Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2014

Supporting Information for:

Semiconducting Liquid Crystalline Block Copolymer Containing Regioregular Poly(3-Hexylthiophene) and Nematic Poly(*n*-Hexyl Isocyanate)

*Mahesh P. Bhatt, Jia Du, Elizabeth A. Rainbolt, Taniya M.S.K. Pathiranage, Peishen Huang, James F. Reuther, Bruce M. Novak, Michael C. Biewer, and Mihaela C. Stefan**

Department of Chemistry, University of Texas at Dallas, Richardson, TX, 75080, USA

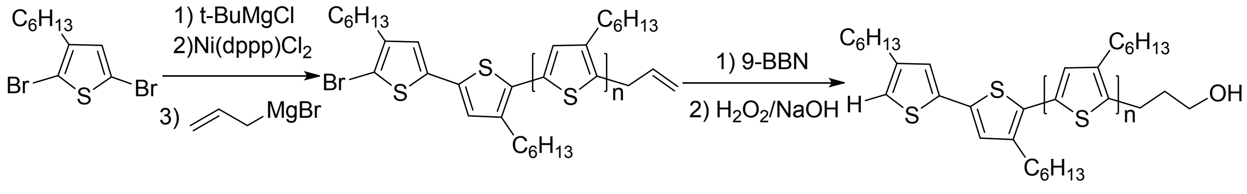
Synthesis of allyl-terminated P3HT

A 250 mL three neck flask with stir bar was flushed with nitrogen for 5 minutes. Tetrahydrofuran (THF) (10 mL) and 2,5-dibromo-3-hexylthiophene (1.63 g) (5.0 mmol) were injected into the flask via syringe. t-Butylmagnesium chloride (2.5 mL), (5.0 mmol) added into the reaction mixture and stirred for 90 minutes. At that point a sample from the reaction mixture was taken and analyzed by GC-MS to monitor the conversion of monomer. Catalyst, Ni(dppp)Cl_2 (0.04 g) (0.07 mmol) was added into the reaction mixture and stirred for 8 minutes. Allyl magnesium bromide (3 mL), (3.0 mmol) was injected into the reaction mixture. The polymer was quenched in methanol and purified by the Soxhlet extraction with methanol, hexane and chloroform. ^{1}H NMR (500 MHz, $CDCl_3$): δH 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.49 (d, 2H), 5.11 (m, 2H), 5.98 (m, 1H), 6.98 (s, 1H), SEC: M_n = 12000 gmol^{-1}; PDI = 1.20.

Synthesis of hydroxypropyl-terminated P3HT

Allyl-terminated P3HT (0.10 g, M_n = 12000 gmol^{-1}) was dissolved in 100 mL of THF under a nitrogen atmosphere. To this solution, 0.5 M of 9-BBN (2 mL, 2 mmol) was added via syringe. The reaction mixture was stirred for 12 h at 40°C. The reaction mixture was cooled to room temperature followed by the addition of a solution of sodium hydroxide (2 mL, 6 M). After 15 min, 2 mL of 33% aqueous solution of H_2O_2 was slowly added to the reaction mixture. After 6 h the polymer was precipitated in methanol and purified by Soxhlet extraction with methanol. The polymer (M_n = 12000gmol^{-1}) was characterized by ^{1}HNMR.

^{1}H NMR (500 MHz, $CDCl_3$): δH 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 1.95 (t, 2H), 2.80 (t, 2H), 3.76 (t, 2H), 6.98 (s, 1H), SEC: M_n = 12000 gmol^{-1}; PDI = 1.20



Scheme S1. Synthesis of hydroxypropyl-terminated P3HT

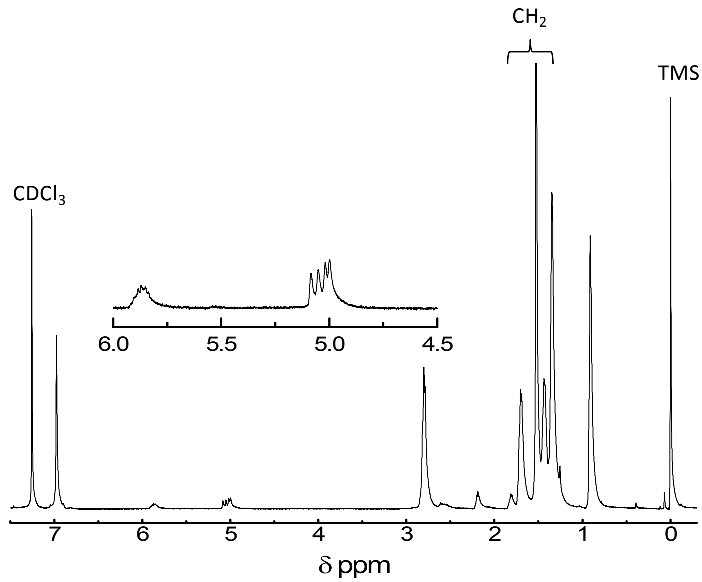


Figure S1. ^{1}H NMR spectrum of allyl-terminated P3HT

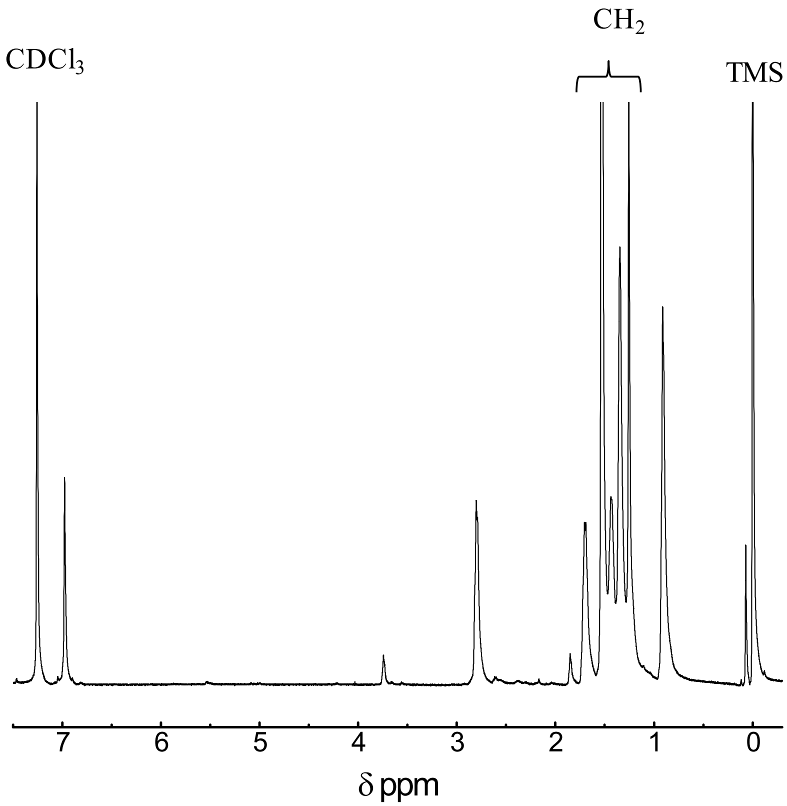


Figure S2. ^{1}H NMR spectrum of hydroxypropyl-terminated P3HT

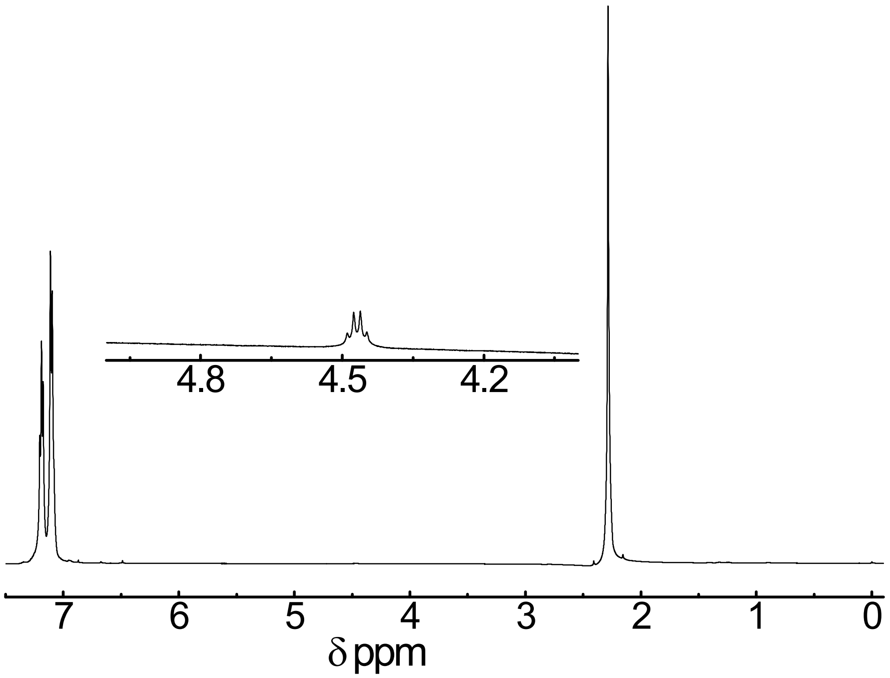


Figure S3. ^{1}H NMR spectrum of titanium propoxide terminated P3HT (before addition of hexyl isocyanate monomer)

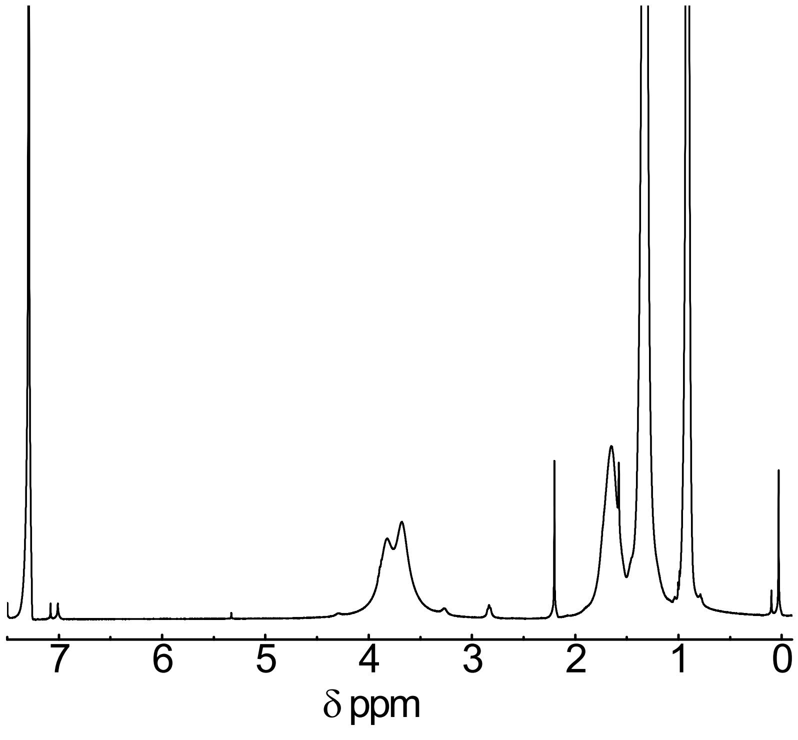


Figure S4. ^{1}H NMR spectrum of P3HT-*b*-PHIC (90 mol% of PHIC determined by ^{1}H NMR, M_n = 21000 gmol^{-1} estimated from SEC with THF eluent and polystyrene calibration)

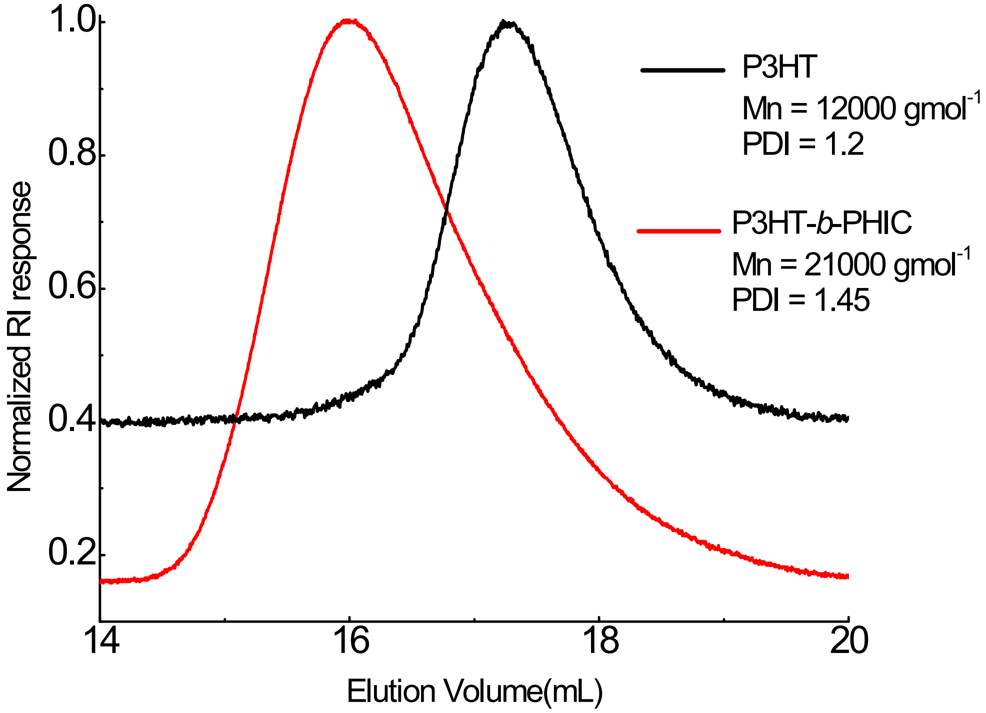
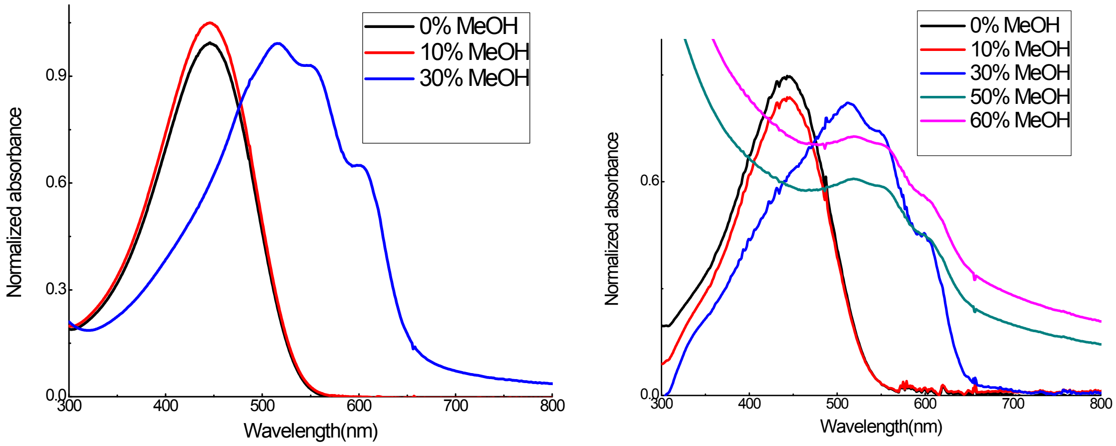


Figure S5. SEC traces of P3HT-*b*-PHIC di block copolymer (red) and precursor P3HT (black) (estimated from SEC with THF eluent and polystyrene calibration)

Synthesis of PHIC using the chiral (R)-BINOL-Ti(IV) diisopropoxide Catalyst

Hexyl isocyanate (1.93 g, 15.2 mmol, Sigma Aldrich, 97%) was used as received and placed in an oven-dried vial in a N_2 atmosphere glove box along with 0.5 mL of dry chloroform. The (R)-BINOL-TI(IV) diisopropoxide catalyst (0.025 g, 56.6 μmol) was added to the stirring solution and the reaction mixture was agitated for 24 hours at room temperature. The crude, gelled product was removed from the glove box and redissolved in about 4 mL of $CHCl_3$. The polymer was then precipitated from MeOH and isolated by vacuum filtration. The product was dried under high vacuum and the precipitation process was repeated once more ensure the removal of residual catalyst. The product was then dried under high vacuum to afford pure product (M_n = 13000 $gmol^{-1}$, PDI = 1.3).



(a) **(b)**

Figure S6. Solvatochromism behavior of (a) P3HT precursor and (b) P3HT-*b*-PHIC in THF/methanol mixtures

Table S1. Solvatochromism data obtained from THF/H_2O

Solvent	**P3HT (λ, nm)**	**P3HT-*b*-PHIC (λ, nm)**
THF	444	448
THF/H_2O (90:10)	501, 549, 605	511, 554, 605
THF/H_2O (70:30)	508, 553, 606	510, 555, 609
THF/H_2O (50:50)	510, 552, 600	519, 555, 610
THF/H_2O (30:70)	N/A	518, 557,610
THF/H_2O (10:90)	N/A	521, 561, 612

Table S2. Solvatochromism data obtained from THF/MeOH

Solvent	P3HT (λ, nm)	P3HT-*b*-PHIC (λ, nm)
THF	444	444
THF/MeOH (90:10)	444	444
THF/ MeOH (70:30)	510, 555, 606	511,555, 604
THF/ MeOH (50:50)	N/A	521, 560, 606
THF/ MeOH (30:70)		523, 558, 616
THF/ MeOH (10:90)	N/A	N/A

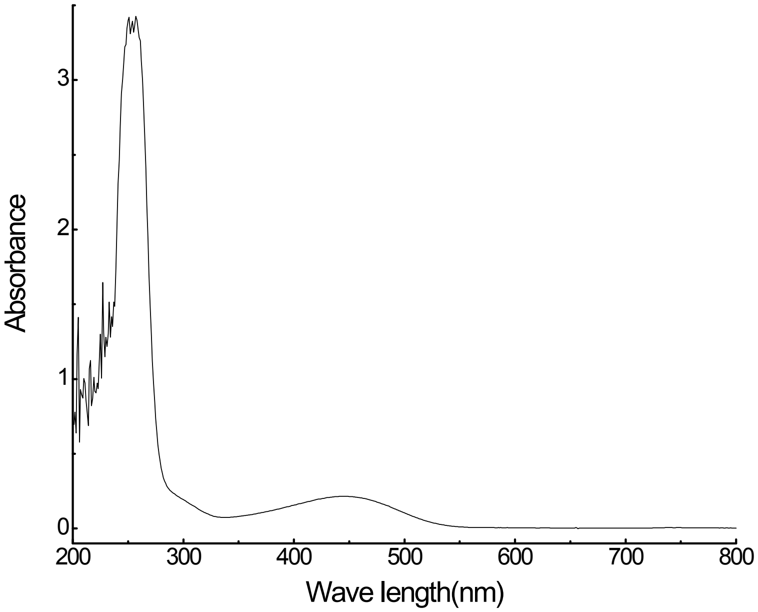


Figure S7. A typical UV-Vis spectrum obtained for the P3HT-*b*-PHIC in THF solution

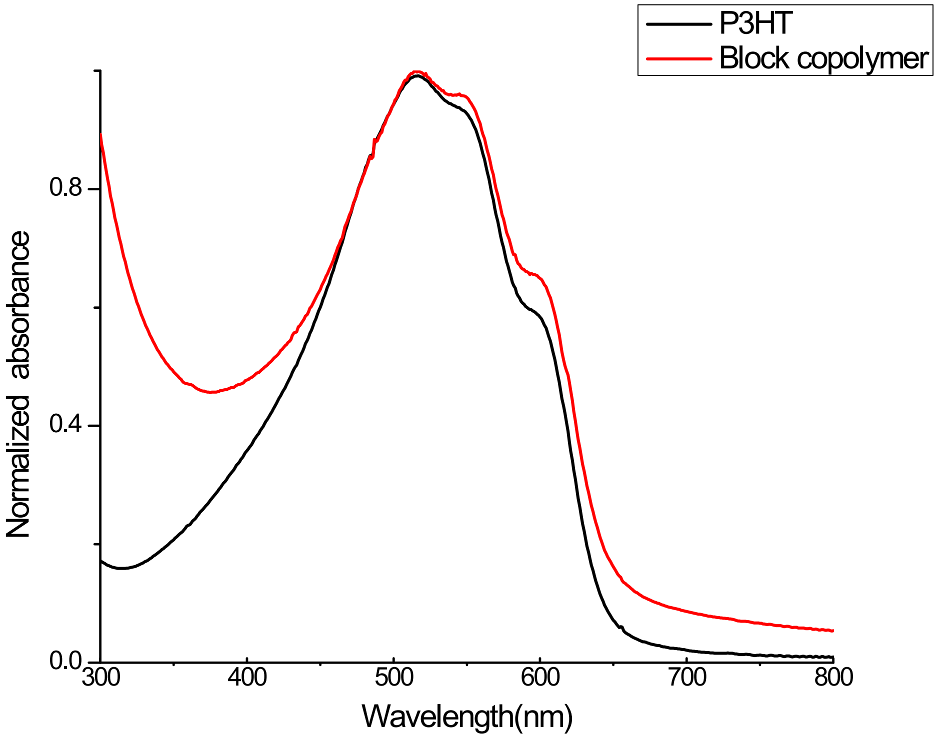


Figure S8. UV-Vis spectra of (a) P3HT precursor and (b) P3HT-*b*-PHIC in thin film deposited on glass slide from THF solution

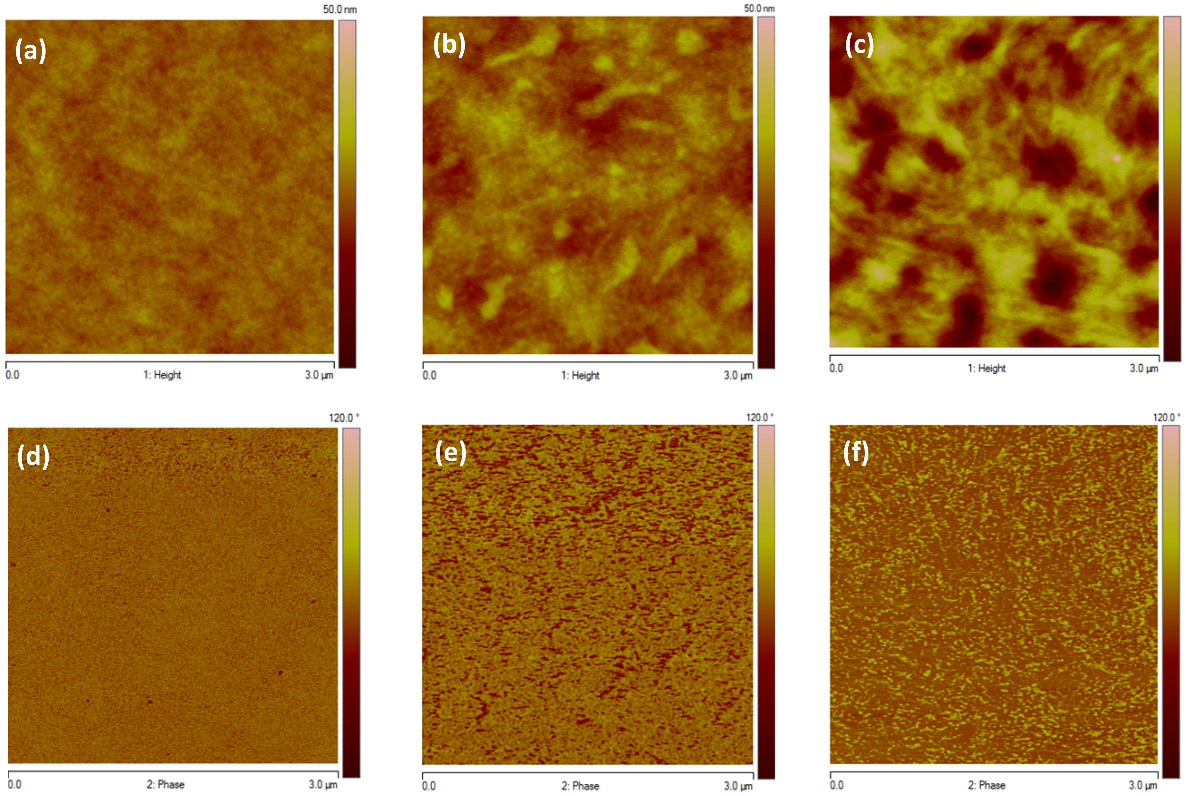


Figure S9. TMAFM images of a 3×3 µm region on solar cell devices. (a) Height and (d) phase images on P3HT:PC$_{61}$BM film; (b) Height and (e) phase images on P3HT:PC$_{61}$BM:15%P3HT-*b*-PHIC film; (c) Height and (f) phase images on P3HT:PC$_{61}$BM:30%P3HT-*b*-PHIC film

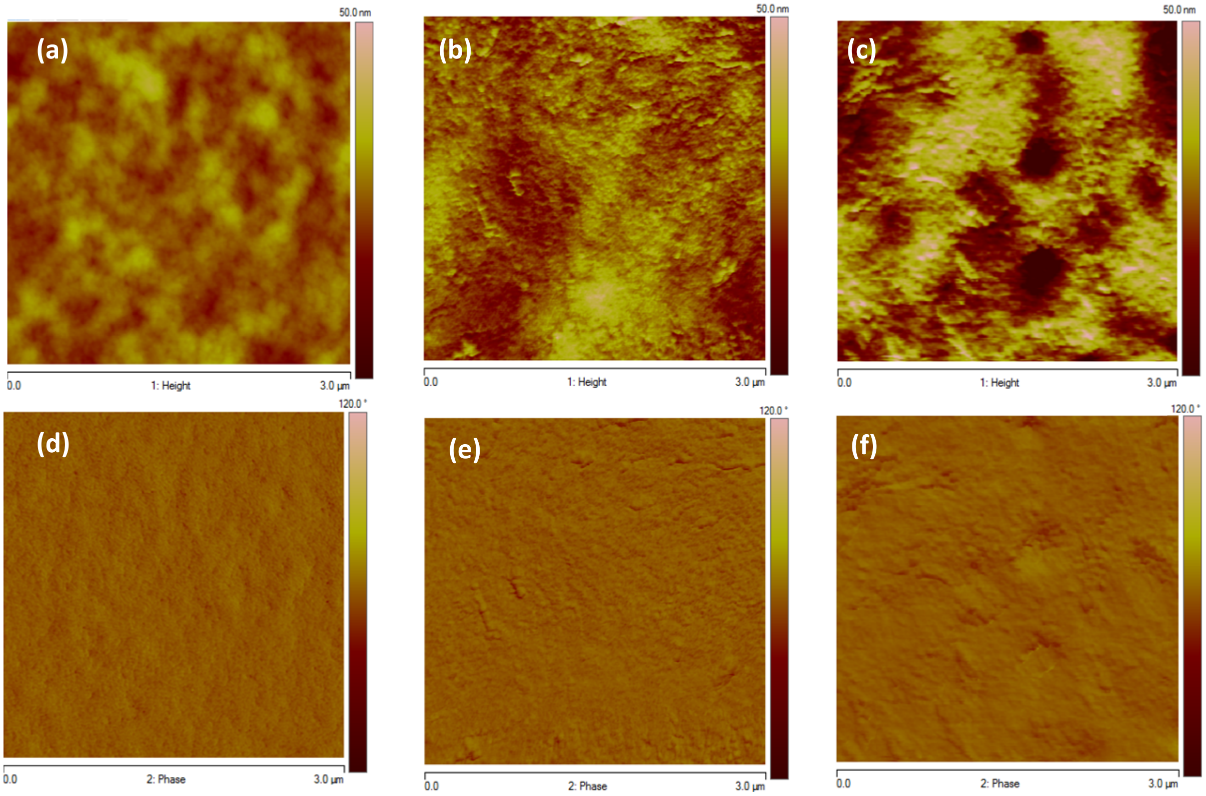


Figure S10. TMAFM images of a 3×3 µm region on solar cell devices. (a) Height and (d) phase images on P3HT:PC$_{71}$BM film; (b) Height and (e) phase images on P3HT:PC$_{71}$BM:15%P3HT-*b*-PHIC film; (c) Height and (f) phase images on P3HT:PC$_{71}$BM:30%P3HT-*b*-PHIC film

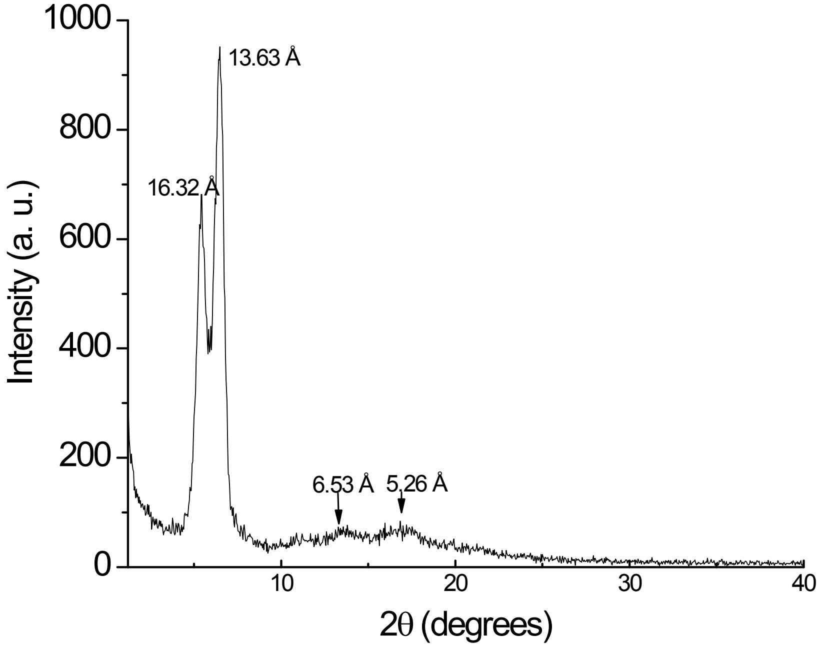


Figure S11. X-Ray diffraction pattern of a PHIC homopolymer (M_n = 13000 gmol^{-1})