Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Polythiophene–*block*–poly(γ-benzyl L-glutamate): Synthesis and study of a new rod–rod block copolymer

Zong-Quan Wu,[†,‡] *Robert J. Ono,*[†] *Zheng Chen,*[†] *Zicheng Li,*[†] *and Christopher W. Bielawski**[†]

[†] *Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, TX 78712*

[‡] *School of Chemical Engineering, Hefei Univ. of Technology, Hefei, Anhui 230009, P. R. China*

bielawski@cm.utexas.edu

General Considerations. All solvents were purchased from Fisher Scientific and used without additional further purification unless otherwise noted. All reagents were purchased from Aldrich, Alfa Aesar, or Fisher, and were used as received. 2,5-Dibromo-3-hexylthiophene, γ-benzyl-L-glutamate *N*-carboxyanhydride (NCA) and 1-azido-3-aminopropane were prepared according to literature procedures.[1,2] THF and DMF were dried over 3 Å molecular sieves and deoxygenated using a Vacuum Atmospheres Company solvent purification system. ^{1}H NMR spectra were recorded using a Varian 300 or 400 spectrometer. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent as an internal standard ($CDCl_3$, 7.26 ppm). Coupling constants (J) are expressed in hertz. Size exclusion chromatography (SEC) was performed at ambient temperature 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 (λ = 450 nm). 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. UV–vis spectra were recorded using a Perkin Elmer Instruments Lambda 35 spectrometer. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC823e under an atmosphere of nitrogen at a heating/cooling rate of 10 °C min^{-1}. Thermogravimetric analyses (TGA) were performed under an atmosphere of nitrogen at a scan rate of 10 °C/min using a Mettler Toledo TGA/SDTA851e equipped with a TSO801RO sample automated loader. Transmission electron microscopy (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 (PTA) 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. Samples for atomic force microscopy (AFM) measurements were prepared by spin casting (1600 rpm) $CHCl_3$ solutions (1 mg mL^{-1}) of the polymer onto pre-cleaned silicon wafers, then placed in covered Petri dishes saturated with $CHCl_3$ vapor for 12 h. AFM images were acquired in tapping mode with a Veeco Series IV Atomic Force Microscope, performed at room temperature under an atmosphere of air using standard silicon cantilevers with

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(1) R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, *Macromolecules* 2001, **34**, 4324.
(2) C. Schatz, S. Louguet, J.-F. Le Meins and S. Lecommandoux, *Angew. Chem. Int. Ed*. 2009, **48**, 2572.

a nominal spring constant of 50 N/m and resonance frequency of ~300 kHz. The images were acquired at a scan frequency of 1 Hz over 1 × 1 μm^2 scan areas.

Representative Procedure for the Synthesis of Ethynyl-Terminated Poly(3-hexylthiophene) (P3HT–C≡CH) (1). A 50 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (1.33 g, 4.16 mmol), dry THF (44 mL), and a stir bar. After adding isopropylmagnesium chloride (2.1 mL, 2.0 M solution in THF), the resulting mixture was stirred at ambient temperature for 2 h. Ni(dppp)Cl_2 (30.0 mg, 0.055 mmol) (dppp = 1,3-bis(diphenylphosphino)propane) was then added in one portion and the resulting dark orange solution stirred for 10 min. Ethynylmagnesium bromide (2.5 mL, 0.5 M in THF) was then added to the mixture via syringe in one portion. After an additional 5 min of stirring, 80 mL of methanol was poured into the reaction flask, which caused a dark purple solid to precipitate. The solid was isolated via filtration, and then washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers, and then dried under vacuum to afford 530 mg (80% yield) of the desired polymer. The microstructure of the polymer was determined by ^1H NMR spectroscopy to be 97% head-to-tail. SEC (THF): M_n = 12.1 kDa, M_w/M_n = 1.10. ^1H NMR ($CDCl_3$, ppm): δ 6.99–6.93 (br, CH thiophene), 3.53–3.46 (s, ethynyl CH), 2.83–2.71 (br, CH_2), 1.74–1.51 (br, CH_2), 1.44–1.37 (br, CH_2), 0.93–0.81 (br, CH_3).

Representative Procedure for the Synthesis of Azide-Terminated PBLG (PBLG–N_3) (2). Using a modified literature procedure,[2] an oven-dried Schlenk tube was charged with a stir bar and γ-benzyl-L-glutamate NCA (510 mg, 1.94 mmol), and dissolved with 4.5 mL of anhydrous DMF. The solution was stirred for 10 min at room temperature, and an anhydrous DMF solution of 1-azido-3-aminopropane (0.05 M, 0.40 mL, 0.02 mmol) was added with a nitrogen flushed syringe. The resulting solution was then stirred under an atmosphere of nitrogen for 40 h at room temperature, at which point the reaction mixture was poured into diethyl ether. The precipitated solids were recovered by filtration, washed with diethyl ether, and dried under vacuum to afford 310 mg (60% yield) of the desired polymer. SEC (DMF) M_n = 11.7 kDa, M_w/M_n = 1.07. ^1H NMR (300 MHz, $CDCl_3$ + 5 % trifluoroacetic acid (TFA), ppm): δ 8.00–8.61 (br, NH), 7.10–7.65 (br, Ar), 4.68–5.30 (br, CO_2CH_2), 3.63–4.21 (br, CH), 2.81–2.42 (br, $CHC\underline{H_2}$), 2.40–1.78 (br, $COC\underline{H_2}C\underline{H_2}CH$).

Representative Procedure for the Synthesis of P3HT–*block*–PBLG (3). A 25 mL flask was charged with P3HT–C≡CH (**1**) (50.0 mg, 4.13 μmol), PBLG–N_3 (**2**) (60 mg, 5.15 μmol), CuBr (3.0 mg, 20 μmol), PMDETA (4.0 mg, 22 μmol) and dry THF (20 mL). The mixture was degassed by one freeze-pump-thaw cycle and was then immersed into an oil bath thermostatted to 55 °C. After stirring for 3 d, the reaction mixture was cooled to ambient temperature and passed through a short column of neutral alumina (eluent = THF) to remove residual catalyst. The crude product was then concentrated and purified by a series of precipitations from methanol and DMF to remove traces of catalyst, ligand, and unreacted PBLG–N_3. The desired product was collected via filtration, washed with methanol, and dried under vacuum in 72% yield (70 mg). ^{1}H NMR ($CDCl_3$, ppm): δ 8.50–8.00 (br, NH of PBLG), 7.34–7.05 (br, Ar of PBLG), 6.98–6.86 (br, CH of P3HT), 5.13–4.80 (br, CO_2CH_2 of PBLG), 3.98–3.73 (br, $COC\underline{H}NH$ of PBLG), 2.86–2.43 (br, CH_2 of P3HT), 2.38–1.87 (br, $C\underline{H_2}C\underline{H_2}CO_2Bn$ of PBLG), 1.75–1.46 (br, CH_2 of P3HT), 1.44–1.11 (br, CH2 of P_3HT), 0.92–0.70 (br, CH_3 of P3HT).

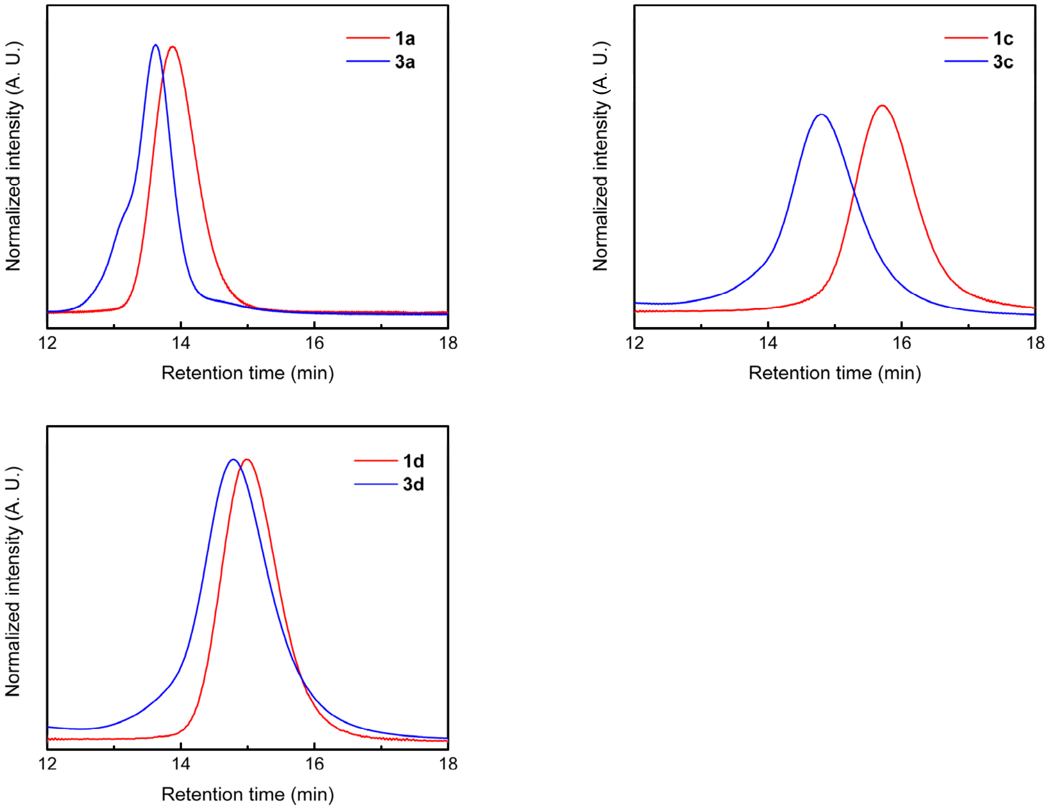

Figure S1. Size exclusion chromatograms of P3HT–C≡CH (**1a–1d**), and their corresponding block copolymers P3HT–*block*–PBLG (**3a–3d**). See Figure 1A for size exclusion chromatograms of **1b** and **3b**.

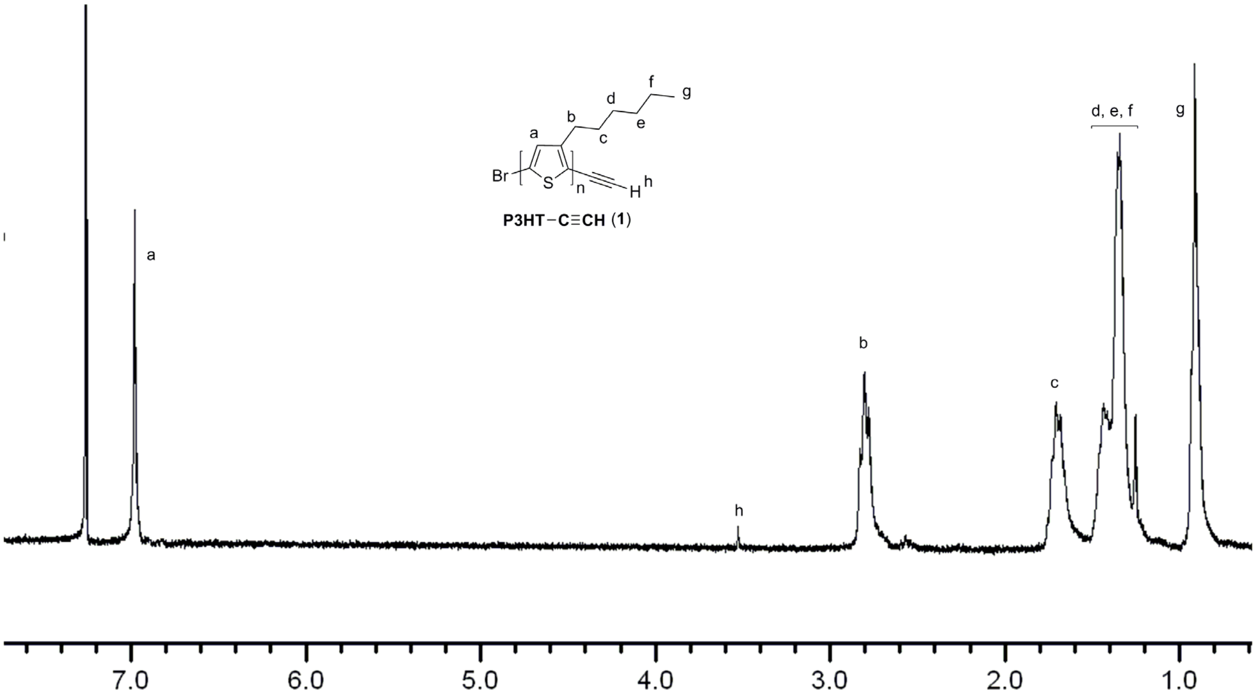

Figure S2. ^{1}H NMR spectrum of P3HT–C≡CH (**1a**) ($CDCl_3$, 25 °C, 300 MHz).

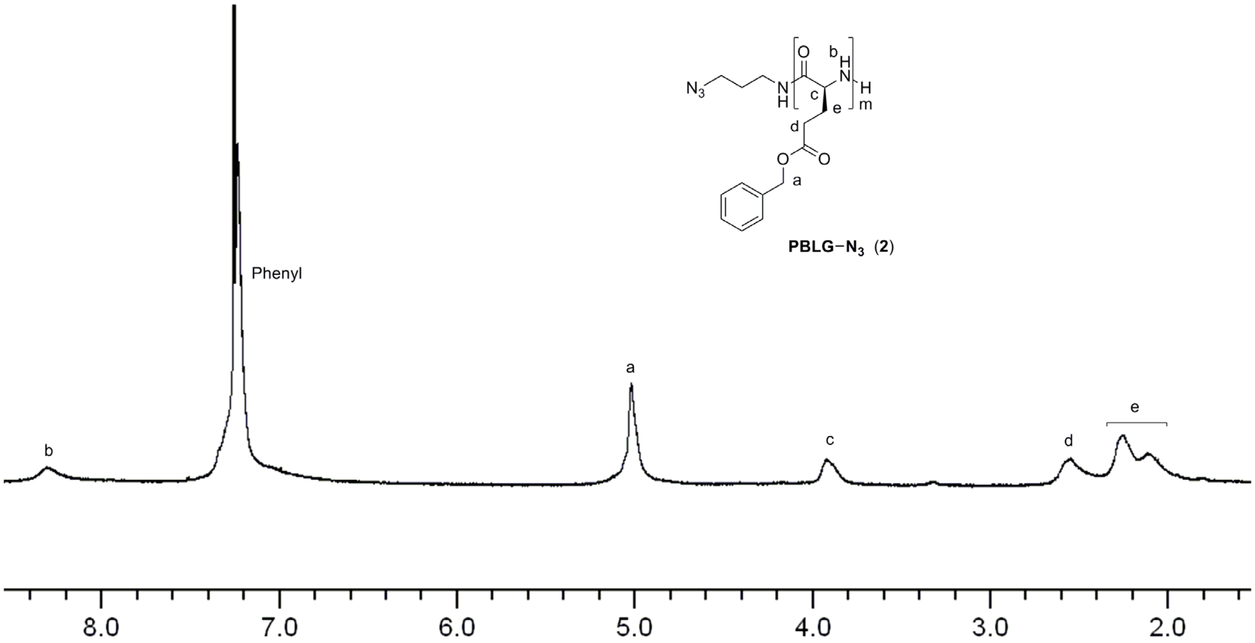

Figure S3. ^{1}H NMR spectrum of PBLG–N_3 (**2a**) ($CDCl_3$ + TFA (5% v/v), 25 °C, 300 MHz).

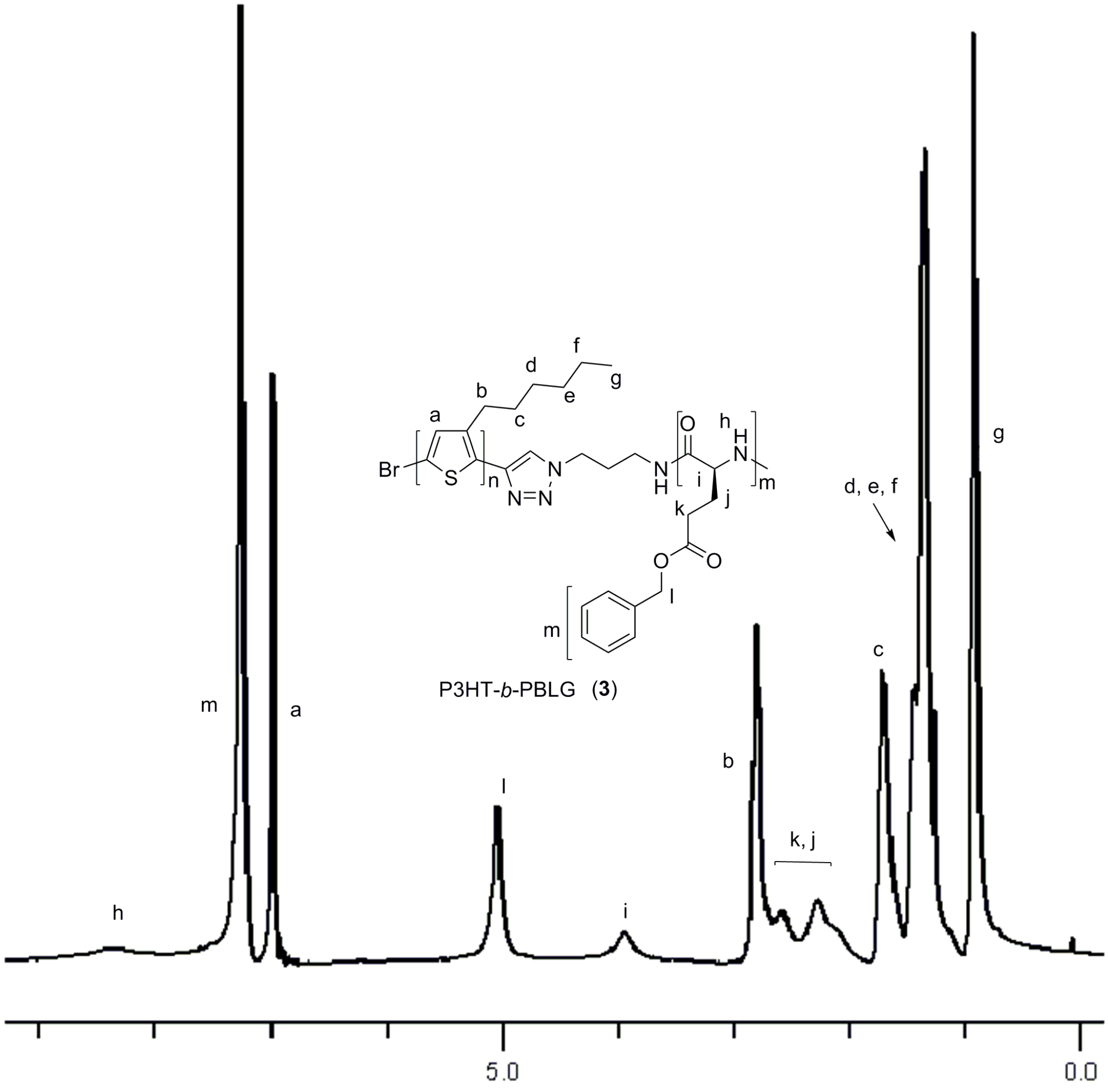

Figure S4. ^{1}H NMR spectrum of P3HT–*block*–PBLG (**3a**) ($CDCl_3$ + TFA (5% v/v), 25 °C, 300 MHz).

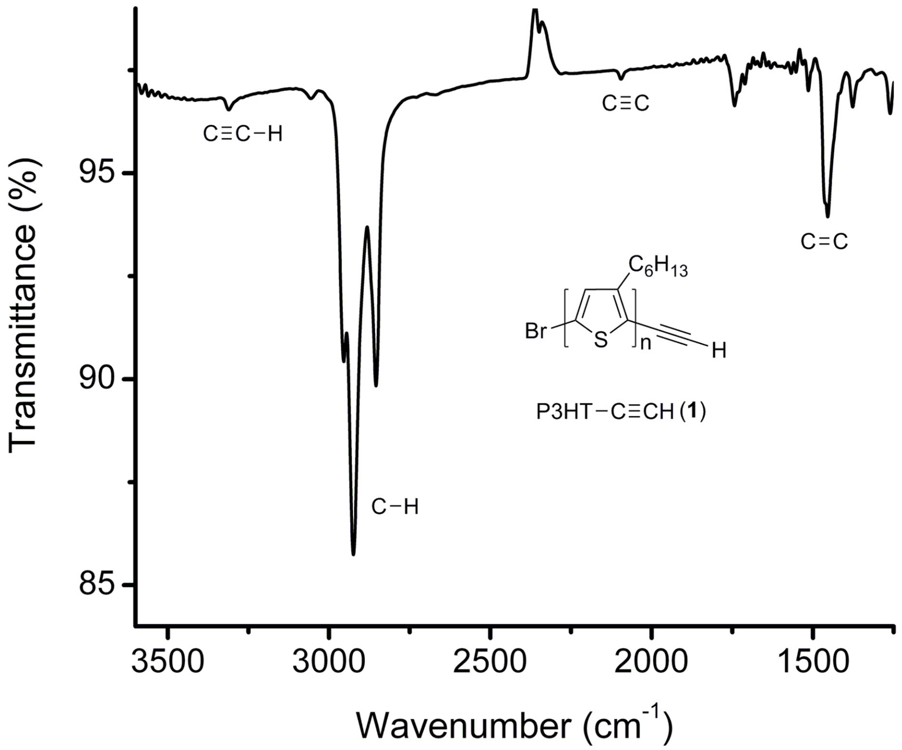

Figure S5. IR spectrum (KBr) of ethynyl-terminated P3HT (P3HT–C≡CH, **1a**).

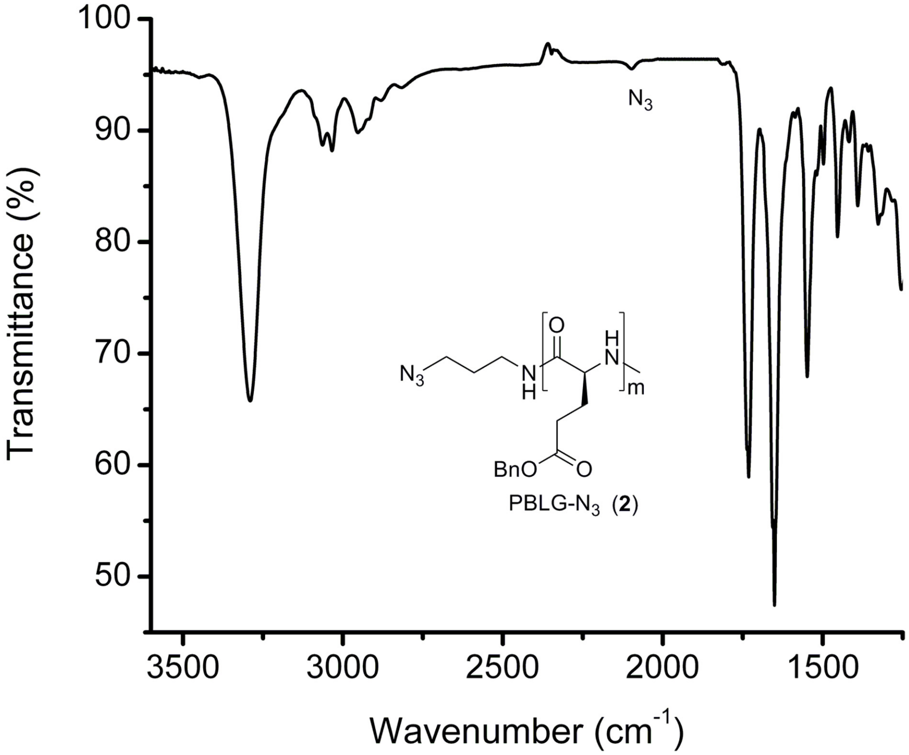

Figure S6. IR spectrum (KBr) of azide-terminated PBLG (PBLG–N_3, **2a**).

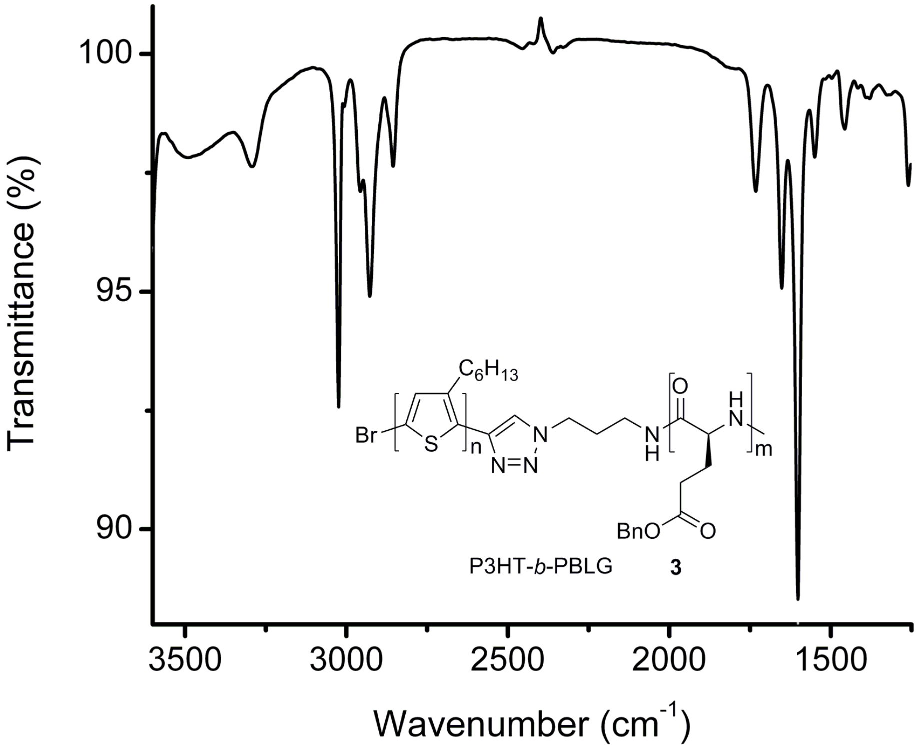

Figure S7. IR spectrum (KBr) of P3HT–*block*–PBLG (**3a**).

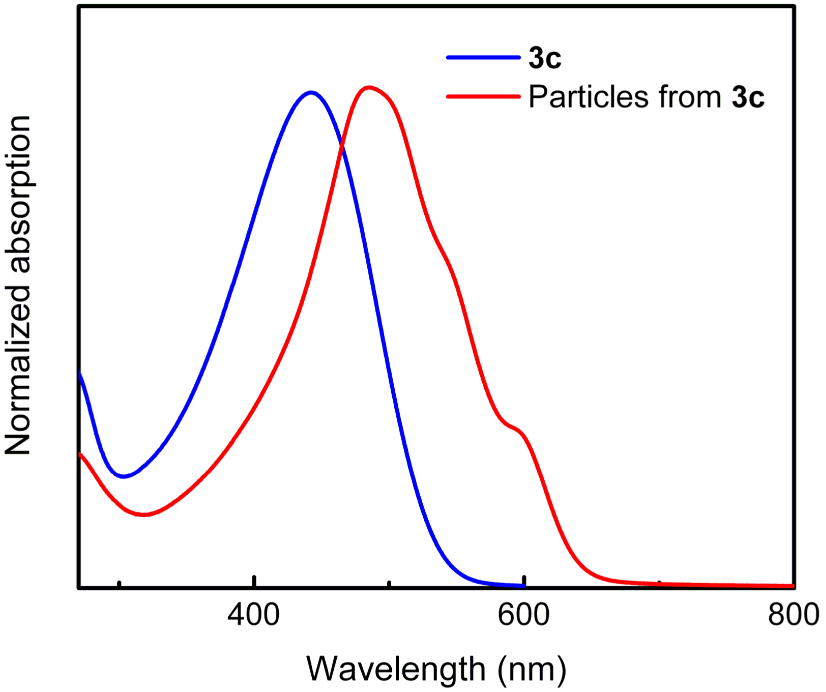

Figure S8. UV-vis spectra of P3HT–*block*–PBLG (**3c**) in THF and the nanoparticles formed from **3c** in THF and DMF (1/1, v/v) at 25 °C.

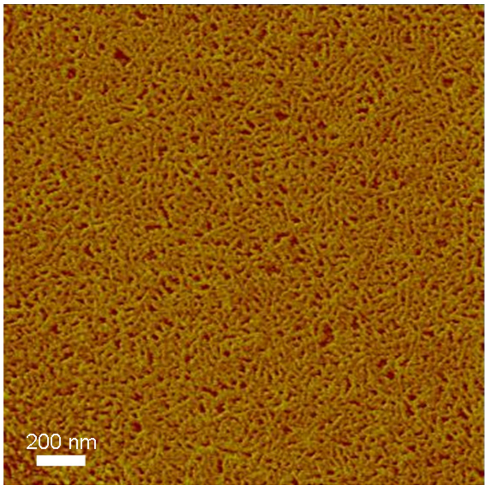

Figure S9. Tapping mode AFM phase image of P3HT–*block*–PBLG **3a** spin casted from $CHCl_3$ (film thickness = 20 nm).

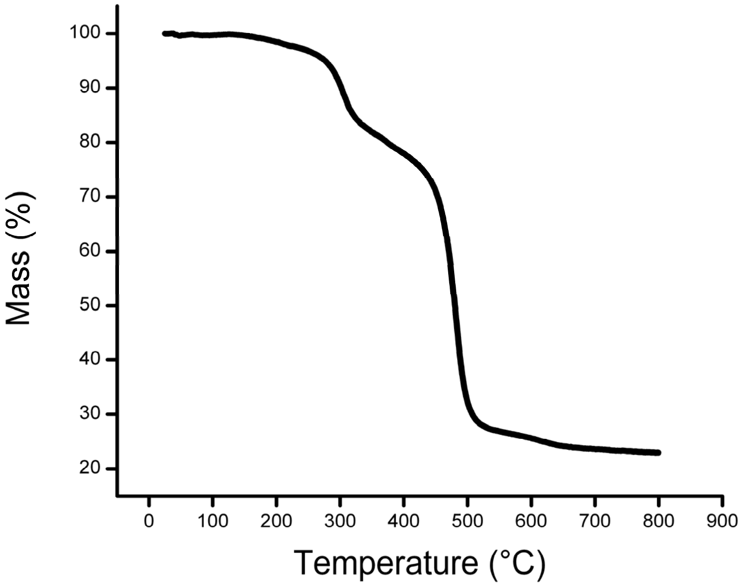

Figure S10. Thermogravigram of **3d**. Conditions: heating rate = 10 °C min^{-1}, nitrogen atmosphere.