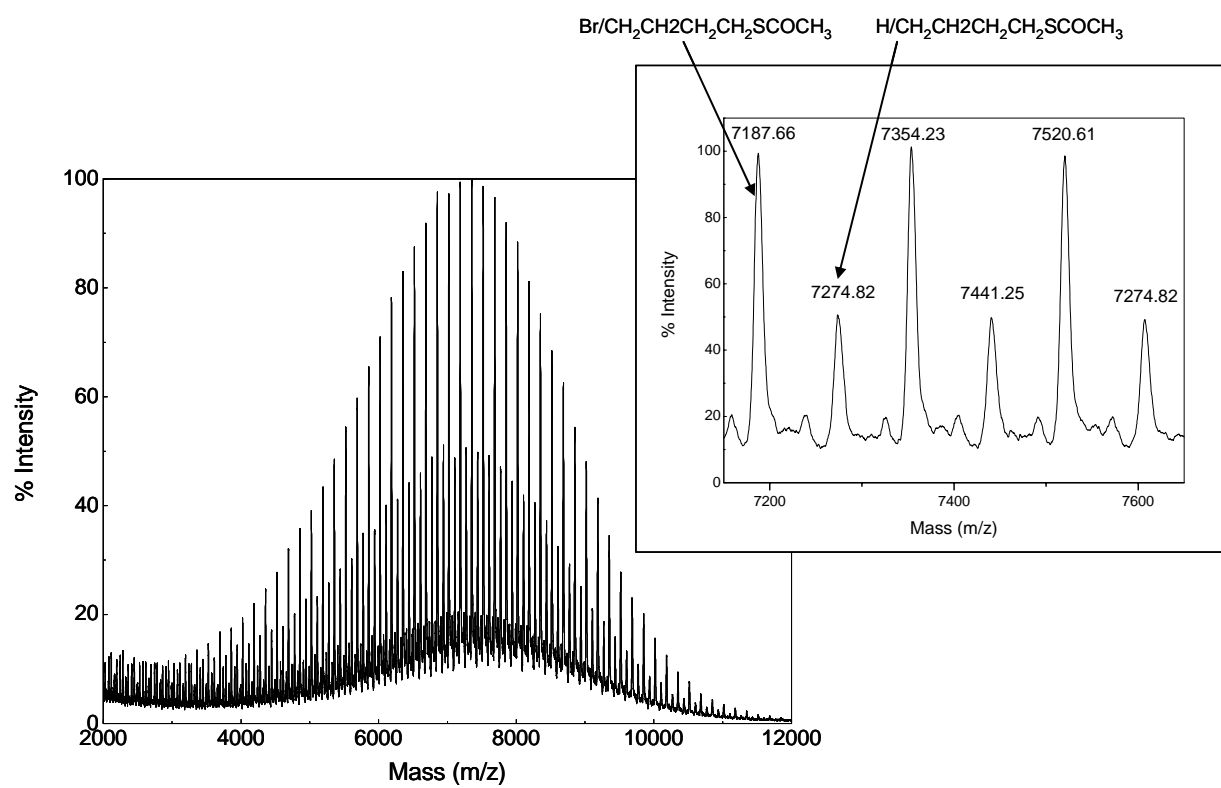


Figure S5. MALDI-TOF MS spectrum of propylthioacetyl-terminated poly(3-hexylthiophene)

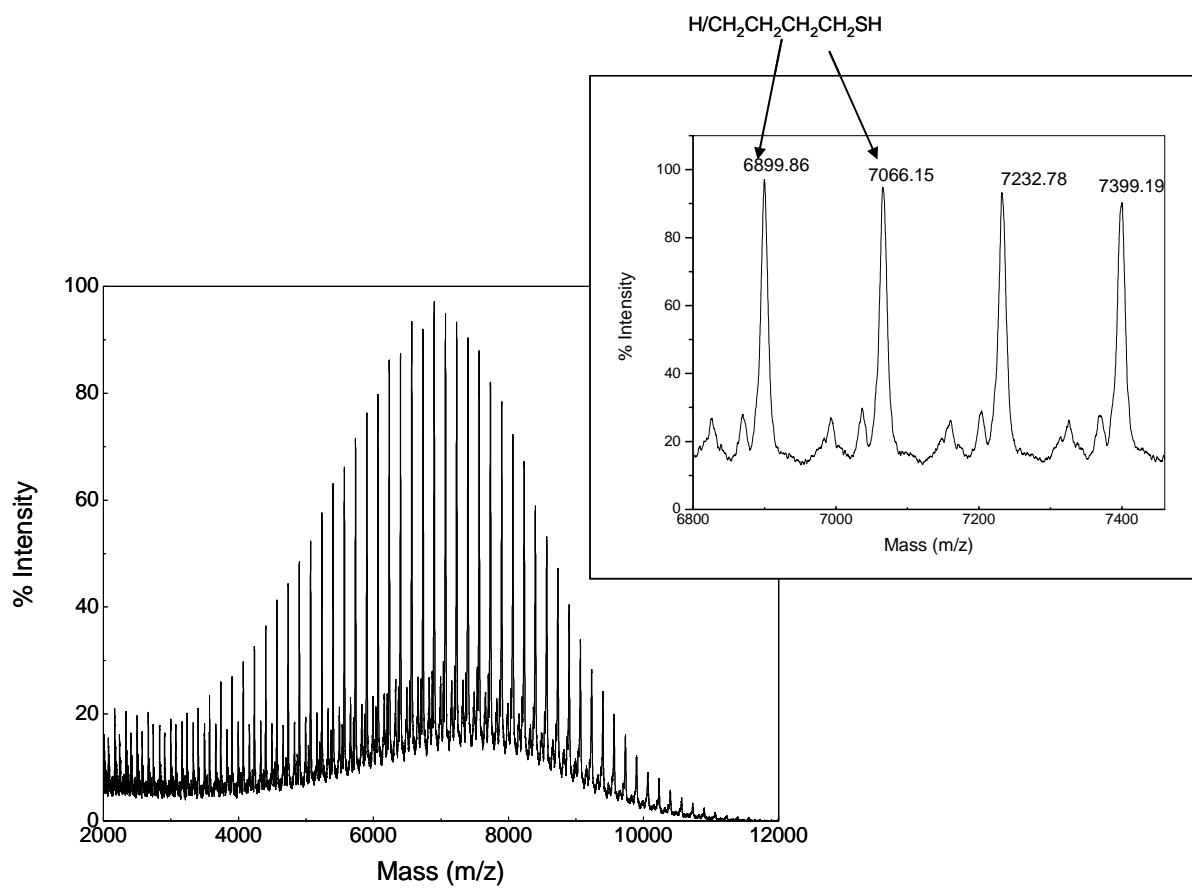


Figure S6. MALDI-TOF MS spectrum of H/propylthiol- terminated poly(3-hexylthiophene)

Photovoltaic Testing

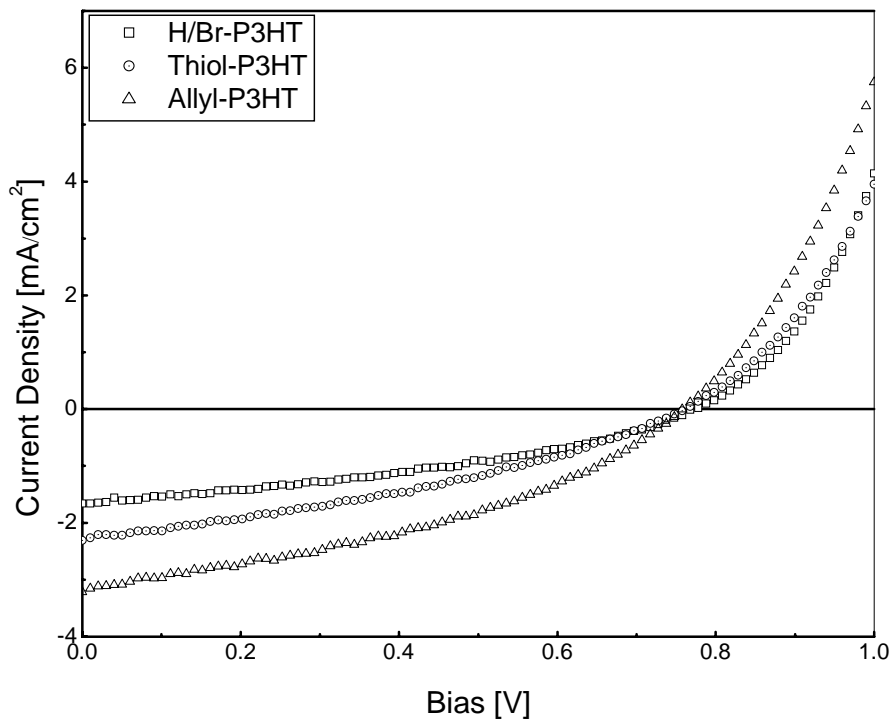


Figure S7. Current-voltage response of P3HT-CdSe blends under AM 1.5 illumination at 100 mW/cm^2 [CdSe] : [P3HT] = 5 : 1 (w/w); samples prepared by slow evaporation from dichlorobenzene/pyridine mixture.

Table 1. Comparison of device performances for CdSe-H/thiol-P3HT blends at different weight ratios.

CdSe: H/thiol-P3HT	Efficiency (%)	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)
5 : 1	0.60	758	2.31	34.7
1.8 : 1	0.25	646	0.94	41.2

AFM Images

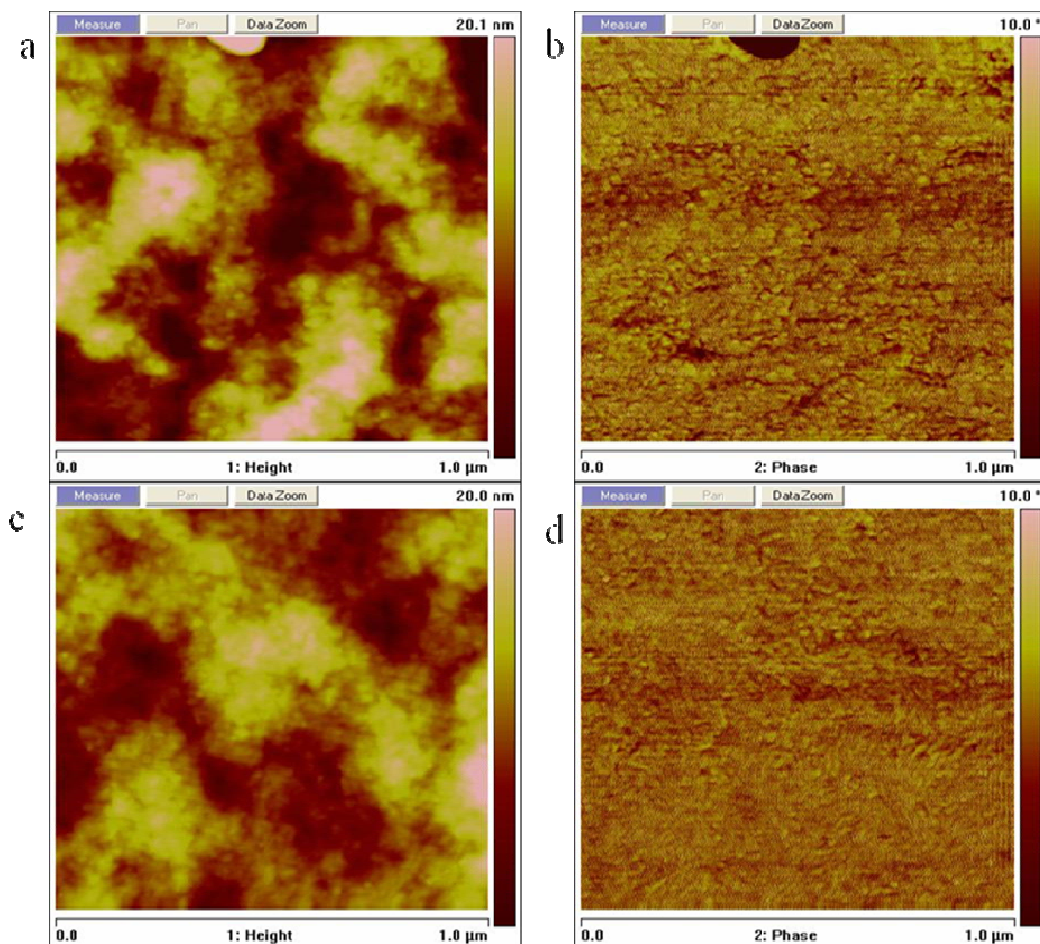


Figure S8. Tapping mode AFM images of blends: a) Height image of CdSe-Br/allyl-P3HT. b) Phase image of CdSe-Br/allyl-P3HT. c) Height image of CdSe-H/thiol-P3HT. d) Phase image of CdSe-H/thiol-P3HT; [CdSe] : [P3HT] = 5 : 1 (w/w); samples prepared by slow evaporation from dichlorobenzene/pyridine mixture.

Optical Properties

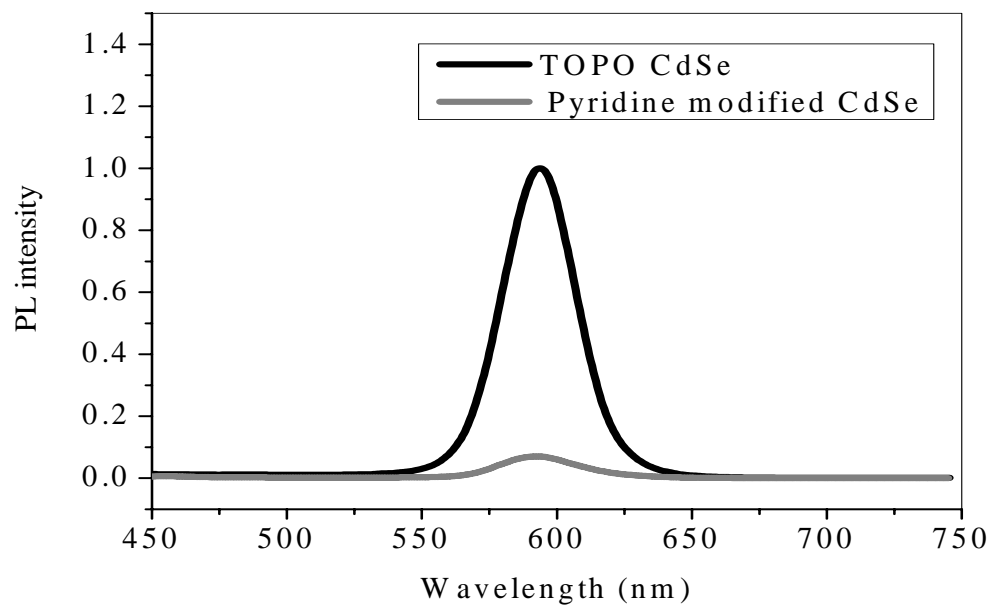
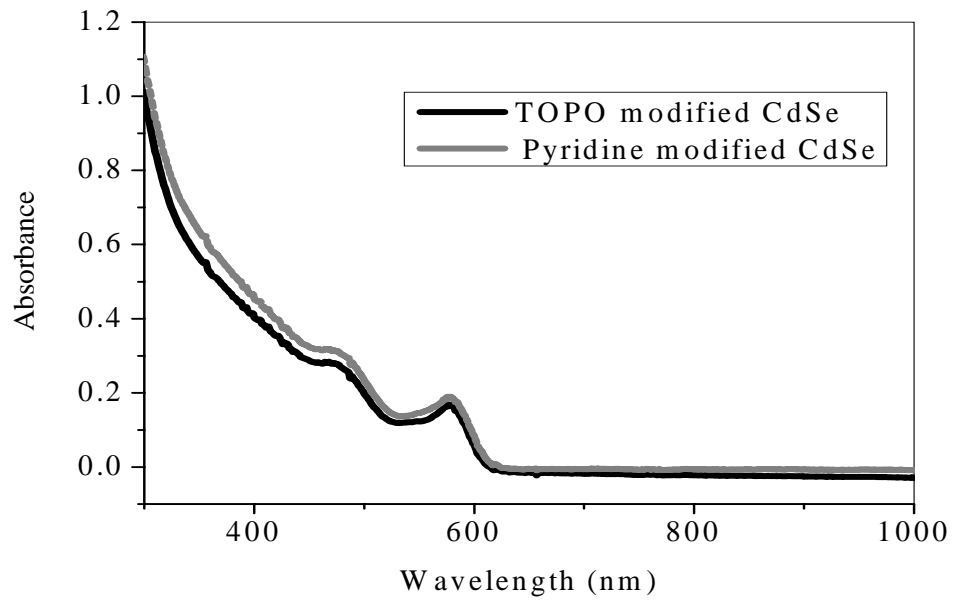


Figure S9. UV-Vis spectra (top) and PL (bottom) for CdSe quantum dots before and after ligand exchange with pyridine.

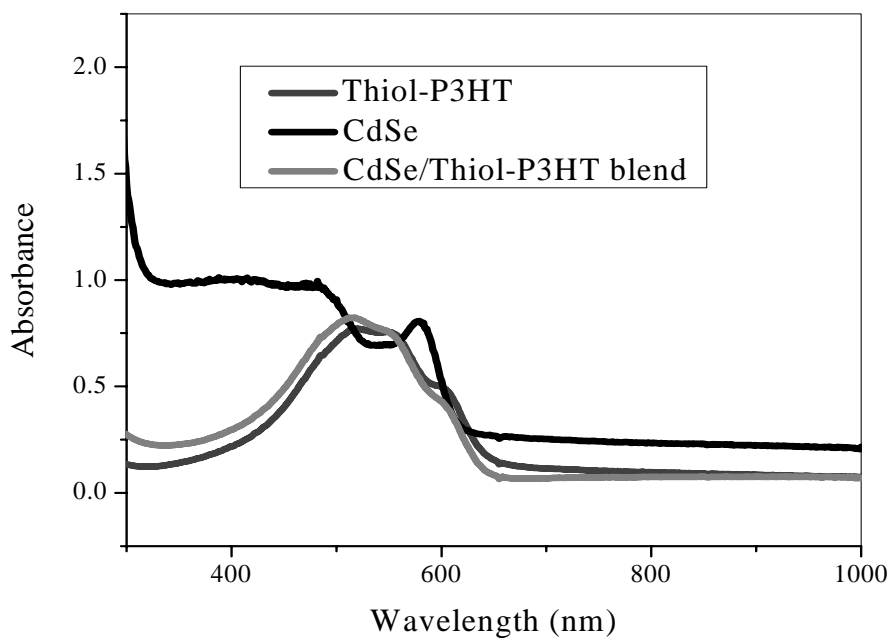


Figure S10. Solid state UV-Vis for pyridine modified CdSe/thiol-P3HT blend. P3HT and CdSe samples were prepared from dichlorobenzene. The blend was prepared in a mixture of dichlorobenzene/pyridine of 95/5 (v/v).

TEM Images

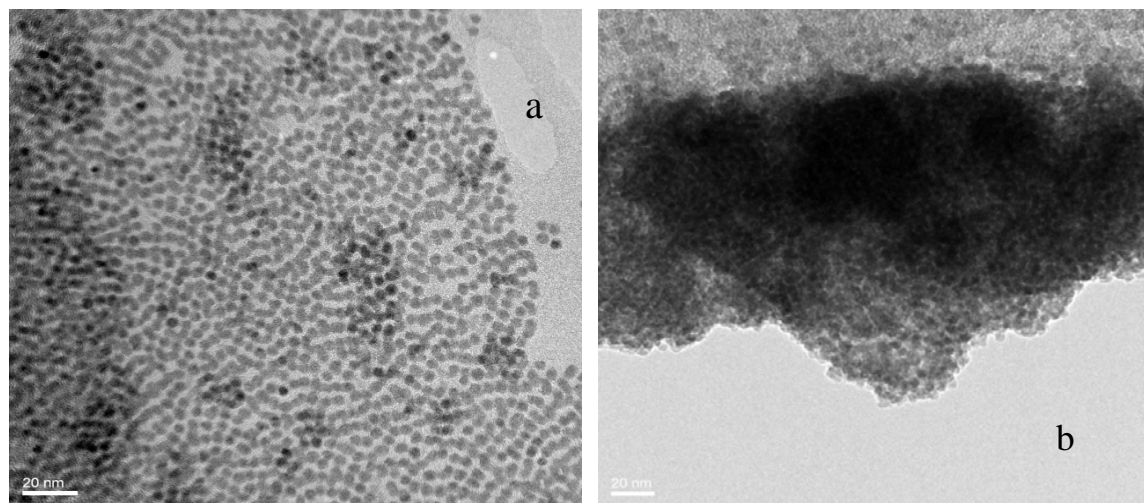


Figure S11. TEM images of a) TOPO capped CdSe. b) CdSe/thiol-P3HT blend.

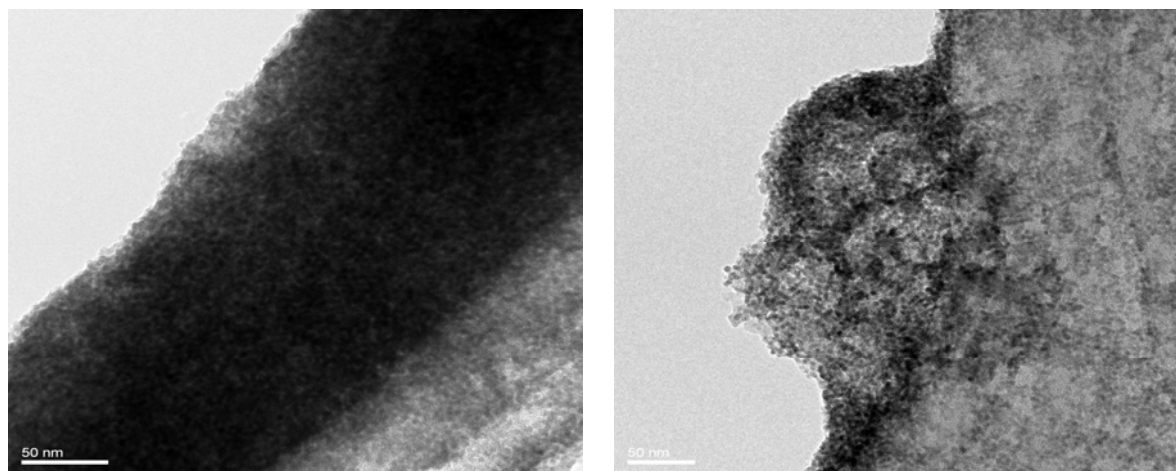


Figure S12. TEM images of CdSe/allyl-P3HT (left) and CdSe/thiol-P3HT blend (right).

References

1. Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, 38 (21), 8649-8656.