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Conjugated Core-Shell Bottlebrush Polymers that Exhibit Crystallization-Driven Self-Assembly

Victor Lotocki,[a] Alicia M. Battaglia,[a] Nahye Moon,[a] Hatem M. Titi,[b] and Dwight S. Seferos[ac]*

[a] Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

[b] Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, H3A 0B8, Canada

[c] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada

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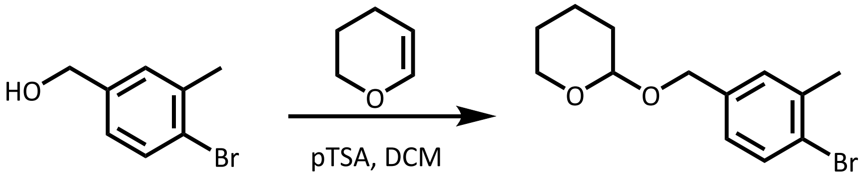
General Considerations

Anhydrous solvents were obtained from an Innovative Technology PureSolv solvent purification system and stored over molecular sieves. 2,5-dibromo-3-hexylthiophene and Grubbs III catalyst were synthesized following literature procedures.[1,2]. All other chemicals were purchased from Sigma-Aldrich and were used as received. Schlenk techniques were used for experiments conducted under argon, and a glovebox was used for experiments conducted under nitrogen.

Instrumentation

Centrifugation was done on an Eppendorf 5702 centrifuge. A Branson 2510 Ultrasonic Cleaner was used for sonication. Nuclear magnetic resonance (NMR) spectra were recorded on Varian MercuryPlus, Agilent VNMRS, and Bruker Avance III NMR spectrometers (400 MHz). MALDI spectra were obtained using a Bruker Autoflex Speed MALDI-TOF mass spectrometer from a matrix of DCTB (2500:1 matrix to sample ratio) cast from chloroform. Gel permeation chromatography was carried out with a Tosoh EcoSEC instrument (model HLC-8320 version 2.01) equipped with two Tosoh TSKgel SuperHM-M columns and a dual-flow refractive-index detector. HPLC grade THF stabilized with 250 ppm BHT was used as eluent at 40 °C with a flow rate of 0.6 mL/min. Calibration curves for SEC analysis were obtained with polystyrene standards. Data processing was performed using the EcoSEC Data Analysis software (version 1.14). Polymer aggregation experiments assessed by UV-visible spectroscopy were performed by layering poor solvents on samples dissolved in chloroform (final concentrations of 0.02 mg/mL) or benzonitrile (final concentrations of 0.2 mg/mL) and aging them in the dark overnight. UV-visible spectra of all samples were then recorded using an Agilent Cary 7000 UV-Vis-NIR Universal Measurement spectrophotometer. Quartz cuvettes with chloroform or benzonitrile served as the blank samples. TEM grids were prepared by drop-casting polymer self-assembly solutions onto 400 mesh copper grids with ultrathin carbon films supported by lacey carbon films and drying overnight. TEM images were obtained on a Hitachi HT7700 TEM at an acceleration voltage of 80 kV. All TEM images were analysed using ImageJ. Grazing incidence wide-angle x-ray scattering (GIWAXS) data was collected using an Anton Paar SAXSpoint 2.0 equipped with a micro-focused X-ray copper source and a 2D Eiger 1 detector. The polymers were drop cast on crystalline silicon wafers from their corresponding solvent mixtures at concentrations of 5 mg/mL. The measurements on these thin films were conducted for 30 minutes per scan. The sample-to-detector distance was 156 mm.

Synthetic Procedures

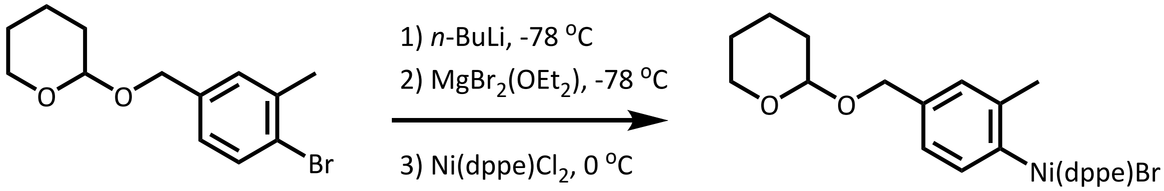


2-((4-bromo-3-methylbenzyl)oxy)tetrahydro-2H-pyran

4-bromo-3-methylbenzyl alcohol (0.500 g, 2.49 × 10^{-3} mol) and 3,4-Dihydro-2H-pyran (0.25 mL, 2.74 × 10^{-3} mol) were added to an argon-filled Schlenk flask containing 10 mL dry DCM. Then. *p*-toluenesulfonic acid (0.142 g, 7.46 × 10^{-3} mol) was slowly added, and the reaction mixture was stirred overnight at room temperature. Upon completion, the reaction was washed with 10% K_2CO_3. Then it was extracted 3x with chloroform from water, washed with brine, and the combined organic extracts were dried with $MgSO_4$. The pure product was isolated using silica gel column chromatography (5:2 Hexanes:Chloroform) as a colourless oil (0.619 g, 87%)

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 1.59-1.91 (6H, m), 2.43 (3H, s), 3.55-3.61 (1H, m), 3.91-3.96 (1H, m), 4.44-4.47 (1H, d), 4.71-4.75 (2H, m), 7.07-7.09 (1H, dd), 7.26-7.27 (1H, d), 7.51-7.53 (1H, d)

^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ_C (ppm) 19.37, 22.89, 25.46, 30.56, 62.20, 68.15, 97.81, 123.87, 126.83, 130.30, 132.28, 137.56, 137.82

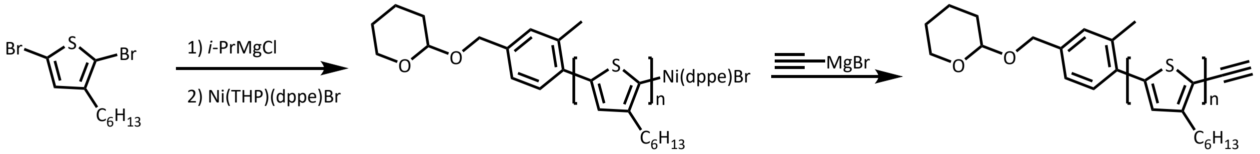


[1,2-Bis(diphenylphosphino)ethane][2-((3-methylbenzyl)oxy)tetrahydro-2H-pyran] nickel (II) bromide (Ni(THP)(dppe)Br)

2-((4-bromo-3-methylbenzyl)oxy)tetrahydro-2H-pyran (0.320 g, 1.12 × 10^{-3} mol) was added to a Schlenk flask which was evacuated and refilled with argon 3 times, filled with 1.5 mL of dry THF, and cooled to -78 °C in a dry ice/acetone bath. While stirring vigorously, *n*-butyllithium (2.5 M, 0.40 mL, 1.01 × 10^{-3} mol) was added dropwise. After stirring for 30 minutes, $MgBr_2(OEt_2)$ (0.4346 g, 1.69 × 10^{-3} mol) was added to the solution all at once. The reaction mixture was kept at -78 °C for 20 minutes, after which the temperature was raised to 0 °C for 10 minutes. In a separate Schlenk flask, $Ni(dppe)Cl_2$ (0.5925 g, 1.12 × 10^{-3} mol) was dispersed in 6 mL of dry THF and cooled to 0 °C. To this second flask was added the initial solution dropwise, and it was left to stir for another 30 minutes. Upon completion, the reaction mixture was filtered, and the filtrate was evaporated to dryness. To this was added a minimal amount of methanol, and the crude mixture was resuspended by ultrasonication. The suspension was centrifuged (4000 rpm, 5 minutes) down and washed two more times with methanol in this manner to yield the final product as a yellow powder (0.315 g, 38%).

^1H NMR (400 MHz, $CDCl_3$): δ_H (ppm)**:** 1.30 (1H, m), 1.57-1.70 (4H, m (H_2O: ~5H)), 1.85 (1H, m), 2.24 (3H, s), 2.30 (1H, m), 2.39-2.53 (2H, m), 3.52 (1H, m), 3.91 (1H, t), 4.26-4.29 (1H, d), 4.51-4.54 (1H, d), 4.62 (1H, s), 6.46 (1H, s), 6.67 (1H, d), 6.72-6.76 (2H, t), 7.07 (2H, t), 7.25-7.29 (2H, m), 7.45 (3H, m), 7.52-7.56 (6H, m), 7.74-7.81 (2H, m), 8.20 (4H, m)

^{31}P NMR (162 MHz, $CDCl_3$) : δ_P (ppm) Br adduct (77.5%): 36.44-36.62 (1P, m), 54.68-54.85 (1P, m); Cl adduct (22.5%): 33.88-33.98 (1P, m), 52.14-52.31 (1P, m)

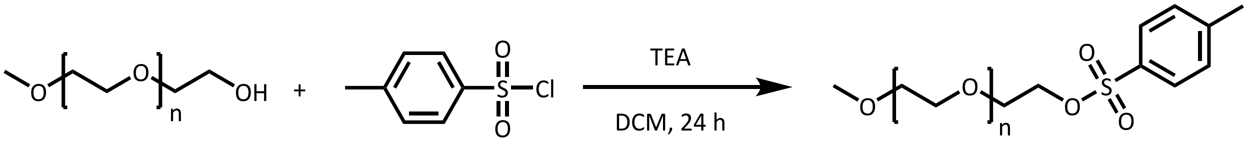


α-tetrahydropyran -ω-ethynyl-poly(3-hexylthiophene) (THP-P3HT–C≡CH)

2,5-dibromo-3-hexylthiophene (0.4815 g, 1.48 × 10^{-3} mol) was added to a flame-dried Schlenk flasked and evacuated. The flask was backfilled with argon and dry THF, and isopropyl MgCl (0.72 mL, 2.0 M, 1.44 × 10^{-3} mol) was added dropwise while stirring. The flask continued to stir for an hour, and then the contents of the flask were quickly transferred to a second Schlenk flask containing Ni(THP)(dppe)Br (0.0492 g, 6.71 × 10^{-5} mol) in THF similarly prepared following Schlenk techniques. The mixture was stirred for 15 minutes before ethynyl MgBr (0.40 mL, 0.5 M, 2.01 × 10^{-5} mol) to end-cap the polymer. The polymer solution was precipitated in methanol, washed with copious amounts of more methanol through a Soxhlet thimble, collected by washing with chloroform, and dried under reduced pressure to yield a purple solid (0.2052 g, 78%, M_{n} (^{1}H NMR) = 3.220 g/mol, M_{n} (GPC) = 3,900 g/mol, $Đ$ = 1.15)

^{1}H NMR (400 MHz, CDCl$_3$): δ_{H} (ppm): 0.93-0.96 (m), 1.29-1.92 (m), 2.53 (3H, s), 2.72-2.86 (m), 3.56 (1H. s), 3.62 (1H, m), 3.98 (1H, m), 4.51-4.54 (1H, d), 4.77-4.84 (2H, m), 6.93-7.01 (m), 7.44-7.46 (1H, d)

^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ_{C} (ppm): 14.13, 22.67, 29.27, 29.49, 30.52, 31.71, 128.62, 130.44, 139.92

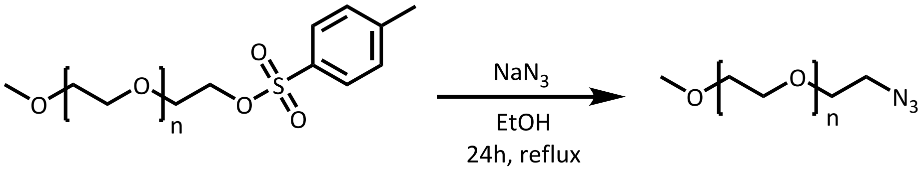


α-methoxy-ω-tosyl-poly(ethylene glycol) (mPEG-OTs)

Polyethylene glycol monomethyl ether 1000 (4.0 g, 4.0 × 10^{-3} mol) was added to a flask and dried under vacuum for one hour. The flask was backfilled with argon, and *p*-toluene sulfonyl chloride (2.288 g, 1.2 × 10^{-3} mol) was added under positive argon pressure. The flask was then filled with DCM, and triethylamine (2.8 mL, 0.02 mol) was added dropwise while stirring. After 24 hours, the solution was extracted 3x from water with chloroform, washed with brine, dried with MgSO$_4$, concentrated, and precipitated in ice-cold ether to yield a white solid (2.21 g, 48%).

^{1}H NMR (400 MHz, CDCl$_3$): δ_{H} (ppm) 2.46 (3H, s), 3.39 (3H, s), 3.49-3.71 (m), 4.16-4.18 (2H, t), 7.35-7.387(2H, d), 7.80-7.82 (2H, d)

^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ_{C} (ppm) 21.64, 59.01 68.68, 69.25, 70.48, 70.58, 71.92, 72. 127.98, 129.83

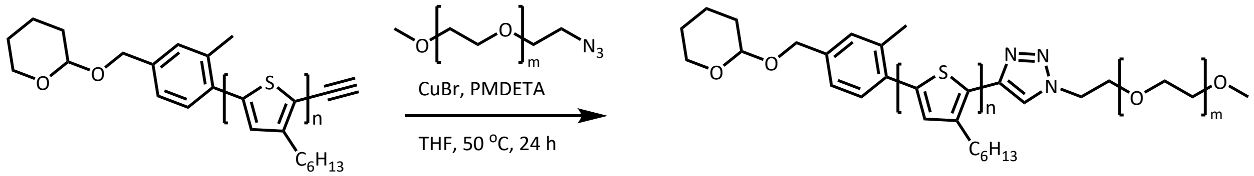


α-methoxy-ω-azido-poly(ethylene glycol) (mPEG-N$_3$)

mPEG-OTs (2.0 g, 1.73 × 10^{-3} mol) and sodium azide (0.5637 g, 8.67 × 10^{-3} mol) were added to a round bottom flask. The flask was filled with anhydrous ethanol, equipped with a condenser, and left to reflux under argon for 24 hours. The reaction mixture was then filtered to remove undissolved salts, and the crude product was extracted 3x with chloroform from water. The organic extracts were washed with brine and dried with MgSO$_4$. The organic fraction was then concentrated and precipitated in ice cold ether to yield the product as a white solid (1.19 g, 67%, M_n (^{1}H NMR) = 1.180 g/mol, M_n (GPC) = 1,100 g/mol, $Đ$ = 1.10)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H (ppm) 3.40 (3H, s), 3.40-3.42 (2H, t), 3.56-3.84 (m)

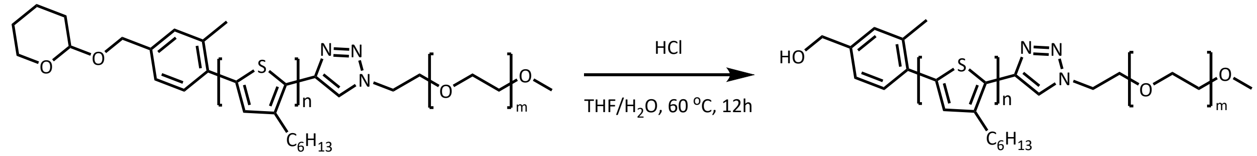
^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ_C (ppm) 50.72, 59.05, 70.05, 70.60, 71.96



α-tetrahydropyran-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (THP-P3HT-*b*-PEG)

THP–P3HT (0.086 g, 2.67 × 10^{-5} mol) and mPEG-N$_3$ (0.0573 g, 5.59 × 10^{-5} mol) were added to a Schlenk flask along with copper(I) bromide (0.0082 g, 5.73 × 10^{-5} mol). The flask was evacuated, backfilled with argon and dry THF. Then, N,N,N′,N″,N″-pentamethyldiethylenetriamine (0.0099 g, 1.15 × 10^{-4} mol) was added to the flask through a rubber septum. The reaction was carried out under argon at 50 °C for 24 hours while stirring. The pure product was obtained following silica gel column chromatography using a 10:1 DCM:methanol eluent (0.081 g, 71%, M_n (^{1}H NMR) = 4,703 g/mol).

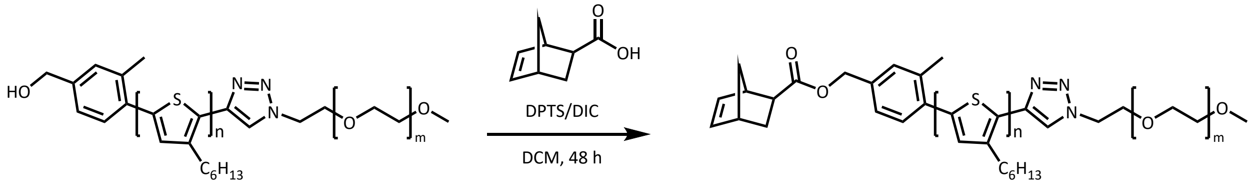
^{1}H NMR (400 MHz, CDCl$_3$): δ_H (ppm) 0.93-0.96 (m), 1.29-1.76 (m), 2.52 (3H, s), 2.81-2.85, 3.41 (3H, s), 3.50-3.85 (m), 3.95-3.98 (2H, t), 4.51-4.54 (1H, d), 4.63-4.65 (2H, t), 4.77-4.83 (2H, m), 6.93-7.03 (m), 7.44 (1H, d), 7.86 (1H, s)



α-hydroxy-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (HO-P3HT-*b*-PEG)

THP–P3HT-*b*-PEG (0.073 g, 1.55 × 10^{-5} mol) was added to a 3-neck flask equipped with a condenser, evacuated, and backfilled with argon and dry THF. Degassed HCl (0.4 M, 1.5 mL) was added to the flask through a rubber septum, and the mixture was stirred for 12 hours at 60 °C. The crude product was concentrated, extracted it 3x with chloroform from water, and dried with brine and $MgSO_4$. The product was obtained after drying under vacuum as a purple solid (0.070 g, 96%, M_n (^{1}H NMR) = 4,667 g/mol, M_n (GPC) = 5.000 g/mol, $Đ$ = 1.10).

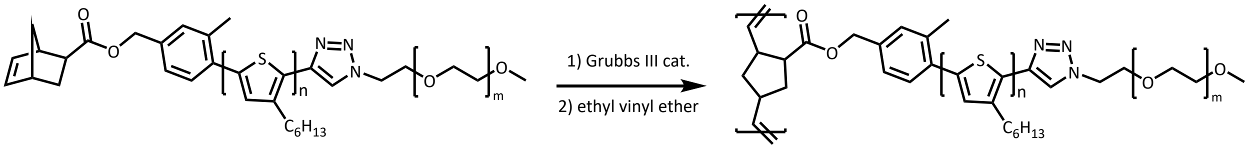
^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.89-0.96 (m), 1.24-1.76 (m), 2.54 (3H, s), 2.82-2.85 (t), 3.41 (3H, s), 3.57-3.70 (m), 3.95-3.97 (2H, t), 4.63-4.64 (2H, t), 4.74 (2H, s), 6.94-7.03 (m), 7.46-7.48 (1H, d), 7.85 (1H, s)



α-norbornene-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (Nor-P3HT-*b*-PEG)

HO–P3HT-*b*-PEG (0.070 g, 1.50 × 10^{-5} mol) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (0.0309 g, 1.05 × 10^{-4} mol) were added to a Schlenk flask. After evacuating and refilling the flask 3x with argon, the flask was filled with dry DCM. Then, exo-5-norbornene carboxylic acid (0.0145 g, 1.05 × 10^{-4} mol) and N,N′-diisopropylcarbodiimide (0.02 mL, 1.05 × 10^{-4} mol) were added, and the reaction mixture was stirred for 48 hours. Upon completion, the crude product was dried, washed with methanol and ether, and isolated by silica gel column chromatography using a 10:1 DCM:methanol eluent (0.042 g, 60%, M_n (^{1}H NMR) = 4,783 g/mol, M_n (GPC) = 5,400 g/mol, $Đ$ = 1.11).

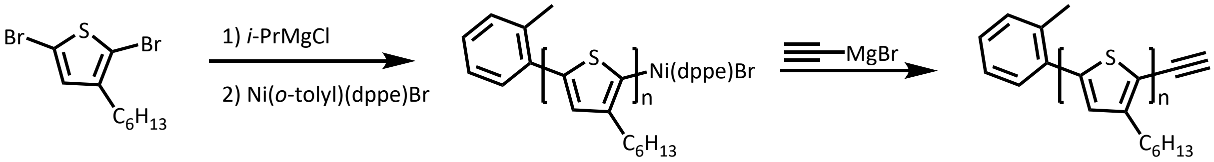
^{1}H NMR (400 MHz, CDCl$_3$): δ_H (ppm) 0.93-0.96 (m), 1.29-1.76 (m), 2.53 (3H, s), 2.82-2.85 (t), 2.97 (1H, m), 3.12 (1H, m), 3.41 (3H, s), 3.57-3.69 (m), 3.96-3.98 (2H, t), 4.63-4.64 (2H, t), 5.16 (2H, s), 6.15-6.18 (2H, m), 6.94-7.03 (m), 7.46-7.48 (1H, d), 7.85 (1H, s)



Polynorbornene-*graft*-(poly(3-hexylthiophene)-*block*-poly(ethylene glycol)) (P3HT-*b*-PEG CSBB)

Nor–P3HT-*b*-PEG (0.0300 g, 6.27 × 10^{-6} mol) added to a vial and dissolved in 1.0 mL of dry chloroform in a nitrogen glove box. Then, a 0.5 mL solution of Grubbs III catalyst (0.133 mg, 1.50 × 10^{-7} mol) was transferred quickly to the macromonomer solution and the mixture was stirred overnight. Upon completion, the polymerization was terminated by the addition of a few drops of ethyl vinyl ether. The crude product was purified by passing it through an alumina plug, dried, and washed with ether (0.024 g, 80%, M_n (GPC) = 84,600 g/mol, $Đ$ = 1.21).

^{1}H NMR (400 MHz, CDCl$_3$): δ_H (ppm) 0.92 (m), 1.29-1.71 (m), 2.82 (m), 3.40 (3H, s), 3.67 (m), 3.96 (2H, t), 4.64 (2H, t), 7.00 (m), 7.84 (1H, s)

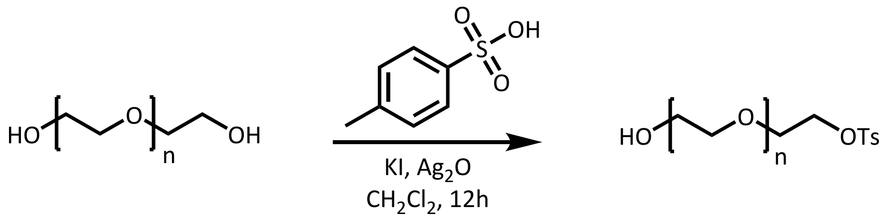


α-*o*-tolyl-ω-ethynyl-poly(3-hexylthiophene) (P3HT–C≡CH)

2,5-dibromo-3-hexylthiophene (0.4861 g, 1.49 × 10^{-3} mol) was added to a flame-dried Schlenk flasked and evacuated. The flask was backfilled with argon and dry THF, and isopropyl MgCl (0.73 mL, 2.0 M, 1.45 × 10^{-3} mol) was added dropwise while stirring. The flask continued to stir for an hour, and then the contents of the flask were quickly transferred to a second Schlenk flask containing Ni(*o*-tolyl)(dppe)Br (0.0396 g, 6.78 × 10^{-5} mol) in THF similarly prepared following Schlenk techniques. The mixture was stirred for 15 minutes before ethynyl MgBr (0.41 mL, 0.5 M, 2.03 × 10^{-4} mol) to end-cap the polymer. The polymer solution was precipitated in methanol, washed with copious amounts of more methanol through a Soxhlet thimble, collected by washing with chloroform, and dried under reduced pressure to yield a purple solid (0.1728 g, 68%, M_n (^{1}H NMR) = 3,128 g/mol, M_n (GPC) = 3,600 g/mol, $Đ$ = 1.18)

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm): 0.93-0.96 (m), 1.29-1.78 (m), 2.53 (3H, s), 2.71-2.86 (m), 3.56 (1H. s), 6.93-7.01 (m), 7.46-7.48 (1H, d)

$^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ_C (ppm): 14.13, 22.67, 29.28, 29.49, 30. 30.53, 31.72, 128.62, 130.50, 133.74, 139.92

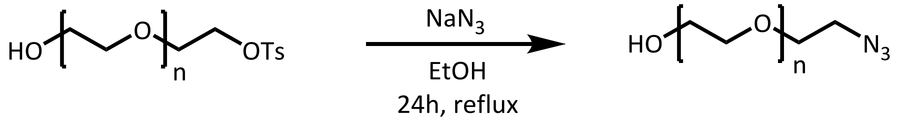


α-hydroxy-ω-tosyl-poly(ethylene glycol) (HO-PEG-OTs)

Polyethylene glycol 1000 (2 g, 2.0×10^{-3}) and silver oxide (0.695 g, $3.0 \times 10^{-3)}$ were added to a 3-neck flask and dried under vacuum for one hour. The flask was filled with argon, dry DCM, and the mixture was stirred for 30 minutes. Potassium iodide (0.066 g, 4.0×10^{-4}) and *p*-toluene sulfonyl chloride (0.400 g, 2.1×10^{-3}) were added under positive argon pressure and the reaction mixture was stirred overnight. Silver oxide was removed from the mixture by centrifugation. The solution was then concentrated and precipitated in diethyl ether in the freezer for 30 minutes to yield a white solid (1.42 g, 62%)

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 2.47 (3H, s), 3.49-3.84 (m), 4.17-4.20 (2H, t), 7.36-7.38 (2H, d), 7.81-7.83 (2H, d)

$^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ_C (ppm) 21.65, 61.69, 68.71, 69.25, 70.29, 70.58, 70.77, 72.54, 128.00, 129.83



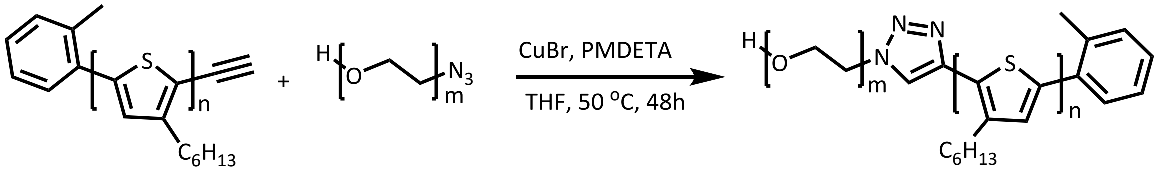
α-hydroxy-ω-azido-poly(ethylene glycol) (HO-PEG-N_3)

HO-PEG-OTs (1.40 g, 1.21×10^{-3}) and sodium azide (0.394 g, 6.07×10^{-3}) were added to a round bottom flask. The flask was filled with ethanol, equipped with a condenser, and left to reflux under argon for 24 hours. The reaction mixture was then filtered to remove undissolved salts, and the crude product was extracted 5x with chloroform from water. The organic extracts were dried with

$MgSO_4$. The organic fraction was then concentrated and precipitated in ice cold ether in a freezer over 30 minutes to yield the product as a white powder (0.791 g, 64%, M_n (^{1}H NMR) = 1,069 g/mol, M_n (GPC) = 700 g/mol, $Đ$ = 1.11)

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 3.40-3.42 (2H, t), 3.48-3.84 (m)

$^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ_C (ppm) 50.70, 61.69, 70.04, 70.26, 70.56, 72.71

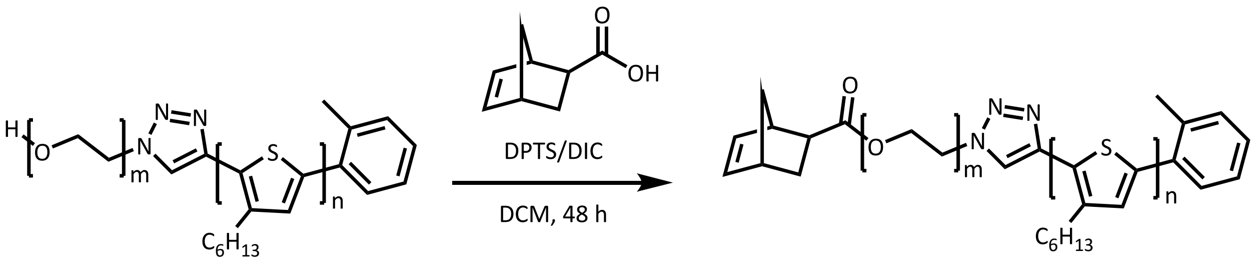


α-*o*-tolyl-ω-hydroxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol)

(HO-PEG-*b*-P3HT)

P3HT (0.1560 g, 4.99 × 10^{-5} mol) and HO-PEG-N_3 (0.1040 g, 1.01 × 10^{-4} mol) were added to a Schlenk flask along with copper(I) bromide (0.0149 g, 1.04 × 10^{-4} mol). The flask was evacuated, backfilled with argon and dry THF. Then, N,N,N′,N″,N″-pentamethyldiethylenetriamine (0..04 mL, 2.08 × 10^{-4} mol) was added to the flask through a rubber septum. The reaction was carried out under argon at 50 °C for 24 hours while stirring. The pure product was obtained following silica gel column chromatography using a 10:1 DCM:methanol eluent (0.098 g, 47%, M_n (^{1}H NMR) = 4,471 g/mol, M_n (GPC) = 4,700 g/mol, $Đ$ = 1.09).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.88-0.96 (m), 1.29-1.76 (m), 2.52 (3H, s), 2.82-2.85 (t), 3.65-3.70 (m), 3.96 (2H, t), 4.64 (2H, t), 6.94-7.03 (m), 7.45 (1H, d), 7.85 (1H, s)

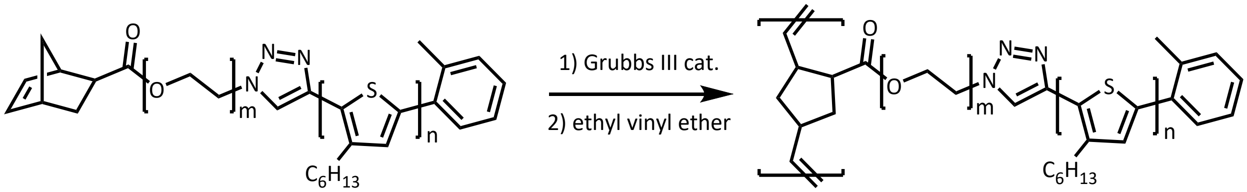


α-*o*-tolyl-ω-norbornene-poly(3-hexylthiophene)-*block*-poly(ethylene glycol)

(Nor-PEG-*b*-P3HT)

HO–P3HT-*b*-PEG (0.091 g, 2.04 × 10^{-5} mol) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (0.033 g, 1.14 × 10^{-4} mol) were added to a Schlenk flask. After evacuating and refilling the flask 3x with argon, the flask was filled with dry DCM. Then, exo-5-norbornene carboxylic acid (0.016 g, 1.14 × 10^{-4} mol) and N,N′-diisopropylcarbodiimide (0.02 mL, 1.14 × 10^{-4} mol) were added, and the reaction mixture was stirred for 48 hours. Upon completion, the crude product was dried, washed with methanol and ether, and isolated by silica gel column chromatography using a 10:1 DCM:methanol eluent (0.062 g, 70%, M_n (^{1}H NMR) = 4,535 g/mol, M_n (GPC) = 4,800 g/mol, $Đ$ = 1.11).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.91-0.96 (m), 1.29-1.76 (m), 2.52 (3H, s), 2.81-2.85 (t), 3.65-3.75 (m), 3.96 (2H, t), 4.26-4.29 (2H, t), 4.63-4.65 (2H, t), 6.14-6.17 (2H, m), 6.94-7.03 (m), 7.45-7.48 (1H, d), 7.85 (1H, s)



Polynorbornene-*graft*-(poly(ethylene glycol)-*block*-poly(3-hexylthiophene)) (PEG-*b*-P3HT ICSBB)

Nor–PEG-*b*-P3HT (0.0481 g, 1.06 × 10^{-5} mol) added to a vial and dissolved in 1.0 mL of dry chloroform in a nitrogen glove box. Then, a 0.5 mL solution of Grubbs III catalyst (0.21 mg, 2.41 × 10^{-7} mol) was transferred quickly to the macromonomer solution and the mixture was stirred overnight. Upon completion, the polymerization was terminated by the addition of a few drops of ethyl vinyl ether. The crude product was purified by passing it through an alumina plug, dried, and washed with ether. Then, the pure product was isolated using a size exclusion column with THF as an eluent (0.033 g, 67%, M_n (GPC) = 70,100 g/mol, $Đ$ = 1.12).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.92-0.96 (m), 1.29-1.73 (m), 2.52 (3H, s), 2.81-2.83 (t), 3.65-3.67 (m), 3.96 (2H, t), 4.63 (2H, t), 6.93-7.03 (m), 7.84 (1H, s)

^{31}P NMR and MALDI-TOF analysis of Ni(THP)(dppe)Br

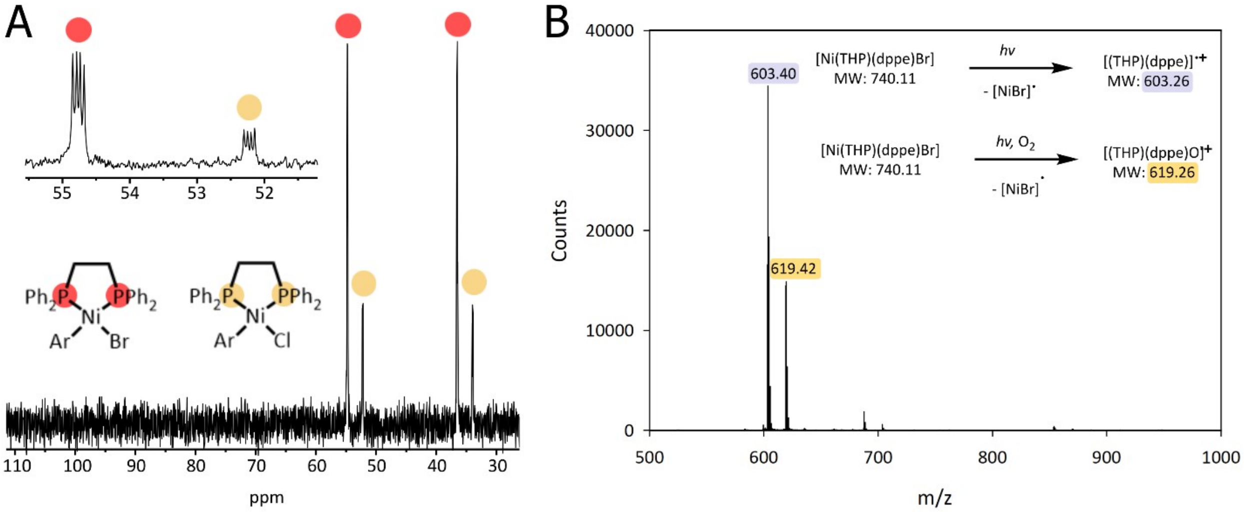


Fig. S1 (A) ^{31}P NMR analysis of Ni(THP)(dppe)X (X = Br, Cl) with labeled adduct signals and (B) MALDI-TOF analysis of Ni(THP)(dppe)X exhibiting ionization-induced NiX elimination with and without oxidation.

Ni(THP)(dppe)Br was obtained as a yellow powder, consistent with previous Ni external initiators, and was washed several times with methanol. Due to the solvent's polarity, bromine-chlorine exchange takes place to form both bromine- and chlorine-Ni(THP)(dppe)X adducts (X = Br, Cl) that are seen as two sets of peaks by ^{31}P NMR.[3–5] Each of these apparent peaks consist of two closely spaced doublets, a consequence of splitting from both the asymmetric ligand environments and the chiral THP protecting group, and they possess coupling constants of $J_{\mathrm{PP}} < 20$ Hz, reflecting a Ni(II) species.[6] The MALDI-TOF spectrum of the product shows two peaks with m/z values consistent with NiBr elimination and rearrangement after instrument-induced ionization and oxidation,[3,5,7] further indicating the identity of the external initiator.

Polymer Molecular Weight Analysis

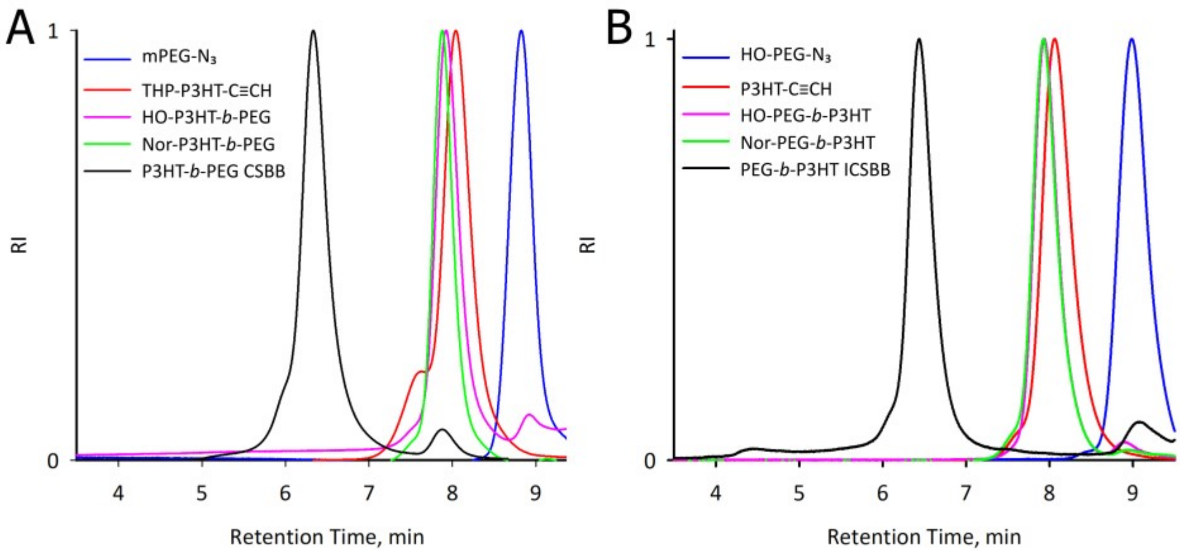


Fig. S2 GPC of (A) P3HT-*b*-PEG CSBB and its polymeric precursors and (B) PEG-*b*-P3HT ICSBB and its polymeric precursors.

Table S1 List of NMR- and GPC-derived parameters of synthesized polymers

Polymer	M_n[a]	M_n[c]	M_w[c]	Đ[d]
mPEG-N$_3$	1,180	1,000	1,100	1.10
THP-P3HT	3,220	3,900	4,500	1.15
HO-P3HT-*b*-PEG	4,670	5,000	5,500	1.10
Nor-P3HT-*b*-PEG	4,780	5,400	6,000	1.11
P3HT-b-PEG CSBB	N/A[b]	84,600	102,700	1.21
HO-PEG-N$_3$	1,070	700	800	1.11
***o*-tolyl-P3HT**	3,130	3,600	4,200	1.18
HO-PEG-*b*-P3HT	4,470	4,700	5,200	1.09
Nor-PEG-*b*-P3HT	4,540	4,800	5,400	1.11
PEG-*b*-P3HT ICSBB	N/A[b]	70,100	78,700	1.12

[a] M_n determined by NMR spectroscopy and rounded to nearest 10.

[b] There are no adequate spectroscopic handles for the CSBB or ICSBB.

[c] M_n and M_w determined by GPC and rounded to nearest 100.

[d] *Đ* determined from unrounded GPC molecular weight data.

Polymer Photophysical Properties

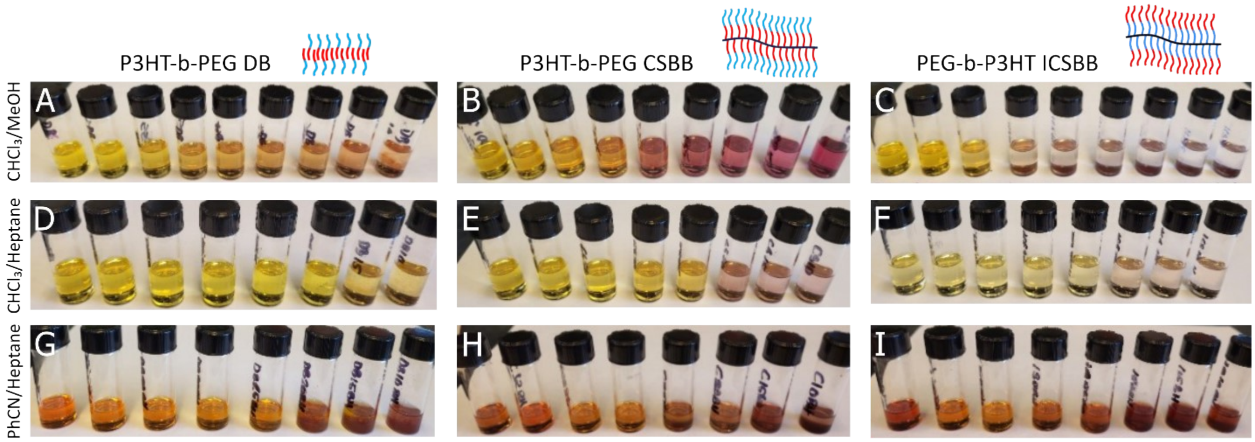


Fig. S3 0.02 mg/mL chloroform solutions of (A, D) P3HT-*b*-PEG diblock copolymer, (B, E) P3HT-*b*-PEG CSBB, and (C, F) PEG-*b*-P3HT ICSBB with 0-90% (A, B, C) methanol or (D, E, F) heptane. 0.2 mg/mL benzonitrile solutions of (G) P3HT-*b*-PEG diblock copolymer, (H) P3HT-*b*-PEG CSBB, and (I) PEG-*b*-P3HT ICSBB with 0-90%heptane.

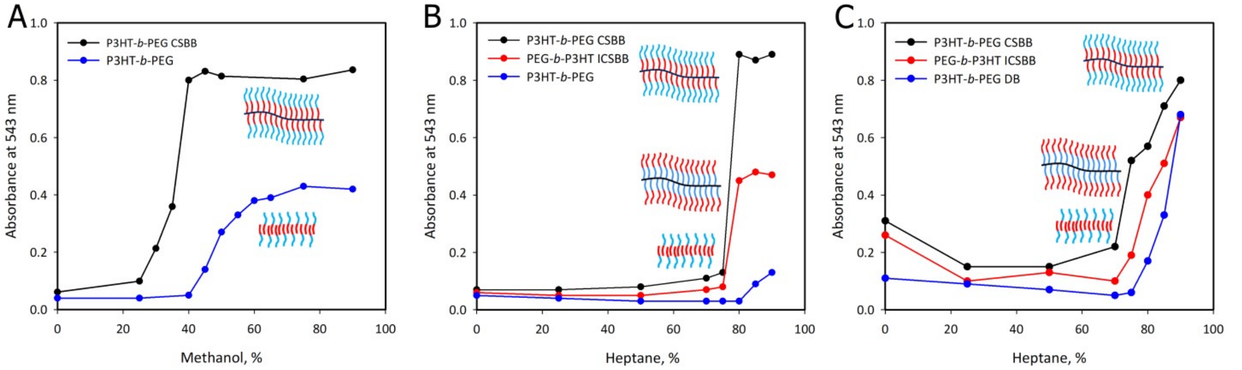


Fig. S4 Plots of UV-visible spectroscopy derived A_{0-1} (absorbance at 543 nm) intensities for polymers as a function of (A) methanol in chloroform solutions, (B) heptane in chloroform solutions, or (C) heptane in benzonitrile solutions as a volume percent. Black = P3HT-b-PEG CSBB, blue = P3HT-b-PEG diblock copolymer, red = PEG-b-P3HT ICSBB.

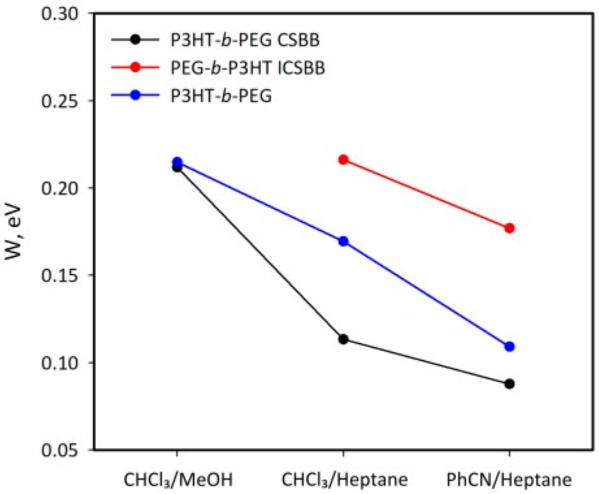


Fig. S5 Free exciton bandwidth calculated from UV-vis spectra of fully aggregated polymers in solution using Equation 1.

$$\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24W/E_p}{1 + 0.073W/E_p}\right)^2 \qquad (1)$$

The free exciton bandwidth (W) of P3HT aggregates can be estimated using Equation 1, which relates W to the absorbance transitions $A_{0\text{-}0}$ and $A_{0\text{-}1}$. The energy of the main intramolecular vibration, C=C, is assumed to be 0.179 eV.[8,9]

GIWAXS Analysis of Bottlebrush Polymers

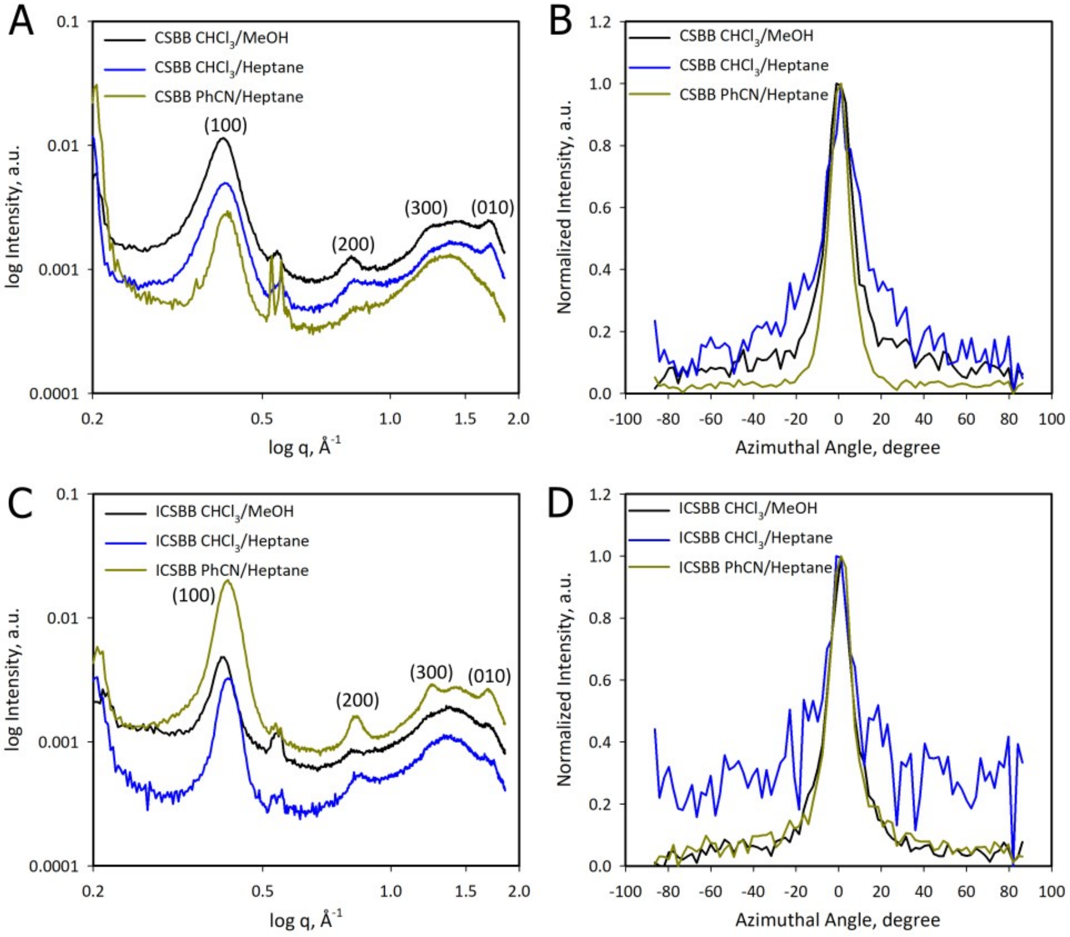


Fig. S6 (A) GIWAXS and (B) azimuthal angle profiles of drop cast CSBB. (C) GIWAXS and (D) azimuthal angle profiles of drop cast ICSBB. Log q was used to emphasize peaks in the upper experimental range.

Grazing incidence wide-angle x-ray scattering (GIWAXS) was performed on bottlebrush polymers drop cast onto crystalline silicon substrates from each binary solvent system. CSBBs show (100) peaks at $q = 0.405$ Å^{-1}, corresponding to P3HT lamellar stacking of 1.55 nm, which agrees with the expected value of 1.6 nm.[10,11] Second order (200) peaks can be observed at $q = 0.801$ Å^{-1} for every solvent system, and a weak third order (300) shoulder can be seen at $q = 1.20$ Å^{-1} for CSBBs self-assembled in chloroform/methanol. In addition, (010) peaks corresponding to π-π stacking are observed at $q = 1.70$ Å^{-1} (0.37 nm) for CSBBs self-assembled in chloroform/methanol and chloroform/heptane, while a weaker shoulder is observed for the self-assembly in benzonitrile/heptane. This π-π stacking agrees with previous crystallographic determination for P3HT.[10,11]

The GIWAXS profiles for the ICSBB largely resemble those of the CSBB. The (100) peaks for the chloroform/heptane and benzonitrile heptane blends appear at q = 0.415 Å^{-1}, resulting in a marginally closer lamellar spacing of 1.51 nm, compared to the CSBB. In contrast, the ICSBB in chloroform/methanol, which largely precipitated out, exhibits a (100) peak at q = 0.399 Å^{-1} (1.57 nm). Second order (200) peaks are observed at q = 0.807, 0.819, and 0.816 Å^{-1} for ICSBBs drop cast from chloroform/methanol, chloroform/heptane, and benzonitrile/heptane, respectively. A third order (300) peak can be seen at q = 1.24 Å^{-1} for the ICSBBs self-assembled in benzonitrile/heptane, while weaker shoulders are observed for the chloroform/methanol and chloroform/heptane conditions. Additionally, (010) peaks are observed at q = 1.68 Å^{-1} (0.37 nm) for the ICSBB in each self-assembly condition, agreeing with previously reported π-π stacking distances for P3HT.

The degree of crystallinity of each self-assembly for each bottlebrush self-assembly could be determined from the azimuthal full width at half-maximum (FWHM) for the (200) peak at each condition. The more prominent (100) peak was not used due to the larger peak offsets between all self-assembly conditions. The azimuthal FWHMs decrease in the order 20.0°, 15.1°, and 11.5° for CSBB self-assemblies drop cast from chloroform/heptane, chloroform/methanol, and benzonitrile/heptane, respectively. ICSBB self-assemblies exhibit azimuthal FWHMs of 18.4°, 13.6°, and 13.1° for the same solvent combinations.

Nanofiber TEM Images

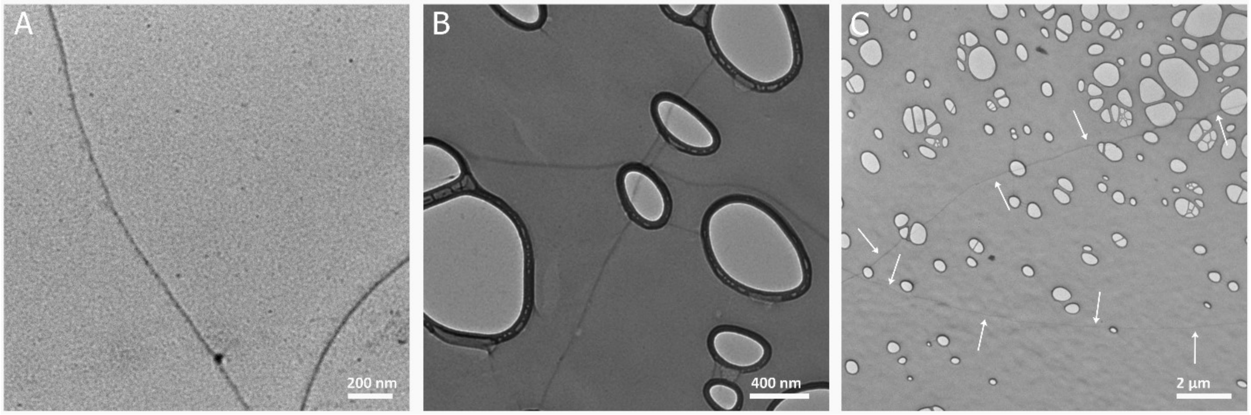


Fig. S7 TEM images of nanofibers formed from P3HT-*b*-PEG CSBB self-assembled in chloroform/heptane at various magnifications. Circular background features are from the lacey carbon film. Scale bars equal (A) 200 nm, (B) 400 nm, and (C) 2 µm.

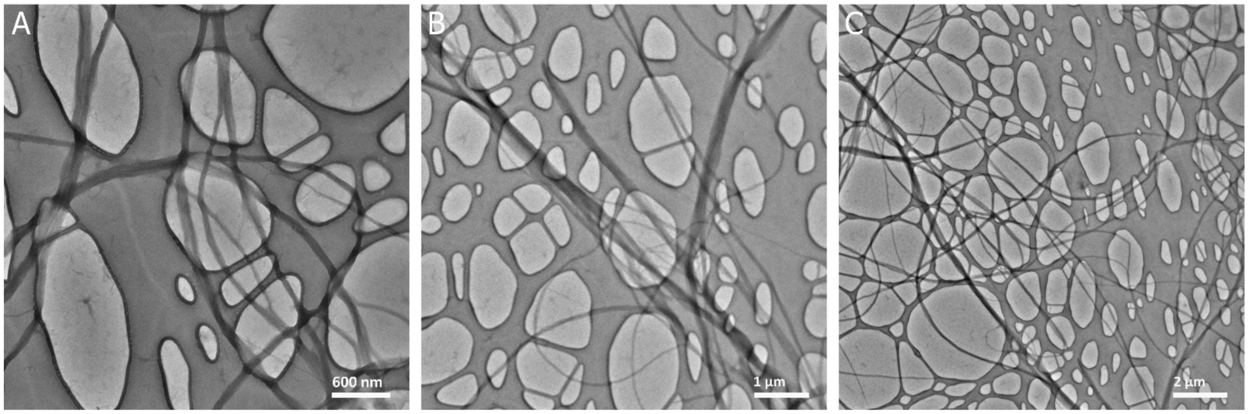


Fig. S8 TEM images of nanofibers formed from PEG-*b*-P3HT ICSBB self-assembled in chloroform/heptane at various magnifications. Circular background features are from the lacey carbon film. Scale bars equal (A) 600 nm, (B) 1 µm, and (C) 2 µm.

NMR Spectra

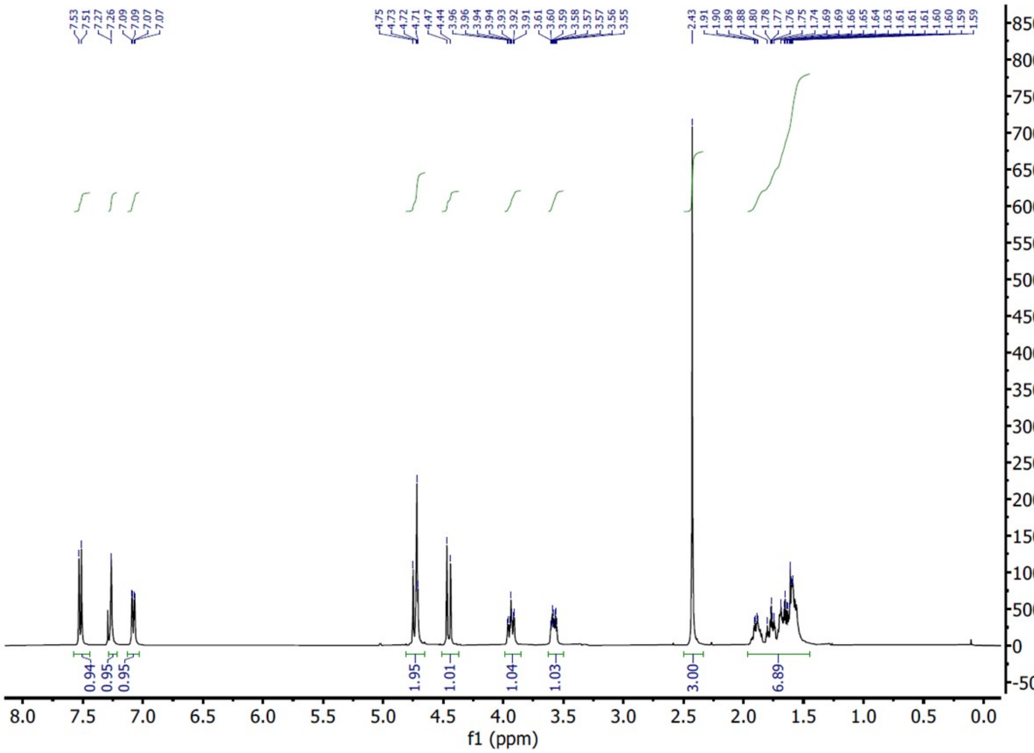


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-((4-bromo-3-methylbenzyl)oxy)tetrahydro-2H-pyran

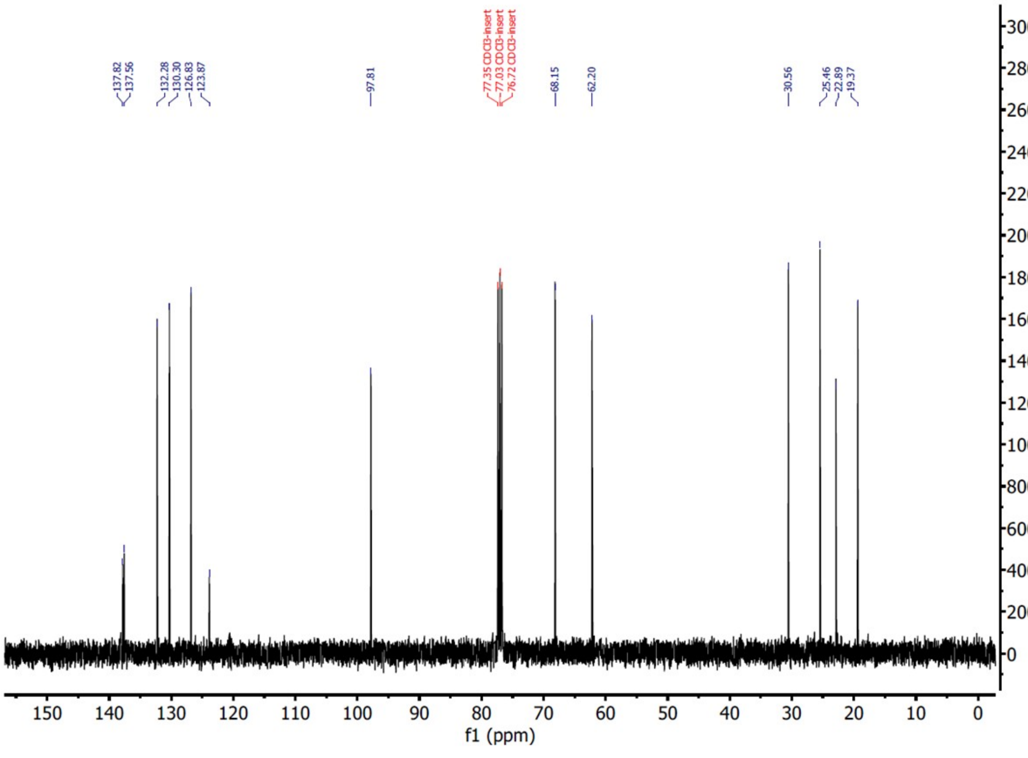


Fig. S10 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-((4-bromo-3-methylbenzyl)oxy)tetrahydro-2H-pyran

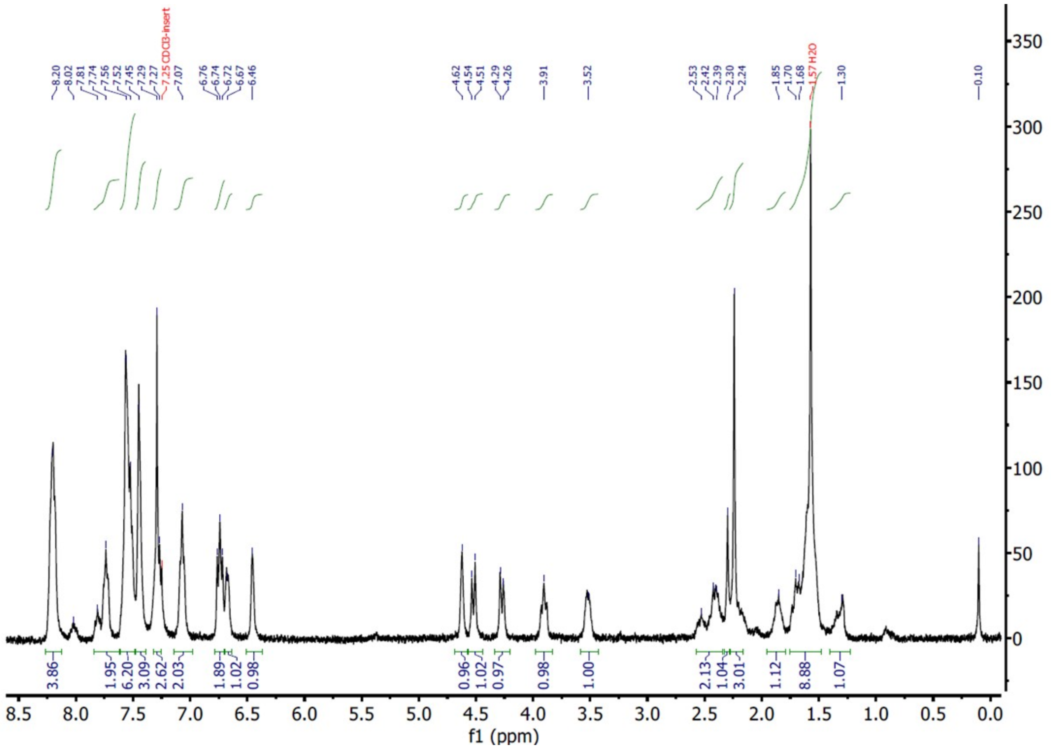


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [1,2-Bis(diphenylphosphino)ethane][2-((3-methylbenzyl)oxy)tetrahydro-2H-pyran]nickel (II) bromide (Ni(THP)(dppe)Br)

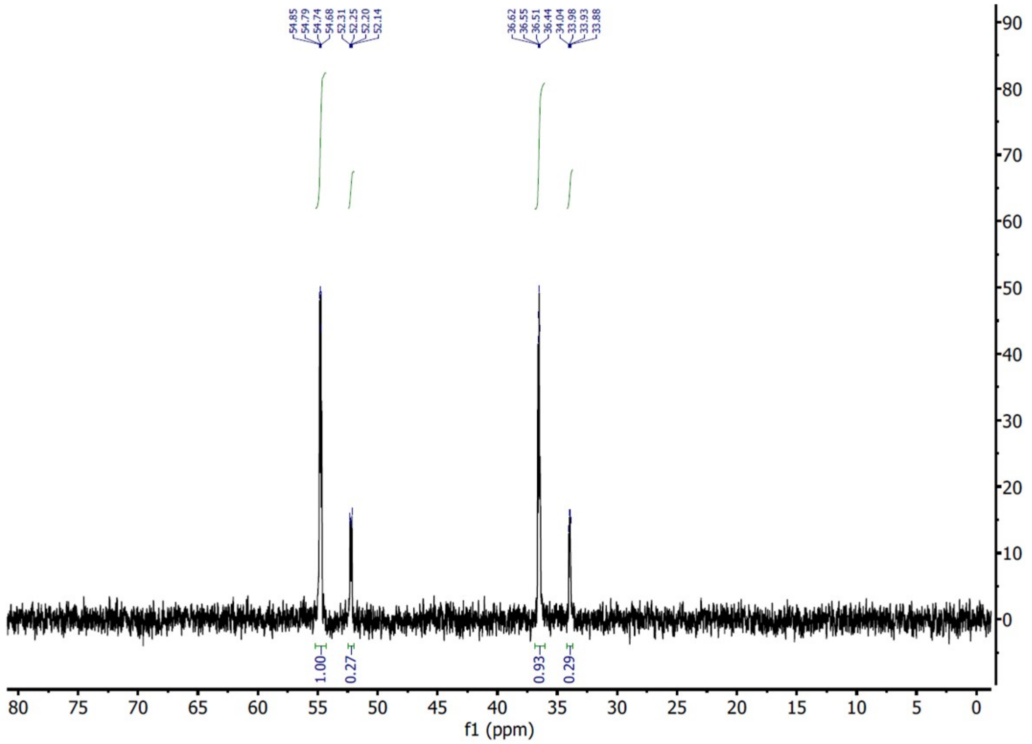


Fig. S12 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of [1,2-Bis(diphenylphosphino)ethane][2-((3-methylbenzyl)oxy)tetrahydro-2H-pyran]nickel (II) bromide (Ni(THP)(dppe)Br)

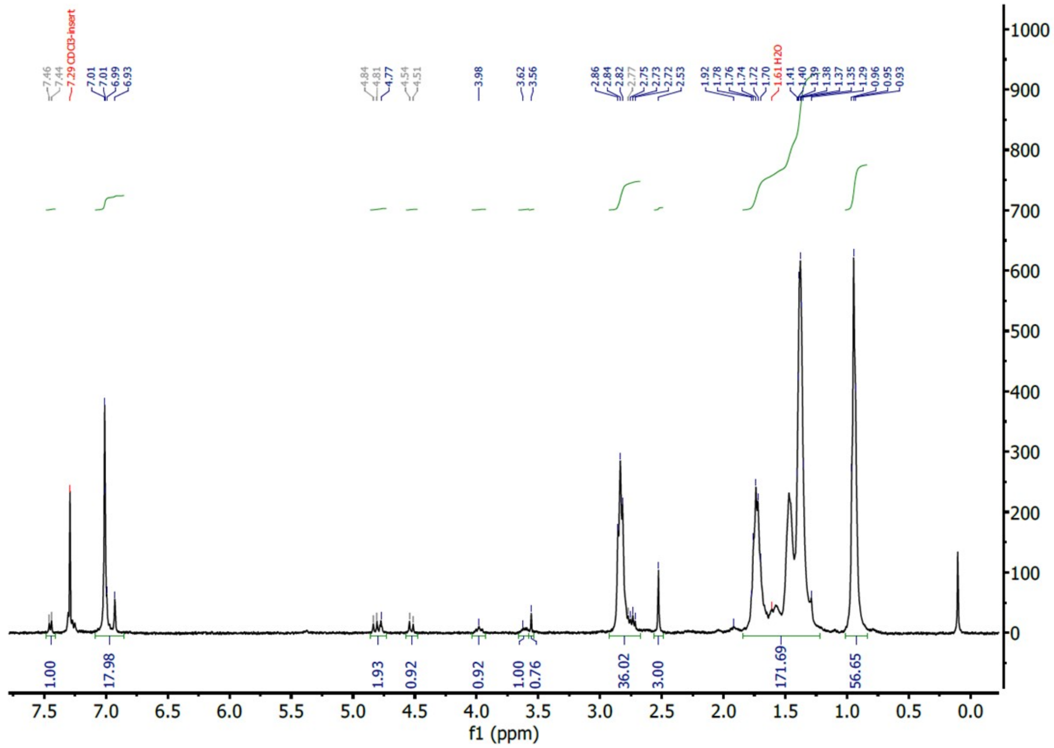


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-tetrahydropyran -ω-ethynyl-poly(3-hexylthiophene) (THP-P3HT–C≡CH)

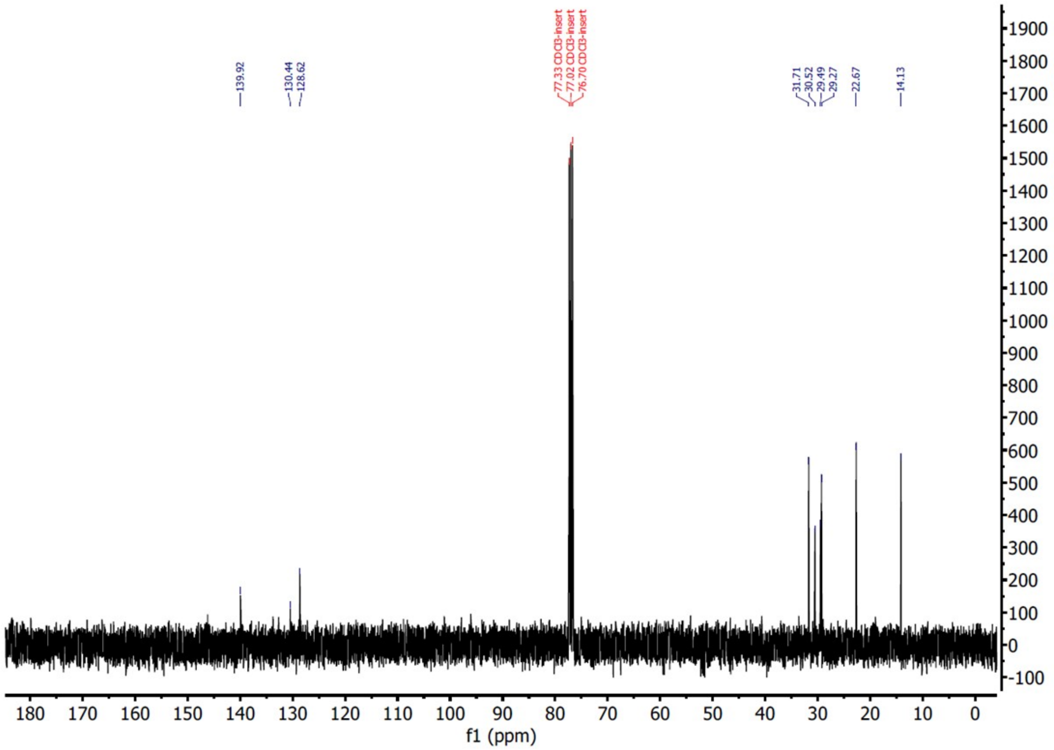


Fig S14. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of α-tetrahydropyran -ω-ethynyl-poly(3-hexylthiophene) (THP-P3HT–C≡CH)

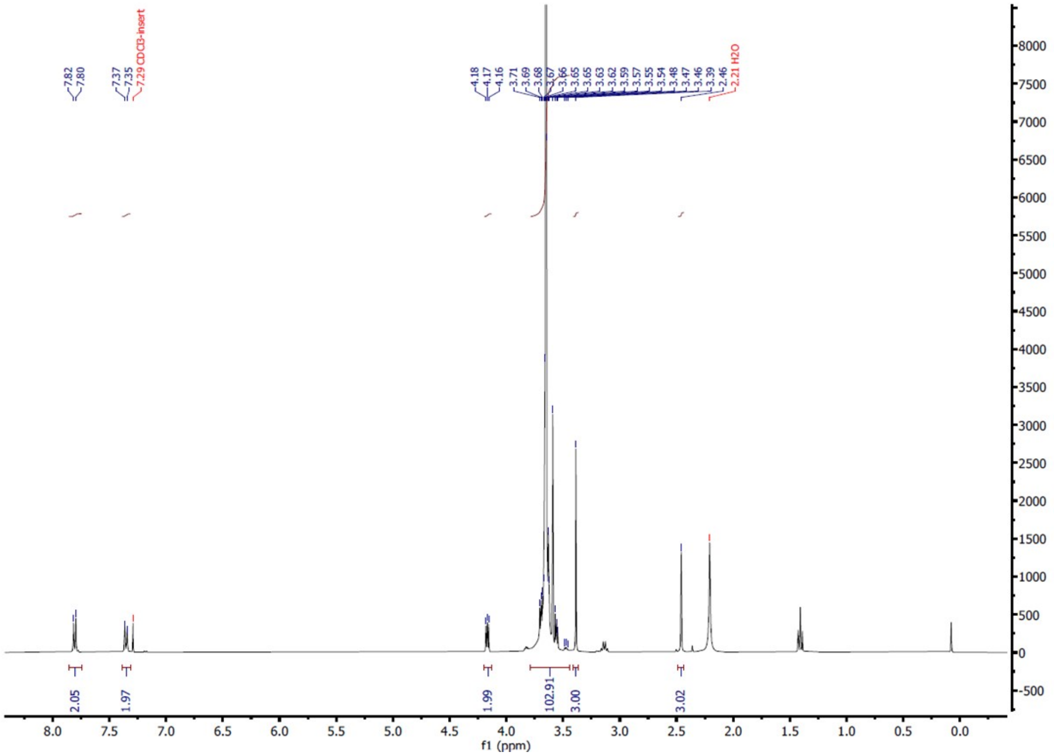


Fig S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-methoxy-ω-tosyl-poly(ethylene glycol) (mPEG-OTs)

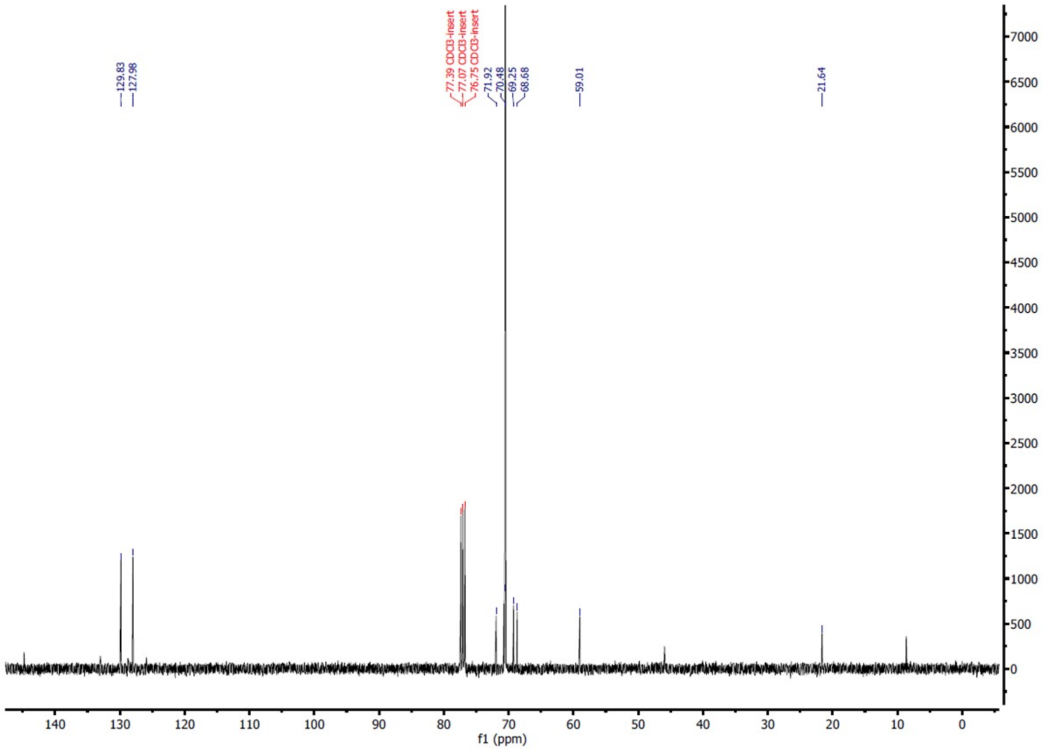


Fig. S16 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of α-methoxy-ω-tosyl-poly(ethylene glycol) (mPEG-OTs)

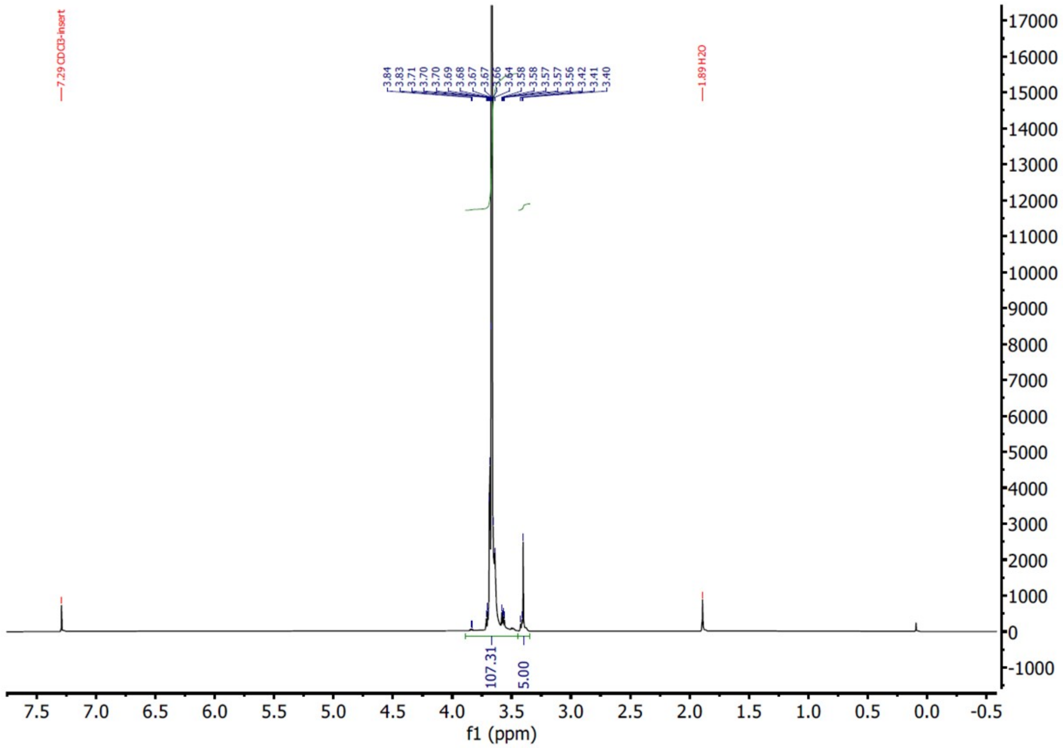


Fig. S17 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of α-methoxy-ω-azido-poly(ethylene glycol) (mPEG-N$_3$)

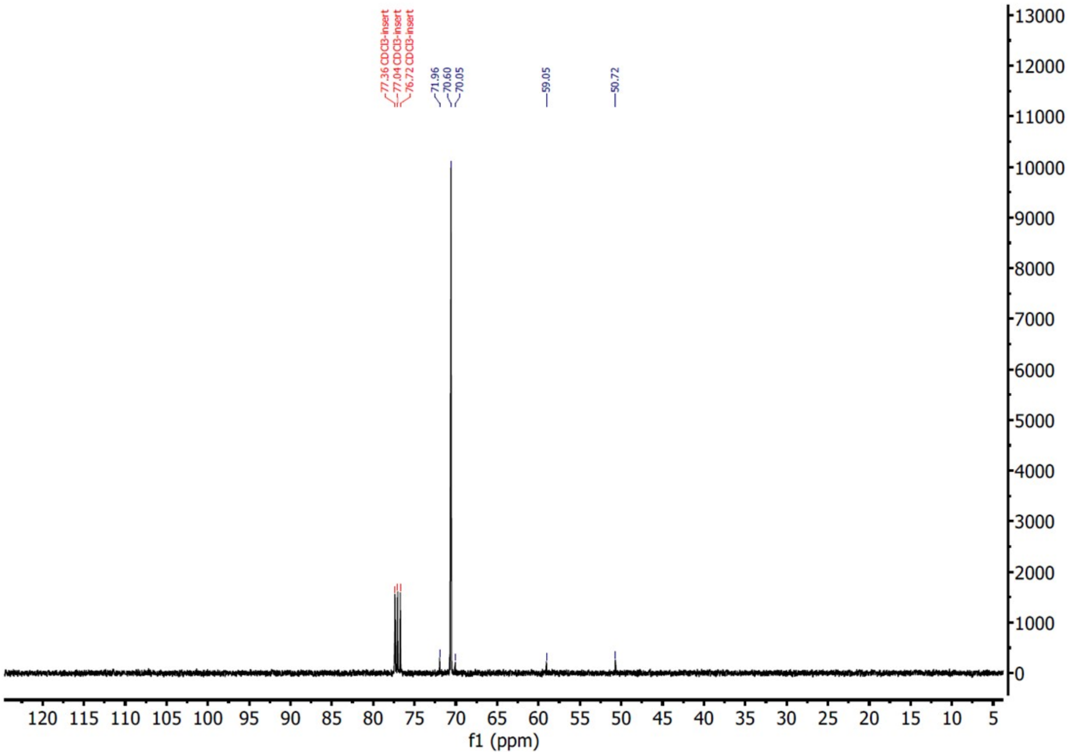


Fig. S18 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of α-methoxy-ω-azido-poly(ethylene glycol) (mPEG-N$_3$)

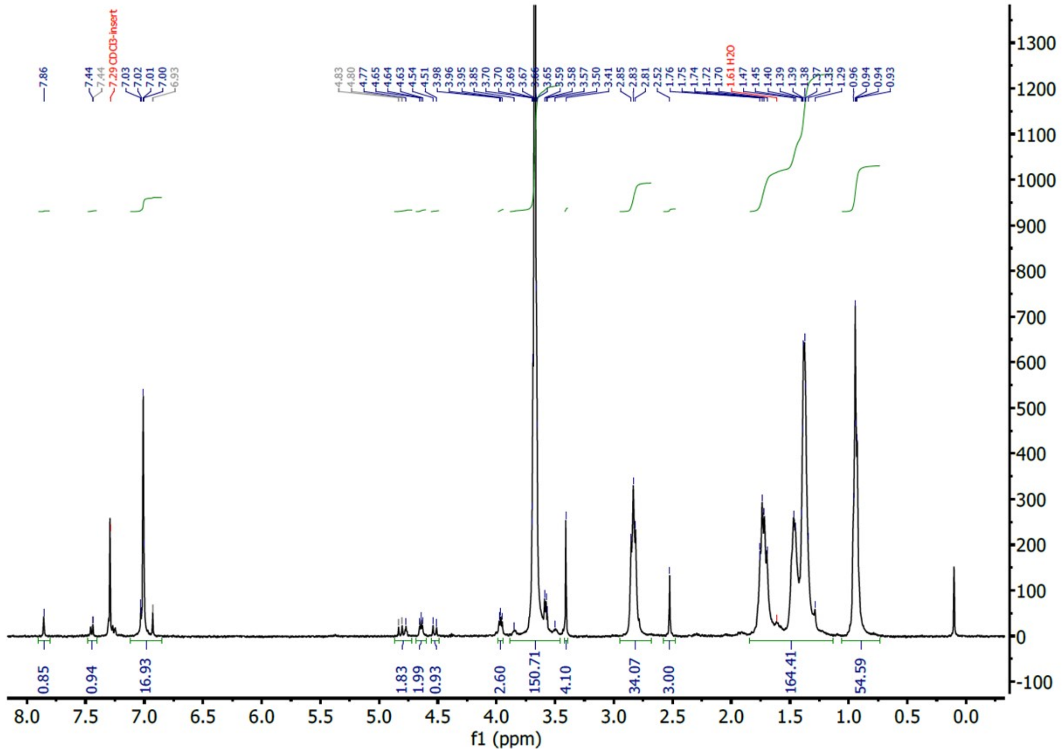


Fig. S19 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of α-tetrahydropyran-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (THP-P3HT-*b*-PEG)

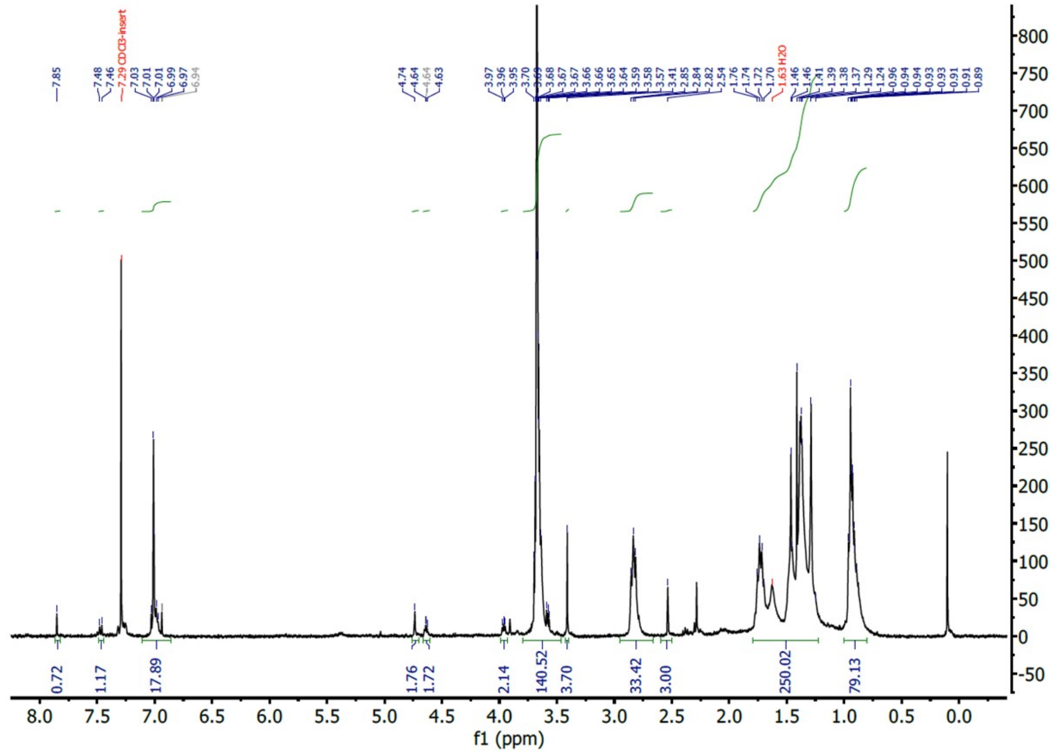


Fig. S20 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of α-hydroxy-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (HO-P3HT-*b*-PEG)

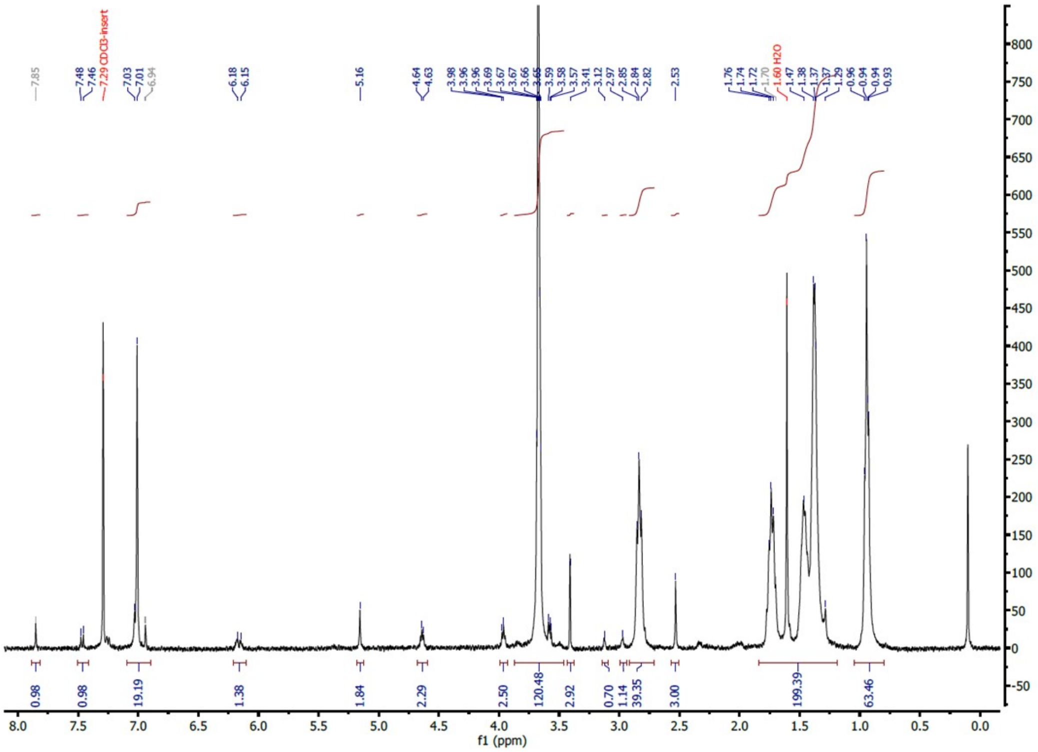


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-norbornene-ω-methoxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (Nor-P3HT-*b*-PEG)

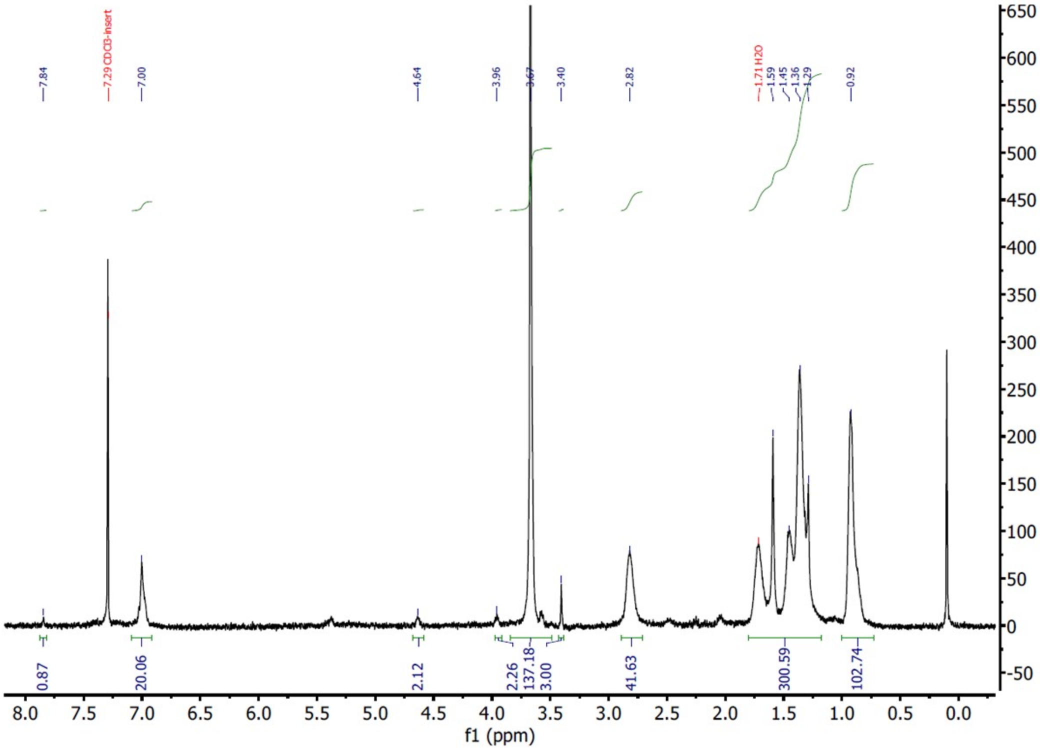


Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polynorbornene-*graft*-(poly(3-hexylthiophene)-block-poly(ethylene glycol)) (P3HT-*b*-PEG CSBB)

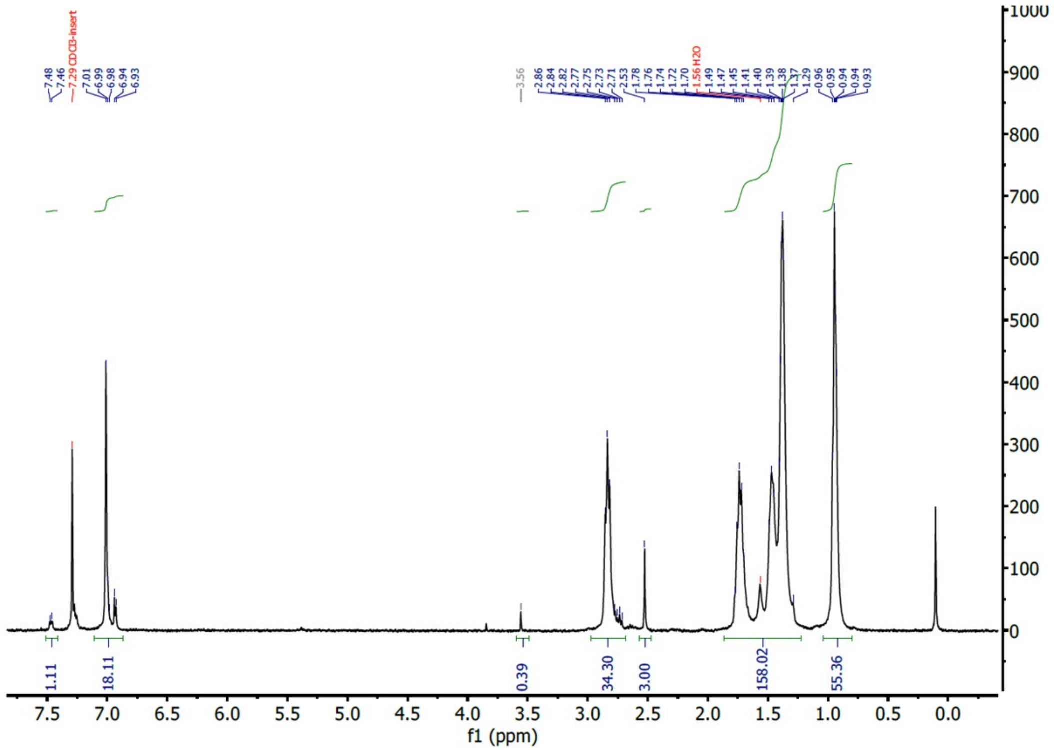


Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-*o*-tolyl-ω-ethynyl-poly(3-hexylthiophene) (P3HT–C≡CH)

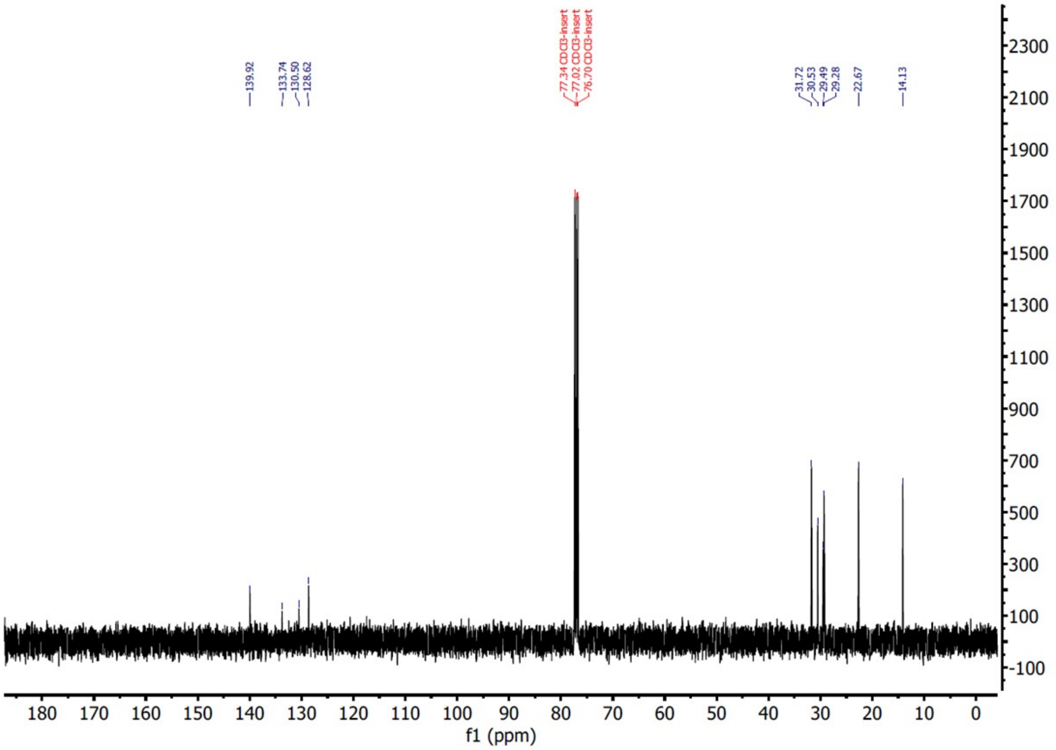


Fig. S24 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of α-*o*-tolyl-ω-ethynyl-poly(3-hexylthiophene) (P3HT–C≡CH)

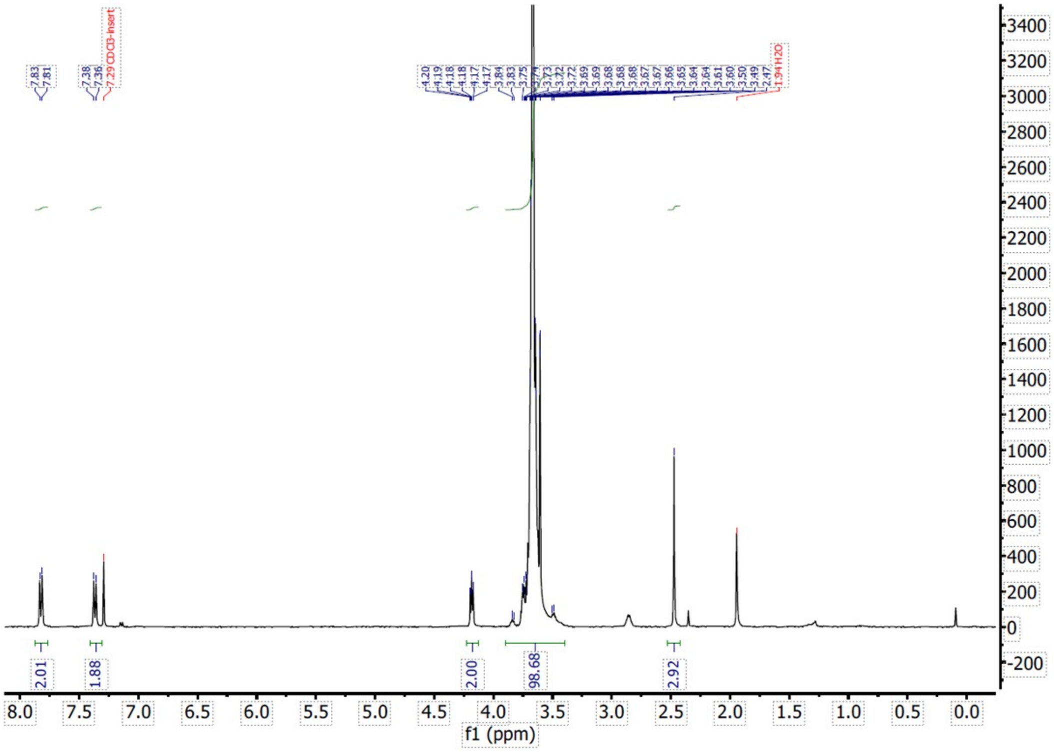


Fig. S25 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of α-hydroxy-ω-tosyl-poly(ethylene glycol) (HO-PEG-OTs)

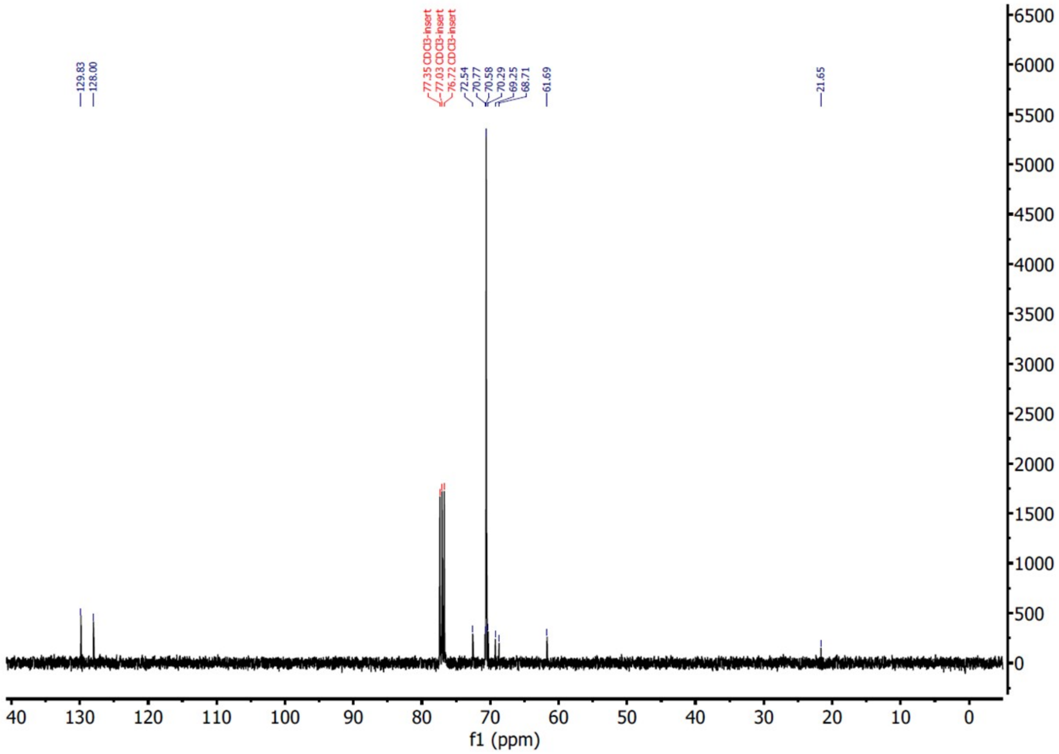


Fig. S26 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of α-hydroxy-ω-tosyl-poly(ethylene glycol) (HO-PEG-OTs)

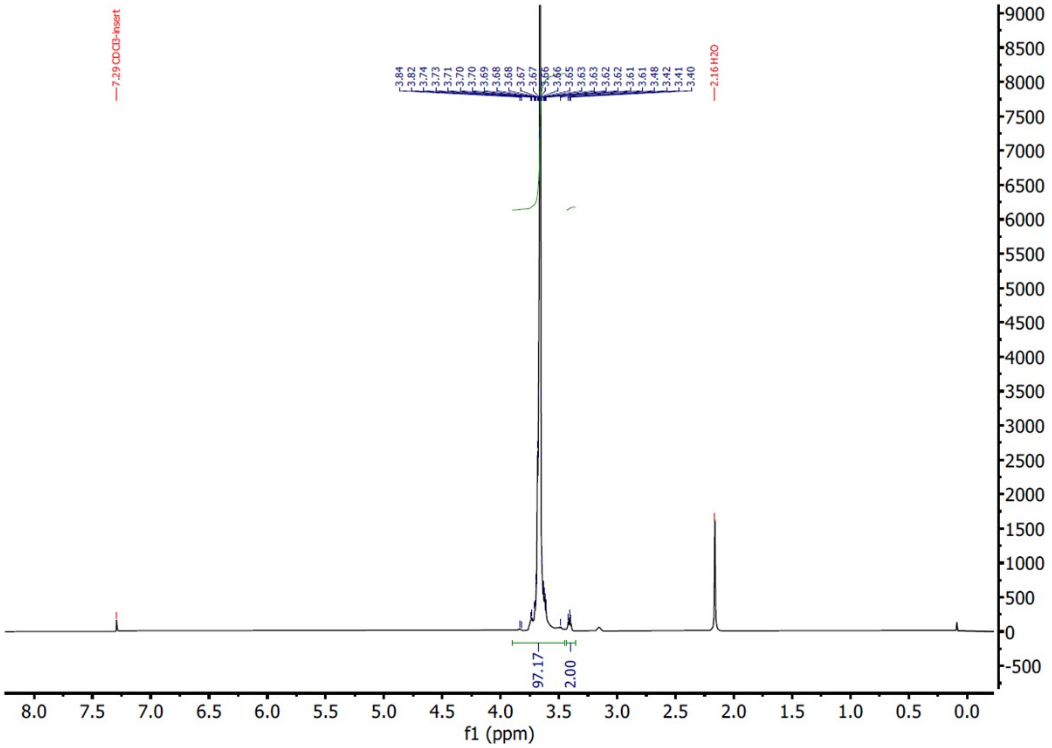


Fig. S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-hydroxy-ω-azido-poly(ethylene glycol) (HO-PEG-N_3)

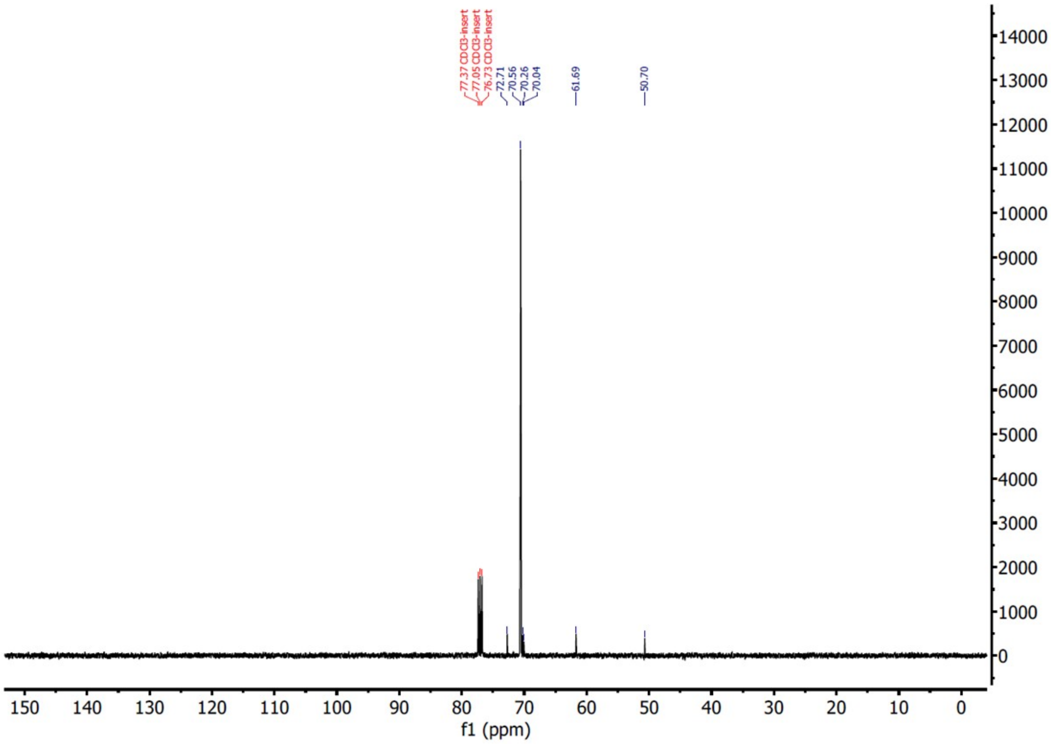


Fig. S28 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of α-hydroxy-ω-azido-poly(ethylene glycol) (HO-PEG-N_3)

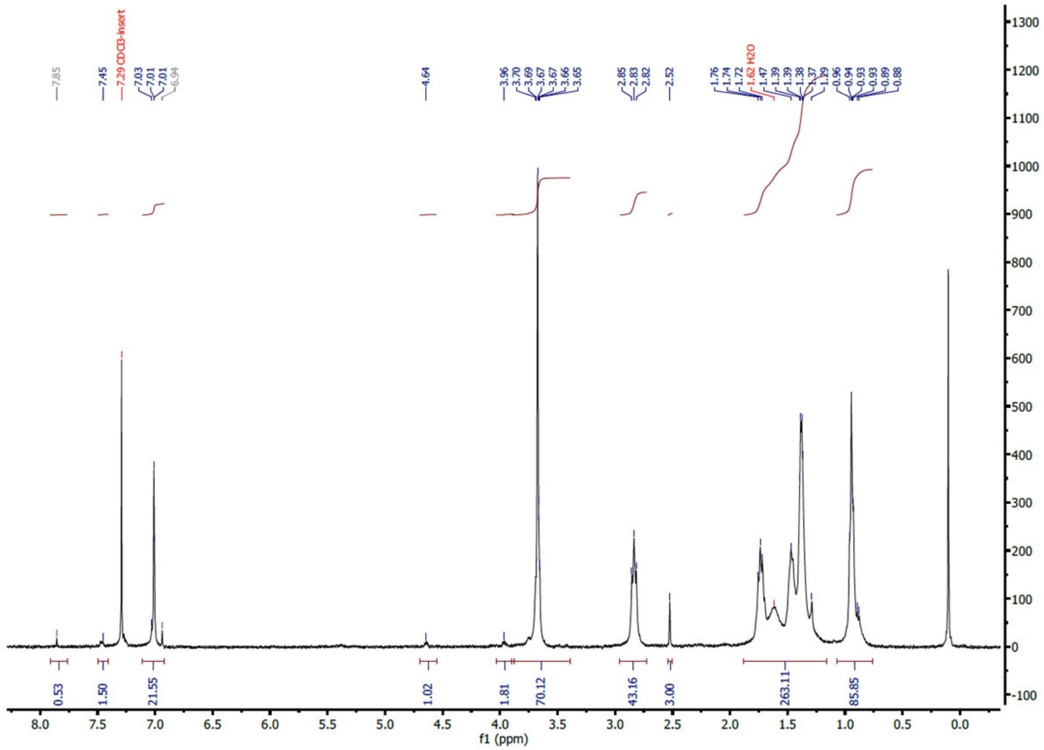


Fig. S29 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-o-tolyl-ω-hydroxy-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (HO-PEG-*b*-P3HT)

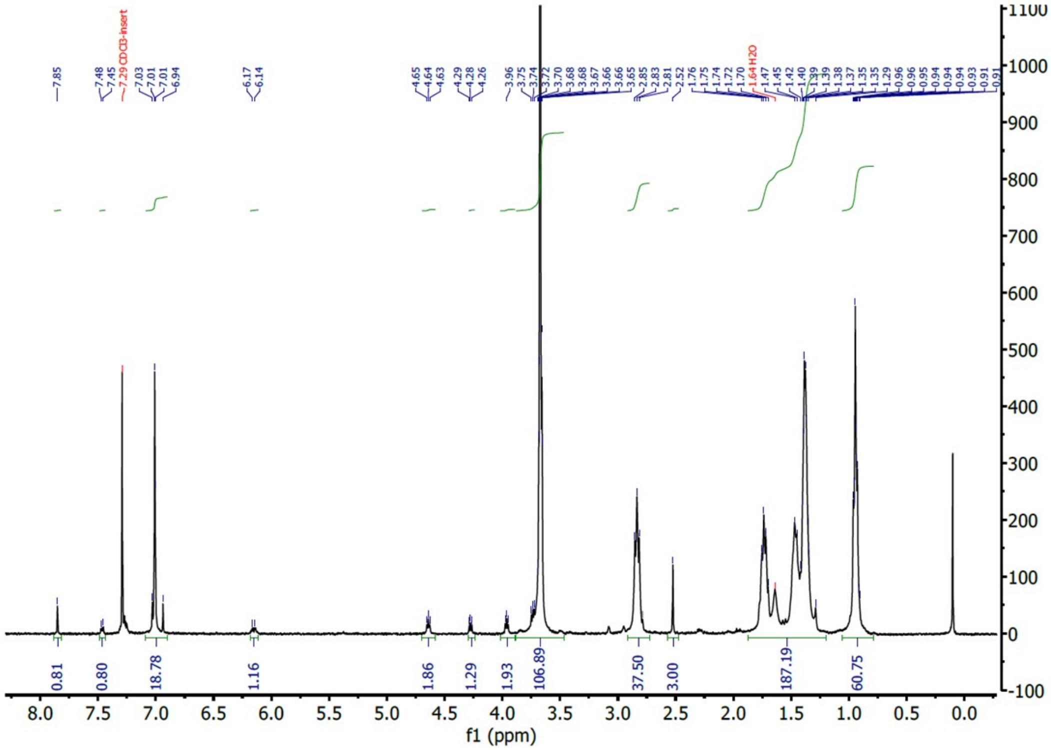


Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of α-o-tolyl-ω-norbornene-poly(3-hexylthiophene)-*block*-poly(ethylene glycol) (Nor-PEG-*b*-P3HT)

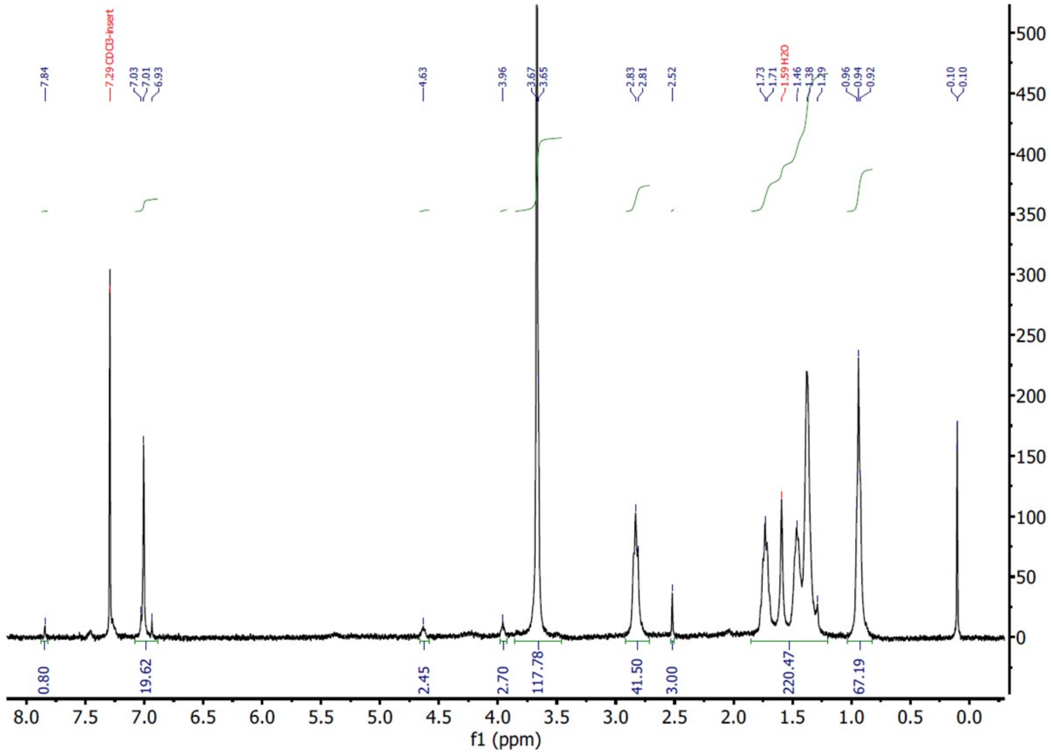


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polynorbornene-*graft*-(poly(ethylene glycol)-block-poly(3-hexylthiophene)) (PEG-*b*-P3HT ICSBB)

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