Electronic Supplementary Material

Amphiphilic poly(alkylthiophene) block copolymers prepared *via* externally initiated GRIM and click coupling

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Instrumentation

Gel-Permeation Chromatography (GPC) Polydispersities were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10000 Å pore sizes) and a Wyatt Technology Optilab reX RI detector. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 ^{o}C.

Nuclear Magnetic Resonance Spectroscopy (NMR) Hydrogen NMR (^{1}H NMR) spectra were recorded using tetramethylsilane as internal standard in $CDCl_3$ on a 400 MHz Bruker multi-nuclear spectrometer. Samples were placed in 5 mm o.d. tubes with the concentration of approximately 20 mg/ml. In the spectra shown below, only major peaks corresponding to the desired product are identified while those corresponding to minor impurities are not listed. The integrated intensities reflect the measured values and may differ slightly from the expected value due to solvent impurities or scatter in the data. NMR spectra are normalized with respect to aliphatic protons on initiator (see H_a and H_b in Fig. 2).

Atomic Force Microscopy (AFM). AFM images were obtained at Argonne National Laboratory Center for Nanoscale Materials with a nanoscope V scanning probe controller (Digital Instruments, Veeco Metrology Group) in peak force mode in air at room temperature using phosphorus n-doped silicon tips (Model VL300). Solid-state samples were prepared by spin-casting aqueous micellar solutions onto clean silicon surfaces.

Ultraviolet-visible (UV-Vis) absorbance and Luminescence spectrometer. UV-Vis spectra were recorded using a Shimadzu UV-2550 UV-Vis spectrophotometer. BCP and micelle solutions were prepared at ~1mg/mL in DI water and filtered immediately prior to measurement.

Dynamic Light Scattering (DLS). DLS spectra were recording using a Malvern Zen 3600 Zetasizer. Polymer micelle solutions were prepared at ~1 mg/mL in DI water and filtered immediately prior to measurement. A minimum of three backscatter measurements were recorded. The absorbance at 633 nm for polymer samples was measured immediately prior to DLS by UV-VIS.

Grazing-Incidence Wide Angle X-ray scattering (GIWAXS) and small-angle X-ray scattering (GISAXS). GIWAXS and GISAXS measurements were carried out at the X9 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. Beamline X9 operates at an energy of 14 keV and images were collected from a Pilatus 1MF camera (Dectris). Using the GIXSGUI package[1] for Matlab (Mathworks), data are corrected for x-ray polarization, detector sensitivity and geometrical solid-angle. Sample detector distance is 370 mm for wide-angle detector and 3091 mm for small-angle detector. Sample measurement and thermal annealing were carried out under vacuum which is in the range of $2\sim3 \times 10^{-6}$ bar.

Materials. Azide functionalized Poly(ethylene glycol) (mPEG-N_3, 5000g/mol) was purchased from NANOCS and used as received. Isopropyl magnesium chloride with lithium chloride complex (iPrMgCl·LiCl, 1.3M), tetrakis(triphenylphosphine)nickel(0) ($Ni(PPh_3)_4$), 4-chloro-3-methlphenol, 1,3-bis(diphenylphosphino)propane (dppp), tetra-*n*-butylammonium fluoride (TBAF) (1.0 M in THF), 5-hexynoic acid (112.13 g/mol), 4-dimethylaminopyridine (DMAP) (122.17 g/mol), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) , 3-hexylthiophene, 3-bromothiophene, (2-ethylhexyl)magnesium bromide (1.0 M in diethyl ether), 1-bromododecane, ethylene carbonate, imidazole, and copper (I) bromide, and *tert*-butyldimethylsilane were purchased from Sigma-Aldrich and used as received. 2,5-dibromo-3-hexylthiophene, 2,5-dibromo-3-(ethylhexyl)thiophene, and 2,5-dibromo-3-dodecylthiophene were synthesized as previously reported.[2] N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) was purchased from TCI America. All other solvents and reagents were purchased from VWR and used as received unless stated otherwise. Chloroform ($CHCl_3$) was dried over molecular sieves (4Å). Silicon wafers were purchased from El-Cat, washed by sonication in DI water and isopropyl alcohol, and dried before use.

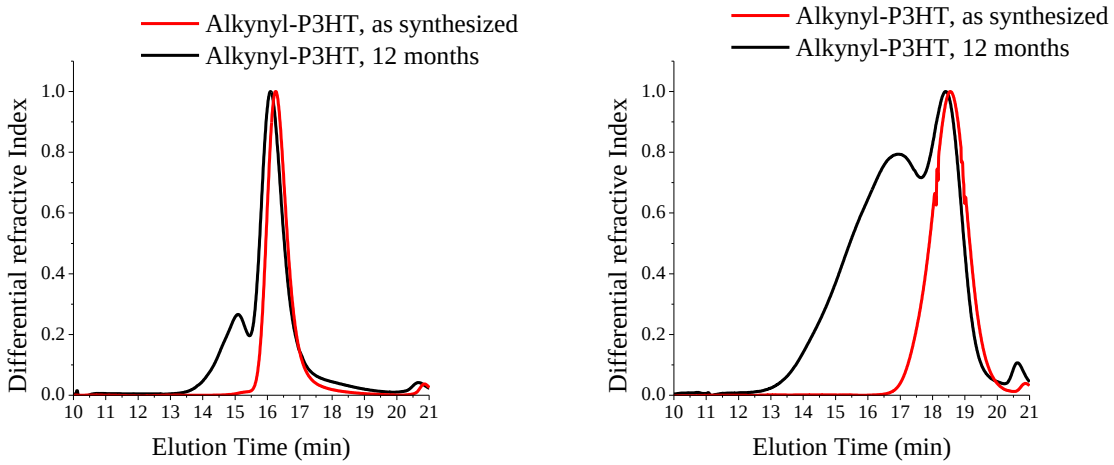

Fig. S1. GPC analysis of alkynyl-P3HT produced using GRIM catalyzed by $Ni(dppp)_2Cl_2$ and quenched with ethynylmagnesium bromide, as previously described[3-4]. Two different molecular weight polymers were analyzed, roughly 15 kg/mol (left) and 5 kg/mol (right). After storage in air under ambient conditions, significant crosslinking of the polymeric product is evident. Both samples show poor solubility in tetrahydrofuran, with poorer solubility for the 15 kg/mol alkynyl-P3HT. The apparent lower degree of crosslinking for the 15 kg/mol sample shown on the left is likely due to the significantly reduced solubility of the crosslinked product, which could not be analyzed by GPC.

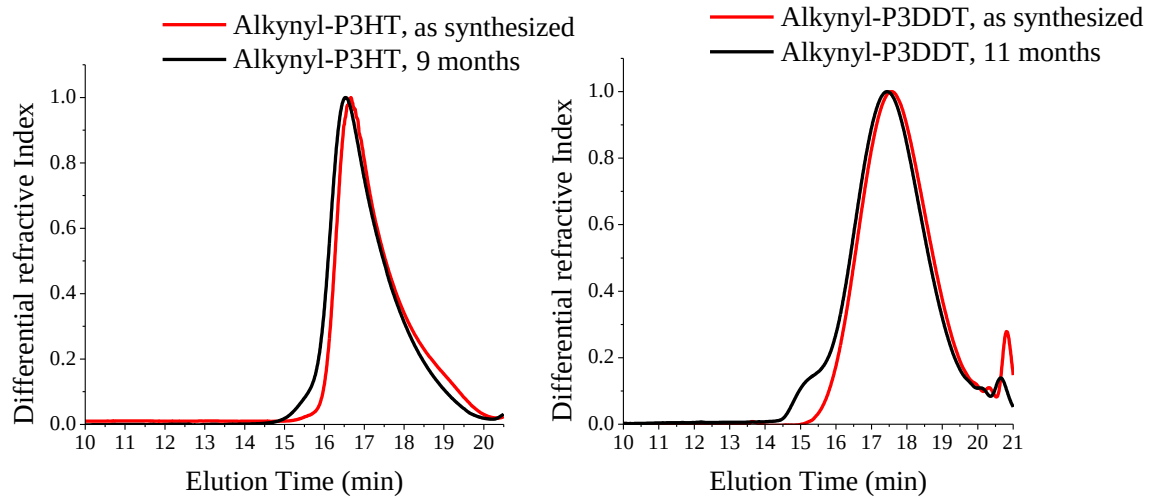

Fig. S2. GPC analysis of alkynyl-P3HT (left) and alkynyl-P3DDT (right) produced using externally initiated GRIM followed by end-group modification, as described in the main text. After storage for up to 11 months in air at ambient conditions, both samples were completely soluble in tetrahydrofuran and exhibited little or no evidence for crosslinking.

2-(4-chloro-3-methylphenoxy)ethanol (1) – The synthetic procedure is a slightly modified from a previous report.[5] 4-chloro-3-methyl phenol (1.80g, 12.6 mmol) and anhydrous K_2CO_3 (3.64g, 26.3 mmol) were dissolved in 40 mL anhydrous N,N-dimethylfomamide (DMF) in a dry 100 mL round-bottom flask. The mixture was stirred at room temperature for 30 minutes before adding ethylene carbonate. The reaction mixture was heated to 100°C and allowed to proceed for 5 h before adding water to quench the reaction and extracting the product with hexanes and ethyl acetate. The organic phase was dried over magnesium sulfate and purified by column chromatography (SiO_2, 40% EtOAc/HX). Yield (recovered): 1.7g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.2 (d, 1.0H, Ar-*H*), 6.8 (d, 1.0H, Ar-*H*), 6.7 (q, 1.0H, Ar-*H*), 4.0 (m, 2.0H, Ar-O-CH_2-C*H*$_2$-OH), 3.9 (m, 2.0H, Ar-O-C*H*$_2$-CH_2-OH), 2.3 (s, 3.0H, Ar-C*H*$_3$), 2.1 (t, 1.0H, Ar-O-CH_2-CH_2-O*H*)

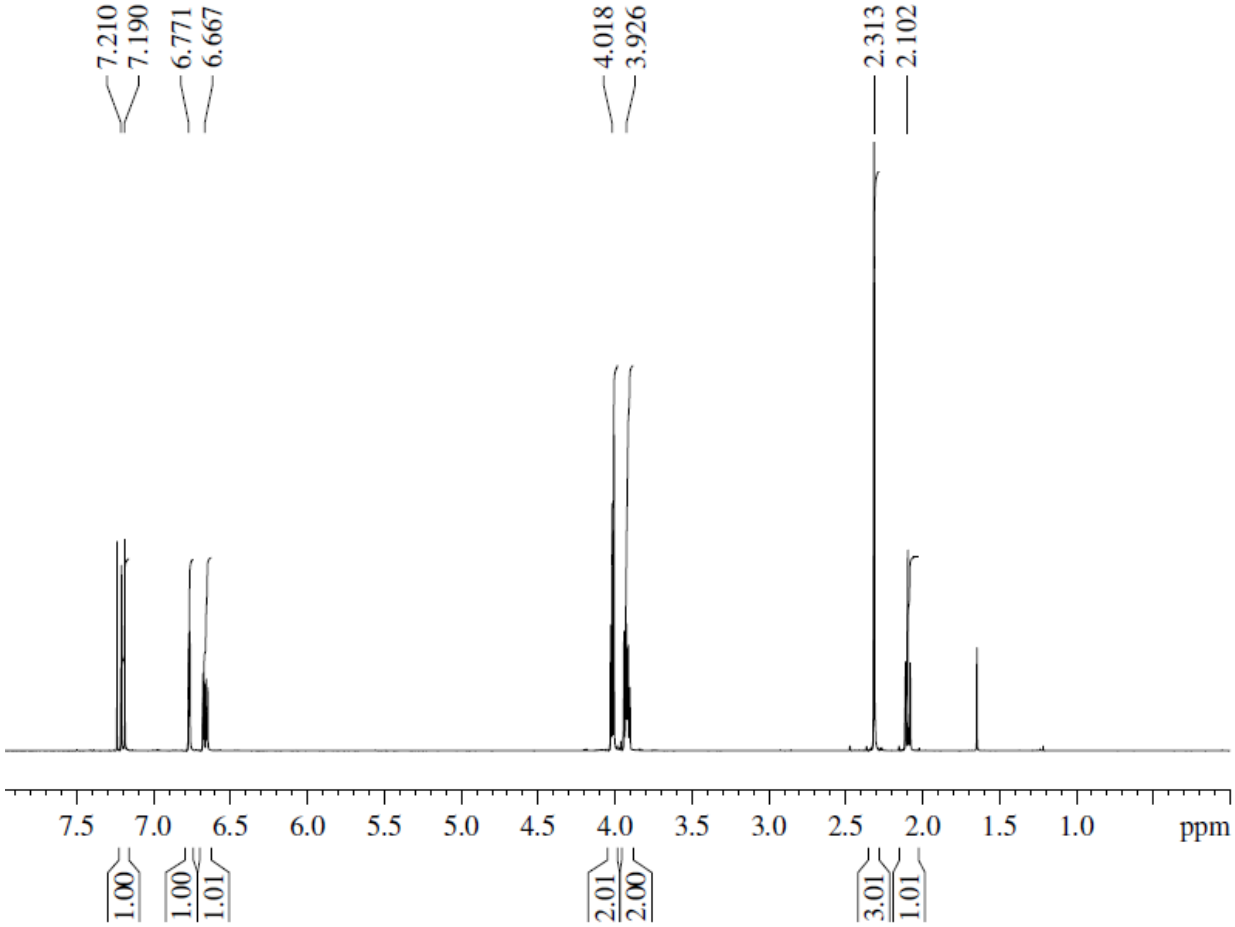

Fig. S3. ^{1}H NMR spectrum of 2-(4-chloro-3-methylphenoxy)ethanol

1-chloro-2-methyl-4-[6-(*t*-butyldimethylsilyloxy)ethoxy]benzene (2) The synthetic procedure is a slightly modified from a previous report.[5] 2-(4-chloro-3-methylphenoxy)ethanol (1.7g, 9.11 mmol) was dissolved in 4mL anhydrous DMF and degassed for 30 minutes by bubbling N_2 through the solution. In a separate flask, *tert*-butyldimethylsilane (2.92g, 19.3 mmol) was dissolved in 5mL DMF and degassed for 30 minutes by bubbling N_2 through the solution. *tert*-butyldimethylsilane was added to the solution of 2-(4-chloro-3-methylphenoxy)ethanol in DMF *via* cannula, and the solution was cooled to 0°C. Next, imidazole (2.62g, 38.6 mmol) was added to the reaction solution, and the reaction was stirred at room temperature. After 5h, the reaction was quenched by the addition of 3mL water, and the product was extracted with hexanes. The organic phase was dried over $MgSO_4$ before isolating the product via column chromatography (SiO_2, 5% EtOAc/HX). Yield (recovered): 2.0g, 74%.^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.2 (d, 1.0H, Ar-*H*), 6.8 (d, 0.98H, Ar-*H*), 6.7 (q, 0.98H, Ar-*H*), 4.0 (m, 4.0H, Ar-O-C*H*$_2$-C*H*$_2$-), 2.3 (s, 2.99H, Ar-C*H*$_3$), 0.9 (m, 9.1H, -Si-C(C*H*$_3$)$_3$), 0.1 (t, 6.1H, -Si-(C*H*$_3$)$_2$)

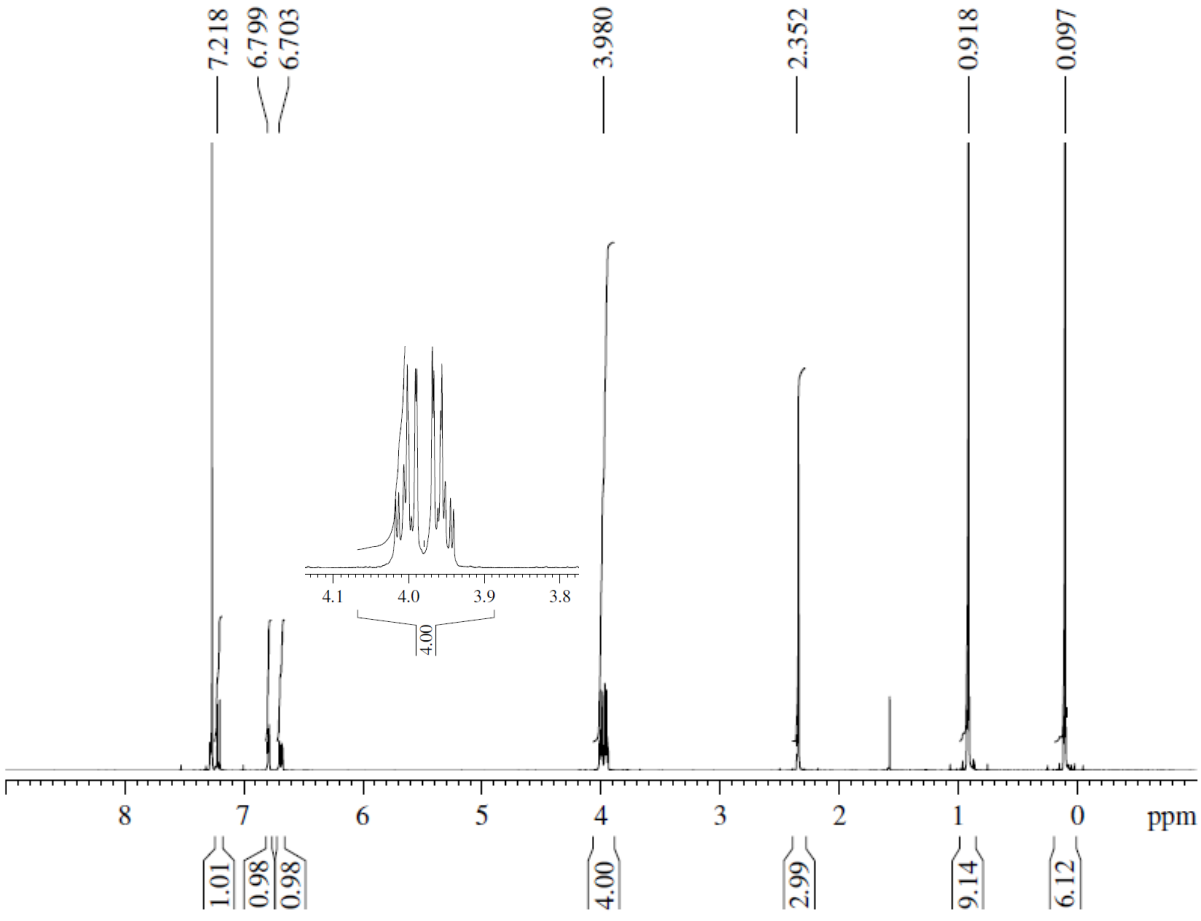

Fig. S4. ^{1}H NMR of 1-chloro-2-methyl-4-[6-(*t*-butyldimethylsilyloxy)ethoxy]benzene

Chloro-]2-methyl-4-[6-*t*-butyldimethylsilyloxy)ethoxy]phenyl] bis(triphenylphosphine) nickel(II) (3). The synthetic procedure is a slightly modified from a previous report.[6] In a nitrogen-filled glovebox, $Ni(PPh_3)_4$ (54 mg, 0.049 mmol) was dissolved in 1mL anhydrous tetrahydrofuran (THF). 1-chloro-2-methyl-4-[6-(*t*-butyldimethylsilyloxy)ethoxy]benzene (100 mg, 0.332 mmol) was added and the solution was allowed to stir overnight, at least 16 h. An aliquot of the reaction solution was removed, dried, and redissolved in toluene for ^{31}P NMR analysis.

^{31}P NMR (400 MHz, C_7H_8, ppm): δ 21.1

Chloro-]2-methyl-4-[6-*t*-butyldimethylsilyloxy)ethoxy]phenyl] 1,3-bis(diphenylphosphino)propane nickel(II) (4). 1,3-bis(diphenylphosphino)propane (80 mg, 0.192 mmol) was dissolved in 1 mL THF and added to the crude reaction solution of **(3)**, and the reaction mixture was stirred at room temperature for 2h. An aliquot of the reaction solution was removed, dried, and redissolved in toluene for ^{31}P NMR analysis. After reacting for 2 h, the crude reaction solution was used to initiate the polymerization of P3AT, as described below.

^{31}P NMR (400 MHz, C_7H_8, ppm): δ 12.1, -4.4, -14.5

General procedure for the preparation of hydroxyl-poly(3-alkylthiophene) (P3AT-OH) – All P3AT-OH were prepared using a similar procedure. In a representative procedure, 2,5-dibromo-3-hexylthiophene (1.91g, 5.86 mmol) was dissolved in anhydrous THF (4.5 mL) in a 100 mL round-bottom flask, and the solution was stirred at 0 ^{o}C for 15 minutes. A solution of isopropyl magnesium chloride with LiCl (1.3 M) in THF (4.51 mL, 5.86 mmol) was added, and the mixture was stirred for 2 hours at 0 ^{o}C. Next, 40 mL of THF was added to the reaction flask followed by the crude reaction solution containing Chloro-[2-methyl-4-[6-*t*-butyldimethylsilyloxy)ethoxy]phenyl] 1,3-bis(diphenylphosphino)propane nickel(II) (0.049 mmol, 2mL). The solution was stirred for an hour and a half before quenching with 5M HCl (2 mL, 10 mmol). TBAF (2mL, 2 mmol) was then added to the reaction flask to remove the silane protecting group, and the reaction mixture was stirred overnight. The final mixture was collected by precipitation in 300 mL of chilled methanol and filtering. The filtered product was washed with acetone and hexanes and dried under vacuum. For P3EHT-OH, the final reaction mixture was concentrated under reduced pressure, washed with water and methanol, and the solid product was collected directly from the flask using a spatula before drying under vacuum.

P3HT-OH ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.0 (s, 114H, Ar-*H*), 4.1 (t, 2.0H, Ar-O-CH_2-C*H*$_2$-OH), 4.0 (m, 2.0H, Ar-O-C*H*$_2$-CH_2-OH), 2.8 (t, 214H, Ar-C*H*$_2$-), 2.49 (s, 4.5H, Ar-C*H*$_3$), 1.7 (m, 260H, Ar-CH_2-C*H*$_2$-), 1.2 - 1.5 (m, 698H, Ar-CH_2-CH_2-(C*H*$_2$)$_3$-CH_3) , 0.9 (t, 347H, Ar-$(CH_2)_5$-C*H*$_3$)

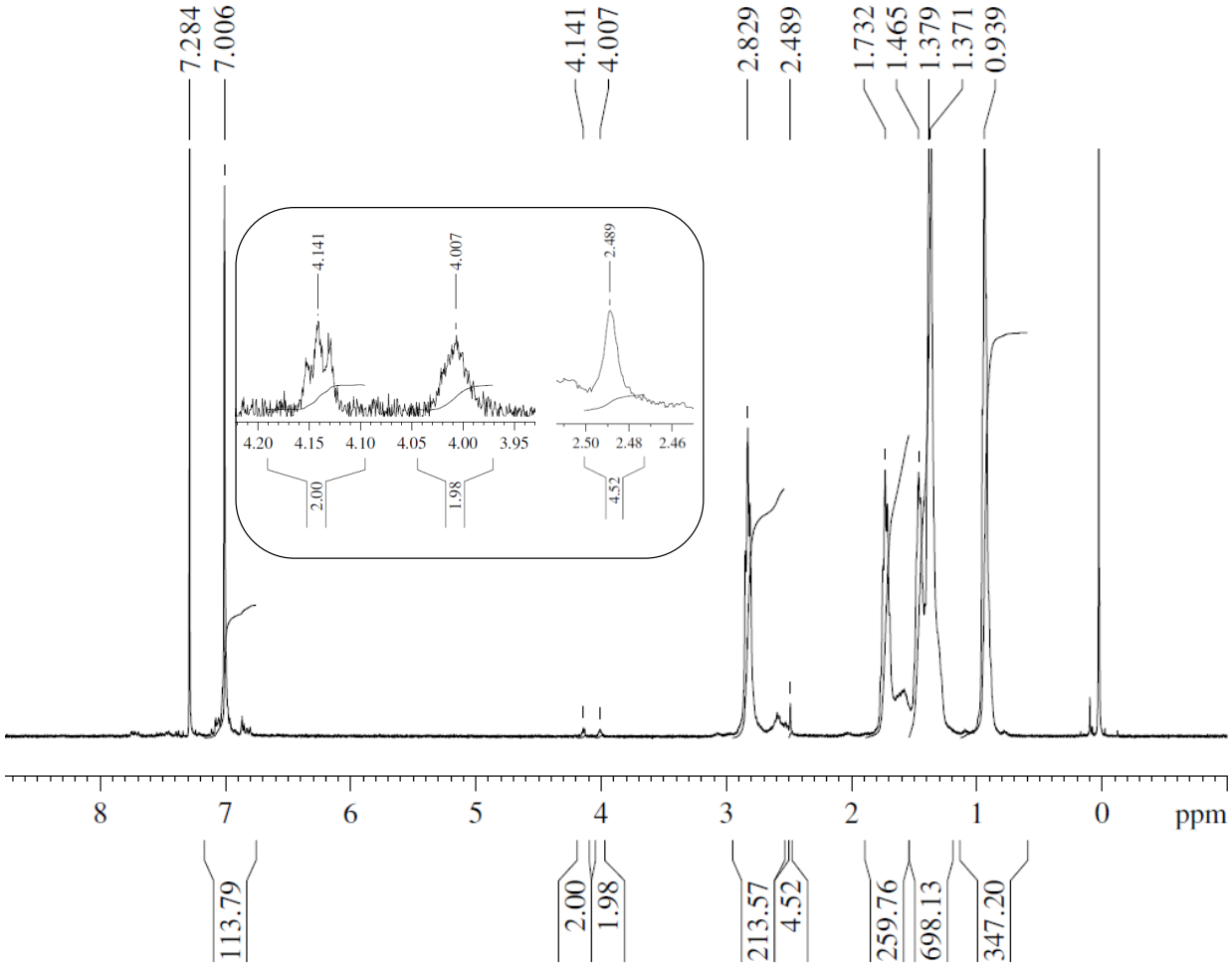

Fig. S5. ^{1}H NMR of P3HT-OH. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup.

P3DDT-OH ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.0 (s, 88H, Ar-*H*), 4.1 (t,1.4H, Ar-O-CH_2-CH_2-OH), 3.98 (t, 2.0H, Ar-O-CH_2-CH_2-OH), 2.8 (m, 175H, Ar-CH_2-), 2.45 (s, Ar-CH_3), 1.7 (m, 152H, Ar-CH_2-CH_2-), 1.2 - 1.5 (m, 1763H, Ar-CH_2-CH_2-$(CH_2)_9$-CH_3), 0.9 (t, 294H, Ar-$(CH_2)_{11}$-CH_3)

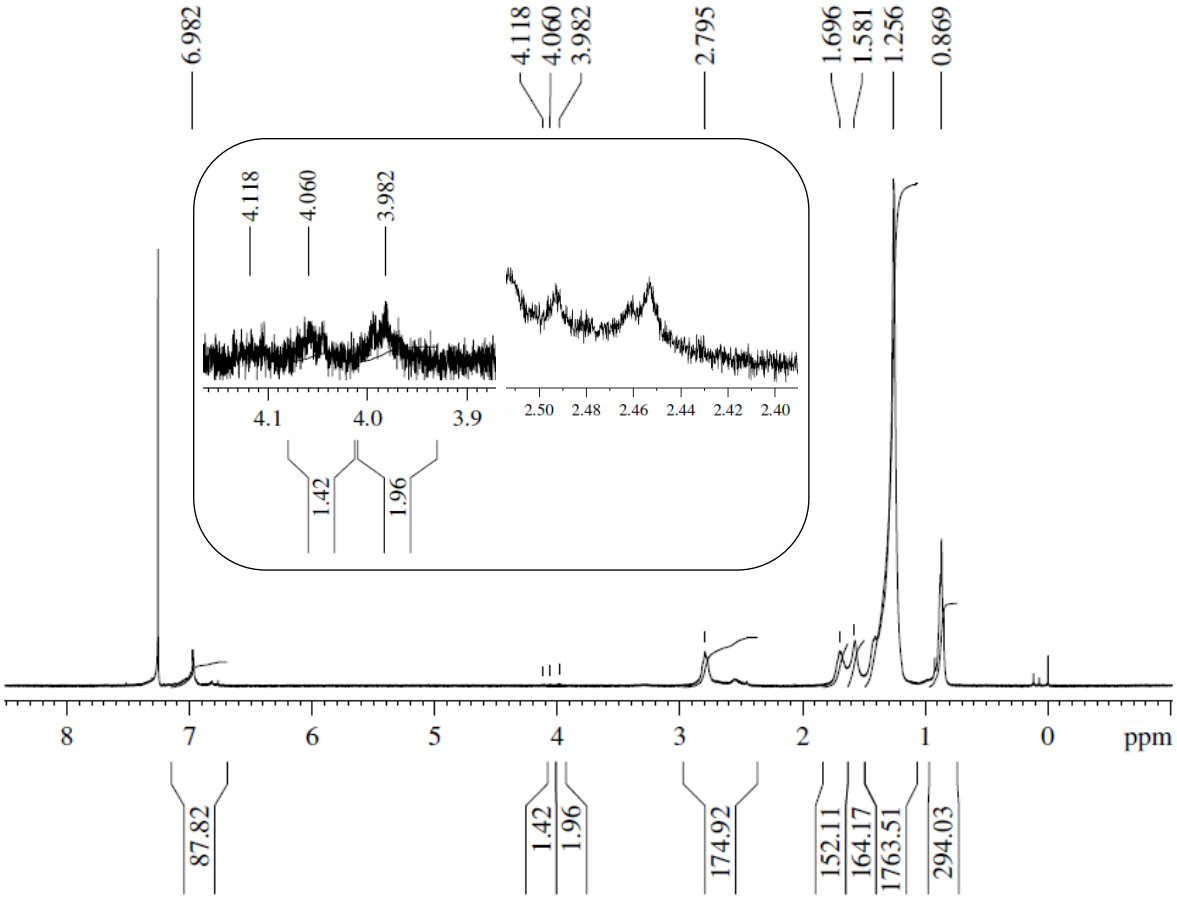

Fig. S6. ^{1}H NMR of P3DDT-OH. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup.

P3EHT-OH ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.9 (s, 88H, Ar-*H*), 4.1 (t, 2.0H, Ar-O-CH_2-CH_2-OH), 3.98 (m, 2.0H, Ar-O-CH_2-CH_2-OH), 2.7 (m, 173H, Ar-CH_2-), 2.45 (s, 3.3H, Ar-CH_3), 1.7 (m, 85H, Ar-CH_2-CH-), 1.3 (m, 770H, Ar-CH_2-CH(CH_2CH_3)-$(CH_2)_3$-), 0.9 (m, 595H, -CH_2-CH(CH_2CH_3)-$(CH_2)_3$-CH_3)

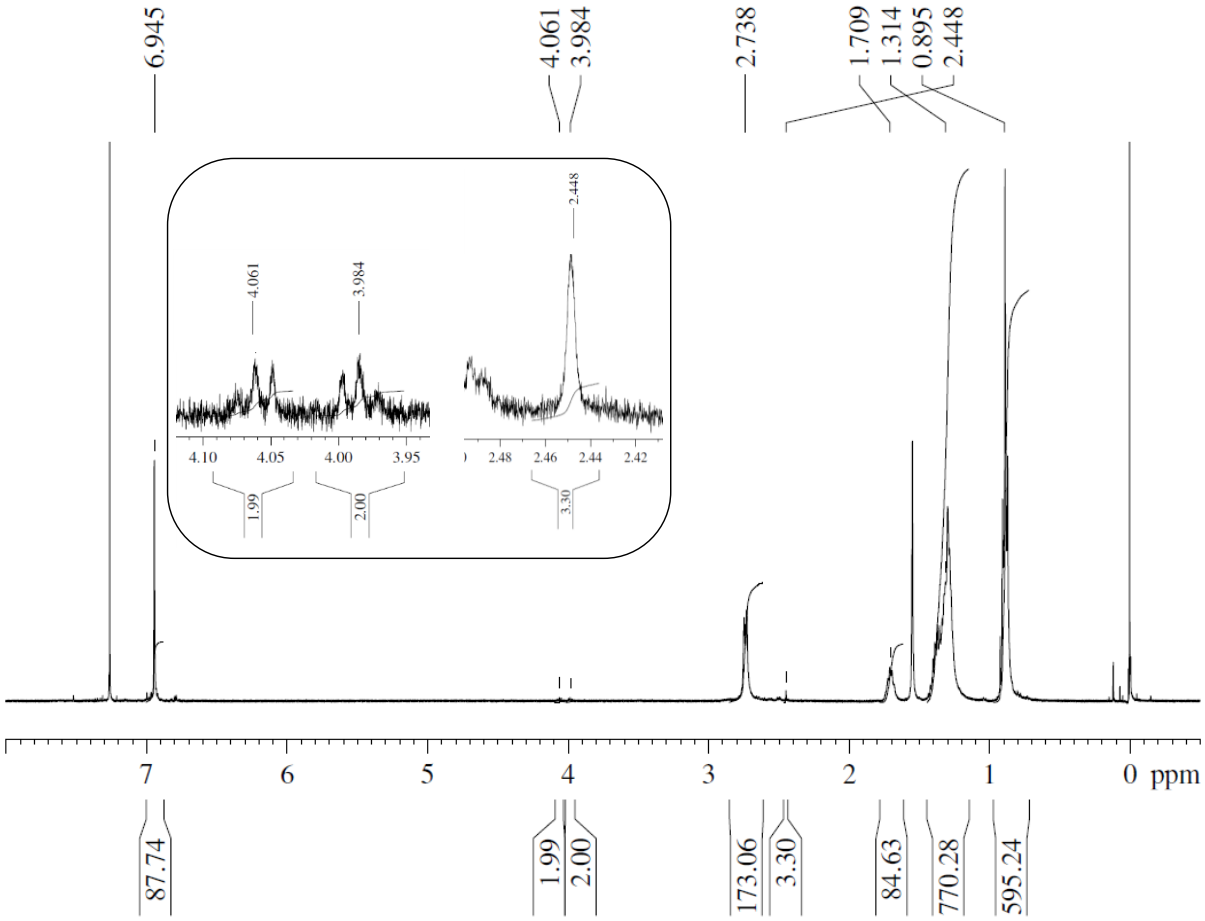

Fig. S7. ^{1}H NMR of P3EHT-OH. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup.

General procedure for the preparation of alkynyl-P3AT– All alkyne end-functionalized P3AT were prepared using a similar procedure. In a representative procedure, P3HT-OH (0.332g, 0.0161 mmol) was dissolved in 20 mL anhydrous $CHCl_3$ in a 100 mL round-bottom flask charged with a stir bar. Hexynoic acid (0.15g, 1.34 mmol) was added to the solution, followed by EDC (0.255 g, 1.33 mmol) and then DMAP (0.06 g, 0.491 mmol0 g/mol). The reaction was left to stir overnight. The following day, the solution was added to a separation funnel with approximately 100 mL of DI water. The organic phase was collected and dried over sodium sulfate. The solvent was removed using a rotary evaporator, and the polymeric product was dissolved in THF and precipitated into approximately 200 mL of chilled methanol. The precipitated product was filtered and washed with acetone. For alkynyl-P3EHT, the final reaction mixture was concentrated under reduced pressure, washed with water and methanol, and the solid product was collected directly from the flask using a spatula before drying under vacuum.

Alkynyl-P3HT ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.0 (s, 101H, Ar-*H*), 4.45 (t, 2.0H, Ar-O-CH_2-C*H*$_2$-OOC-), 4.20 (t, 2.0H, Ar-O-C*H*$_2$-CH_2-OOC-), 2.8 (t, 196H, Ar-C*H*$_2$-), 2.45 (s, 3.9H, Ar-C*H*$_3$), 1.7 (m, 176H, Ar-CH_2-C*H*$_2$-), 1.2 - 1.5 (m, 617H, Ar-CH_2-CH_2-(C*H*$_2$)$_3$-CH_3) , 0.9 (t, 302H, Ar-$(CH_2)_5$-C*H*$_3$)

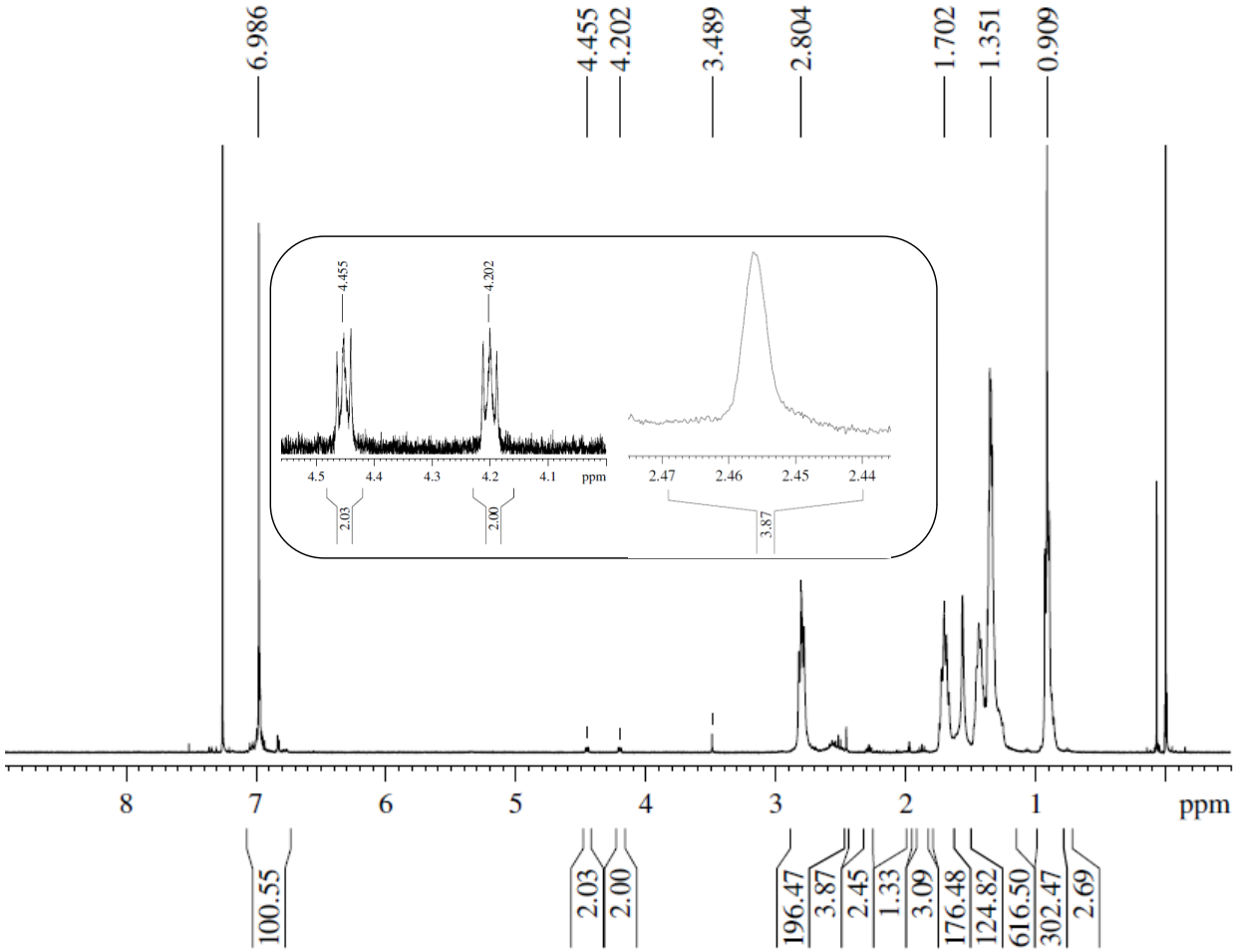

Fig. S8. ^{1}H NMR of P3HT-alkyne. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup.

Alkynyl-P3DDT ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.0 (s, 112H, Ar-*H*), 4.45 (m, 2.0H, Ar-O-CH_2-C*H*$_2$-OOC-), 4.20 (m, 2.0H, Ar-O-C*H*$_2$-CH_2-OOC-), 2.8 (m, 201H, Ar-C*H*$_2$-), 2.45 (s, 6.7H), 1.7 (m, 238H, Ar-CH_2-C*H*$_2$-), 1.1 - 1.5 (m, 1925H, Ar-CH_2-CH_2-(C*H*$_2$)$_9$-CH_3), 0.8-1.0 (m, 325H, Ar-CH_2-CH_2-$(CH_2)_9$-C*H*$_3$)

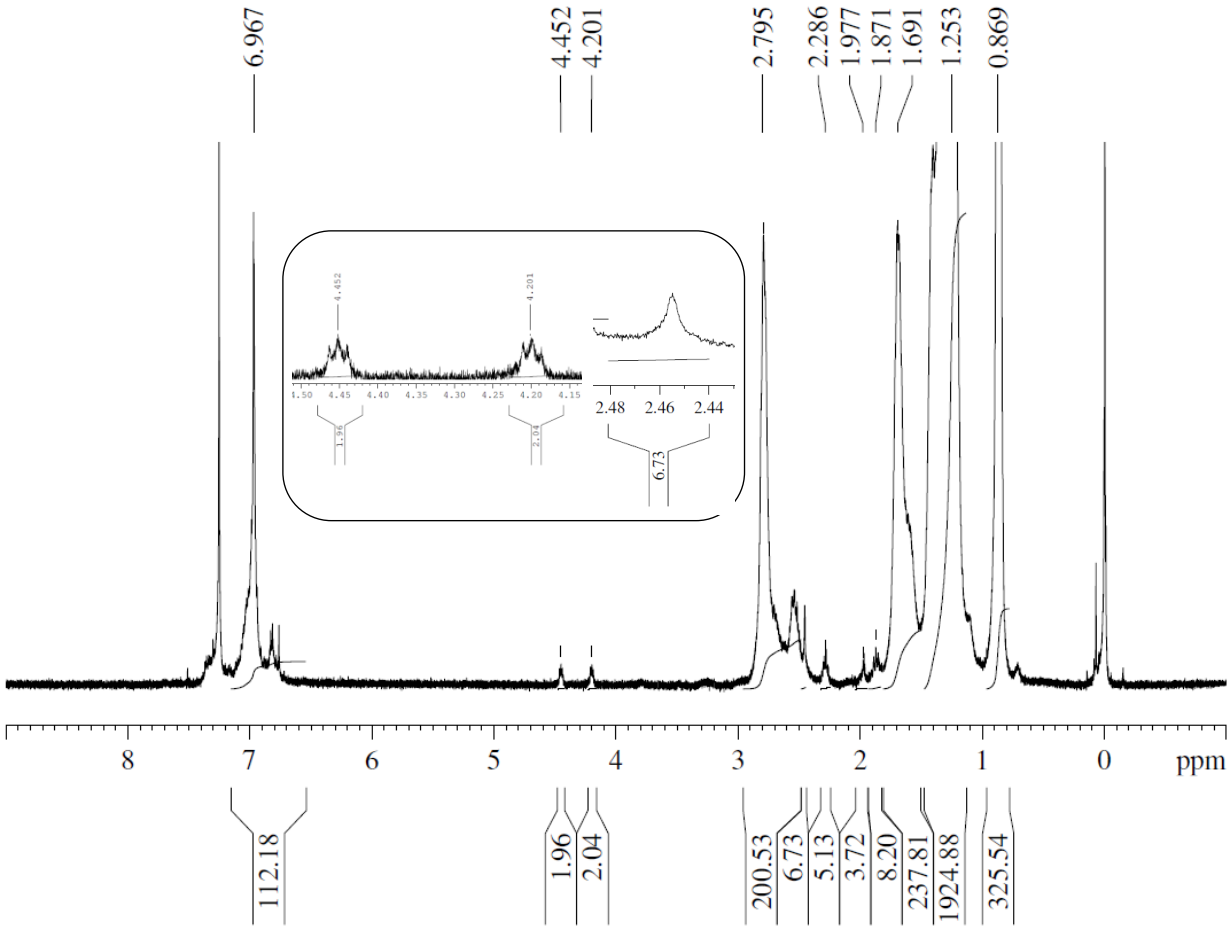

Fig. S9. ^{1}H NMR of P3DDT-alkyne. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup.

Alkynyl-P3EHT ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.9 (s, 125H, Ar-*H*), 4.45 (m, 2.0H, Ar-O-CH_2-C*H*$_2$-OOC-), 4.2 (m, Ar-O-C*H*$_2$-CH_2-OOC-), 2.7 (m, 248H, Ar-C*H*$_2$-), 1.7 (m, 147H, Ar-CH_2-C*H*-), 1.0 - 1.4 (m, 1227H, Ar-CH_2-CH(C*H*$_2$CH$_3$)-(C*H*$_2$)$_3$-), 0.7 - 1.0 (m, 911H, -CH_2-CH(CH_2C*H*$_3$)-(CH_2)$_3$-C*H*$_3$)

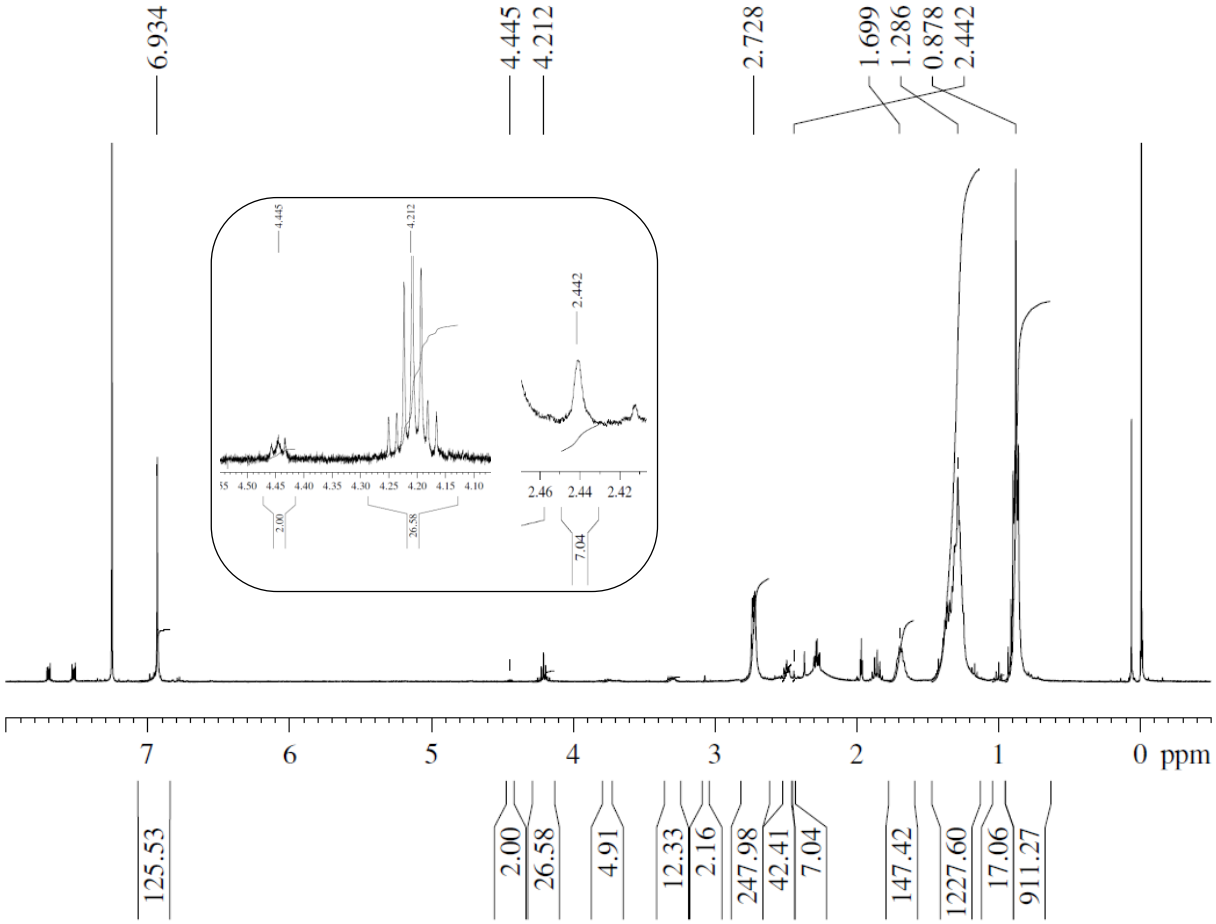

Fig. S10. ^{1}H NMR of P3EHT-alkyne. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup. In addition to the peaks corresponding to P3EHT-alkyne identified above, a significant number of solvent impurities were also present in this product. We found this was typical of P3EHT due to its rubbery nature and increased solubility in a broader range of solvents.

General procedure for the preparation of P3AT-*b*-PEG block copolymers – All P3AT-*b*-PEG block copolymers were prepared using the same technique, except where otherwise noted. In a representative procedure, alkynyl-P3HT (0.29 g, 0.021 mmol), PEG (0.20 g, 0.04 mmol), and CuBr (0.058 g, 0.4 mmol) were added to a 50 mL round bottom flask. The flask was evacuated and refilled with nitrogen. 20 mL anhydrous THF was added to the reaction flask and the resulting solution was purged with nitrogen by needle and stirred for 10 minutes. PMDETA (0.1 mL, 0.48 mmol) was injected into to the reaction and the solution was purged by needle for an additional 20 minutes. The reaction flask was kept stirring in a 45^{o}C oil bath overnight. The solution was purified by passing through an Al_2O_3 column. The purified solution was fully dried using a rotary evaporator and was subsequently dissolved in THF. The product was collected by precipitation into methanol (which will remove excess PEG) and filtration. The filtered product was washed with acetone.

P3HT-*b*-PEG: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): **Triazole ring:** 7.52 (s, -N_5HC_2-), **P3HT block:** 7.0 (s, 113H, Ar-*H*), 4.44 (t, 2.0H, Ar-O-CH_2-C*H*$_2$-OOC-), 4.19 (t, 2.1H, Ar-O-C*H*$_2$-CH_2-OOC-), 2.8 (t, 222H, Ar-C*H*$_2$-), 2.45 (s, 4.9H, Ar-C*H*$_3$), 1.7 (m, 201H, Ar-CH_2-C*H*$_2$-), 1.2 - 1.5 (m, 720H, Ar-CH_2-CH_2-(C*H*$_2$)$_3$-CH_3) , 0.9 (t, 353H, Ar-$(CH_2)_5$-C*H*$_3$) **PEG block:** 4.5 (t, 2H,-CH_2-C*H*$_2$- N_5HC_2-), 3.80 - 3.88 (m, 4.8H, ,-O-C*H*$_2$-C*H*$_2$-N_5HC_2-), 3.6 (s, 529H, -OC*H*$_2$C*H*$_2$-)

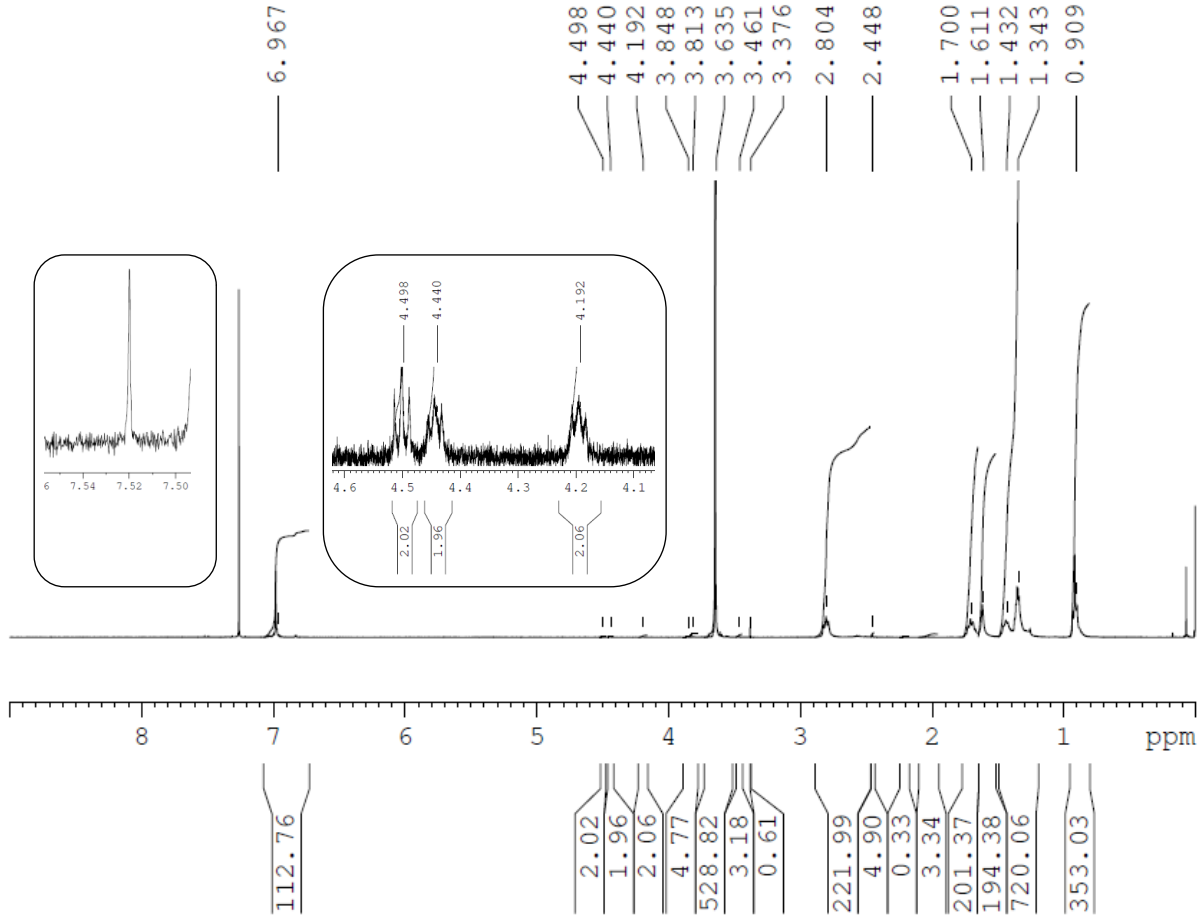

Fig. S11. ^{1}H NMR of P3HT-*b*-PEG. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup (δ = 4.44 ,4.19), from the triazole ring (δ = 7.52) and from PEG aliphatic protons near the triazole linkage (δ = 4.5).

P3DDT-*b*-PEG ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): **Triazole ring:** 7.52 (s, -N_5HC_2-), **P3DDT block:** 7.0 (s, 94H), 4.45 (m, 2.0H, Ar-O-CH_2-CH_2-OOC-), 4.2 (m, 3H, Ar-O-CH_2-CH_2-OOC-), 2.8 (t, 177H, Ar-CH_2-), 2.45 (s, Ar-CH_3), 1.7 (t, 375H, Ar-CH_2-CH_2-), 1.15-1.5 (s, 1856H, Ar-CH_2-CH_2-(CH_2)$_9$-CH), 0.8-1.0 (t, 342H, Ar-CH_2-CH_2-$(CH_2)_9$-CH_3) **PEG block:** 4.5 (t, 2.2H, -CH_2-CH_2-N_5HC_2 -), 3.80 - 3.88 (m, 5.1H, ,-O-CH_2-CH_2-N_5HC_2-), 3.6 (s, 699H, -OCH_2CH_2-),

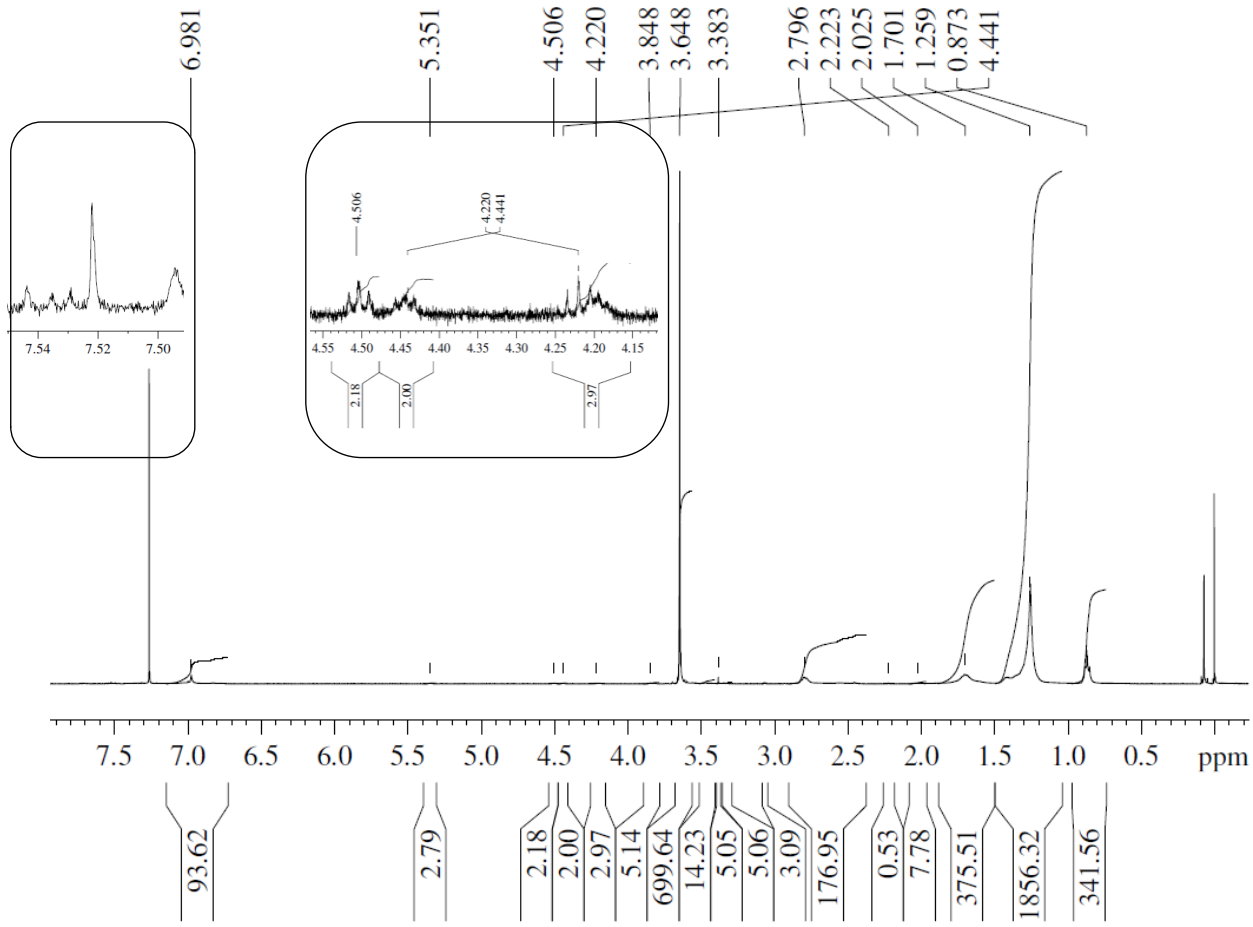

Fig. S12. ^{1}H NMR of P3DDT-*b*-PEG. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup (δ = 4.44 ,4.22), from the triazole ring (δ = 7.52) and from PEG near the triazole linkage (δ = 4.5). Minor solvent impurities contribute to the measured peak intensity at δ = 4.22.

P3EHT-*b*-PEG ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): **Triazole ring:** 7.52 (s, -N_5HC_2-), **P3EHT block:** 6.9 (s, 120H, Ar-*H*), 4.45 (m, 2.8H, Ar-O-CH_2-CH_2-OOC-), 4.2 (m, 2H, Ar-O-CH_2-CH_2-OOC-), 2.7 (m, 224H, Ar-CH_2-), 2.45 (s, Ar-CH_3), 1.7 (m, 124H, Ar-CH_2-CH-), 1.2 - 1.4 (m, 1152H, Ar-CH_2-CH(CH_2CH_3)-(CH_2)$_3$-), 0.8 - 1.0 (m, 832H, -CH_2-CH(CH_2CH_3)-(CH_2)$_3$-CH_3) **PEG block:** 4.5 (t, 1.8H, -CH_2- CH_2-N_5HC_2-), 3.80 - 3.88 (m, 2.9H, ,-O-CH_2-CH_2-N_5HC_2-), 3.6 (s, 503H, -OCH_2CH_2-),

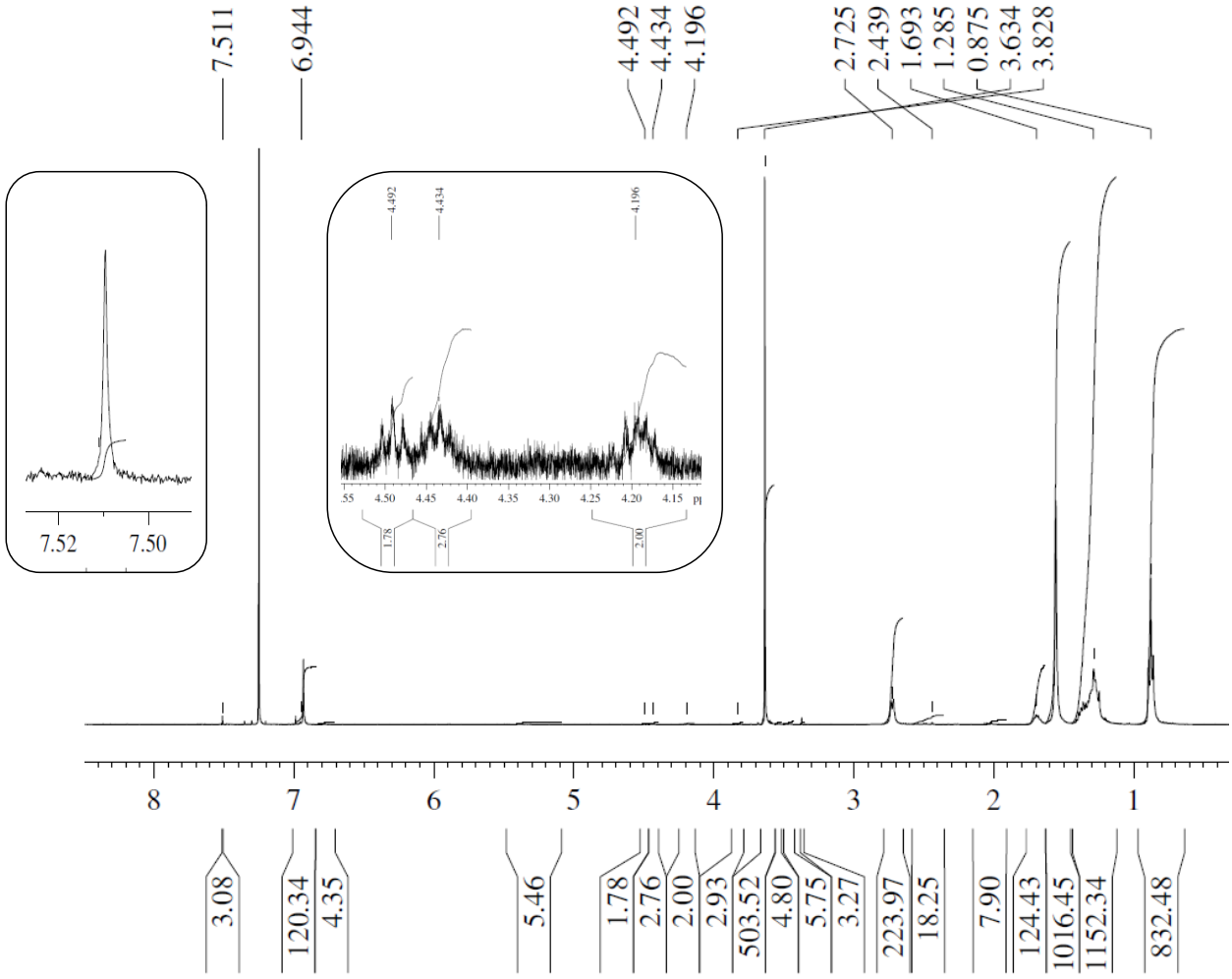

Fig. S13. ^{1}H NMR of P3EHT-*b*-PEG. The inset shows protons from the initiating species (**3**) incorporated into the polymer endgroup (δ = 4.44 ,4.20), from the triazole ring (δ = 7.52) and from PEG near the triazole linkage (δ = 4.49).

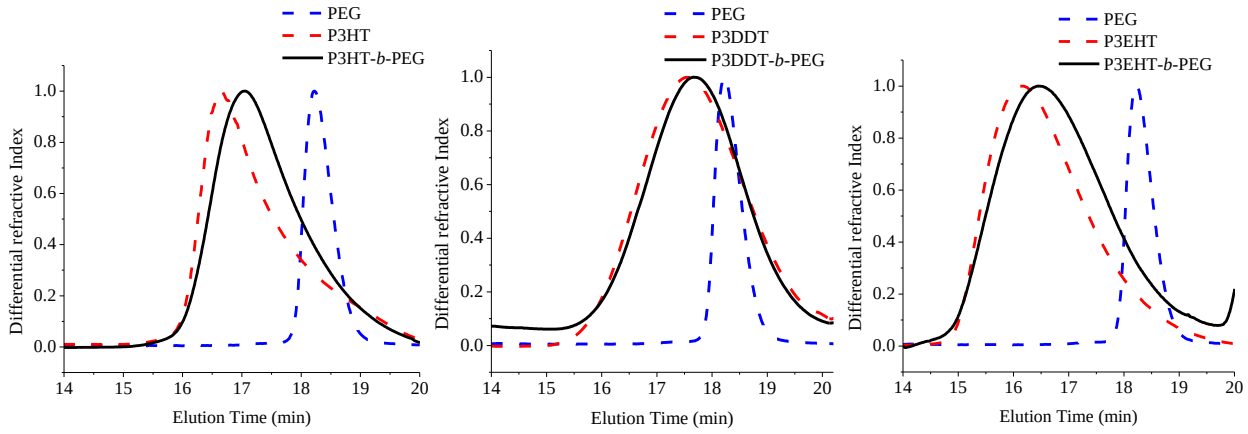

Fig S14. GPC analysis of P3AT-*b*-PEG block copolymers. Note that in all cases a single, broad peak is evidenced for the final block copolymer product, indicating no residual PEG is present. All samples show only a modest shift in the molecular weight distribution, as expected due to the relatively small size of the PEG block. All block copolymer samples show a slight shift to longer elution times, which typically corresponds to lower molecular weights. We believe this shift to longer elution times is indicative of reduced THF solubility after click coupling. This results in a smaller average hydrodynamic size for the final block copolymer relative to the starting P3AT block.

General procedure for the preparation of P3AT-b-PEG micelles in water – All P3AT-*b*-PEG micelles in water were prepared using the same technique, except where otherwise stated. In a representative procedure, P3HT-*b*-PEG (60 mg), was dissolved in THF (5.14 g, 5.78 mL), giving a solution with a concentration of approximately 1 mg/ml. A volume of methanol, approximately equal to that of THF was added to the solution. The solution was filtered (by syringe filter) into a dialysis bag which was then immersed in DI water. The bag was immersed for approximately 24 hours, and the DI water was changed after 7 hours. The final solution was filtered to remove insoluble aggregates and obtain a clear, colored solution with dispersed P3AT-*b*-PEG block copolymers. The solution was repeated for P3AT macroreagents, and as shown below, no dispersion of the block copolymers into water was observed. The resulting aqueous phase is clear, with no indication of P3AT homopolymer disperse, as expected due to the hydrophobicity of P3AT.

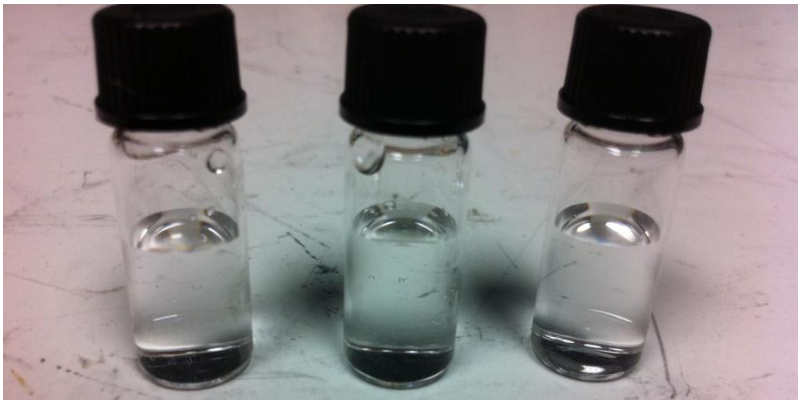

Fig S15. Aqueous phases after dispersion of P3HT (left), P3DDT (middle), and P3EHT (right) in water using dialysis as described above. The images show that P3AT cannot be dispersed in water, but as shown in Fig. 3 P3AT-*b*-PEG are readily dispersed in water.

Atomic Force Microscopy analysis of P3AT-*b*-PEG micelles

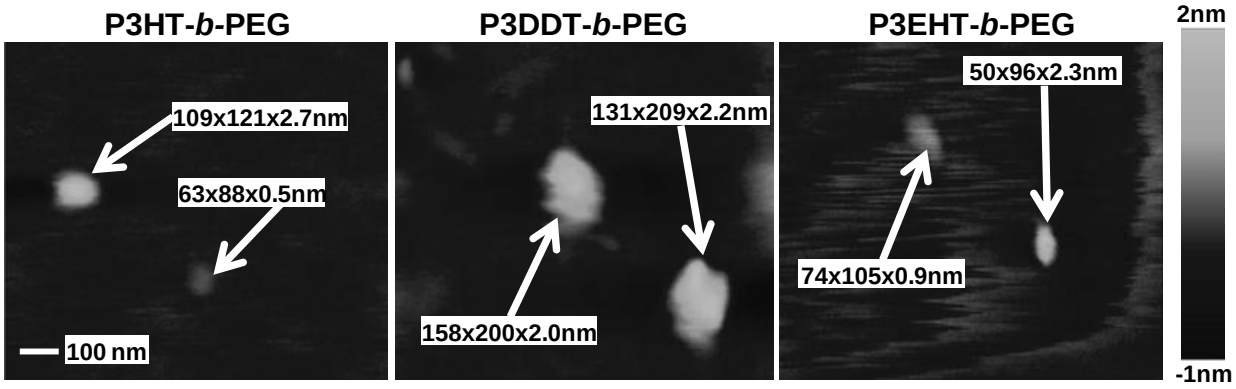

Fig. S16. AFM height images of individual micelles spin coated onto Si substrates. Scale bar is the same for all images. Note that the micelles are flattened in the dry state, with micellar heights roughly 2 nm or smaller for all samples. The numbers indicate the micelle width, length, and height, respectively.

GISAXS analysis of P3DDT-*b*-PEG and P3EHT-*b*-PEG thin films.

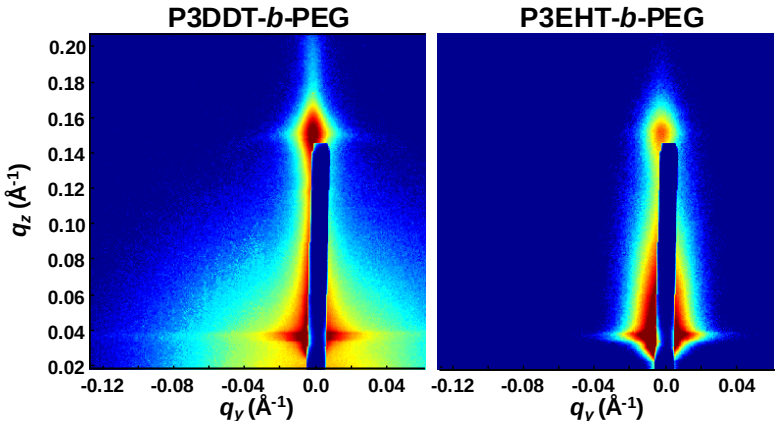

Fig. S17 GISAXS analysis for P3DDT-*b*-PEG (left) and P3EHT-*b*-PEG (right) thin films on silicon. Sample films were prepared by spin-casting from chloroform (10 mg/mL) and film thickness is roughly 100 nm. Both samples show a broad reflection near 0.15 Å^{-1}.

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