

Electronic Supporting Information

**Influence of Functionalized Side Chains of Polythiophene Diblock
Copolymers on the Performance of CdSe Quantum Dot (QD) Hybrid Solar
Cells**

*Chandima Bulumulla,^a Jia Du,^a Katherine E. Washington,^a Ruvanthi N. Kularatne,^a Hien Q.
Nguyen,^a Michael C. Biewer,^a Mihaela C. Stefan^{a,b*}*

*mci07100@utdallas.edu

^aDepartment of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas,
75080

^bDepartment of Bioengineering, University of Texas at Dallas, Richardson, Texas, 75080

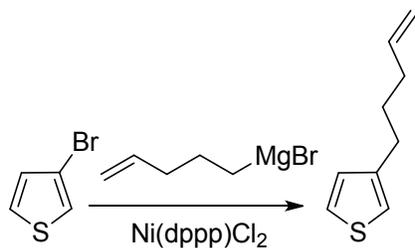
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1. Materials, monomer and polymer synthesis

Materials: All commercial chemicals were purchased from Aldrich and Fisher chemicals and were used without further purification unless otherwise noted. All the reactions were conducted under a nitrogen atmosphere using oven-dried glassware. Tetrahydrofuran (THF) was dried over sodium/benzophenone ketyl and distilled prior to use. 2,5-dibromo-3-hexylthiophene (**M1**), regioregular P3HT (**P1**) and allyl-terminated P3HT (**P2**) were synthesized according to previously published procedures.^{1, 2} Size exclusion chromatography (SEC) data were obtained on a Viscotek VE3580 system equipped with viscoGEL columns (GMHHR-M) connected to a refractive index and UV detectors. HPLC grade THF was used as the eluent with 1 mL/min rate at 30 °C with GPC_{max} as the sample module. Calibration based on polystyrene standards were applied to determine the molecular weights. ¹H NMR spectra were recorded on a 500 MHz Bruker AVANCE IIITM spectrometer using deuterated chloroform as the solvent. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), br. s (broad singlet), m (multiplet). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was carried out using Nicolet 380 FTIR.

3-Pentenylthiophene:

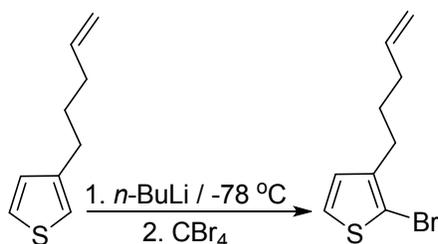


To a clean 100 mL three neck round bottom flask was added magnesium turnings (24.0 mmol, 0.57 g) and dry diethyl ether (40 mL) under N₂. The solution was cooled to 0 °C while adding 5-bromo-1-pentene (23.5 mmol, 2.4 mL) dropwise with a few drops of 1,2-dibromoethane. The ice

bath was removed and gently refluxed for 2 hours. To a separate clean 100 mL three neck round bottom flask was added 3-bromothiophene (20.3 mmol, 1.9 mL), Ni(dppp)Cl₂ (0.19 mmol, 0.10 g) and dry diethyl ether (20 mL) under N₂. Grignard reagent was cannulated into the flask containing the catalyst and refluxed overnight. The reaction was quenched by pouring the contents in the flask to a beaker containing ice. Crude compound was extracted with ether (3×30 mL), washed with water (3×30 mL), brine (50 mL) and dried over anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure and pure compound was afforded by column chromatography with hexane as the eluent (1.43 g, Yield = 47.8 %).

¹H NMR (500 MHz, CDCl₃): δ_H 1.73 (m, 2H), 2.09 (q, 7.1 Hz, 2H), 2.65 (t, 7.7 Hz, 2H), 5.00 (m, 2H), 5.83 (m, 1H), 6.94 (m, 2H), 7.24 (dd, 4.8 Hz and 3 Hz, 1H); EIMS (M⁺) m/z calcd for C₉H₁₂S 152.07, found 152.1

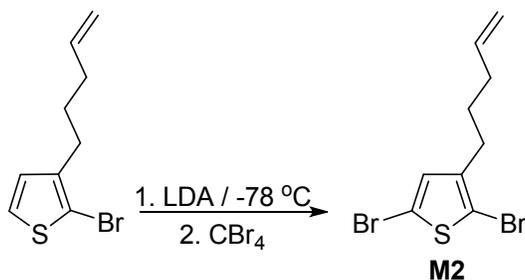
2-Bromo-3-pentenyl thiophene:



To a clean 100 mL three neck round bottom flask was added 3-pentenylthiophene (6.57 mmol, 1.00 g) with dry THF (20 mL) under N₂. The flask was cooled to -78 °C and 2.5 M *n*-BuLi (7 mmol, 2.8 mL) was added dropwise to the solution mixture. The solution was allowed to stir at -78 °C for 1.5 hours and the temperature was raised to -40 °C. At this time, CBr₄ (13.79 mmol, 4.573 g) in THF (10 mL) was added in one portion and stirred for 1 hour at room temperature. Reaction was quenched in ice and the organic layer was extracted with diethyl ether (3×30 mL), washed with DI water (3×30 mL), brine (50 mL) and dried over anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure and the pure compound was obtained by column chromatography with hexane as the eluent (0.83 g, Yield = 54.5 %).

^1H NMR (500 MHz, CDCl_3): δ_{H} 1.68 (m, 2H), 2.07 (q, 7.2 Hz, 2H), 2.56 (t, 7.7 Hz, 2H), 5.00 (m, 2H), 5.80 (m, 1H), 6.81 (s, 1H), 6.88 (d, 1.5 Hz, 1H); EIMS (M^+) m/z calcd for $\text{C}_9\text{H}_{11}\text{BrS}$ 231.15, found 232.0

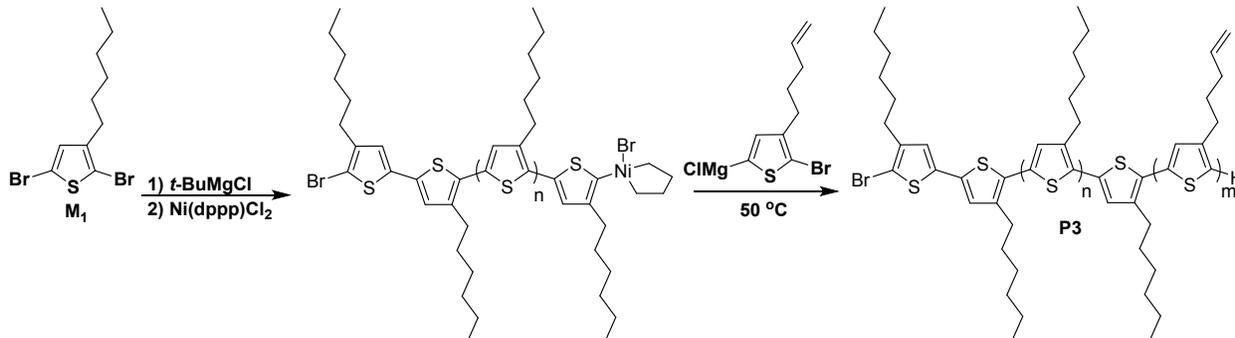
2, 5-Dibromo-3-pentenylthiophene (M2):



An oven dried 100 mL three neck round bottom flask was charged with diisopropylamine (9.48 mmol, 1.33 mL) with THF (30 mL) under N_2 . To the flask was added 2.5 M *n*-BuLi (4.31 mmol, 1.74 mL) to generate LDA at $-78\text{ }^\circ\text{C}$ and stirred for 1 hour. 2-Bromo-3-pentenylthiophene (4.31 mmol, 0.97 g) was added to the pot in one portion and reacted for 1 hour. At this time CBr_4 (4.74 mmol, 1.57 g) in THF (5 mL) was injected to the flask and reacted for 1 hour followed by quenching with ice. Organic layer was extracted with diethyl ether (3×30 mL), washed with DI water (3×30 mL), brine (50 mL) and dried over anhydrous MgSO_4 and filtered. The solvent was removed under reduced pressure and pure compound was obtained by column chromatography with hexane as the eluent (0.83 g, Yield = 54.5 %).

^1H NMR (500 MHz, CDCl_3): δ_{H} 1.65 (m, 2H), 2.07 (q, 7.2 Hz, 2H), 2.52 (t, 7.7 Hz, 2H), 5.00 (m, 2H), 5.80 (m, 1H), 6.78 (s, 1H); EIMS (M^+) m/z calcd for $\text{C}_9\text{H}_{10}\text{Br}_2\text{S}$ 310.05, found 309.9

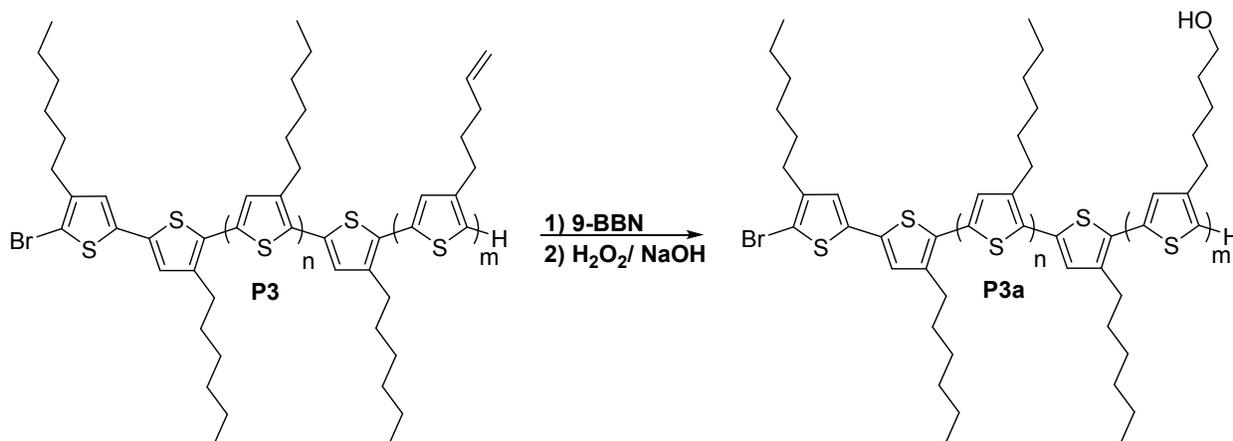
Synthesis of Polymer P3:



To a solution of 2,5-dibromo-3-hexylthiophene (**M1**) (9.12 mmol, 2.97 g) in THF (12.4 mL) (*Flask A*) was added *tert*-butylmagnesium chloride (9.12 mmol, 4.56 mL) under N_2 at room temperature. With an offset of 30 mins, to a solution of 2,5-dibromo-3-pentenylthiophene (**M2**) (4.51 mmol, 1.41 g) in THF (12.4 mL) (*Flask B*) was added *tert*-butylmagnesium chloride (4.51 mmol, 2.25 mL) under N_2 at $40\text{ }^\circ\text{C}$. After 2 hours a sample was withdrawn from flask A and conversion was analyzed using GCMS. To *flask A*, Ni(dppp)Cl_2 (0.147 mmol, 79.5 mg) was quickly added and a sample was withdrawn and crashed in methanol to check the molecular weight. Another sample was withdrawn from *flask B* at this time to check for the conversion using GCMS. The contents of the *flask B* was cannulated to *flask A*. After stirring at $50\text{ }^\circ\text{C}$ for 2 hours, the mixture was cooled to room temperature and precipitated in methanol. The precipitate was filtered and washed with methanol (24 h), hexane (24 h), and extracted with chloroform (3 h) in a Soxhlet apparatus. The chloroform fraction was concentrated and dried to yield the polymer **P3**.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ_{H} 0.91 (t, 6.6Hz, 3H), 1.30–1.47 (m, 6H), 1.70 (m, 2H), 1.81 (m, 2H), 2.20 (m, 2H), 2.80 (t, 7.4 Hz, 2H), 5.04 (m, 2H), 5.88 (m, 1H), 6.98 (s, 1H); SEC: $M_n = 10,094\text{ g mol}^{-1}$, PDI = 1.37.

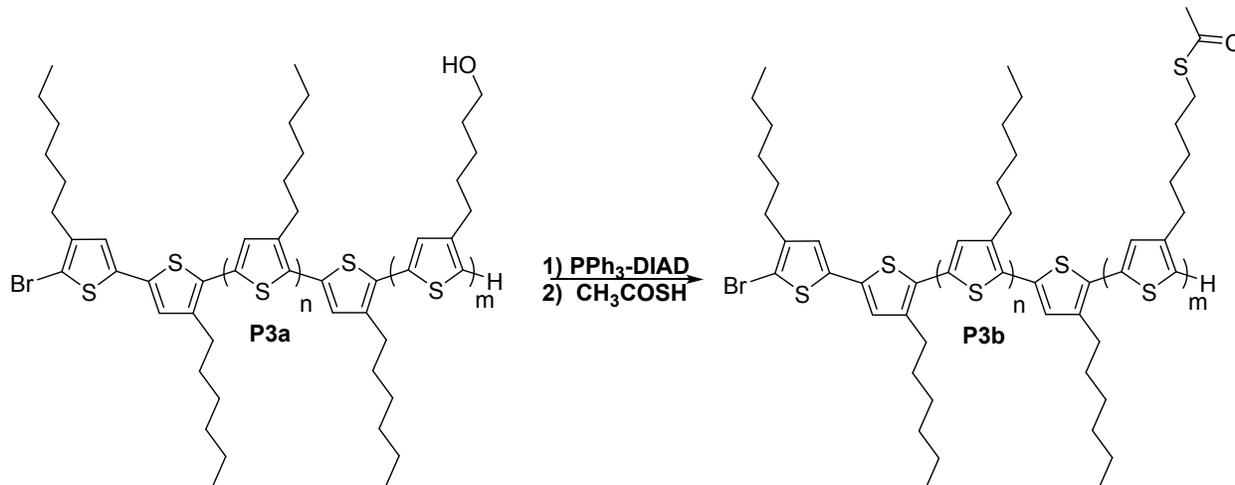
Synthesis of Polymer P3a:



To a solution of polymer **P3** (0.08 mmol, 0.80 g) dissolved in anhydrous THF (50 mL) was added 0.5 M 9-BBN solution (8 mmol, 16 mL) under N₂. The solution was stirred for 12 hours at 40 °C, at which point a 6 M NaOH solution (16 mL) was added to the reaction flask followed by stirring at 40 °C for 15 minutes. Flask was cooled to room temperature and 33% aqueous solution of hydrogen peroxide (16 mL) was added slowly. After heating at 40 °C for 12 hours, polymer was isolated by precipitation with methanol. Precipitate was filtered and washed with methanol (24 h), hexane (24 h), and finally extracted with chloroform (3h) in a Soxhlet apparatus. The chloroform fraction was concentrated and dried to yield the polymer **P3a**.

¹H NMR (500 MHz, CDCl₃): δ_H 0.91 (t, 6.6 Hz, 3H), 1.30–1.47 (m, 10H), 1.70 (m, 4H), 2.80 (t, 7.4 Hz, 4H), 3.67 (br, 2H), 6.98 (s, 2H); SEC: M_n = 10,938 g mol⁻¹, PDI = 1.49.

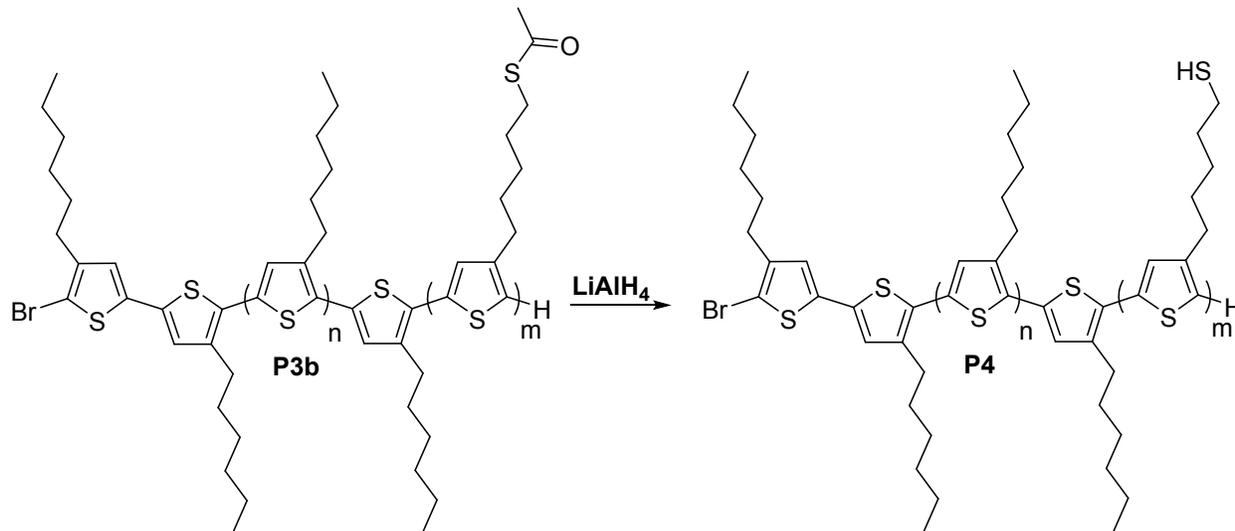
Synthesis of Polymer **P3b**:



To a solution of triphenyl phosphine (7.5 mmol, 1.95 g) in anhydrous THF (25 mL) was added diisopropyl azodicarboxylate (DIAD) (7.5 mmol, 1.5 mL) at -30 °C under N₂. The DIAD-PPh₃ adduct was formed as a pale yellow precipitate after 30 minutes. At this time the flask was removed from the cooling bath and allowed to warm to room temperature. To the flask was dropwisely added a solution of polymer **P3a** (0.075 mmol, 0.75 g) and thiolacetic acid (7.5 mmol, 0.5 mL) in THF (20 mL). After heating at 40 °C for 8 hours, the polymer was isolated by precipitation with methanol. Precipitate was filtered and washed with methanol (24 h), hexane (24 h), and finally extracted with chloroform (3h) in a Soxhlet apparatus. The chloroform fraction was concentrated and dried to yield the polymer **P3b**.

¹H NMR (500 MHz, CDCl₃): δ_H 0.91 (t, 6.6 Hz, 3H), 1.30–1.47 (m, 10H), 1.70 (m, 4H), 2.31 (s, 3H), 2.80 (t, 7.4 Hz, 4H), 2.98 (t, 7.0 Hz, 2H), 6.98 (s, 2H); SEC: M_n = 10,965 g mol⁻¹, PDI = 1.49.

Synthesis of Polymer P4:



To a solution of polymer **P3b** (0.06 mmol, 0.60 g) in anhydrous THF (50 mL) was added LiAlH_4 (6 mmol, 0.22 g) under N_2 . Solution was stirred at 40 °C for 4 hours followed by precipitation in methanol/ HCl (100 mL) mixture. Precipitate was filtered and washed with methanol (24 h), hexane (24 h) and finally extracted with chloroform (3h) in a soxhlet apparatus. Chloroform fraction was concentrated and dried to yield the polymer **P4**.

^1H NMR (500 MHz, CDCl_3): δ_{H} 0.91 (br, 3H), 1.30–1.47 (m, 12H), 1.69 (br, 4H), 2.61 (t, 10 Hz, 2H), 2.80 (br, 4H), 6.98 (s, 2H); SEC: $M_n = 10,147 \text{ g mol}^{-1}$, PDI = 1.49.

2. ^1H NMR spectra of monomers and polymers

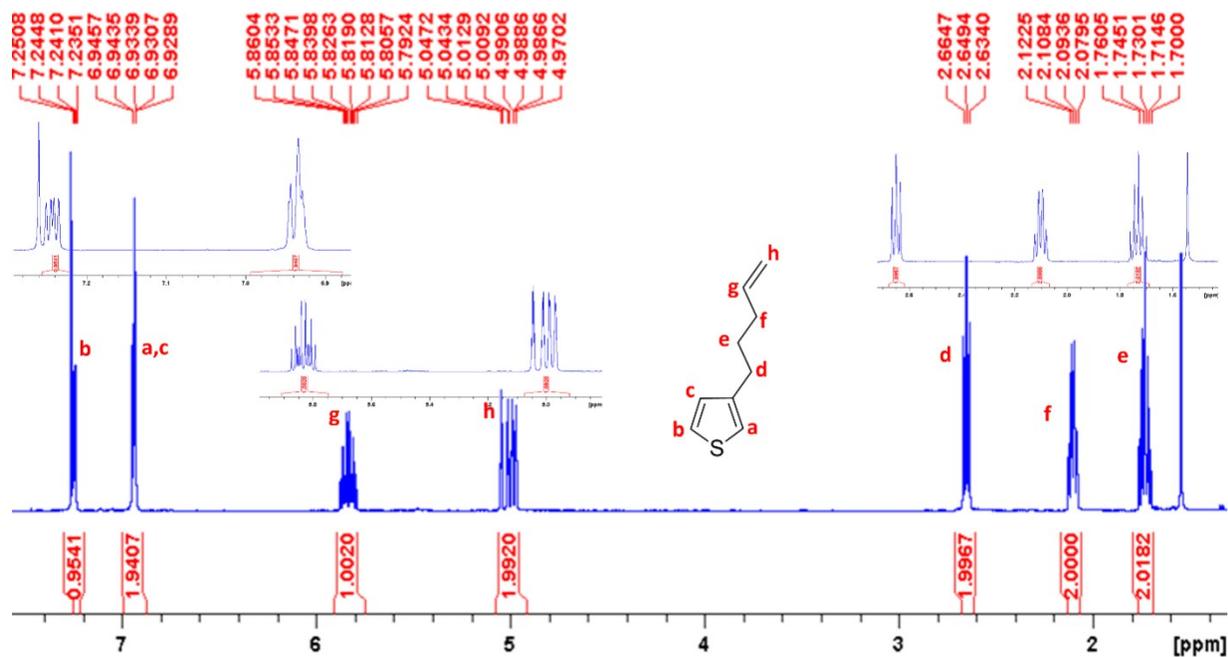


Fig. S1 ^1H NMR of 3-pentenylthiophene

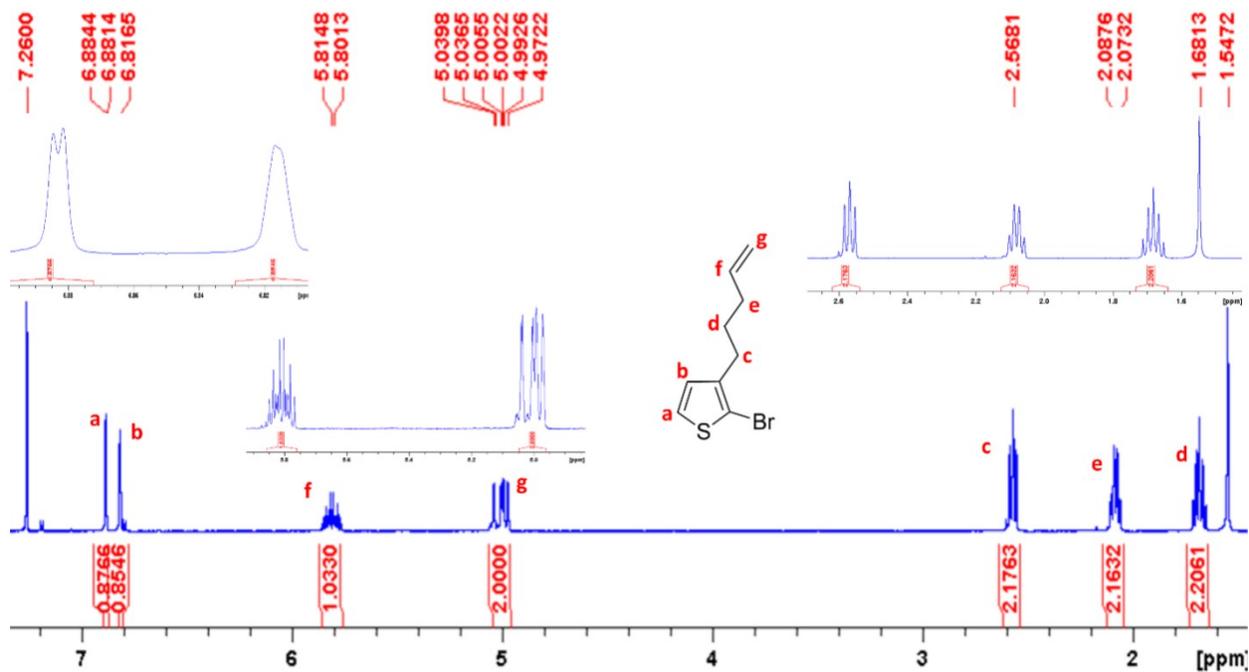


Fig. S2 ^1H NMR of 2-bromo-3-pentenylthiophene

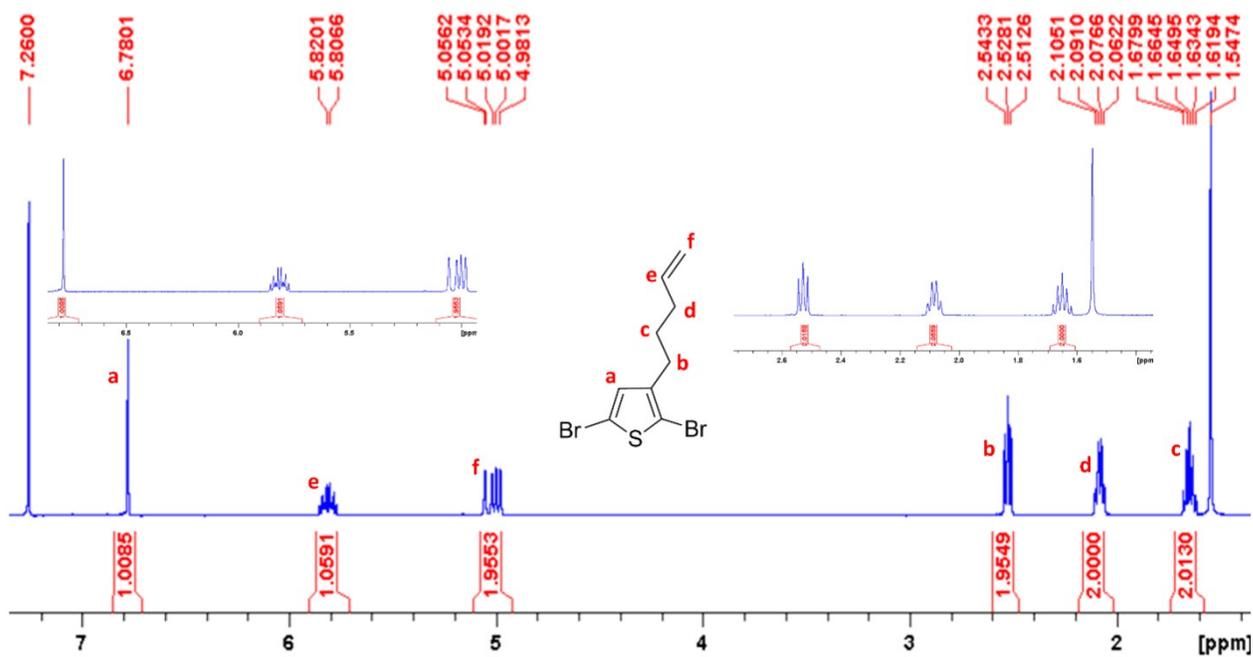


Fig. S3 ¹H NMR of 2,5-dibromo-3-pentenylthiophene (M2)

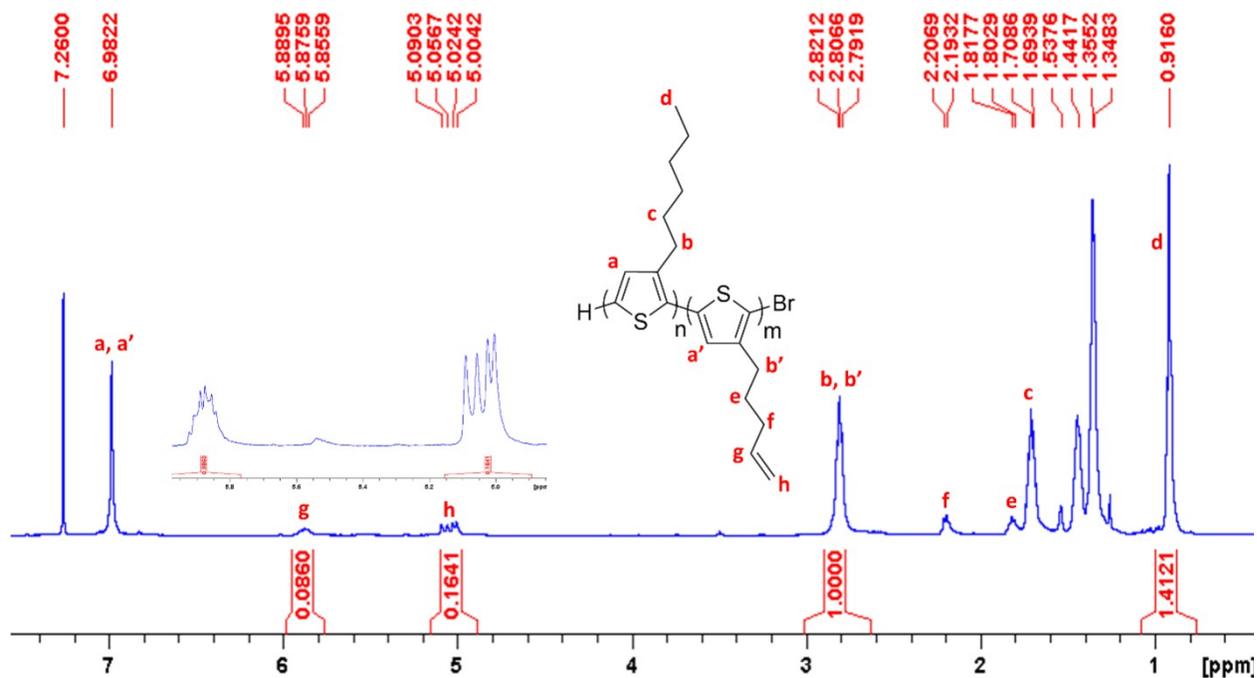


Fig. S4 ¹H NMR of polymer P3

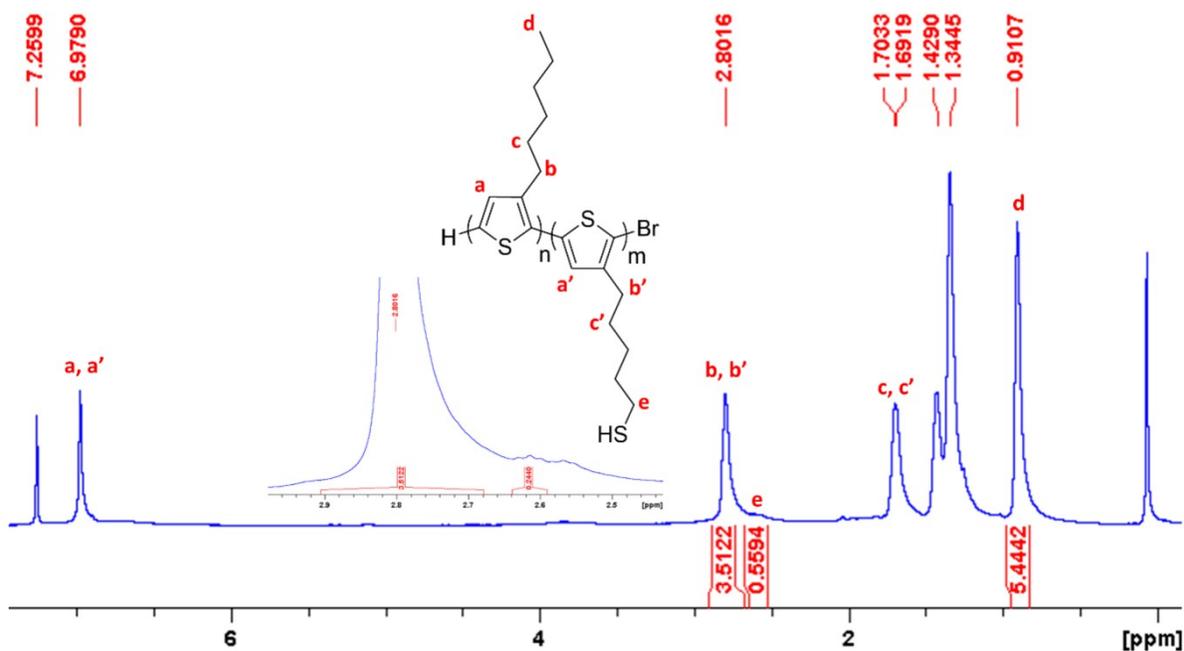


Fig. S7 ^1H NMR of Polymer P4

3. CdSe QD synthesis and colloidal ligand exchange

Nearly monodispersed nanocrystals were synthesized using a previously published procedure with slight modifications.² In a typical reaction, cadmium oxide (1 mmol, 128.4 mg), oleic acid (20 mmol, 5.65 g) and trioctylphosphine oxide (5 mmol, 1.93 g) were combined in a 50 mL three neck round bottom flask and degassed at 150 °C. After 1.5 hours flask was purged with N_2 and heated until an optically clear solution is obtained. The temperature of the clear solution was adjusted to 250 °C and a solution of Se powder (1 mmol, 78.96 mg) in 1.33 mL of trioctylphosphine was swiftly injected to the flask. After 2 mins, the heating mantle was removed and quickly cooled to 150 °C by purging air. At 70 °C, 10 mL of toluene was added to prevent solidification of excess ligands. Nanocrystals were precipitated using methanol and collected by centrifugation followed by washing with methanol more than three times. For the ligand exchange, the precipitated CdSe

QDs were dissolved in a minimum amount of toluene and refluxed with anhydrous pyridine for 24 hours. Pyridine coated CdSe QDs were recovered by precipitation with excess hexane and dried by blowing N₂. For the preparation of the photoactive layer, polymers were blended with nanocrystals with a weight ratio of 1:5 in chlorobenzene/pyridine mixture (95/5 v/v) to have a total concentration of 22.5 mg/ mL.

4. Polymer: CdSe QD hybrid photovoltaic device fabrication

Patterned ITO glasses were cleaned with DI water, acetone, toluene and isopropanol successively for 10 mins and treated in UV-ozone for 30 minutes. A 30 nm thick layer of PEDOT: PSS was spin coated on the ITO glass and annealed at 150 °C for 10 mins in a nitrogen filled glovebox. The photoactive layer was spin coated (1000 RPM, 45 s) onto the PEDOT: PSS coated ITO glass. The blend film was dried for 5 s and dipped in a solution containing 0.01 M EDT in acetonitrile for 30 s followed by rinsing with pure acetonitrile. The devices were annealed at 120 °C for 10 minutes and loaded to high vacuum chamber to deposit a 100 nm thick Al cathode. I-V testings were carried out using a Keithley 2400 interfaced with Labview software. The solar simulator used was an ORIEL 67005 equipped with a Xe lamp calibrated to 100 mW cm⁻² with a Si photodiode purchased from PV measurements Inc.

5. UV-Vis Spectra of polymers

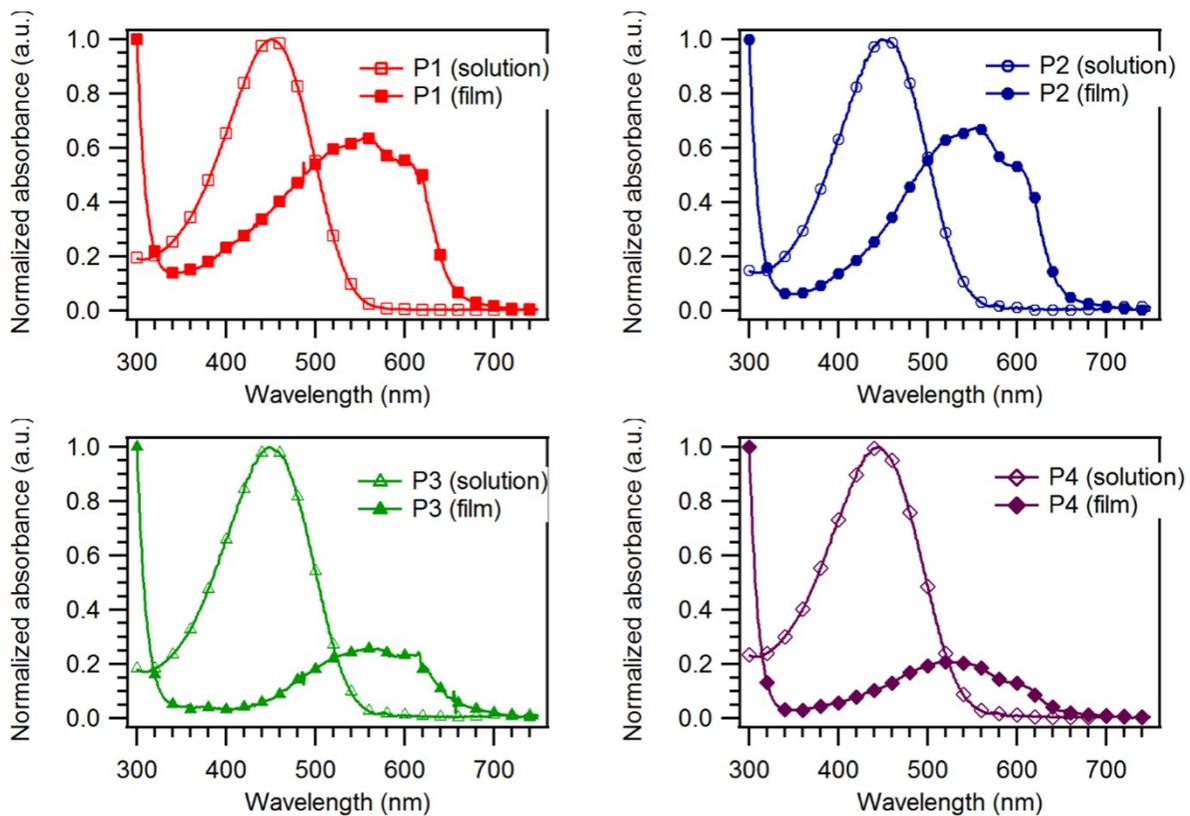


Fig. S8 UV-Vis spectra of polymers in chloroform solutions and films

6. Evidence of ligand exchange on CdSe QDs using pyridine

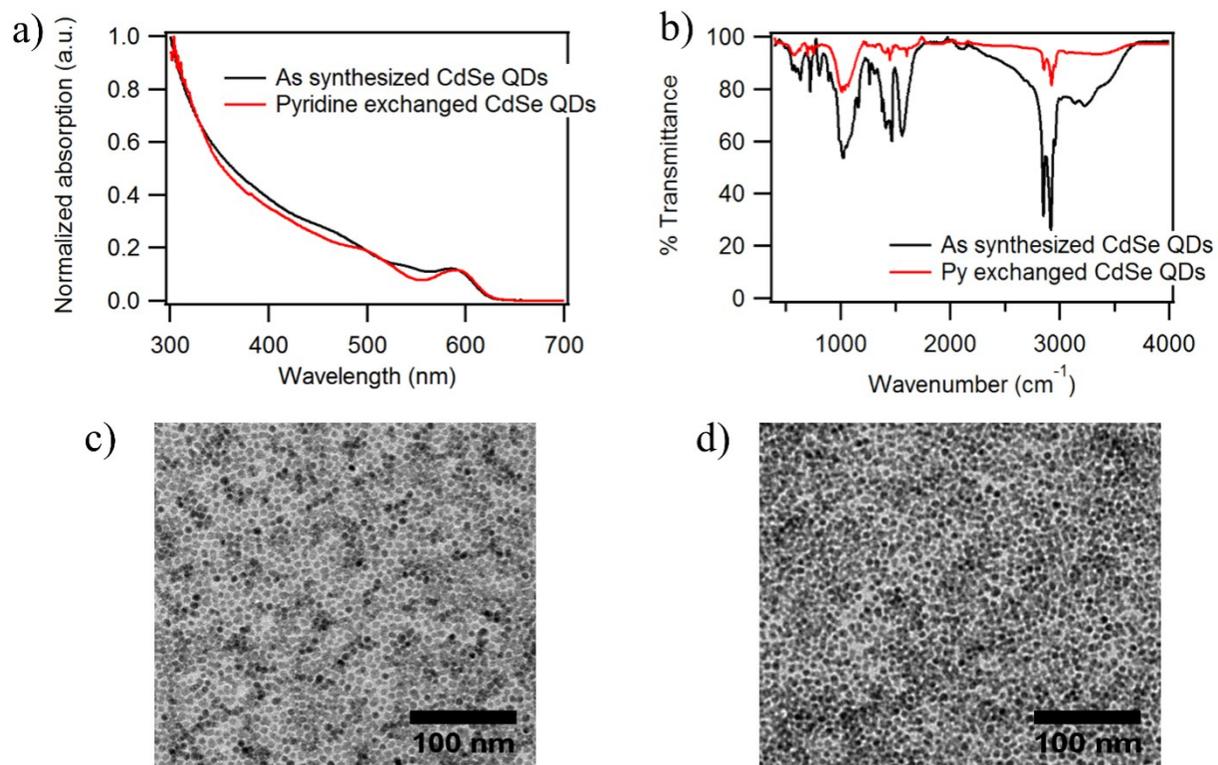


Fig. S9 a) UV-Vis and b) FTIR spectra of CdSe QDs before and after the ligand exchange with pyridine, TEM image of CdSe QDs c) before and d) after ligand exchange with pyridine

7. Cyclic voltammetry data

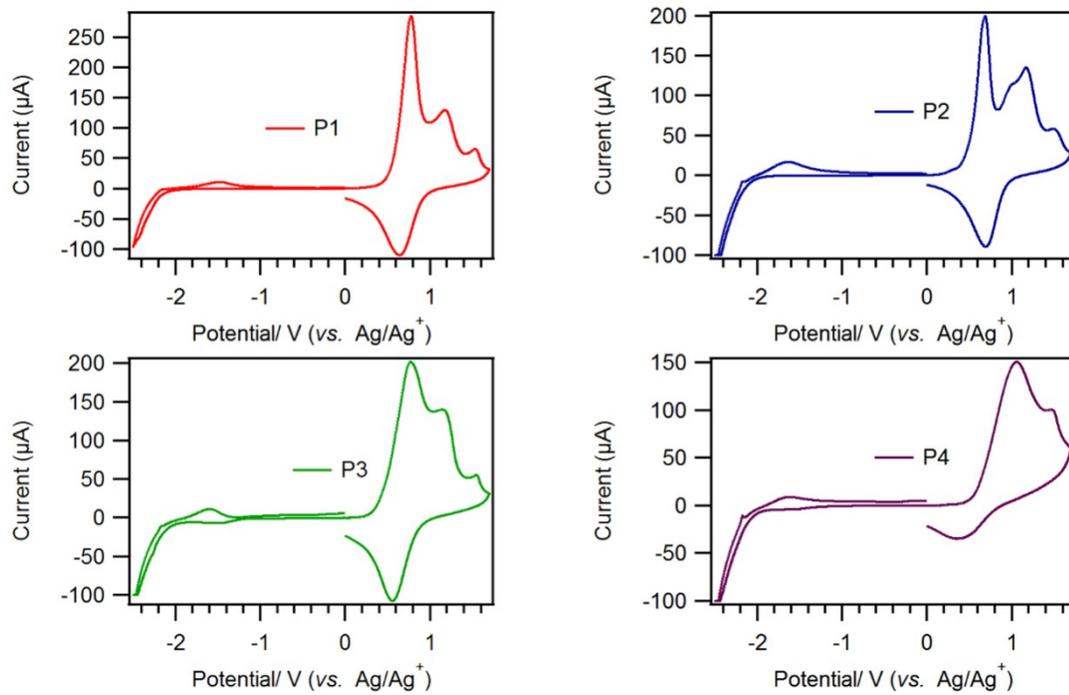


Fig. S10 Cyclic voltammograms of polymer films

8. Photoluminescence quenching data

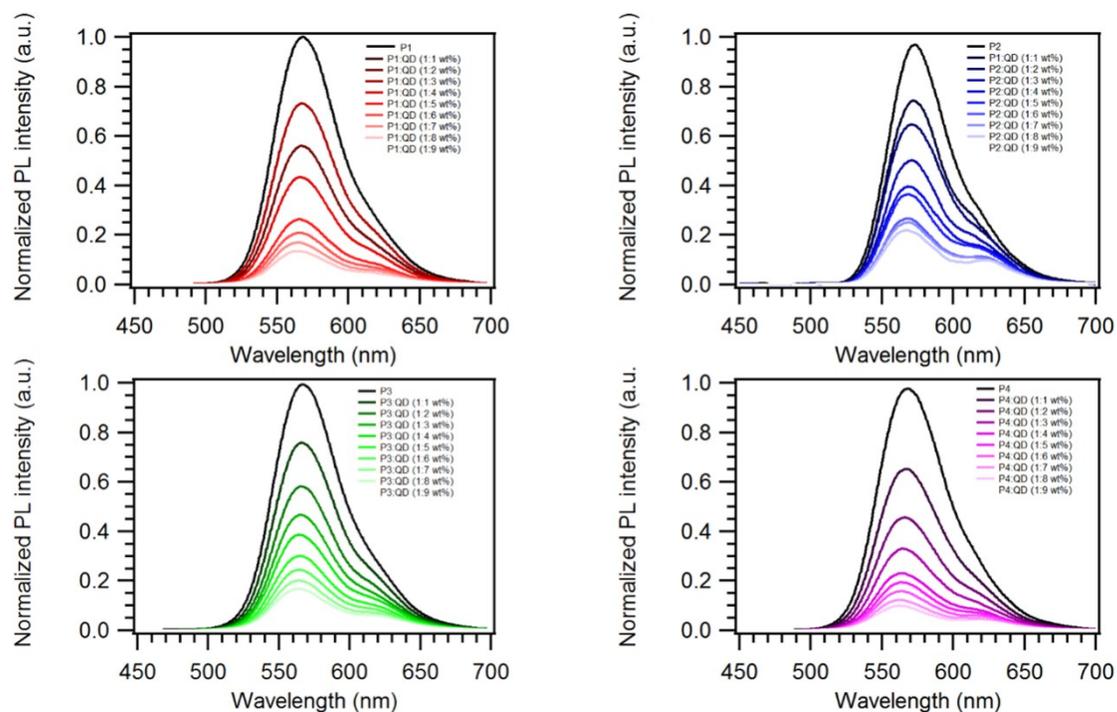


Fig. S11 Photoluminescence quenching data for polymer: CdSe QDs blends in different weight ratios

9. References

1. Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D., *Macromolecules* 2005, **38**, 8649-8656.
2. Palaniappan, K.; Murphy, J. W.; Khanam, N.; Horvath, J.; Alshareef, H.; Quevedo-Lopez, M.; Biewer, M. C.; Park, S. Y.; Kim, M. J.; Gnade, B. E.; Stefan, M. C., *Macromolecules* 2009, **42**, 3845-3848.