

## Electronic Supporting Information

### Synthesis and Self-Assembly of Poly(3-hexylthiophene)-*block*-Poly(acrylic acid)

Zicheng Li, Robert J. Ono, Zong-Quan Wu and Christopher W. Bielawski\*

Department of Chemistry & Biochemistry, The University of Texas, Austin, Texas 78712 (USA)

E-mail: bielawski@cm.utexas.edu

<b>General Considerations</b>	S2
<b>Transmission Electron Microscopy (TEM)</b>	S2
<b>Dynamic Light Scattering (DLS)</b>	S2
<b>Representative Procedure for the Synthesis of PtBA</b>	S3
<b>Representative Procedure for the Synthesis of PtBA-N<sub>3</sub></b>	S3
<b>Representative Procedure for the Synthesis of P3HT-C≡CH.</b>	S3
<b>Representative Procedure for the Synthesis of P3HT-<i>b</i>-PtBA</b>	S4
<b>Representative Procedure for the Synthesis of P3HT-<i>b</i>-PAA</b>	S4
<b>Procedure for the Synthesis of P3HT-C≡C-TMS</b>	S4
<b>Procedure for Micelle Assembly</b>	S4
<b>Figure S1.</b> <sup>1</sup> H NMR spectra of bromide- and azide-terminated PtBA.	S5
<b>Figure S2.</b> IR spectra of PtBA-bromide, PtBA-azide and P3HT- <i>b</i> -PtBA.	S5
<b>Figure S3.</b> <sup>1</sup> H NMR spectrum of ethynyl-terminated poly(3-hexylthiophene).	S6
<b>Figure S4.</b> <sup>1</sup> H NMR spectra of P3HT <sub>96</sub> - <i>b</i> -PtBA <sub>170</sub> and P3HT <sub>96</sub> - <i>b</i> -PAA <sub>170</sub> .	S6
<b>Figure S5.</b> Gel permeation chromatograms of P3HT- <i>b</i> -PtBA.	S7
<b>Figure S6.</b> Gel permeation chromatograms of P3HT <sub>50</sub> -C≡CH.	S7
<b>Figure S7.</b> UV-vis spectra of P3HT- <i>b</i> -PAA (THF solution and micelle solution).	S8
<b>Figure S8.</b> DLS histograms for P3HT <sub>96</sub> - <i>b</i> -PtBA <sub>170</sub> and P3HT <sub>29</sub> - <i>b</i> -PAA <sub>112</sub> .	S8
<b>Figure S9.</b> <sup>1</sup> H NMR spectrum of P3HT-C≡C-TMS.	S9
<b>Figure S10.</b> Gel permeation chromatogram of P3HT <sub>25</sub> -C≡C-TMS.	S9

**General Considerations.** All solvents were purchased from Fisher Scientific and used without additional purification unless otherwise noted. Prior to use, *t*-butyl acrylate (*t*BA) was filtered through a short plug of alumina to remove the 4-methoxyphenol (MEHQ) stabilizer. All other chemicals were purchased from Aldrich, Alfa Aesar, or Fisher, and were used as received. 2,5-Dibromo-3-hexylthiophene was prepared according to literature procedures.<sup>1</sup> THF was dried over 3Å molecular sieves and deoxygenated using a Vacuum Atmospheres Company solvent purification system. The separation tubing used for dialysis (molecular weight cutoff or MWCO = 6–8 kDa) were purchased from Spectrum Medical Industries Inc. <sup>1</sup>H NMR spectra were recorded using a Varian Gemini (300 MHz or 400 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent as an internal standard (CDCl<sub>3</sub>, 7.24 ppm; THF-*d*<sub>8</sub>, 1.73 and 3.58 ppm). Gel permeation chromatography (GPC) was performed on a Viscotek system equipped with a VE 1122 pump, a VE 7510 degasser, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-3078) thermostated to 30 °C (using a ELDEX CH 150 column heater) and arranged in series or on a home-built system equipped with a Waters Model 510 HPLC pump, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-3078) arranged in series, and a Waters 486 Tunable Absorbance Detector. Molecular weight and polydispersity data are reported relative to polystyrene standards in tetrahydrofuran (THF). IR spectra were recorded using Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. Differential scanning calorimetry analyses were performed on a Mettler Toledo DSC 823<sup>e</sup>. UV–vis spectra were recorded using a Perkin Elmer Instruments Lambda 35 spectrometer.

**Transmission electron microscopy (TEM).** TEM was performed in bright-field mode with a TECNAI Spirit Biotwin at 80 kV accelerating voltage. Samples for TEM measurements were diluted with equal volume of 1 wt% aqueous solution of phosphotungstic acid stain and cast onto carbon-coated copper mesh grids. Micrographs were collected at 100,000× magnification. The number average particle diameters ( $D_{avg}$ ) and standard deviations were generated from the analysis of a minimum of 150 particles from at least three different micrographs.

**Dynamic Light Scattering (DLS).** Hydrodynamic diameters ( $D_h$ ) and size distributions were measured in aqueous media by DLS. The custom-built DLS instrument consisted of a Brookhaven Instruments Limited (Worcestershire, U.K.) system, a model BI-9000AT digital correlator, a model EMI-9865 photomultiplier, and a model 17 mW He-Ne laser (NSG America, SELFOC micro-lens, 1.8 mm diameter, 0.25 pitch) operated at 632.8 nm. Measurements were performed at 20 °C. Prior to analysis, solutions were filtered through a 0.45 μm Millex GV PVDF membrane filter (Millipore Corp., Medford, MA) to remove dust particles. Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 ratio spaced channels, an initial delay of 2 μs, a final delay of 100 ms, and a duration of 3 min. A photomultiplier aperture was used and the incident laser intensity was adjusted to obtain a photon counting of between 200 and 300 kcps. Only data in which the measured and calculated baselines of the intensity autocorrelation function agreed to within 0.1% were used to calculate particle sizes. The calculations of the particle size distributions and distribution averages were

---

(1) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.

performed with the ISDA software package (Brookhaven Instruments), which employed single-exponential fitting, cumulants analysis, and non-negatively constrained least-squares (CONTIN) particle size distribution analysis routines. All determinations were made in triplicate.

**Representative Procedure for the Synthesis of Poly(*t*-butyl acrylate) (PtBA).** An oven-dried 100 mL flask was charged with copper(I) bromide (365 mg, 2.54 mmol), *t*-butyl acrylate (20.0 g, 156 mmol), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (440 mg, 2.54 mmol), and a stir bar. After one freeze-pump-thaw cycle, ethyl 2-bromoisobutyrate (248 mg, 1.27 mmol) was added using nitrogen flushed syringes. After three additional freeze-pump-thaw cycles, the reaction mixture was warmed to ambient temperature and placed in an oil bath at 65 °C. After stirring the mixture for 120 min, the reaction was quenched by immersion of the flask in liquid nitrogen. The reaction mixture was then taken up in THF and passed through a short column of neutral alumina (eluent = THF) to remove the residual catalyst. The polymer mixture was then concentrated, precipitated into cold methanol/water mixture (50/50 v/v) (3×), and collected via filtration (16.6 g, 80% yield). Data for PtBA<sub>112</sub>: GPC:  $M_N = 14.6$  kDa,  $M_W/M_N = 1.32$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 4.05 (broad overlapping m, CH<sub>3</sub>CH<sub>2</sub>O and CHBr end groups), 2.30-2.10 (broad, CH of the polymer backbone), 1.88-1.68 (broad, *meso* CH<sub>2</sub> of the polymer backbone), 1.65-1.30 (broad, *meso* and *racemo* CH<sub>2</sub> of the polymer backbone and (CH<sub>3</sub>)<sub>3</sub>C). Using end-group analysis, the  $M_N = 14.5$  kDa. FTIR (KBr): 3448, 2981, 2933, 1734, 1367, 1259, 1150, 846 cm<sup>-1</sup>.

**Representative Procedure for the Synthesis of PtBA-N<sub>3</sub>.** A 50 mL flask was charged with PtBA ( $M_N = 7.4$  kDa, 410 mg, 55 μmol), NaN<sub>3</sub> (36 mg, 550 μmol), DMF (8 mL), and a stir bar. The resulting mixture was stirred at 50 °C for 12 h and then cooled to ambient temperature. After adding CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and water (50 mL), the organic phase was separated and extracted with water (4 × 50 mL), and then dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the residual solvent under reduced pressure afforded the desired product in 87% yield (350 mg). Data for PtBA<sub>57</sub>-N<sub>3</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 4.05 (broad m, CH<sub>3</sub>CH<sub>2</sub>O), 3.78 (broad, CH-N<sub>3</sub>), 2.30-2.10 (broad, CH of the polymer backbone), 1.88-1.68 (broad, *meso* CH<sub>2</sub> of the polymer backbone), 1.70-1.30 (broad, *meso* and *racemo* CH<sub>2</sub> of the polymer backbone and (CH<sub>3</sub>)<sub>3</sub>C). FTIR (KBr): 3450, 2980, 2123, 1730, 1560, 1459, 1369, 1259, 1150, 846 cm<sup>-1</sup>.

**Representative Procedure for the Synthesis of Poly(3-hexylthiophene)-C≡CH (P3HT-C≡CH).** A 50 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (500 mg, 1.53 mmol), dry THF (12 mL), and a stir bar. After adding isopropylmagnesium chloride (0.76 mL, 2.0 M solution in THF), the resulting mixture was placed in an oil bath at 50 °C for 2 h. Upon cooling to ambient temperature, Ni(dppp)Cl<sub>2</sub> (16.6 mg, 2 mol%; dppp = 1,3-bis(diphenylphosphino)propane) and, after 10 min, ethynylmagnesium bromide (0.4 mL, 0.5 M in THF) were added to the mixture. After an additional 5 min, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers. The purple solid was then dried under vacuum to afford 150 mg (60% yield) of the desired polymer. The microstructure of the polymer was determined by <sup>1</sup>H NMR spectroscopy to be 97% head-to-tail. GPC:  $M_N = 4.9$  kDa,  $M_W/M_N = 1.24$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 6.98 (s, CH of the thiophene ring), 3.52 (s, terminal ethynyl CH), 2.80 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.71 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.50-1.30 (broad m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.90 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Representative Procedure for the Synthesis of P3HT-*b*-PtBA.** A 25 mL flask was charged with P3HT-C≡CH (26.4 mg, 5.38 μmol), PtBA-N<sub>3</sub> (80.5 mg, 5.55 μmol), CuBr (1.5 mg, 10 μmol), PMDETA (2.0 mg, 11 μmol) and dry THF (10 mL). The mixture was degassed by one freeze-pump-thaw cycle and was then immersed into an oil bath thermostatted to 40 °C. After stirring for 24 h, the reaction mixture was passed through a short column of neutral alumina (eluent = THF) to remove the residual catalyst. The crude product was then concentrated and precipitated into methanol to remove unreacted PtBA-N<sub>3</sub>. The desired product was collected in 60% yield (67 mg) *via* filtration. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 6.98 (s, CH of the thiophene ring), 2.81 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.30-2.10 (broad, CH of the polymer backbone), 1.90-1.75 (broad, *meso* CH<sub>2</sub> of the polymer backbone), 1.71 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.50-1.30 (broad m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *meso* and *racemo* CH<sub>2</sub> of the PtBA backbone and (CH<sub>3</sub>)<sub>3</sub>C), 0.90 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

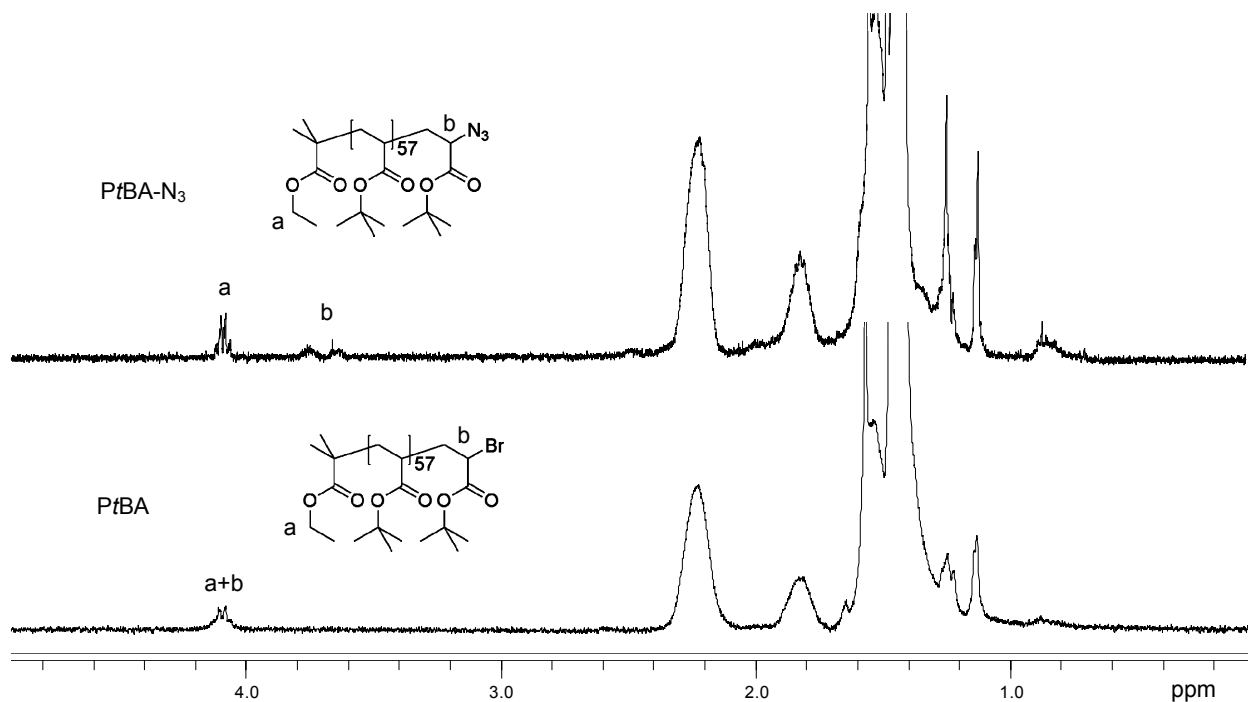
**Representative Procedure for the Synthesis of P3HT-*b*-PAA.** After dissolving P3HT<sub>96</sub>-*b*-PtBA<sub>170</sub> (14.3 mg, 0.35 μmol) in chloroform (5 mL), trifluoacetic acid (0.20 mL, 33 mmol) was added. The reaction mixture was allowed to stir at room temperature for 24 h, after which the solvent was removed under reduced pressure. The resulting crude solid was then washed with cold hexanes and dried under reduced pressure to afford the desired product (9.5 mg, 97% yield). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 7.08 (s, CH on the thiophene ring), 2.85 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.55-2.38 (broad, CH of the polymer backbone), 2.00-1.85 (broad, *meso* CH<sub>2</sub> of the polymer backbone), 1.75-1.30 (broad m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *meso* and *racemo* CH<sub>2</sub> of the PAA backbone), 0.98 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Procedure for the Synthesis of Poly(3-hexylthiophene)-C≡C-TMS (P3HT-C≡C-TMS).** The polymerization was conducted analogously to the synthesis of P3HT-C≡CH by quenching the polymerization with 2-(trimethylsilyl)ethynylmagnesium bromide.<sup>2</sup> Following precipitation into methanol and collection by filtration, the isolated solids were washed with excess methanol, and subjected to Soxhlet extraction with chloroform. The polymer was isolated from the chloroform solution upon evaporation of the residual solvent in 78% yield. GPC: *M*<sub>N</sub> = 4.6 kDa, *M*<sub>W</sub>/*M*<sub>N</sub> = 1.33. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 6.96 (s, CH of the thiophene ring), 2.78 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.69 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.50-1.30 (broad m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.90 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.25 (s, Si(CH<sub>3</sub>)<sub>3</sub>).

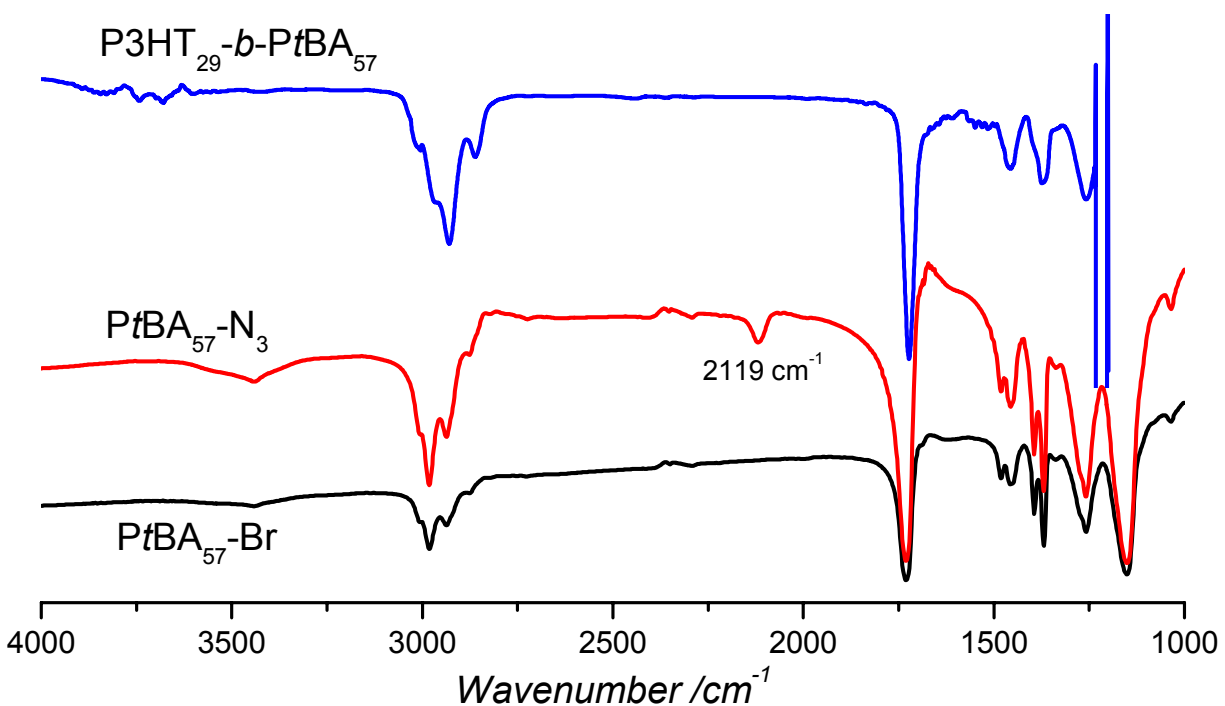
**Procedure Used for Micelle Assembly.** To a round-bottom flask equipped with a magnetic stir bar was added P3HT-*b*-PAA followed by THF (8.0 mL). The resulting mixture was stirred for 2 h at room temperature to ensure that a homogeneous solution had formed (final polymer concentration = *ca.* 1.0 mg/mL). To this solution, an equal volume of de-ionized water (8.0 mL) was added dropwise *via* a syringe pump over 3 h. The mixture was then stirred for 12 h at room temperature before being transferred to a pre-soaked dialysis tube and then dialyzed against de-ionized water for 4 d, which afforded a transparent purple micelle solution (*ca.* 16 mL) with the final polymer concentration in the range of 0.20 to 0.30 mg/mL.

---

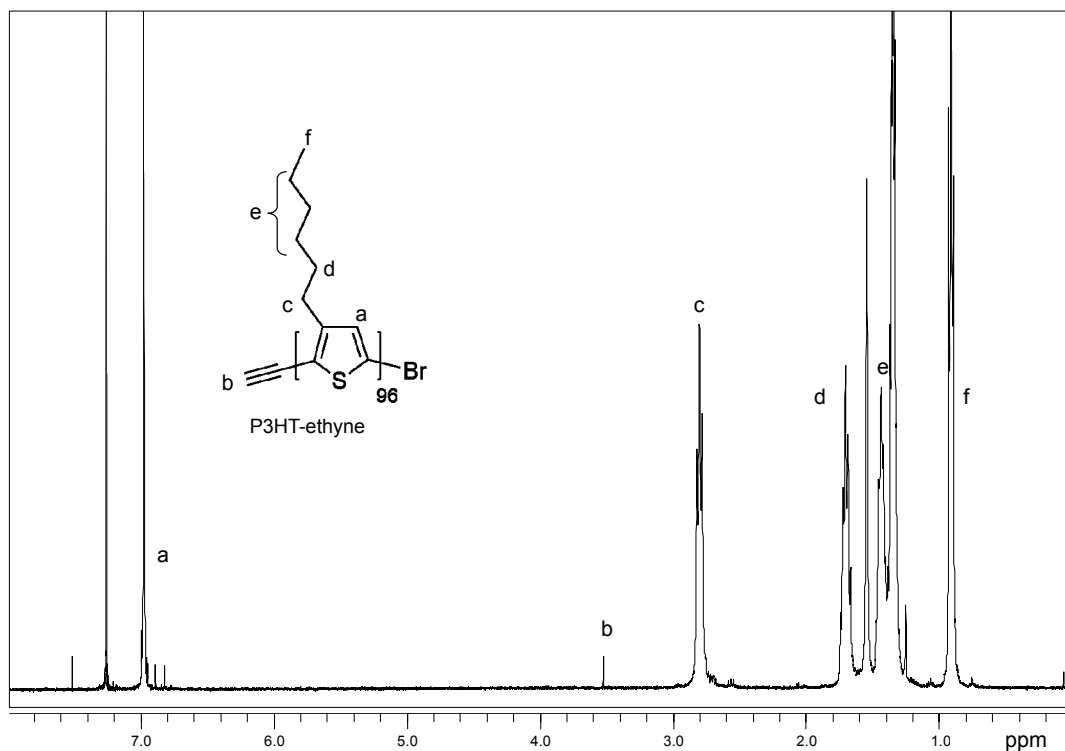
(2) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 3093–3096.



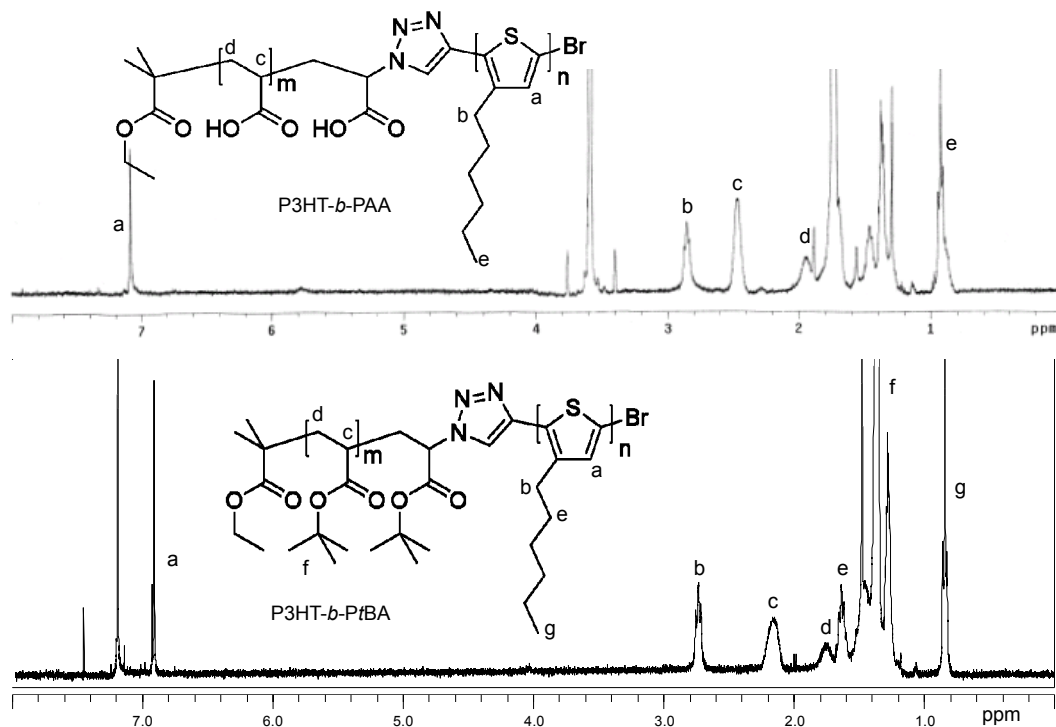
**Figure S1.** Representative  $^1\text{H}$  NMR spectra of (top) azide- and (bottom) bromide-terminated PtBA ( $\text{CDCl}_3$ ).



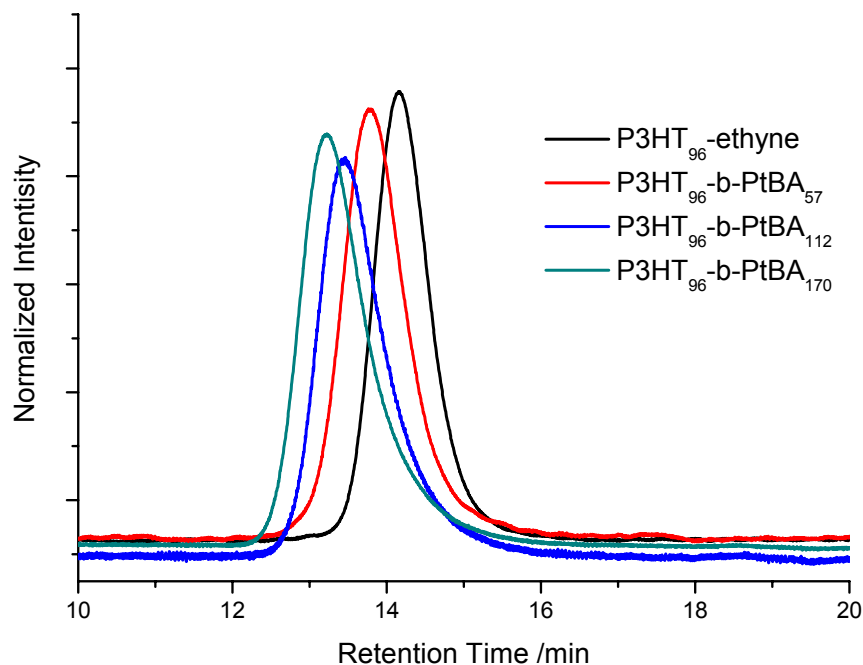
**Figure S2.** Representative IR spectra (KBr) of bromide-terminated PtBA (black), azide-terminated PtBA (red) and P3HT-*b*-PtBA (blue). The signal at  $2119\text{ cm}^{-1}$  was assigned to the azide stretching frequency.



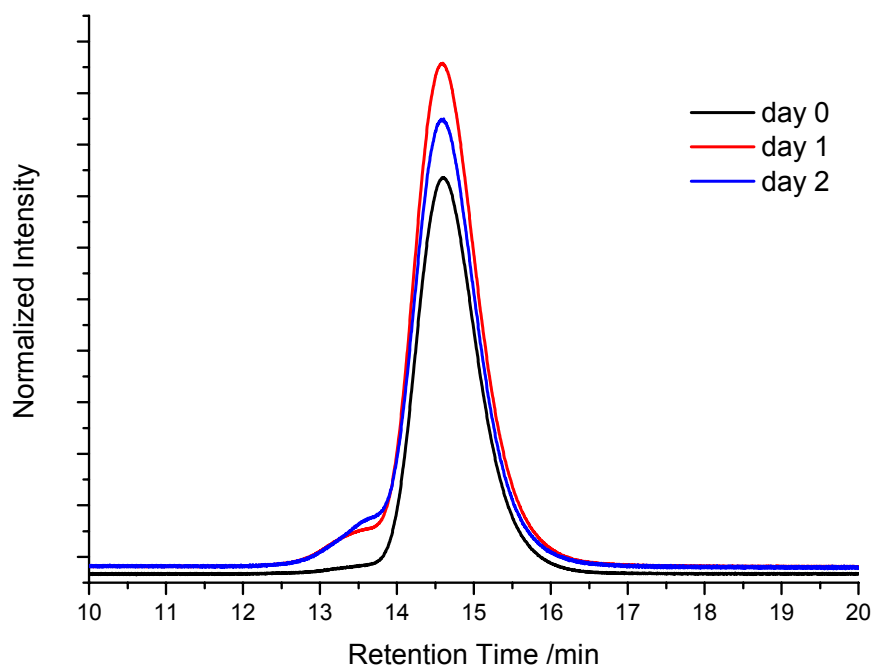
**Figure S3.** Representative  $^1\text{H}$  NMR spectrum of ethynyl-terminated poly(3-hexylthiophene) ( $\text{CDCl}_3$ ).



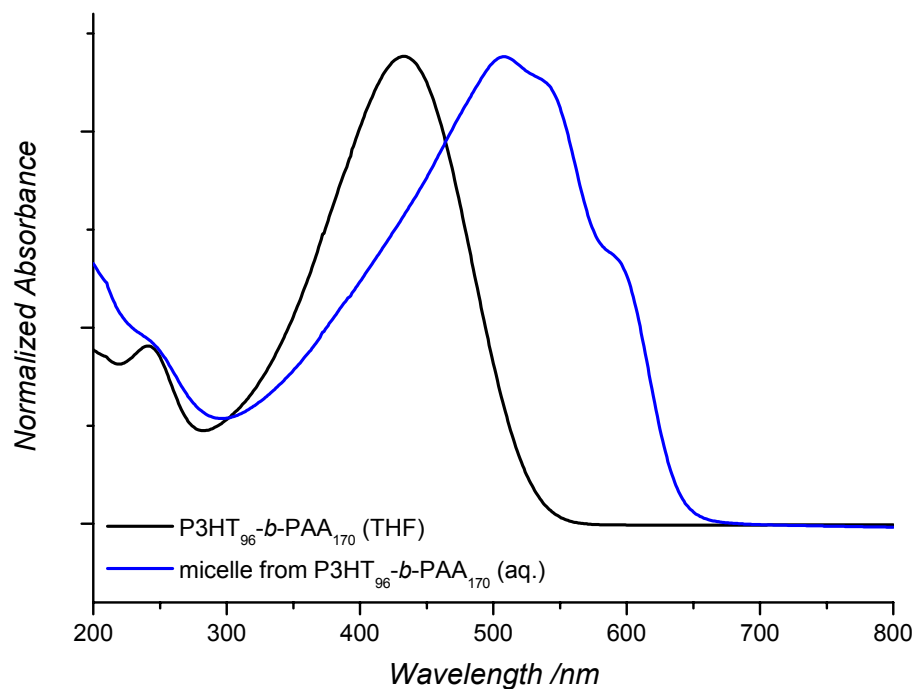
**Figure S4.** Representative  $^1\text{H}$  NMR spectra of (bottom) P3HT<sub>96</sub>-*b*-PtBA<sub>170</sub> ( $\text{CDCl}_3$ ) and (top) P3HT<sub>96</sub>-*b*-PAA<sub>170</sub> (THF- $d_8$ ).



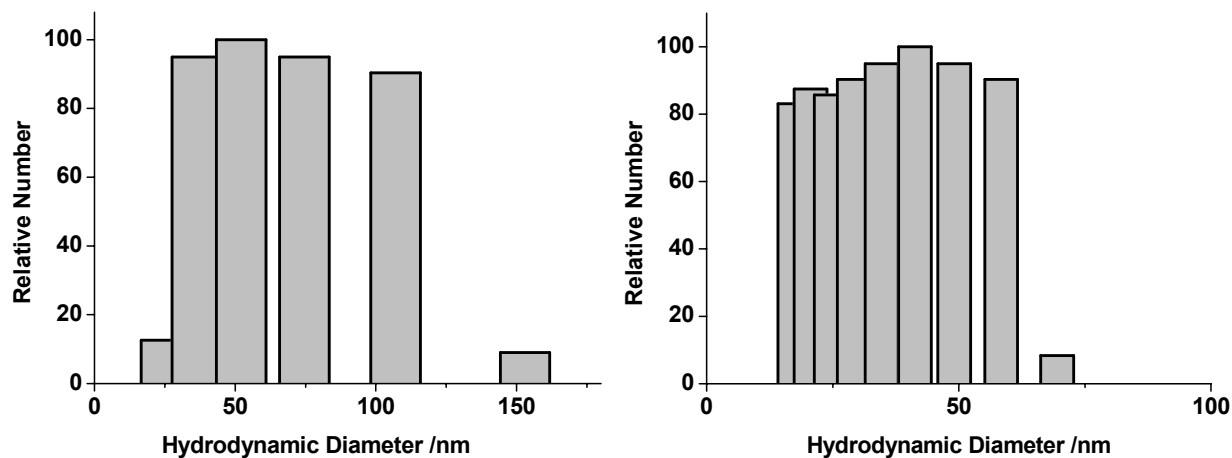
**Figure S5.** Gel permeation chromatograms (UV/vis detection at 450 nm) of P3HT-*b*-PtBA synthesized using freshly prepared P3HT-C≡CH: P3HT<sub>96</sub>-C≡CH (black), P3HT<sub>96</sub>-*b*-PtBA<sub>57</sub> (red), P3HT<sub>96</sub>-*b*-PtBA<sub>112</sub> (blue) and P3HT<sub>96</sub>-*b*-PtBA<sub>170</sub> (green).



**Figure S6.** Gel permeation chromatograms (UV/vis detection at 450 nm) of P3HT<sub>50</sub>-C≡CH (— immediately after reaction mixture was isolated using the improved procedure reported in the main text; — after being stored at ambient conditions for 24 h in the solid state; — after being stored at ambient conditions for 48 h in the solid state).

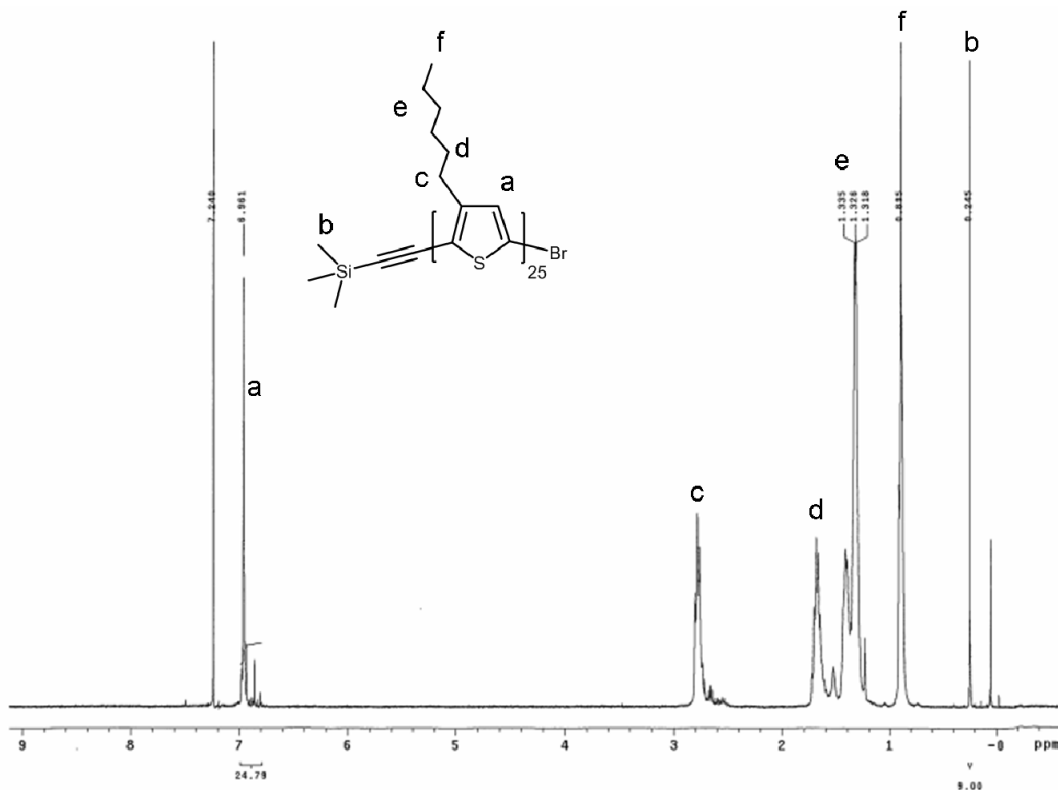


**Figure S7.** UV-vis spectra of a THF solution of P3HT-*b*-PAA (black) and an aqueous micelle solution assembled from P3HT-*b*-PAA (blue).

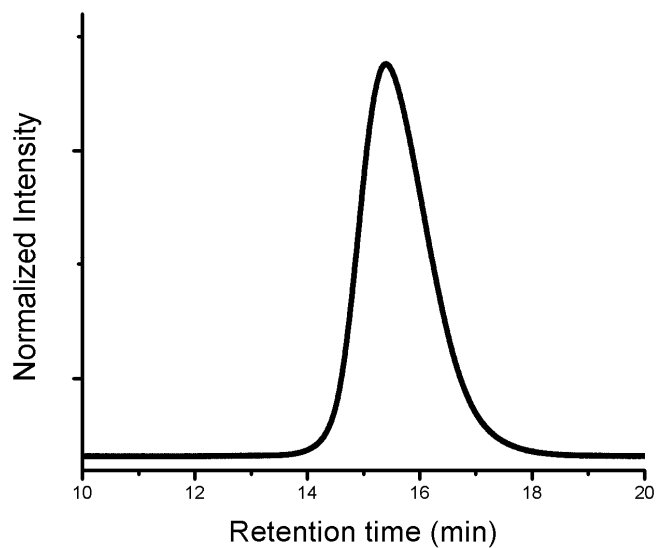


**Figure S8.** DLS histograms of micelles prepared from (left) P3HT<sub>96</sub>-*b*-PAA<sub>170</sub> and (right) P3HT<sub>29</sub>-*b*-PAA<sub>112</sub> (right). The hydrodynamic diameters were intensity averaged.





**Figure S9.** <sup>1</sup>H NMR spectra of P3HT-C≡C-TMS (CDCl<sub>3</sub>).



**Figure S10.** Gel permeation chromatogram (UV-vis detection at 450 nm) of TMS protected ethynyl-P3HT (P3HT<sub>25</sub>-C≡C-TMS), taken after Soxhlet treatment and storage in the solid state under ambient conditions for four days.