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Random Copolymers Outperform Gradient and Block Copolymers in Stabilizing Organic Photovoltaics

*Chen Kong, Byeongseop Song, Emily A. Mueller, Jinsang Kim, and Anne J. McNeil**

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I. Materials

Flash chromatography was performed on SiliCycle silica gel (40–63 µm). Thin layer chromatography was performed on MACHEREY-NAGEL TLC plates (pre-coated with 0.20 mm silica gel 60 with fluorescent indicator UV254). $Ni(COD)_2$ was purchased from Strem Chemicals. Lithium diisopropylamide (LDA, 2.0 M in THF/n-heptane/ethylbenzene, 59/28/13 v/v) was purchased from Acros Organics. 2,5-Dibromo-3-hexylthiophene (DB3HT) was purchased from ArkPharm and purified by dissolving in hexanes, decoloring with carbon powder, stirring for 2 h, filtering through a plug of silica gel and concentrating *in vacuo*. [6,6]-phenyl C61-butyric acid methyl ester ($PC_{61}BM$) was purchased from Nano-C Inc. *N*-Bromosuccinimide (NBS) was purchased from Sigma Aldrich, recrystallized from water and dried over P_2O_5. Isopropylmagnesium chloride (iPrMgCl, 2.0 M in THF, 25 mL), Molybdenum(VI) oxide, (MoO_3, 99.97% trace metals basis), zinc acetate dihydrate ($Zn(OAc)_2 \bullet 2H_2O$), and 2-methoxyethanol (2ME) were purchased from Sigma Aldrich. Silver pellets (Ag, 99.99% purity) were purchased from Kurt J. Lesker Company. MoO_3 and Ag pellets were loaded into an Angstrom Engineering AMOD thermal evaporation chamber. All other reagent grade materials and solvents were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar, or Fisher and used without further purification unless otherwise noted. THF was dried and deoxygenated using an mBraun Innovative Technology solvent purification system composed of activated alumina, a copper catalyst, and molecular sieves. Any water used for reactions or work-ups was deionized. The glovebox in which specified procedures were carried out was an MBraun LABmaster 130 with a N_2 atmosphere and H_2O levels below 4 ppm. Compounds **S1,**[1] **S2,**[1] **3,**[2] and **4–7**[3] were prepared using modified literature procedures.

II. General Experimental

<u>*NMR Spectroscopy:*</u> ^1H, ^{13}C and ^{31}P spectra for all compounds were acquired in deuterated solvents on a Varian MR400 operating at 400, 100, and 162 MHz or a Varian VNMRS 500 operating at 500, 126, and 202 MHz, respectively. For ^1H and ^{13}C spectra, the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. For 31P spectra, the chemical shift data are reported in units of δ (ppm) relative to 85% H_3PO_4 in H_2O. All NMR spectra were recorded at r.t.

Mass Spectrometry: HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

Infrared Spectroscopy: IR data were recorded using Thermo Scientific Nicolet iS50 FT-IR spectrometer.

Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry: Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was carried out on a Bruker AutoFlex Speed MALDI-TOF in positive-ion reflectron mode using using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Samples were prepared by dissolving a 2.5 μL of a 1 mg/mL solution of polymer in THF/toluene (99:1 v/v) in 2.5–10 μL of 1 M DCTB in $CHCl_3$. Samples were diluted in DCTB in varying ratios (to ensure good signal/noise) and then spotted on a MALDI 96-well plate and air dried. The data were analyzed using flexAnalysis.

Gel Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580–377,400) at 40 °C in THF on a Malvern Viscotek GPCMax VE2001 equipped with two Viscotek LT-5000L 8 mm (ID) × 300 mm (L) columns and analyzed with Viscotek TDA 305 (with UV-PDA Detector Model 2600). All data shown refer to the absorbance at 254 nm. Samples were dissolved in THF/toluene (99:1 v/v) (with mild heating), and passed through a 0.2 μm PTFE filter prior to analysis.

Gas Chromatography: Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl–95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column.

Thin Film Preparation: Fused silica wafers (from University Wafer) were cut into square substrates (~1.5 cm x 1.5 cm) and cleaned via rubbing with undiluted Hellmanex III followed by rinsing with DI water. The substrates were then sonicated for 15 min in each of the following solvents: DI water, acetone, and iPrOH. The clean substrates were then dried in an oven at 80 °C for 8 h and stored in a clean petri dish wrapped in aluminum foil. P3HT, $PC_{61}BM$, and copolymer were each dissolved separately in 1,2-dichlorobenzene (*o*-DCB) (30 mg/mL) and stirred at 60 °C for 2 h. The solutions were then combined (1:1:X, P3HT:$PC_{61}BM$:copolymer, 30 mg/mL overall), stirred for 18 h at 60 °C, filtered, then spin-casted onto the clean silica substrate at 800 rpm for 3 min. The thin films were characterized with optical microscopy and UV-Vis spectroscopy before and after thermal annealing in a vacuum oven (–711.2 mmHg) at 150 °C for 60 min. Thin film thickness was determined by variable-angle spectroscopic ellipsometry by spin-casting onto silicon wafers. Near-infrared (1100 nm–1600 nm) spectroscopic data were recorded by J.A. Woollam M-2000 ellipsometer followed by thickness measurement by Cauchy-model fitting.[4]

Optical Microscopy: The annealed thin film samples were examined using a Leica DMCB optical microscope with a 40x objective lens. Images were recorded with an attached QICAM Fast 1394 digital video camera and analyzed with ImageJ.

Image Processing with ImageJ: Images were saved as .tiff files to open in the ImageJ software. Once loaded, the images were converted to black and white by clicking “Image” and selecting “Color,” then “Split Channels” from the dropdown menu. Three images were generated and the “(blue)” channel image was selected for further analysis. The image background was subtracted by clicking “Process” then “Subtract Background” from the dropdown menu which opened a new window. The default rolling ball radius (50 pixels) was used and “light background” was checked to ensure even background subtraction. In the “Image” tab, “Adjust” then “Threshold” were selected, opening a new window showing the minimum and maximum threshold limits for detecting particles (dark domains), now depicted in red on the image. Selecting “Apply” defined the particle sizes/areas and displayed them in black on the image. To calculate the black particle percent area, “Analyze” then “Analyze Particles” was selected. In the resulting window, the size was set to “0.0005-infinity” then “display results,” “summary,” “include holes” and “clear results” were checked and “OK” was selected. The tabulated data points and results summary (with % area of particles relative to whole image), each appeared in separate windows.

UV-Vis Spectroscopy: UV-Vis spectra of thin films were acquired using a Thermo Scientific Evolution 220 UV-Vis spectrophotometer.

Cyclic Voltammetry (CV): The electrochemical measurements were performed on a CH Instruments electrochemical analyzer. A glassy carbon electrode, Pt wire, and Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. A ferrocene/ferrocenium (Fc/Fc+) redox couple was used as the internal standard which is assumed to have an absolute energy level of -4.8 eV.[5]

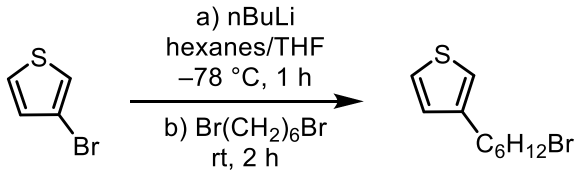
Bulk Heterojunction Solar Cell Device Fabrication and Measurement: All processing was completed in an ultra-high puritiy (<1ppm of H_2O and O_2) glovebox from LC Technology Solutions, INC. Solar cell devices have the following inverted structure: glass/ITO/ZnO(40 nm)/blend/MoO_3(20 nm)/Ag(100 nm). The indium tin oxide (ITO) substrate was cleaned with detergent, sonicated in DI water, acetone, and iPrOH for 10 min each, then exposed to 245 nm ultraviolet light under oxygen flow for 15 min. ZnO sol–gel solution was prepared by dissolving zinc acetate dihydrate ($Zn(OAc)_2 \bullet 2H_2O$, Sigma Aldrich) in 2-methoxyethanol (2ME, Sigma Aldrich) (0.5 M). Monoethanolamine (0.5 M) was added as a stabilizer and the mixture was vigorously stirred at 60 °C for 4 h. The solution was then cooled to r.t. and aged for > 24 h. The prepared ZnO solution was spin-casted on ITO coated glass substrates at 3000 rpm for 60 s, followed by thermal annealing in air at 150 °C for 20 min. Polymer solutions were prepared as described above in *o*-DCB and heated at 60 °C for 12 h before spin-casting in an ultra-high purity (< 1 ppm of H_2O and O_2) N_2 glovebox. The polymer solutions were spin-casted at 800 rpm for 180 s, generating thin films (175 ± 10 nm). After spin-casting the polymers, the films were either thermally annealed (for 15, 45, 90 min) then transferred, or directly transferred to an Angstrom Engineering AMOD thermal evaporation chamber. Molybdenum masks with 1 mm radius circular openings were placed on the sample, determining 3.14 mm^2 of the device size. MoO_3 and Ag were evaporated onto the film at a rate of 1 Å/s under the base pressure of 3×10^{-7} torr.

J-*V* characteristics of the devices were recorded by a HP 4156a semiconductor parameter analyzer. The transparent glass/ITO side was illuminated with simulated AM 1.5G at 1 sun intensity (100 mW/cm^2). The intensity of the solar simulator was calibrated by the National Renewable Energy Laboratory (NREL)-traceable Si reference cell. The reverse bias saturation current (J_o) was obtained from the *J*-*V* curve at -1 bias voltage in the dark. The series resistance (Rs) of each device was extracted from the inverse slope of the *J*-*V* curve at the open circuit voltage (V_{OC}).

Conductive Atomic Force Microscopy (c-AFM): An Asylum Research MFP-3D atomic force microscope was used for both phase images and conductive-tip atomic force microscopy (c-AFM) images. Phase images of the spin-casted polymer (175 nm) on ITO/ZnO (40 nm) were obtained under tapping mode. The c-AFM images were obtained under the contact-mode using a Pt-Ir5-coated tip (spring constant 0.2 N/m). For the hole or electron current measurements, the spin-casted polymer (175 nm) on ITO/MoO_3 (10 nm) or ITO/ZnO (40 nm) was scanned under 1.5 V of applied bias in reference to an ITO substrate. The average current and standard deviation were obtained from the current distribution over a 1×2 μm scanned area.

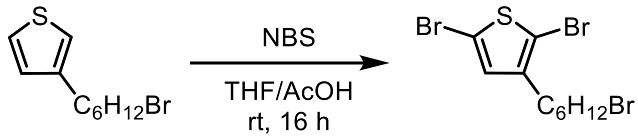
Differential Scanning Calorimetry (DSC): All DSC experiments were performed under N_2 on a TA Instruments Q2000 differential scanning calorimeter equipped with a TA RCS cooling accessory. The C_{60}-functionalized copolymers were weighed directly into low-mass aluminum Tzero DSC pans with hermetic lids. Solutions of P3HT, copolymer, and $PC_{61}BM$ for blends were prepared the same way as for thin films. The solutions were then drop cast while hot through a 0.2 μm PTFE filter onto clean glass substrates and the solvent was removed *in vacuo* over 24 h. The dried films were then scraped from the glass substrates onto weigh paper and the resulting solid was weighed into low-mass aluminum Tzero DSC pans with hermetic lids. All sample masses were ~3.2 mg. The temperature was ramped at a rate of 10 °C/min for heating up to 150 °C or 295 °C and cooling to -60 °C over three cycles. The third cycle was used for analysis.

III. Small Molecule Synthetic Procedures



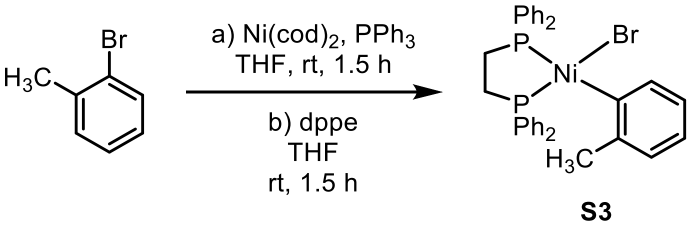
S1

3-(6-bromohexyl)thiophene (S1): To a 200 mL oven-dried Schlenk flask under N_2 were added 3-bromothiophene (2.00 mL, 21.3 mmol, 1.00 equiv) and dry, degassed hexanes (50 mL). The flask was cooled to –78 °C. A solution of n-butyllithium in hexanes (2.65 M, 7.70 mL, 20.4 mmol, 0.96 equiv) was added dropwise over 10 min and the solution was stirred for an additional 10 min. Then THF (5 mL) was injected dropwise over 15 min and the solution was stirred for an additional 1 h. During this time, a white precipitate formed in a transparent, yellow supernatant. The supernatant was removed via cannula transfer and replaced with hexanes/THF (10/1 v/v, 55 mL). 1,6-Dibromohexane (13.1 mL, 85.2 mmol, 4.0 equiv) was then added. The slurry was warmed to r.t. and stirred for 2 h. The reaction was quenched with saturated aq. $NaHCO_3$ (50 mL) and extracted with Et_2O (100 mL). The organic layer was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, treated with decolorizing carbon, filtered, and concentrated *in vacuo* to give a viscous orange oil. Excess 1,6-dibromohexane was removed by distillation (0.20 torr, 55 °C) and the remaining oil was purified by silica gel column chromatography (EtOAc/hexane gradient from 0/100 to 2/98 v/v) to obtain a clear, colorless oil (2.2 g, 42%). HRMS (EI): Calcd. for $C_{10}H_{15}BrS$ $[M]^+$ 246.0078; found, 246.0084.



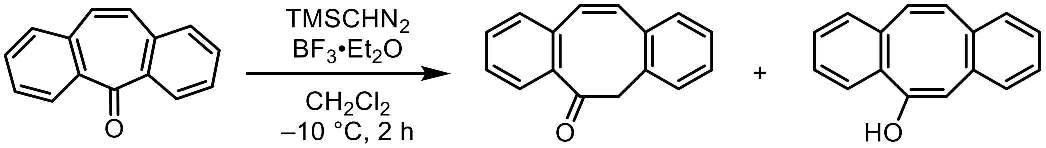
S1 **S2**

2,5-dibromo-3-(6-bromohexyl)thiophene (S2): To an oven-dried 100 mL round-bottom flask were added **S1** (2.40 g, 9.71 mmol, 1.00 equiv), THF (25 mL) and AcOH (25 mL). Recrystallized NBS (4.32 g, 24.3 mmol, 2.50 equiv) was added and the solution was stirred at r.t. for 16 h. The reaction was quenched using saturated aq. $NaHCO_3$ (50 mL) and extracted with Et_2O (100 mL). The organic layer was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting orange oil was purified by silica gel column chromatography (EtOAc/hexane gradient from 1/99 to 4/96 v/v) to obtain a clear, colorless oil (3.0 g, 77%). HRMS (EI): Calcd. for $C_{10}H_{13}Br_3S$ $[M]^+$ 401.8288; found, 401.8283.



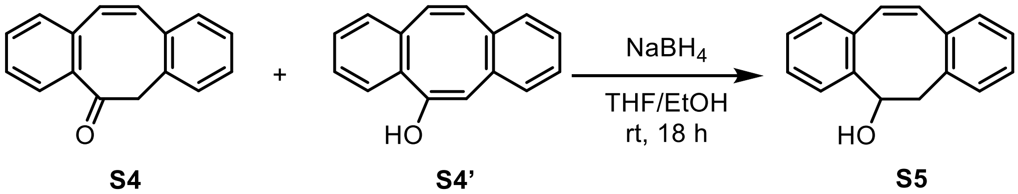
S3

(*o*-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (S3): Ni(cod)$_2$ (275 mg, 1.00 mmol, 1.00 equiv) and PPh$_3$ (538 mg, 2.05 mmol, 2.05 equiv) were added to a 20 mL vial equipped with a stir bar in the glovebox. To this vial was added THF (5 mL) and the solution was stirred for 5 min. Then 2-bromotoluene (132 µL, 1.10 mmol, 1.10 equiv) was added and the solution was stirred at r.t. for 1.5 h. Then, 1,2-bis(diphenylphosphino)ethane (dppe) (438 mg, 1.10 mmol, 1.10 equiv) was added and stirred for 1.5 h. Hexane (15 mL) was slowly added as the top layer and the mixture was cooled to –35 °C for 24 h. The resultant yellow precipitate was isolated by filtration inside the glovebox, washed with hexanes (10 mL) and recrystallized from CH$_2$Cl$_2$/hexanes (20 mL) at –35 °C to afford a fine yellow powder (375 mg, 60%). HRMS (EI): Calcd. For $C_{33}H_{31}BrNiP_2$ $[M]^+$ 626.0438; found, 626.0447.

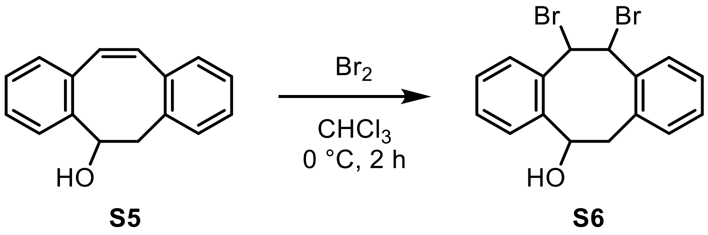


S4 **S4’**

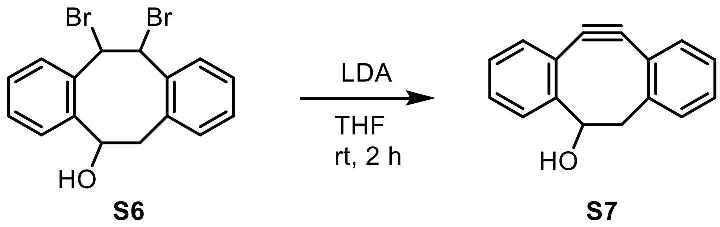
6*H*-Dibenzo[a,e]cyclooctatrien-5-one (S4): In a N$_2$ flushed 100 mL round-bottom flask was added dibenzosuberenone (3.10 g, 15.0 mmol, 1.00 equiv) and BF$_3$·OEt$_2$ (2.80 mL, 22.7 mmol, 1.50 equiv) in CH$_2$Cl$_2$ (30 mL). The solution was cooled to –10 °C. A 0.75 M solution of trimethylsilyl diazomethane in CH$_2$Cl$_2$ (32.0 mL, 24.0 mmol, 1.60 equiv) was added to the solution dropwise over 1 h and then stirred at –10 °C for an additional 2 h. Then AcOH (0.2 mL) was added to quench the reaction. The mixture was poured into ice water (150 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 100 mL) and the combined organic layers were washed with brine (100 mL), dried over MgSO$_4$, and filtered. The filtrate was concentrated *in vacuo* and the crude product was purified by silica gel column chromatography (hexanes/CH$_2$Cl$_2$ gradient from 90/10 to 30/70, v/v) to give dibenzocyclooctenone (**S4**) as a white solid (1.13 g, 34%) and dibenzocyclooctadienol (**S4’**) as a viscous transparent liquid (2.1 g, 63%). HRMS (EI): Calcd. For $C_{16}H_{12}O$ $[M]^+$ 220.0888; found, 220.0884.



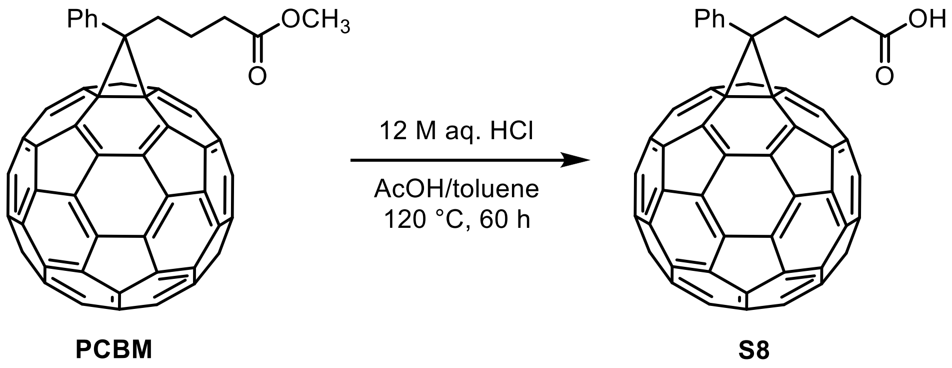
5,6-Dihydro-dibenzo[a,e]cycloocten-5-ol (S5): Sodium borohydride (0.388 g, 10.3 mmol, 2.00 equiv) was slowly added to a stirred solution of **S4**/**S4’** (1.13 g, 5.13 mmol, 1.00 equiv) in THF/EtOH (1/1, v/v, 60 mL). The reaction was stirred at r.t. for 18 h, then quenched by slow addition of AcOH (0.5 mL). The mixture was concentrated *in vacuo*, and the yellow residue was dissolved in CH_2Cl_2 (50 mL) and washed with brine (50 mL). The aqueous layer was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layers were dried over $MgSO_4$, treated with decolorizing carbon, filtered and concentrated *in vacuo* to give a white solid (723 mg, 63%). HRMS (EI): Calcd. For $C_{16}H_{14}O$ $[M]^+$ 222.1045; found, 222.1046.



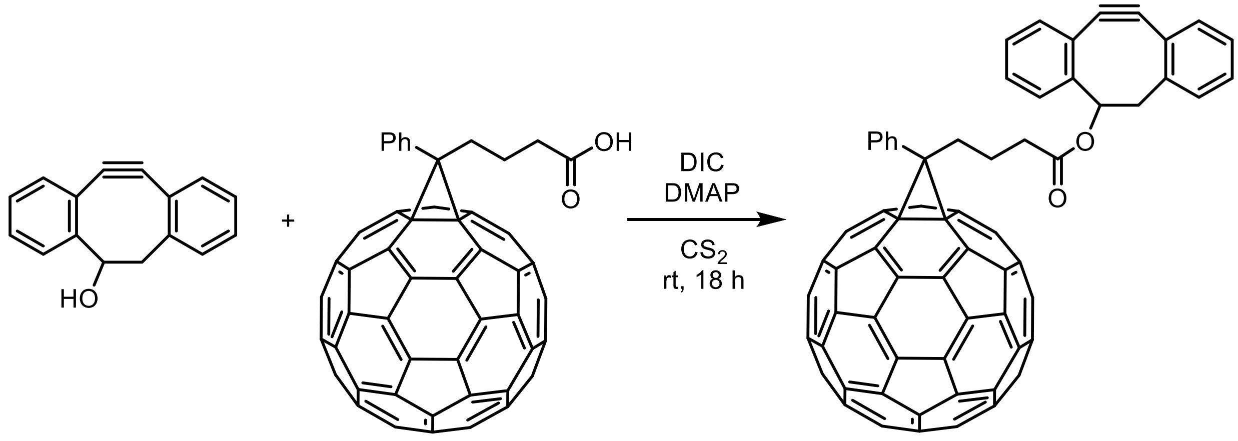
11,12-Dibromo-5,6,11,12-tetrahydro-dibenzo[a,e]cycloocten-5-ol (S6): Into a N_2 filled round-bottom flask was added **S5** (0.642 g, 2.89 mmol, 1.00 equiv) in $CHCl_3$ (15 mL) and the resulting solution was cooled to 0 °C using an ice-water bath. A solution of Br_2 (0.150 mL, 2.93 mmol, 1.01 equiv) in $CHCl_3$ (5 mL) was added dropwise over 3 minutes. After stirring for 2 h, the resulting solution was quenched with saturated aq. $Na_2S_2O_3$ (20 mL), and washed with water (20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*, affording a yellow oil. The crude product was purified by silica gel column chromatography (CH_2Cl_2/hexanes gradient from 5/95 to 70/30 v/v) to obtain a viscous, colorless oil (480 mg, 44%). HRMS (EI): Calcd for $C_{16}H_{13}BrO$ $[M–HBr]^+$ 300.0150; found, 300.0156.



5,6-Dihydro-11,12-didehydro-dibenzo[a,e]cycloocten-5-ol (S7): Under an N_2 atmosphere, **S6** (480 mg, 1.26 mmol, 1.00 equiv) was dissolved in THF (15 mL) at r.t. and a solution of commercial lithium diisopropylamide (LDA) (2.0 M in THF, 2.50 mL, 5.00 mmol, 4.00 equiv) was added dropwise over 5 min. The reaction solution was stirred for 2 h, and then quenched by the dropwise addition of water (0.5 mL). The resulting mixture was concentrated *in vacuo* and the resulting yellow oil residue was purified by silica gel column chromatography (hexanes/CH_2Cl_2 gradient from 75/25 to 0/100, v/v) to give a white solid (174 mg, 63%). HRMS (EI): Calcd. For $C_{16}H_{11}O$ $[M–H]^+$ 219.0810; found, 219.0806.

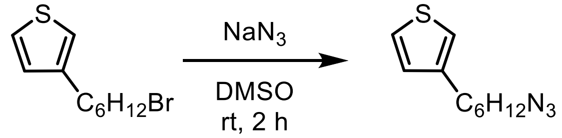


phenyl-C_{61}-butyric acid (S8): Phenyl-C_{61}-butyric acid methyl ester (PCBM) (550 mg, 0.604 mmol, 1.00 equiv) was dissolved in toluene (80 mL) and AcOH (40 mL) in a 350 mL bomb flask then aq. HCl (12 M, 20 mL) was added. The flask was sealed and heated to 120 °C for 60 h with vigorous stirring. The mixture was then cooled to r.t. The now heterogeneous organic layer was separated from the aquous layer and filtered. The resulting brown solid was washed sequentially with MeOH, acetone, toluene, and Et_2O (30 mL each), to afford a brown powder (541 mg, quant). The product was carried to the next step without further purification. HRMS (ESI-): Calcd. For $C_{71}H_{11}O_2$ $[M–H]^-$ 895.0765; found, 895.0750.



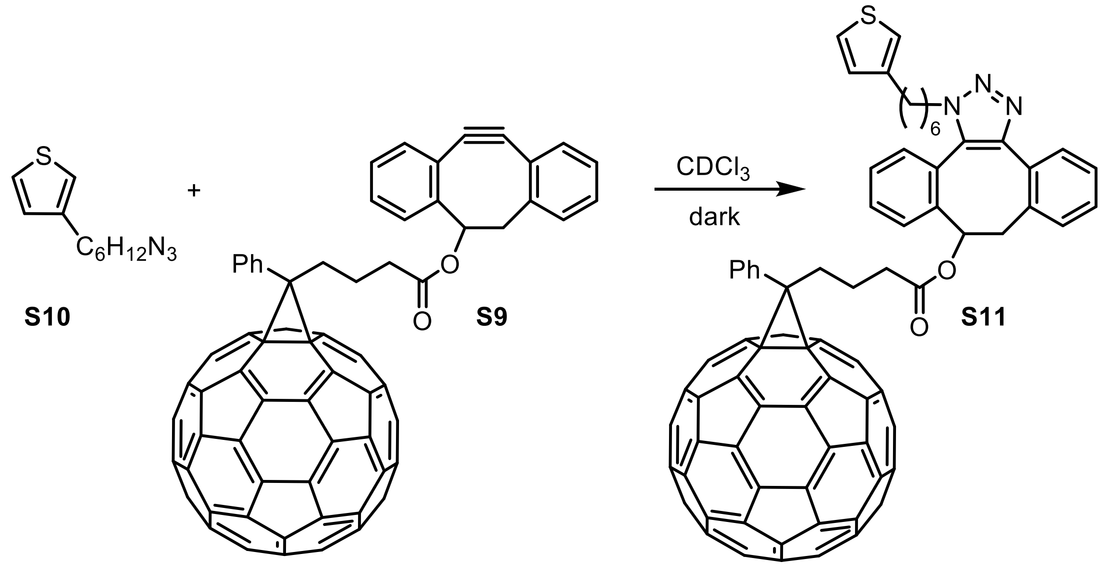
S7 **S8** **S9**

PCB-DIBO (S9): Under an N_2 atmosphere, **S8** (300 mg, 0.334 mmol, 1.00 equiv) was suspended in CS_2 (15 mL) in a 50 mL round-bottom flask. Then **7** (81 mg, 0.37 mmol, 1.1 equiv) and 4-dimethylaminopyridine (41 mg, 0.34 mmol, 1.0 equiv) were added, followed by diisopropylcarbodiimide (DIC) (57 µL, 0.37 mmol, 1.1 equiv). The reaction was stirred at r.t. in the dark for 18 h and then quenched with H_2O (1 mL). Then the organic layer was washed with H_2O (20 mL) and brine (20 mL), then concentrated *in vacuo*. The resulting brown solid was purified by silica gel column chromatography (CH_2Cl_2/hexane gradient from 10/90 to 100/0 v/v), affording a dark brown powder (300 mg, 82%). MALDI-TOF-MS: Calcd. For $C_{87}H_{22}O_2$ [M] 1099.162; found,1100.422.



S1 **S10**

3-(6-azidohexyl)thiophene (S10): In a 20 mL vial equipped with a stir bar, **S1** (288 mg, 1.17 mmol, 1.00 equiv) was dissolved in DMSO (5 mL). Sodium azide (160 mg, 2.46 mmol, 2.10 equiv) was then added. The reaction mixture was stirred for 10 min and then sonicated for 3 min to facilitate sodium azide dissolution. Then the solution was stirred for 2 h at r.t. before quenching with H_2O (5 mL). The mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The oil was purified by silica gel column chromatography (hexanes/EtOAc gradient from 100/0 to 90/10, v/v) to give a yellow oil (207 mg, 85%). HRMS (EI): Calcd. For $C_{10}H_{15}NS$ $[M–N_2]^+$ 181.092; found, 181.0921.



3AHT-PCB-DIBO (S11): In a 20 mL vial, **S9** (25.6 mg, 0.0233 mmol, 1.00 equiv) and **S10** (5.2 mg, 0.025 mmol, 1.10 equiv) were added. Then $CDCl_3$ (1.5 mL) was added and the solution was transferred to a NMR tube. ^1H NMR spectra were collected at 10 min, 8 h, 29 h and 43 h. At 29 h, **S10** (2 mg, 0.010 mmol, 0.4 equiv) was added to the NMR tube and then an additional spectrum was acquired to show starting material peak reappearance. IR spectra were also collected at 8 h and at 29 h (after the second addition of **S10**). The resulting solution was concentrated *in vacuo* and the resulting solid was purified by silica gel column chromatography (CH_2Cl_2/MeOH gradient from 100/0 to 90/10 v/v) to give a dark brown solid that was a mixture of regioisomers (23.3 mg, 76%). MALDI-TOF-MS: Calcd. For $C_{97}H_{37}N_3O_2S$ [M] 1308.264; found 1308.894.

IV. Small Molecule NMR Spectra

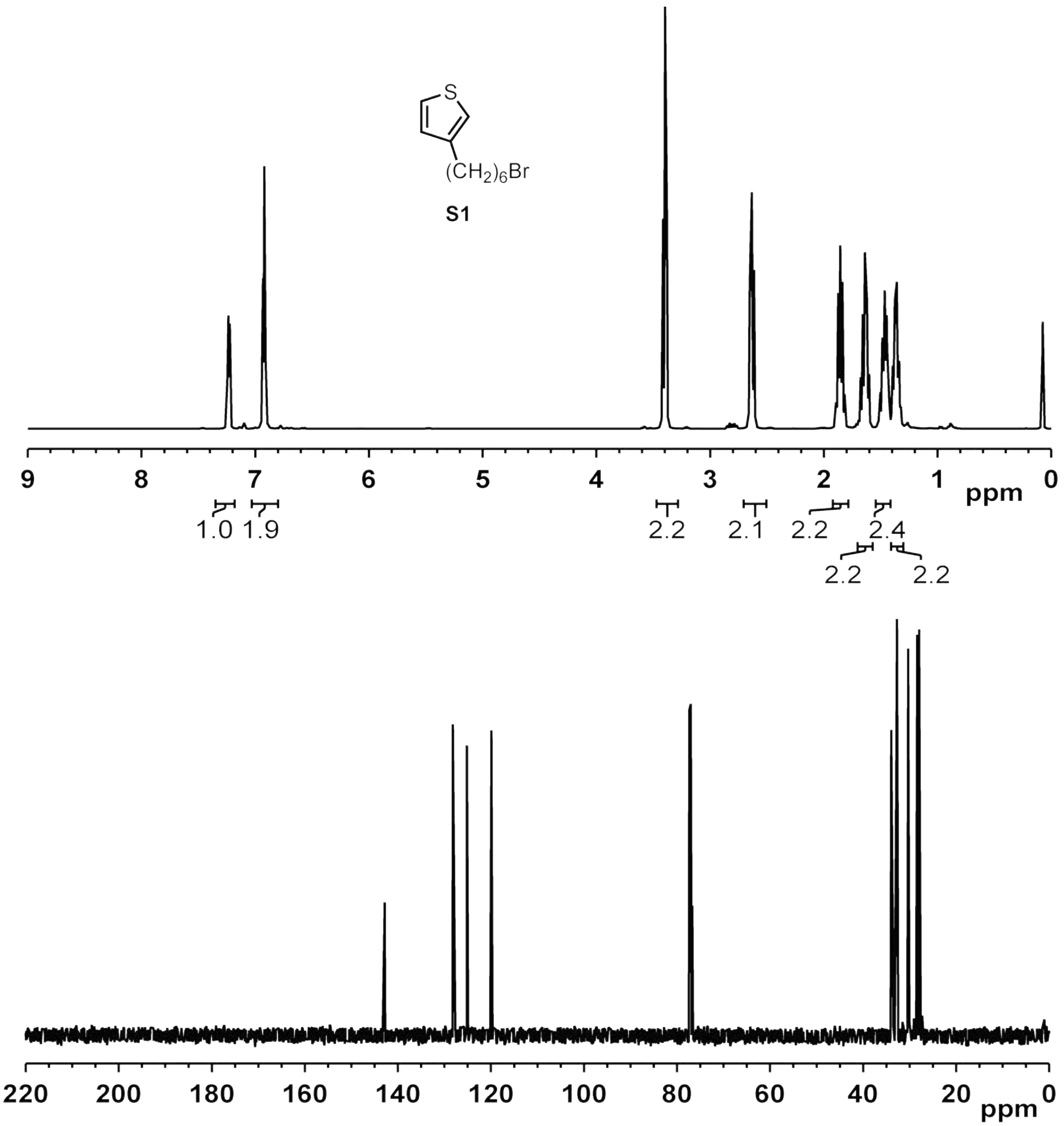


Figure S1. NMR spectra for **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 4.8, 2.9 Hz, 1H), 6.92 (m, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.86 (m, 2H), 1.64 (m, 2H), 1.46 (m, 2H), 1.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.84, 128.19, 125.16, 119.89, 33.96, 32.71, 30.32, 30.11, 28.38, 27.97.

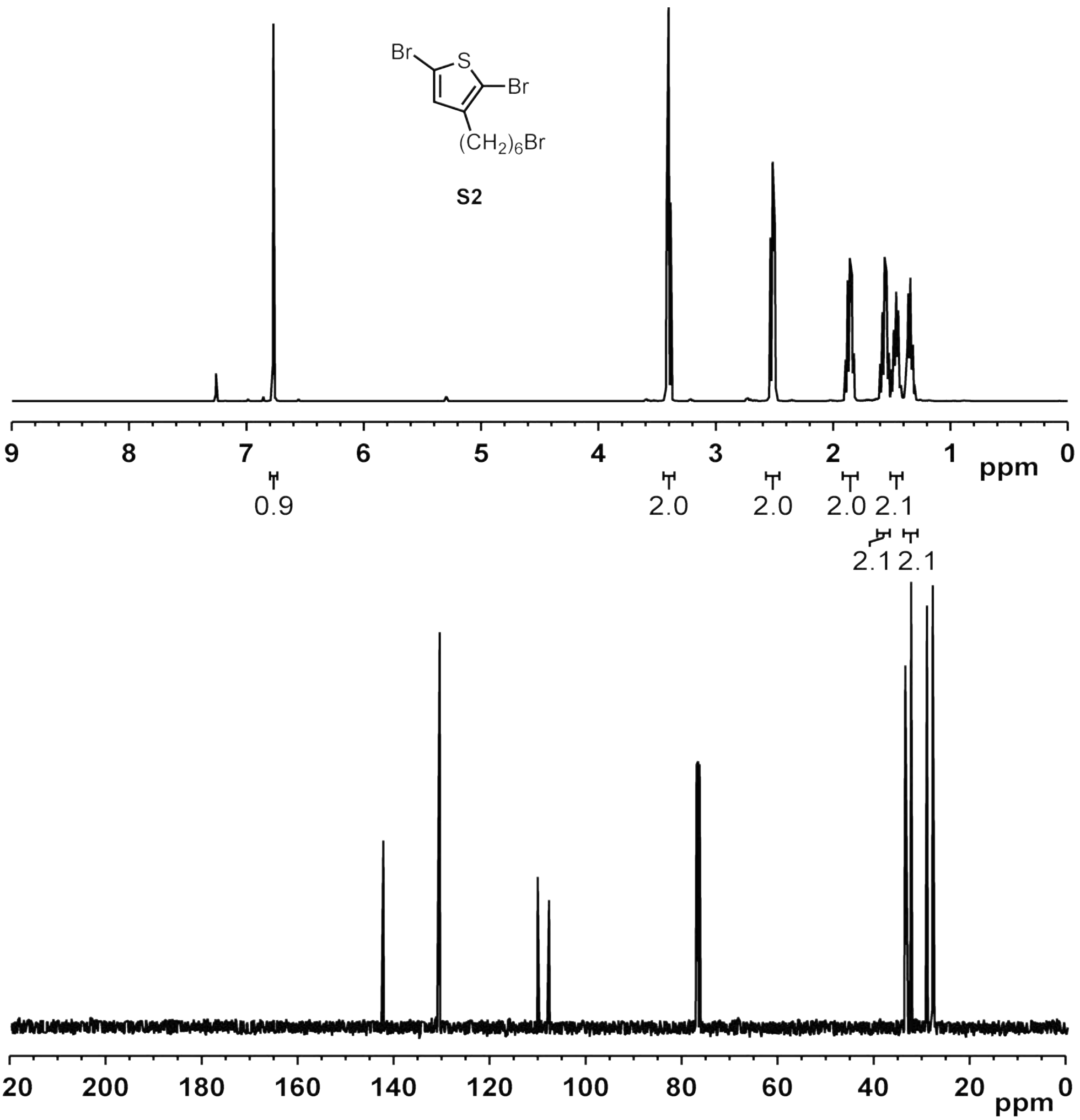


Figure S2. NMR spectra for **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.86 (m, 2H), 1.56 (m, 2H), 1.46 (m, 2H), 1.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.59, 130.86, 110.44, 108.07, 33.86, 32.64, 29.35, 29.29, 28.15, 27.87.

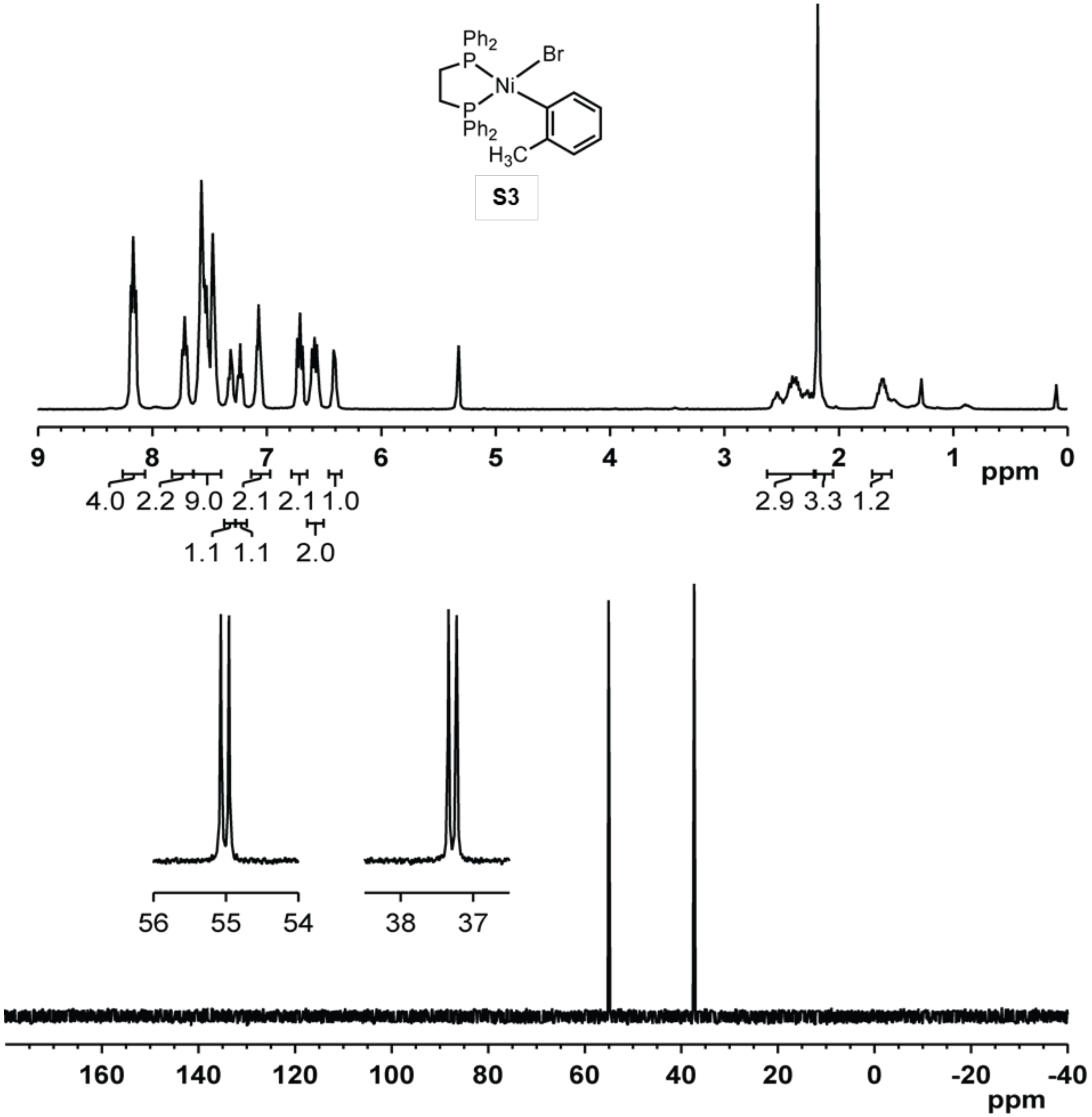


Figure S3. NMR spectra for **S3**. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.16 (m, 4H), 7.72 (app t, *J* = 8.3 Hz, 2H), 7.51 (m, 9H), 7.31 (app t, *J* = 7.2 Hz, 1H), 7.23 (app t, *J* = 6.4 Hz, 1H), 7.07 (app t, *J* = 6.5 Hz, 2H), 6.71 (m, 2H), 6.58 (m, 2H), 6.41 (d, *J* = 6.6 Hz, 1H), 2.39 (m, 3H), 2.18 (s, 3H), 1.61 (m, 1H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 55.01 (d, *J* = 18.3 Hz), 37.28 (d, *J* = 18.2 Hz).

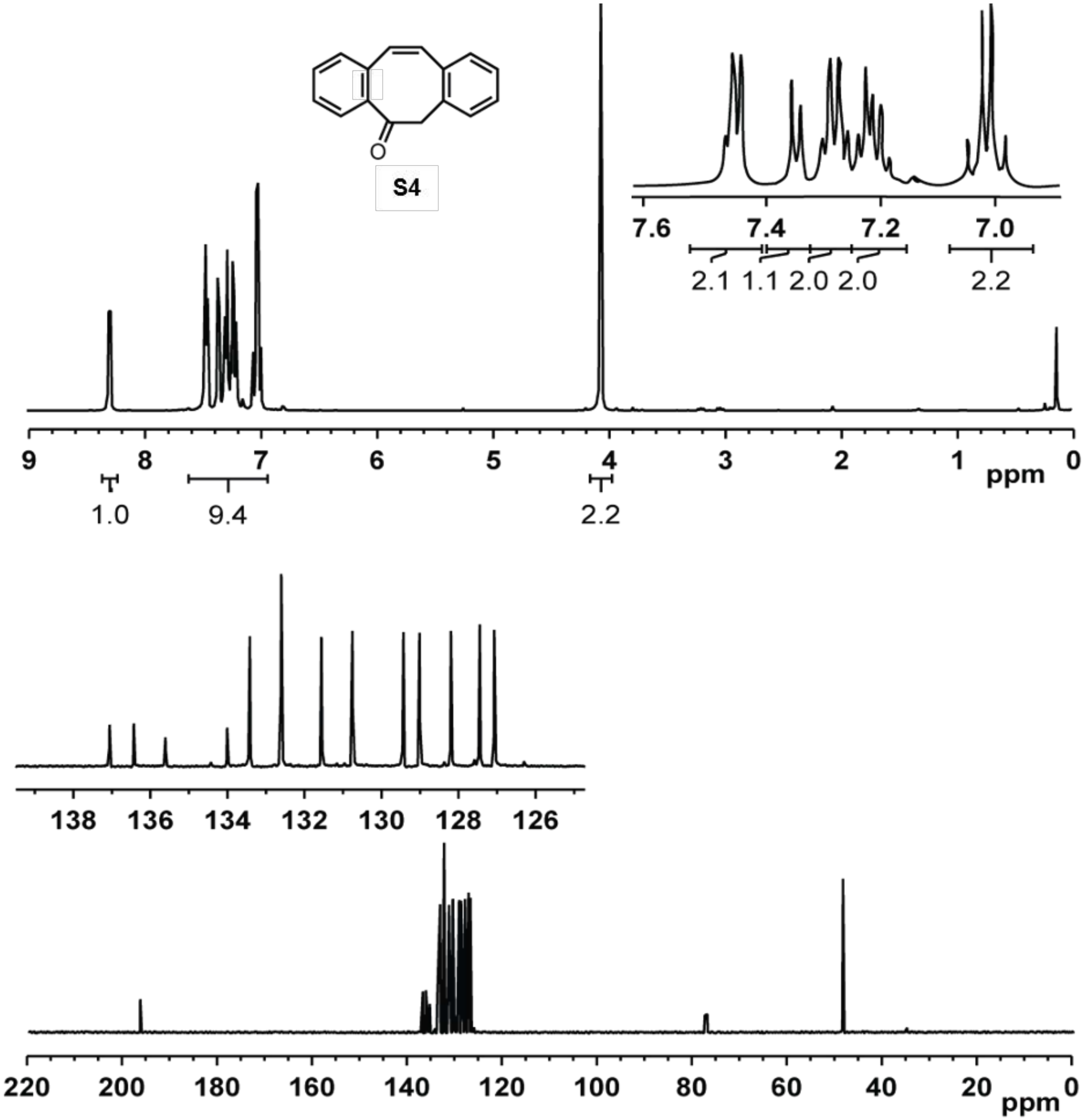
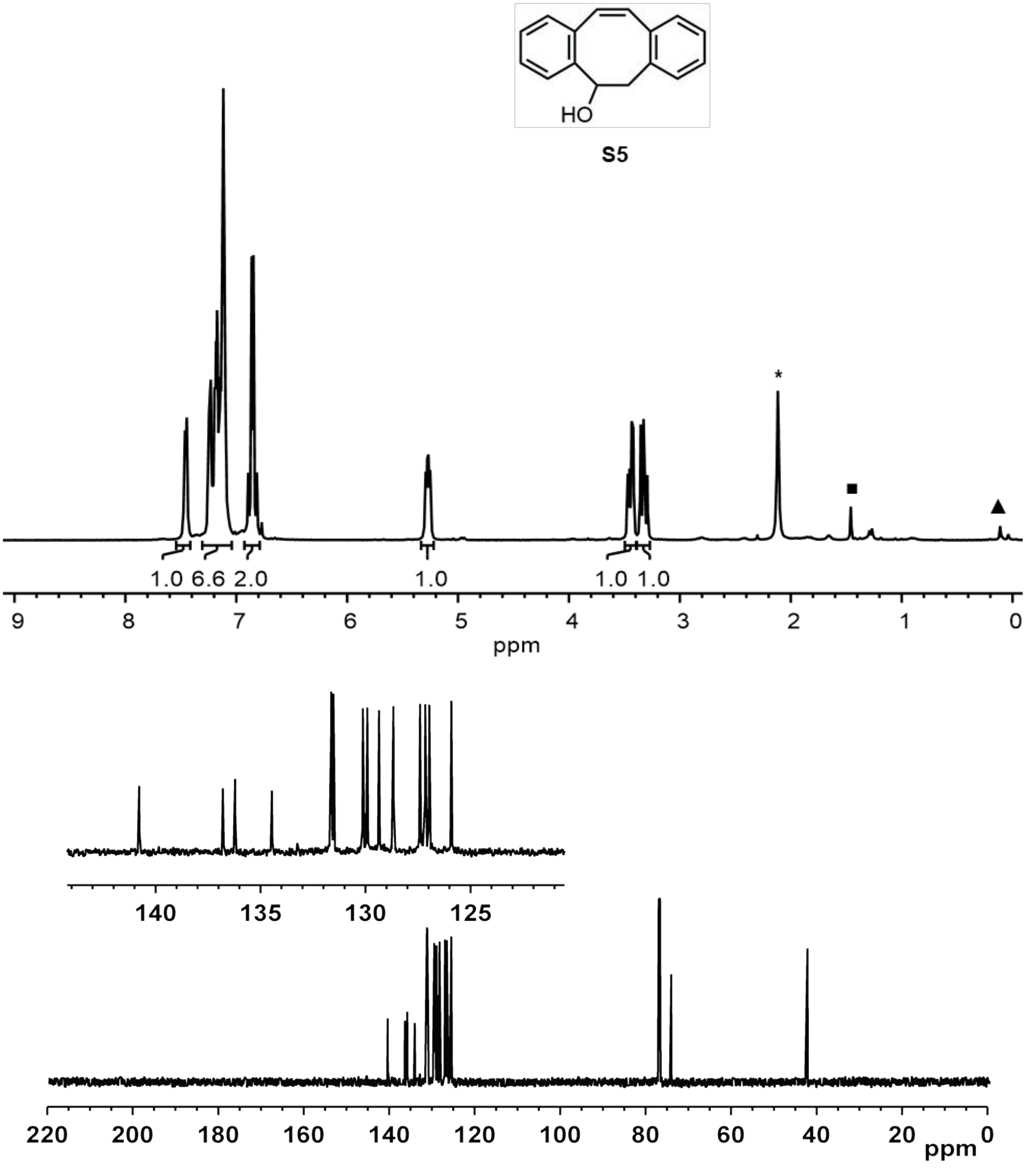


Figure S4. NMR spectra for **S4**. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.46 (m, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.28 (m, 2H), 7.21 (m, 2H), 7.02 (m, 2H), 4.06 (s, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 196.58, 137.06, 136.43, 135.61, 134.01, 133.42, 132.60, 131.56, 130.76, 129.43, 129.01, 128.20, 127.45, 127.07, 48.60.



S5

Figure S5. NMR spectra for **S5**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 1H), 7.17 (m, 7H), 6.84 (m, 2H), 5.27 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.45 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.32 (dd, *J* = 13.6, 10.2 Hz, 1H). *Acetone, ■ H_2O, ▲ grease. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.78, 136.79, 136.21, 134.46, 131.63, 131.53, 130.12, 129.91, 129.36, 128.67, 127.40, 127.15, 126.96, 125.91, 74.46, 42.59.

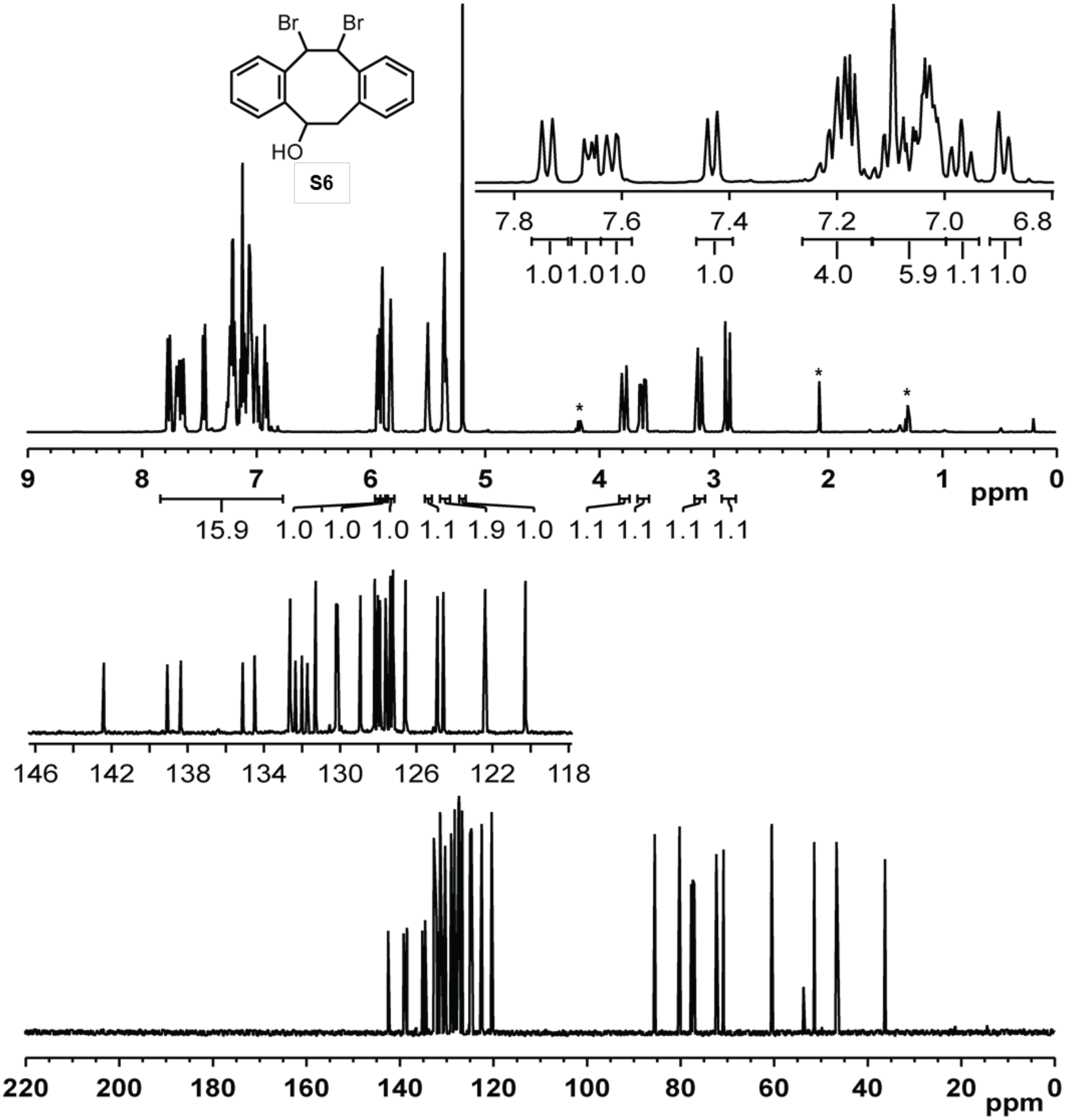


Figure S6. NMR spectra for **S6** (a 1:1 mixture of diastereomers). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (m, 1H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.23-7.18 (m, 4H), 7.01-7.11 (m, 6H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 5.90 (d, *J* = 5.5 Hz, 1H), 5.87 (d, *J* = 2.2 Hz, 1H), 5.80 (s, 1H), 5.47 (t, *J* = 3.2 Hz, 1H), 5.33 (t, *J* = 5.0 Hz, 2H), 5.17 (s, 1H), 3.75 (dd, *J* = 16.1, 1.2 Hz, 1H), 3.59 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.10 (dd, *J* = 16.1, 3.7 Hz, 1H), 2.85 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.40, 139.07, 138.36, 135.11, 134.49, 132.62, 132.35, 132.01, 131.72, 131.28, 130.21, 130.14, 128.93, 128.18, 128.01, 127.90, 127.61, 127.36, 127.22, 126.57, 124.88, 124.58, 122.39, 120.27, 85.40, 80.09, 72.24, 70.70, 60.40, 51.31, 46.53, 36.16. *EtOAc

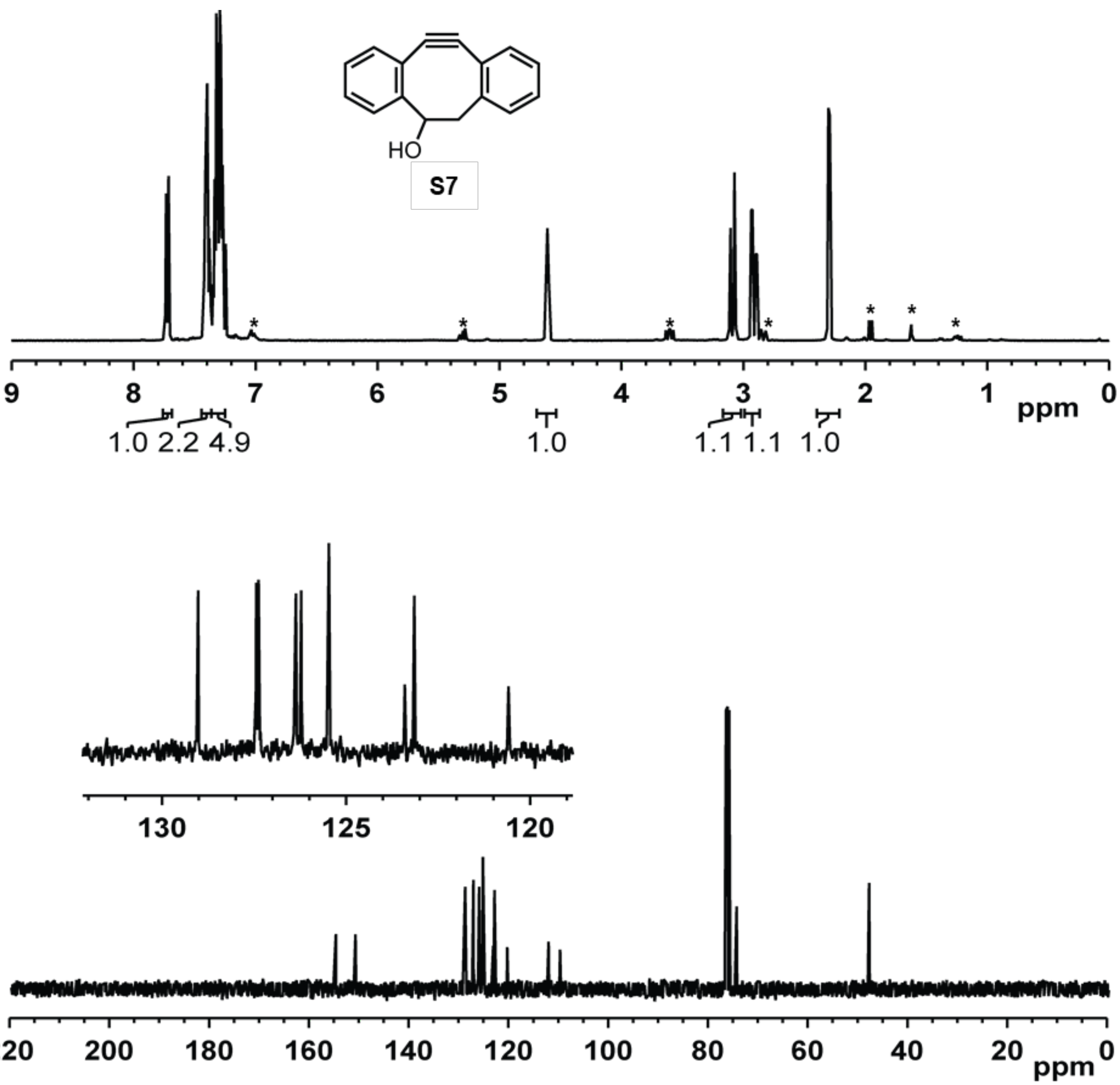


Figure S7. NMR spectra for **S7**. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, J = 7.8 Hz, 1H), 7.40 (m, 2H), 7.30 (m, 5H), 4.60 (bs, 1H), 3.09 (dd, J = 14.7, 2.1 Hz, 1H), 2.91 (dd, J = 14.7, 3.7 Hz, 1H), 2.30 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.67, 151.75, 129.76, 128.18, 128.11, 127.10, 126.96, 126.20, 126.19, 124.14, 123.88, 121.33, 113.04, 110.73, 75.34, 48.78. *unknown and unresolvable impurity

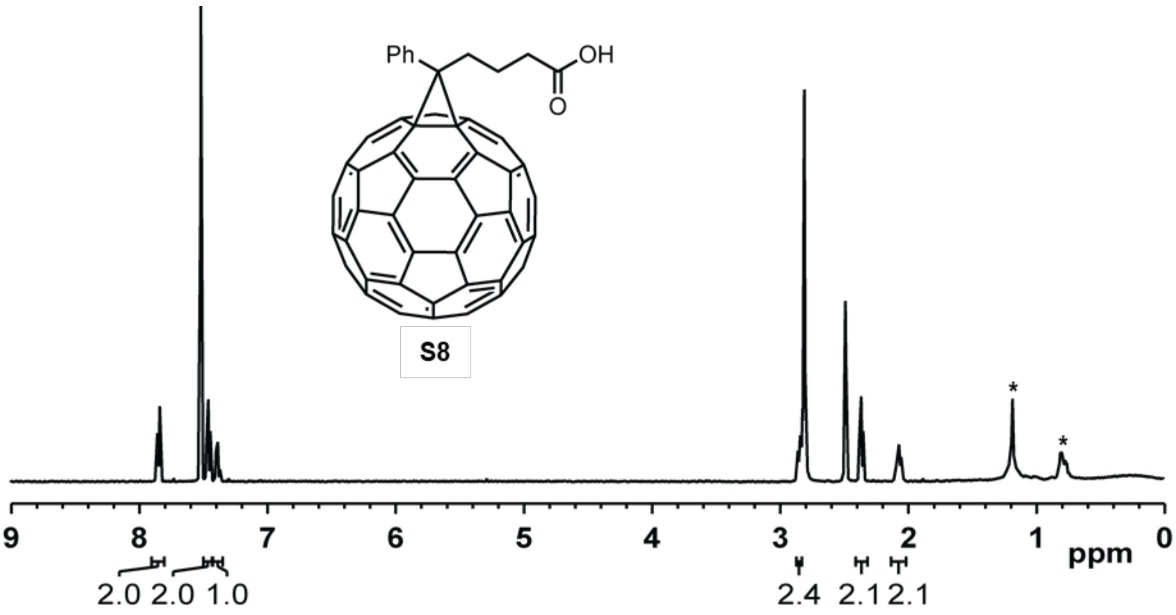


Figure S8. NMR spectrum for **S8**. ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6/CS_2 3:1:1) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.46 (m, 2H), 7.38 (m, 1H), 2.84 (m, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.07 (m, 2H). *grease

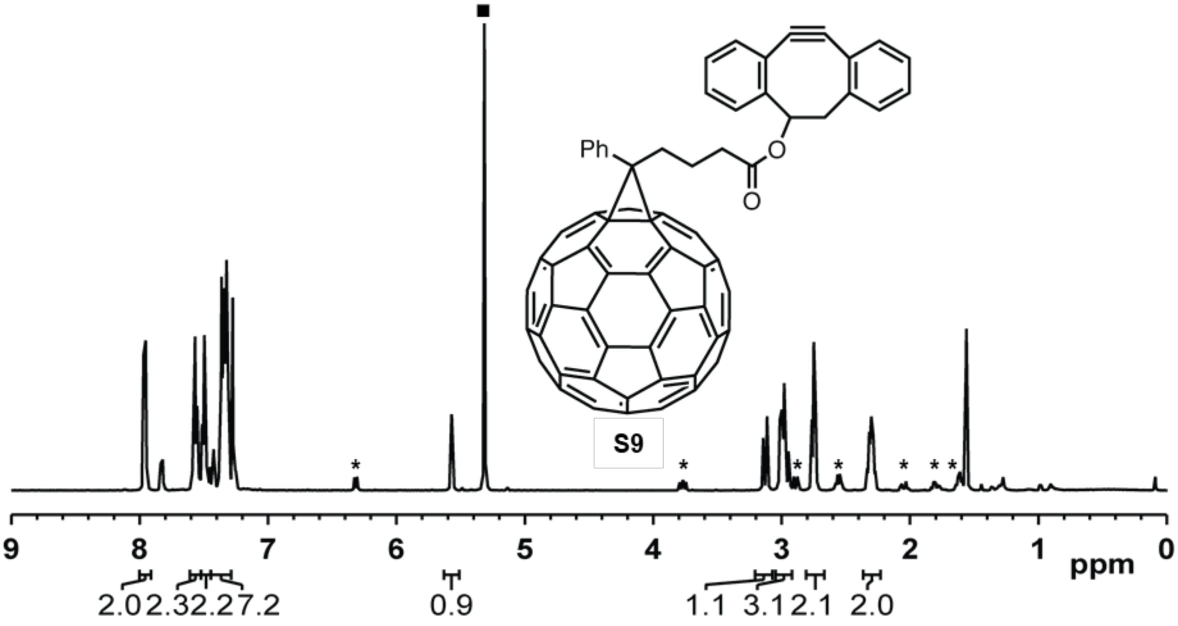


Figure S9. NMR spectrum for **S9**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (m, 2H), 7.50 (m, 2H), 7.35 (m, 7H), 5.57 (s, 1H), 3.13 (m, 1H), 2.98 (m, 3H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.31 (m, 2H). *unknown and unresolvable impurity. ■DCM

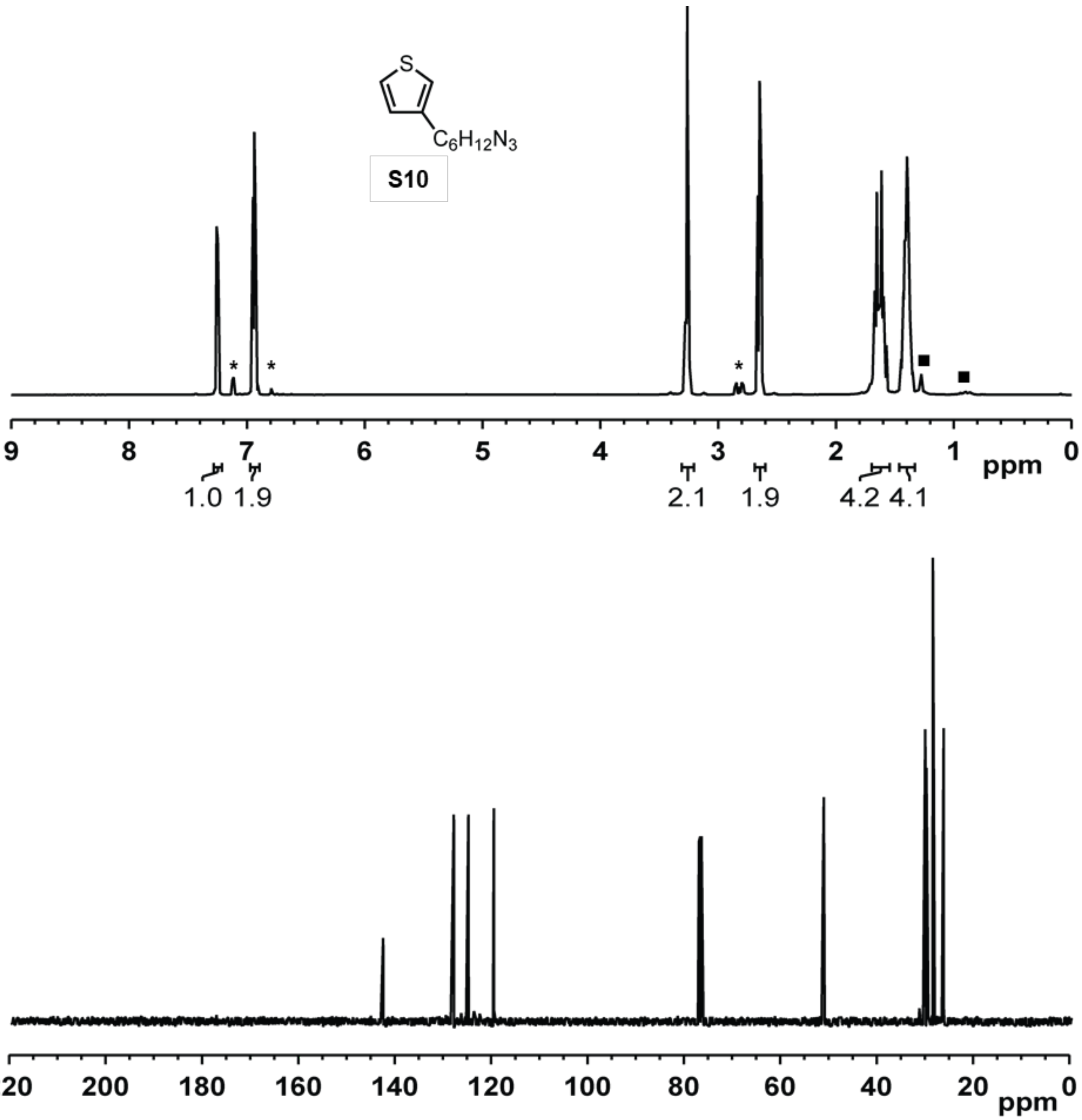


Figure S10. NMR spectrum for **S10**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 4.8, 3.0 Hz, 1H), 6.94 (m, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.63 (m, 4H), 1.40 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.86, 128.19, 125.17, 119.89, 51.42, 30.37, 30.13, 30.12, 28.78, 26.55. *unknown and unresolvable impurity, ■grease

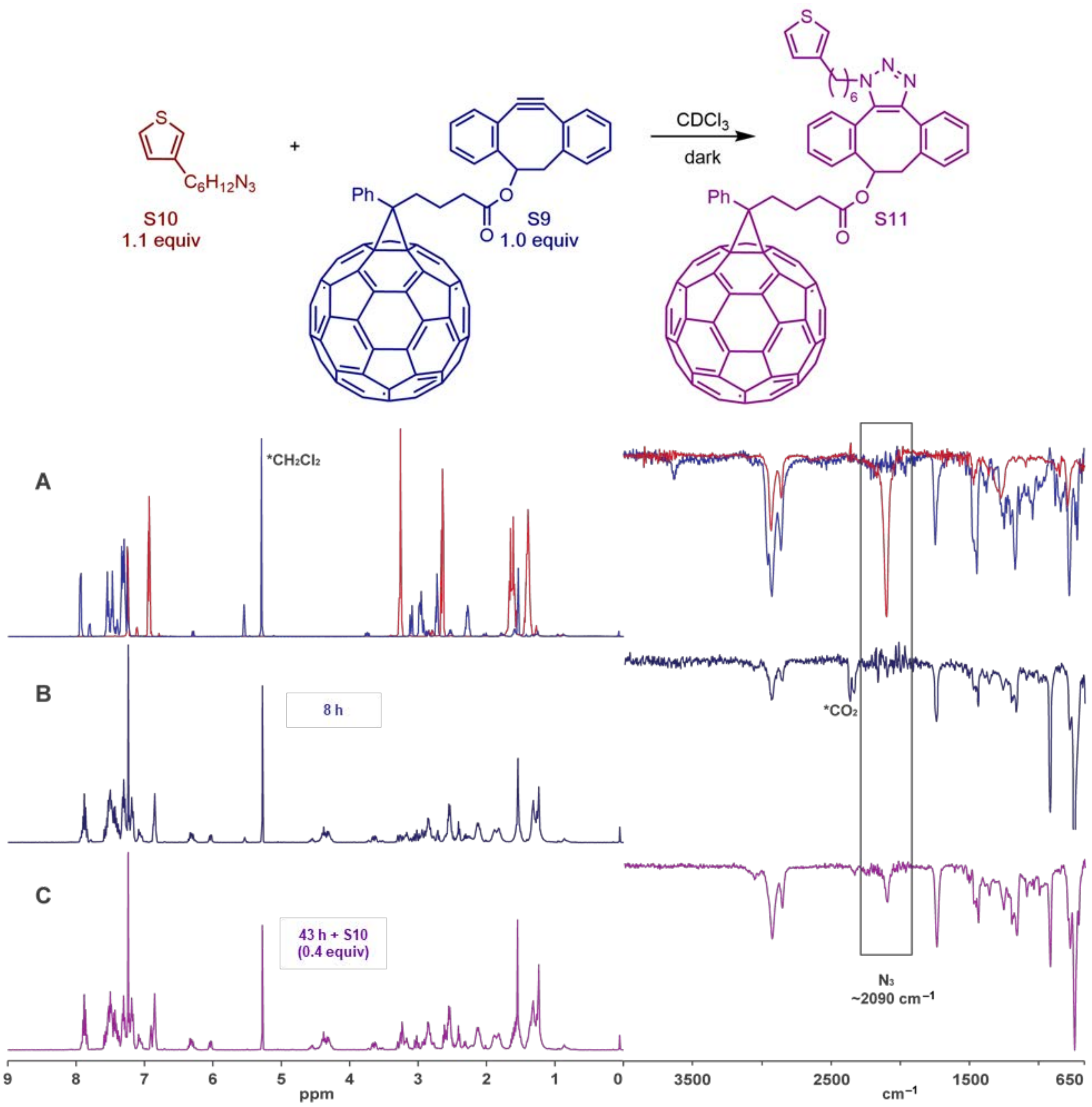


Figure S11. ^{1}H NMR (left) and IR (right) spectra for (A) **S10** (red) and **S9** (blue) overlay. (B) Reaction solution at 8 h with unreacted **S9**. (C) After 29 h additional **S10** (0.4 equiv) was added and the spectrum shows reaction solution after 43 h with unreacted **S10**. Note that two regioisomers of the triazole are formed in the click reaction.

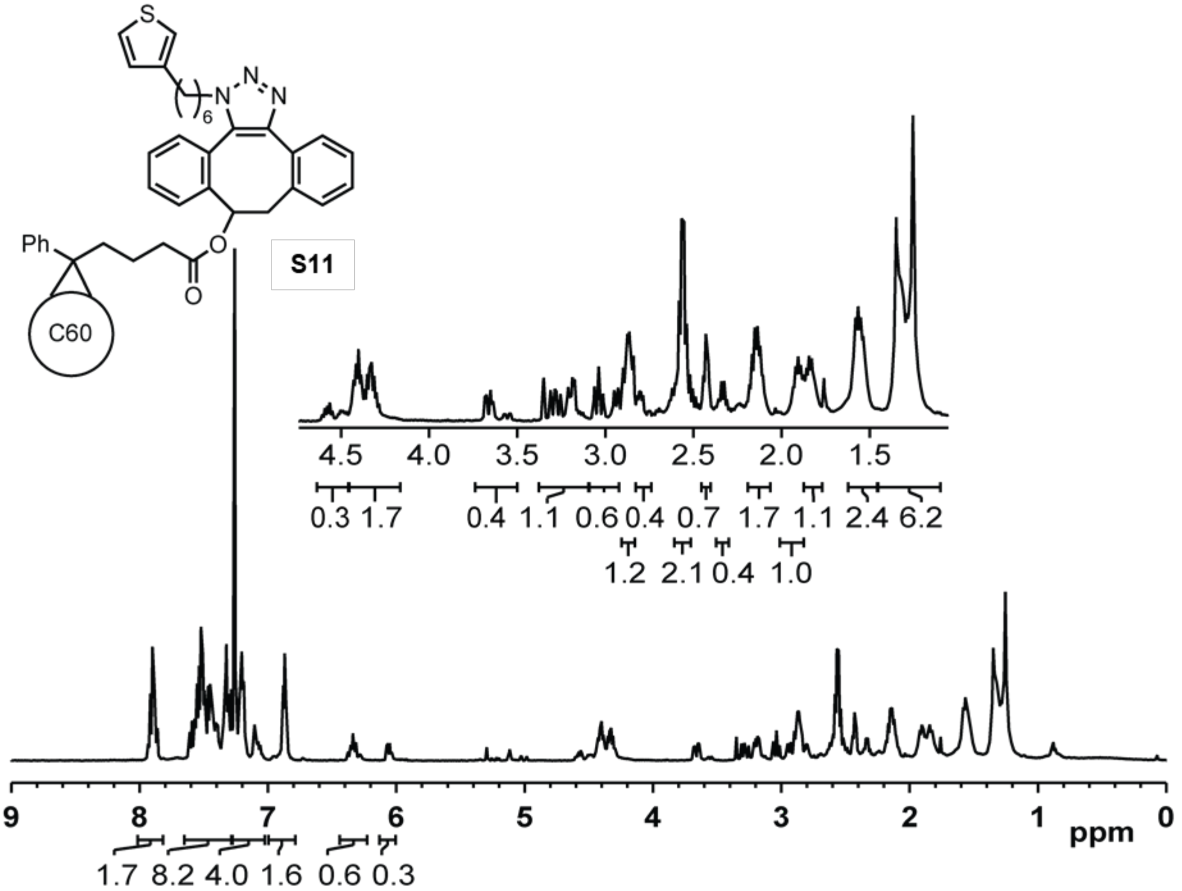
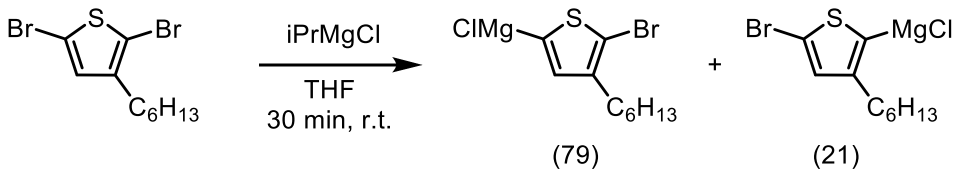


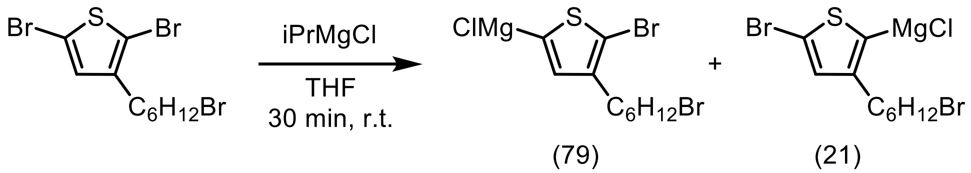
Figure S12. NMR spectrum for **S11** (a mixture of regioisomers and diastereomers). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (m, 2H), 7.46 (m, 8H), 7.19 (m, 4H), 6.87 (m, 2H), 6.33 (m, 0.6H), 6.05 (m, 0.3H), 4.58 (m, 0.3H), 4.36 (m, 1.7H), 3.61 (m, 0.4H), 3.25 (m, 1H), 3.00 (m, 0.6H), 2.87 (m, 1H), 2.80 (m, 0.4H), 2.56 (q, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 0.7H), 2.33 (q, *J* = 7.2 Hz, 0.4H), 2.14 (m, 1.7H), 1.90 (m, 1H), 1.84 (m, 1H), 1.57 (m, 2H), 1.31 (m, 6H).

V. Polymerization Procedures and Data



HT

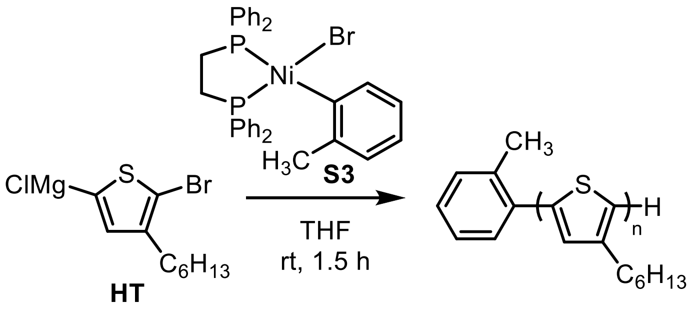
3HT monomer activation: In the glovebox, 2,5-dibromo-3-hexylthiophene (117 mg, 0.359 mmol, 1.00 equiv) was dissolved in THF (3 mL) in an 8 mL vial equipped with a stir bar. iPrMgCl (2.0 M in THF, 160 µL, 0.32 mmol, 0.89 equiv) was added and stirred at r.t. for 30 min. An aliquot (0.5 mL) was quenched with 6 M aq. HCl (0.1 mL), extracted with $CHCl_3$ (2 x 1 mL), dried over $MgSO_4$, filtered, and analyzed by GC, showing a mixture of **HT** regioisomers in a 79:21 ratio. Note that only the major regioisomer undergoes polymerization with precatalyst **S3**, giving highly regioregular materials. Fresh solution of **HT** was synthesized before every polymerization.



S2

BrHT

BrHT monomer activation: In the glovebox, **S2** (149 mg, 0.368 mmol, 1.00 equiv) was dissolved in THF (3 mL) in an 8 mL vial equipped with a stir bar. iPrMgCl (2.0 M in THF, 160 µL, 0.320 mmol, 0.87 equiv) was added and the reaction stirred at r.t. for 30 min. An aliquot (0.5 mL) was quenched with 6 M aq. HCl (0.1 mL), extracted with $CHCl_3$ (2 x 1 mL), dried over $MgSO_4$, filtered and analyzed by GC, showing a mixture of **BrHT** regioisomers in a 79:21 ratio. Note that only the major regioisomer undergoes polymerization with precatalyst **S3**, giving highly regioregular materials. Fresh solution of **BrHT** was synthesized before every polymerization.



Poly(3-hexylthiophene) (P3HT): To an oven-dried 500 mL round-bottom flask, a 0.17 M solution of **HT** (15 mL, 2.5 mmol, 250 equiv) in THF was added and diluted with THF (250 mL). A 0.010 M solution of precatalyst **S3** (1.0 mL, 0.010 mol, 1.0 equiv) in THF was injected and the solution was stirred at r.t. for 1.5 h. The polymerization was quenched with 6 M aq. HCl (30 mL), and precipitated with MeOH (200 mL). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with acetone, MeOH, hexane, CH_2Cl_2 and $CHCl_3$. The $CHCl_3$ fraction was dried *in vacuo* to afford **P3HT** as a dark purple solid (374 mg, 80%). Gel permeation chromatography (GPC) after purification: M_n = 61.8 kg/mol, Đ = 1.26.

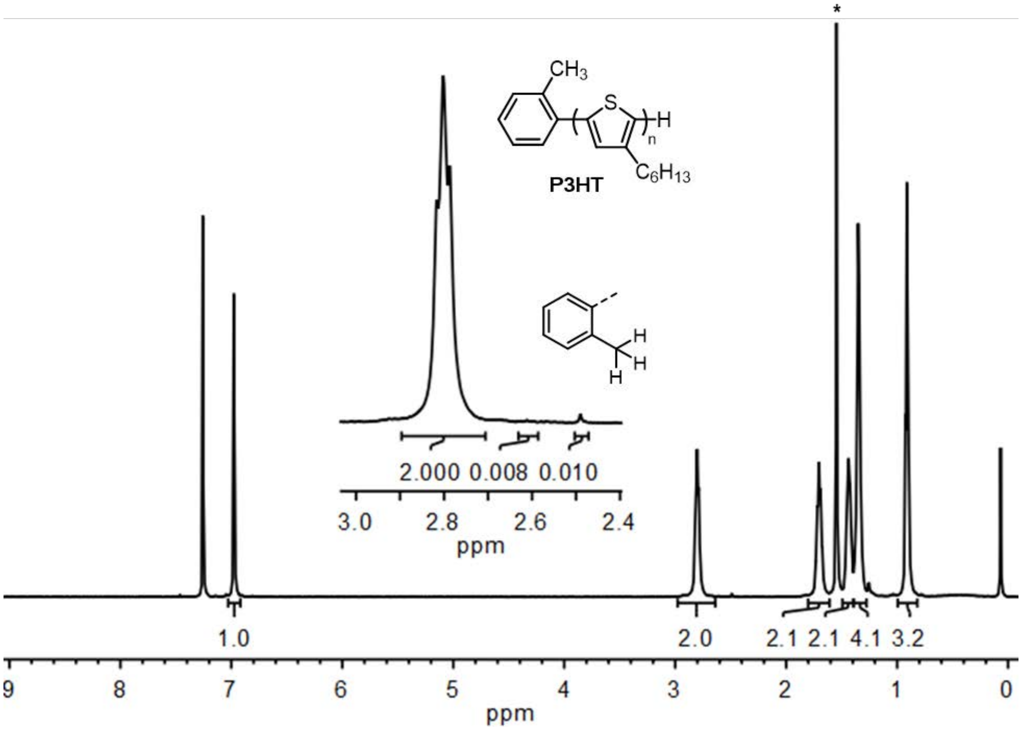
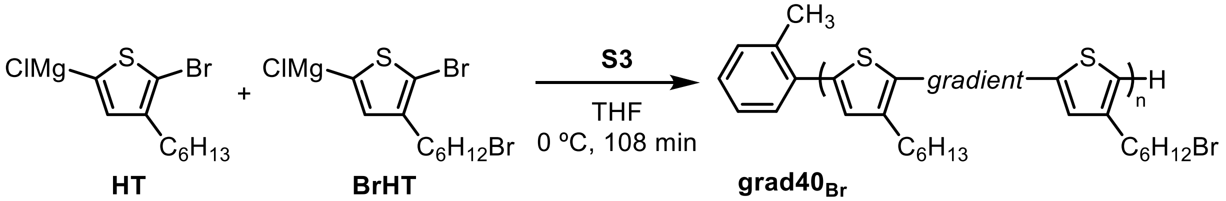


Figure S13. NMR spectrum for **P3HT**. ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1H), 2.80 (t, *J* = 7.9 Hz, 2H), 1.71 (m, 2H), 1.43 (m, 2H), 1.35 (m, 4H), 0.99 (m, 3H). ^1H NMR shows >99% regioregularity and M_n = 49.8 kg/mol based on end-group analysis (inset). The M_n obtained by GPC is an overestimation by a factor of 1.2, in reasonable agreement with a previous report.[6] *H_2O

Copolymers for compositional studies



Poly(3-hexylthiophene-*grad*-3-(6-bromohexyl)thiophene)60:40 (grad40$_{\text{Br}}$). In the glovebox, to an oven-dried 50 mL Schlenk flask, a 0.122 M solution of **HT** (2.40 mL, 0.293 mmol, 54.0 equiv) in THF was added and diluted with THF (10 mL). The Schlenk flask was capped and removed from the glovebox, put under N_2 and cooled to 0 °C. In a 20 mL vial, a 0.0863 M solution of **BrHT** (1.70 mL, 0.147 mmol, 27.0 equiv) in THF was added and diluted with THF (1.3 mL). The solution of **BrHT** was taken out of the glovebox with a syringe and affixed to the syringe pump. A 0.010 M solution of precatalyst **S3** (0.54 mL, 5.4 µmol, 1.0 equiv) in THF was taken out of the glovebox in a plastic syringe and injected to the solution of **3HT**. After 2 min 48 s, the syringe pump was activated to inject **BrHT** at a rate of 0.1 mL/min. Aliquots (2 mL) were removed at 7, 17, 35 (addition completed), 69 and 108 min (reaction completed) and quenched with 6 M aq. HCl (2 mL). The resulting solution was then extracted with $CHCl_3$ (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford crude polymer. The samples were analyzed by GC for monomer conversion and GPC for M_n. Then these samples were purified (see below) and analyzed by ^{1}H NMR spectroscopy to determine the cumulative mole fraction of **BrHT**.

Purification of aliquots for NMR spectroscopic analysis: The first aliquot was purified using silica gel column chromatography (CH_2Cl_2/hexane gradient from 0/100 to 100/0 v/v). The crude polymers from the remaining aliquots were dissolved in a minimal amount of $CHCl_3$ and precipitated with cold MeOH (10 mL). The resulting mixture was centrifuged for 15 min, the clear supernatant was decanted and the reddish purple precipitate was collected and dried *in vacuo*.

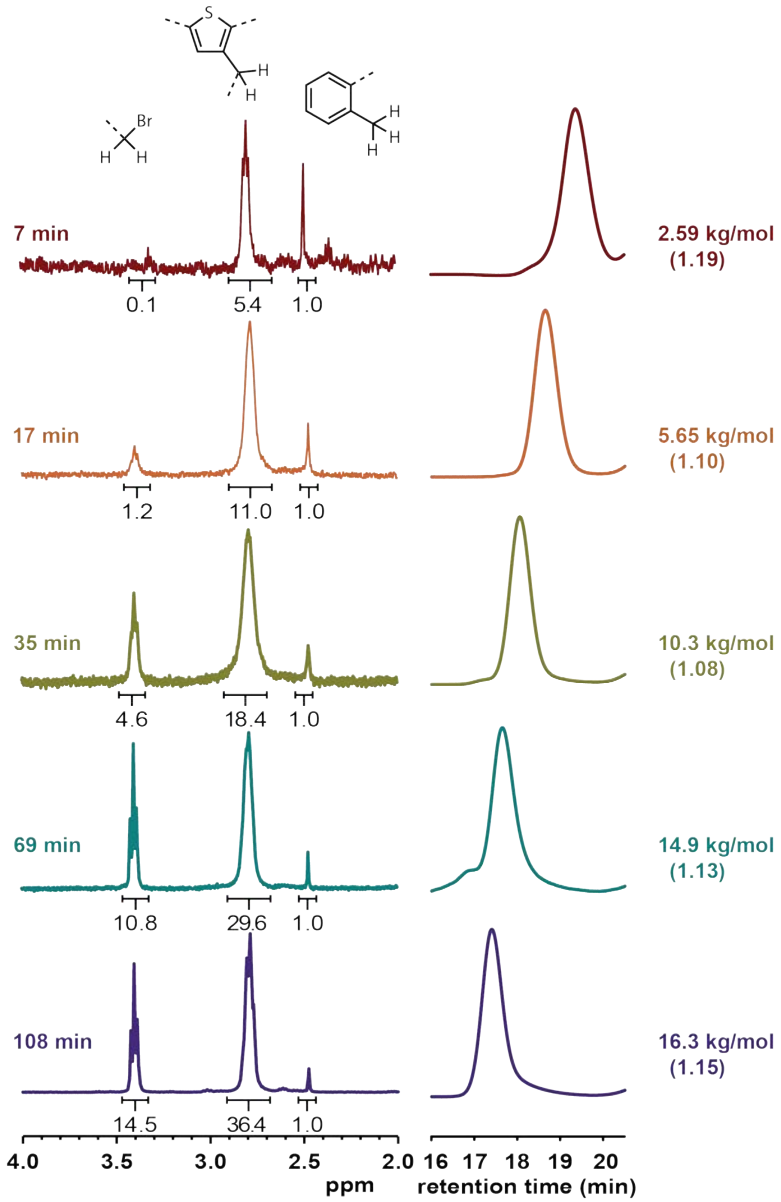


Figure S14. ^{1}H NMR spectra (left) and GPC curves (right) for aliquots drawn during the synthesis of **grad40**$_{\mathbf{Br}}$. GPC data are labeled with M_n (top) and Đ (in parenthesis, bottom).

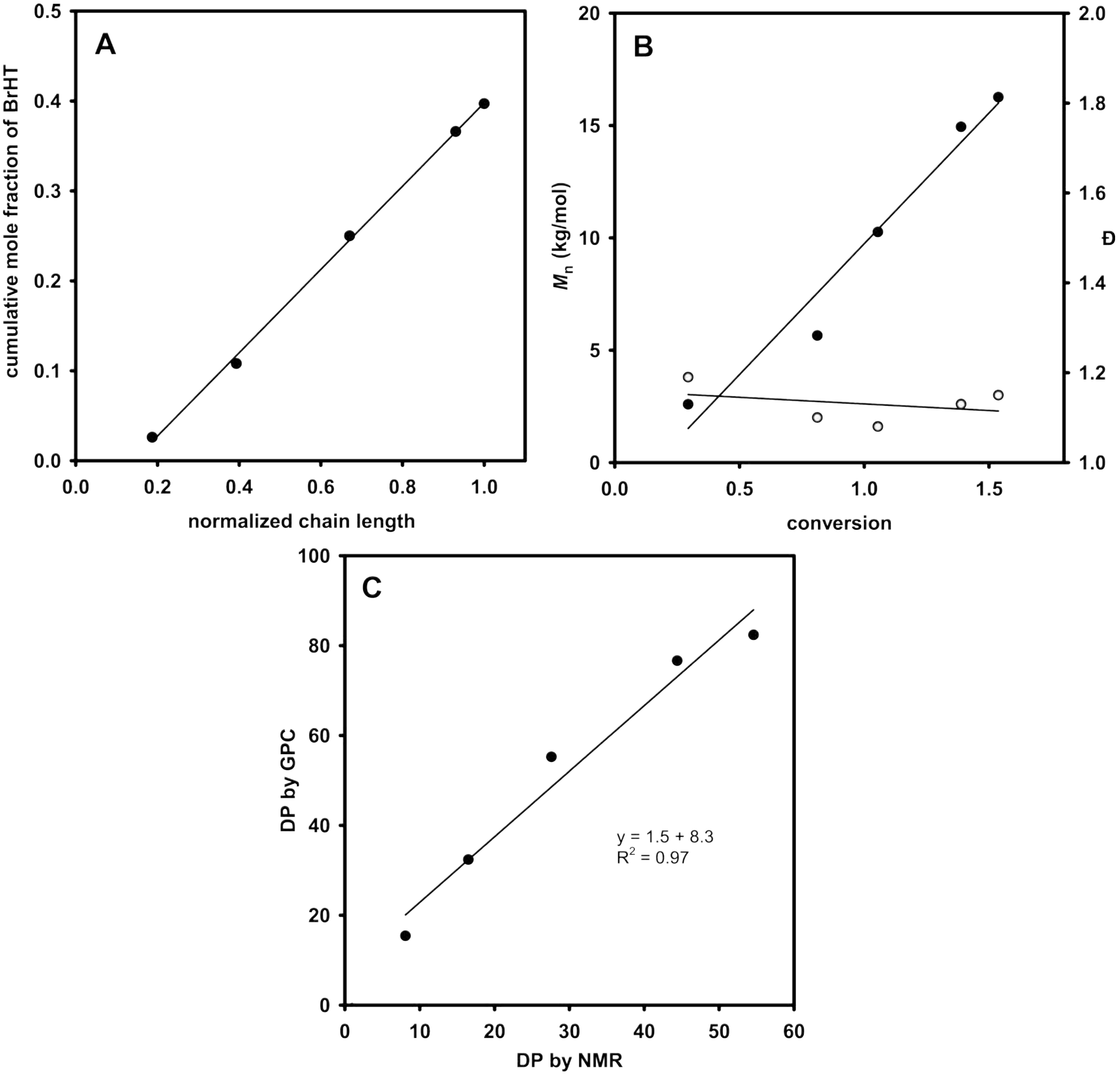
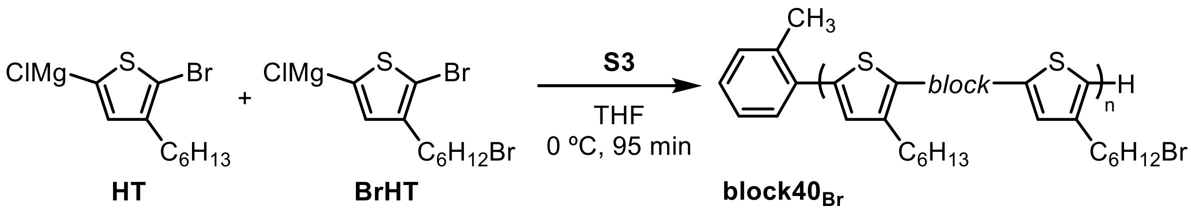


Figure S15. (A) Plot of the cumulative mole fraction of monomer **BrHT** in **grad40$_{Br}$** as a function of normalized chain length, (B) M_n (filled circles, ●) and Đ (open circles, ○) versus % conversion, and (C) comparison of the degree of polymerization (DP) obtained by GPC and ^{1}H NMR spectroscopic analysis of end groups. DP = M_n/ average repeat unit MW. Comparing the results of these two methods, it appears that GPC overestimates the DP of these copolymers by a factor of approximately 1.5, in reasonable agreement with a previous report.[6]



Poly(3-hexylthiophene-*block*-3-(6-bromohexyl)thiophene)60:40 (block40$_{Br}$). In the glovebox, to an oven-dried 50 mL Schlenk flask, a 0.123 M solution of **HT** (3.00 mL, 0.369 mmol, 48.0 equiv) in THF was added and diluted with THF (25 mL). The Schlenk flask was capped and removed from the glovebox, put under N_2 and cooled to 0 °C. A 0.010 M solution of precatalyst **S3** (0.77 mL, 7.7 µmol, 1.0 equiv) in THF was added to the solution of **HT**. After 30 min, a 0.123 M solution of **BrHT** (2.00 mL, 0.246 mmol, 32 equiv) in THF was injected into the reaction solution. Aliquots (2 mL) were removed at 12, 34, 40, 50, 66 and 95 min (reaction completed), and quenched with 6 M aq. HCl (2 mL). The resulting solutions were then extracted with $CHCl_3$ (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford crude polymer. The samples were analyzed by GC for monomer conversion and GPC for M_n. Then these samples were purified (see page S25) and analyzed by ^{1}H NMR spectroscopy to determine the cumulative mole fraction of **BrHT**.

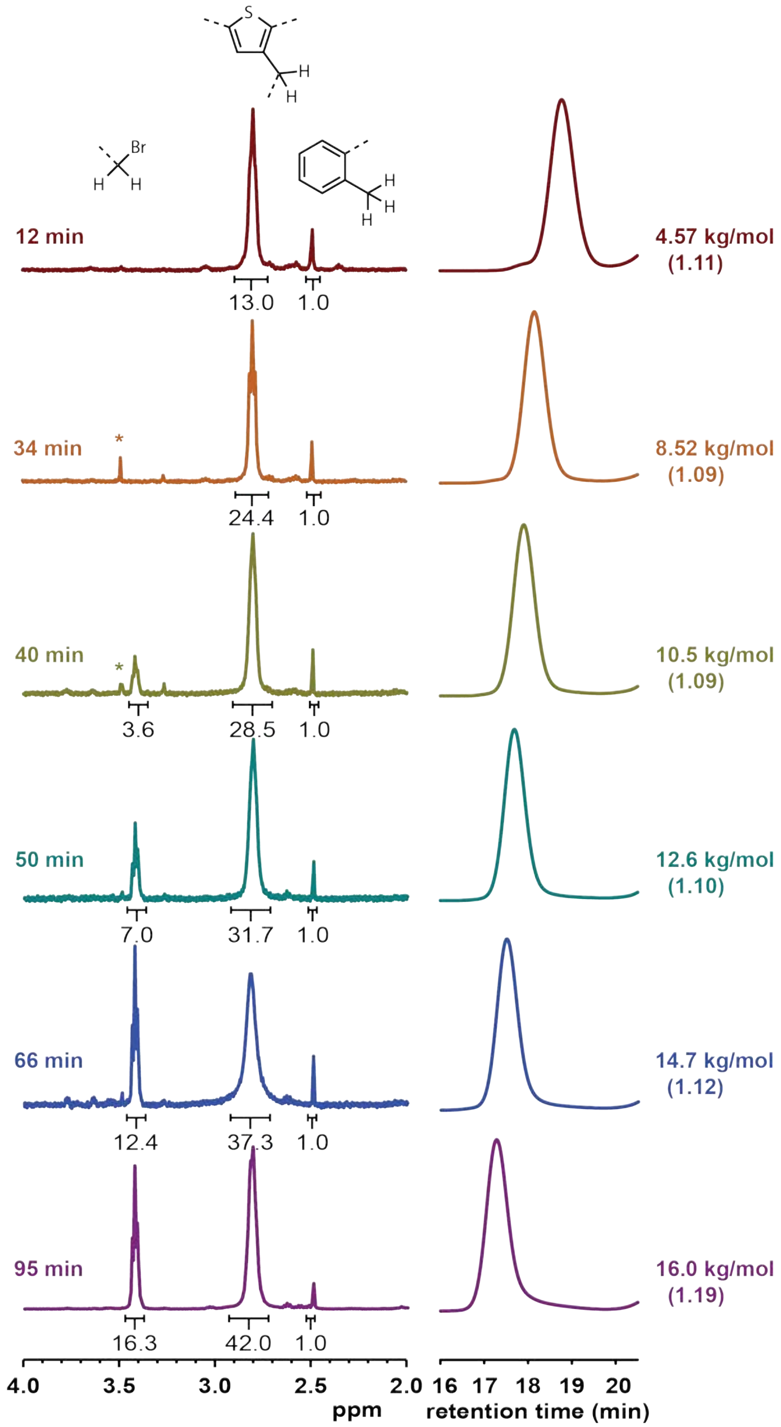


Figure S16. ^{1}H NMR spectra (left) and GPC curves (right) for aliquots drawn during synthesis of **block40$_{\mathbf{Br}}$** at various times. (* labeled as residual solvents, 3.49 ppm for MeOH.) GPC data is labeled with M_n (top) and Đ (in parenthesis, bottom).

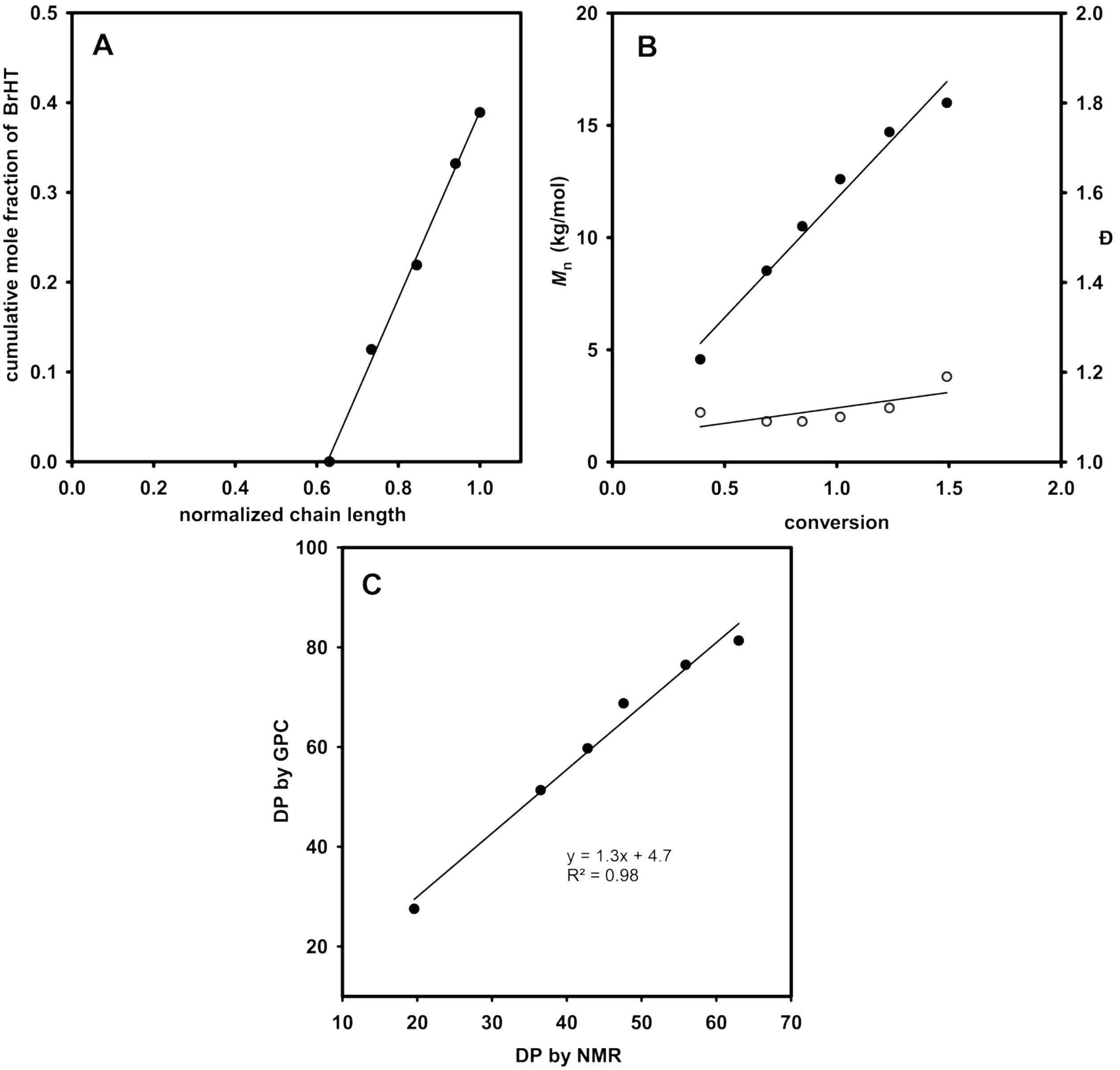
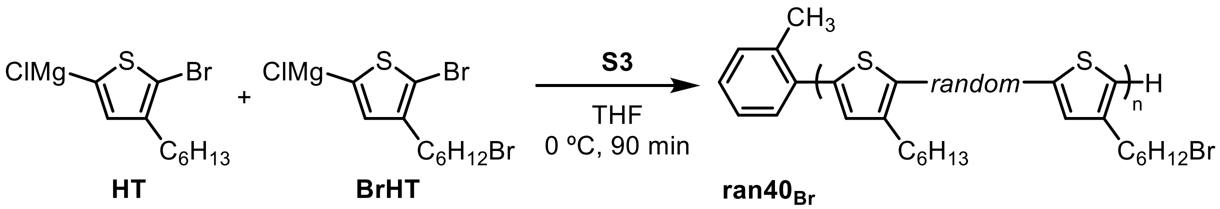


Figure S17. (A) Plot of the cumulative mole fraction of monomer **BrHT** in **block40**$_{\mathbf{Br}}$ as a function of normalized chain length, (B) M_n (filled circles, ●) and Đ (open circles, ○) versus % conversion, and (C) comparison of the degree of polymerization (DP) obtained by GPC and ^{1}H NMR spectroscopic analysis of end groups. DP = M_n/ average repeat unit MW. Comparing the results of these two methods, it appears that GPC overestimates the DP of these copolymers by a factor of approximately 1.3, in reasonable agreement with a previous report.[6]



Poly(3-hexylthiophene-*random*-3-(6-bromohexyl)thiophene)60:40 (ran40$_{\mathbf{Br}}$). In the glovebox, to an oven-dried 50 mL Schlenk flask, a 0.131 M solution of **HT** (2.20 mL, 0.288 mmol, 48.0 equiv) in THF and a 0.103 M solution of **BrHT** (1.87 mL, 0.192 mmol, 32.0 equiv) in THF were added and diluted with THF (15 mL). The Schlenk flask was capped and removed from glovebox, put under N_2 and cooled to 0 °C. Then a 0.010 M solution of precatalyst **S3** (0.60 mL, 6.0 μmol, 1.0 equiv) in THF was added. Aliquots (2 mL) were taken at 11, 25, 45, 60 and 90 min (reaction completed), and the reaction was quenched with 6 M aq. HCl (2 mL). The resulting solution was then extracted with $CHCl_3$ (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford crude polymer. The samples were analyzed by GC for monomer conversion and GPC for M_n. Then these samples were purified (see page S25) and analyzed by ^{1}H NMR spectroscopy to determine the cumulative mole fraction of **BrHT**.

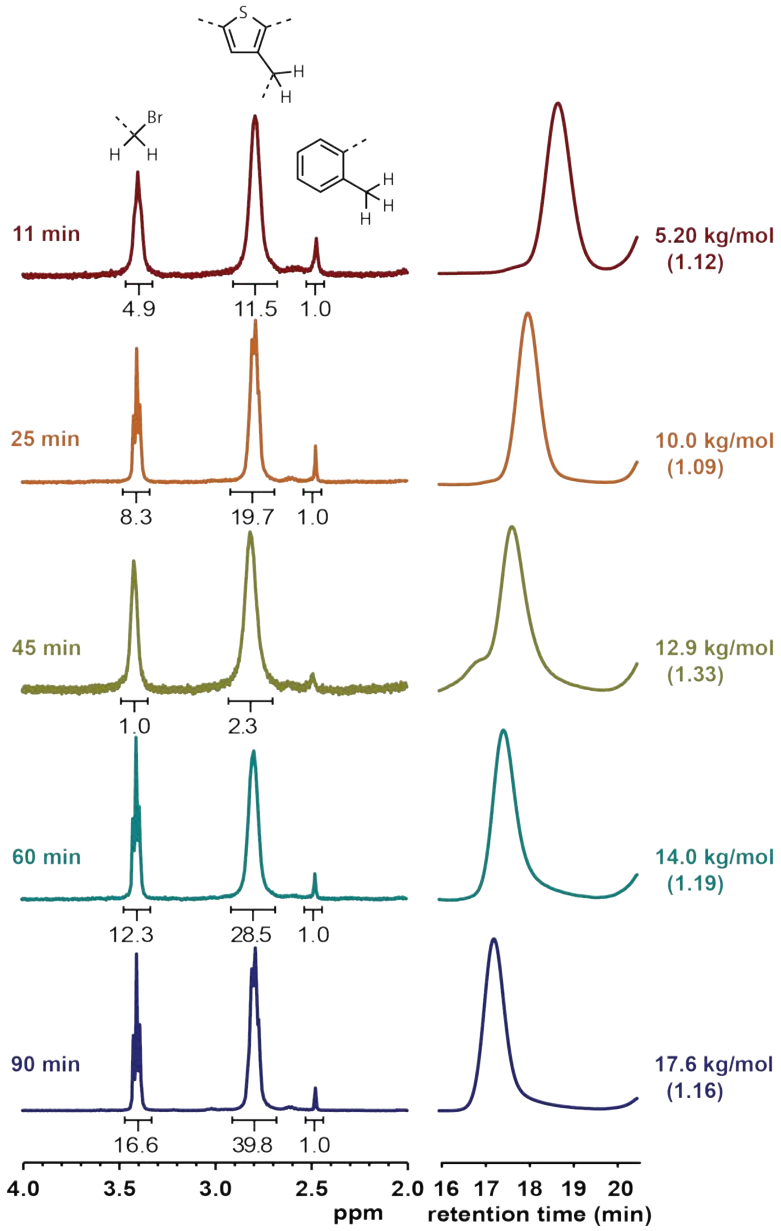


Figure S18. ^{1}H NMR spectra (left) and GPC curves (right) for aliquots drawn during the synthesis of **ran40$_{\mathbf{Br}}$** at various times. GPC data is labeled with M_n (top) and Đ (in parenthesis, bottom).

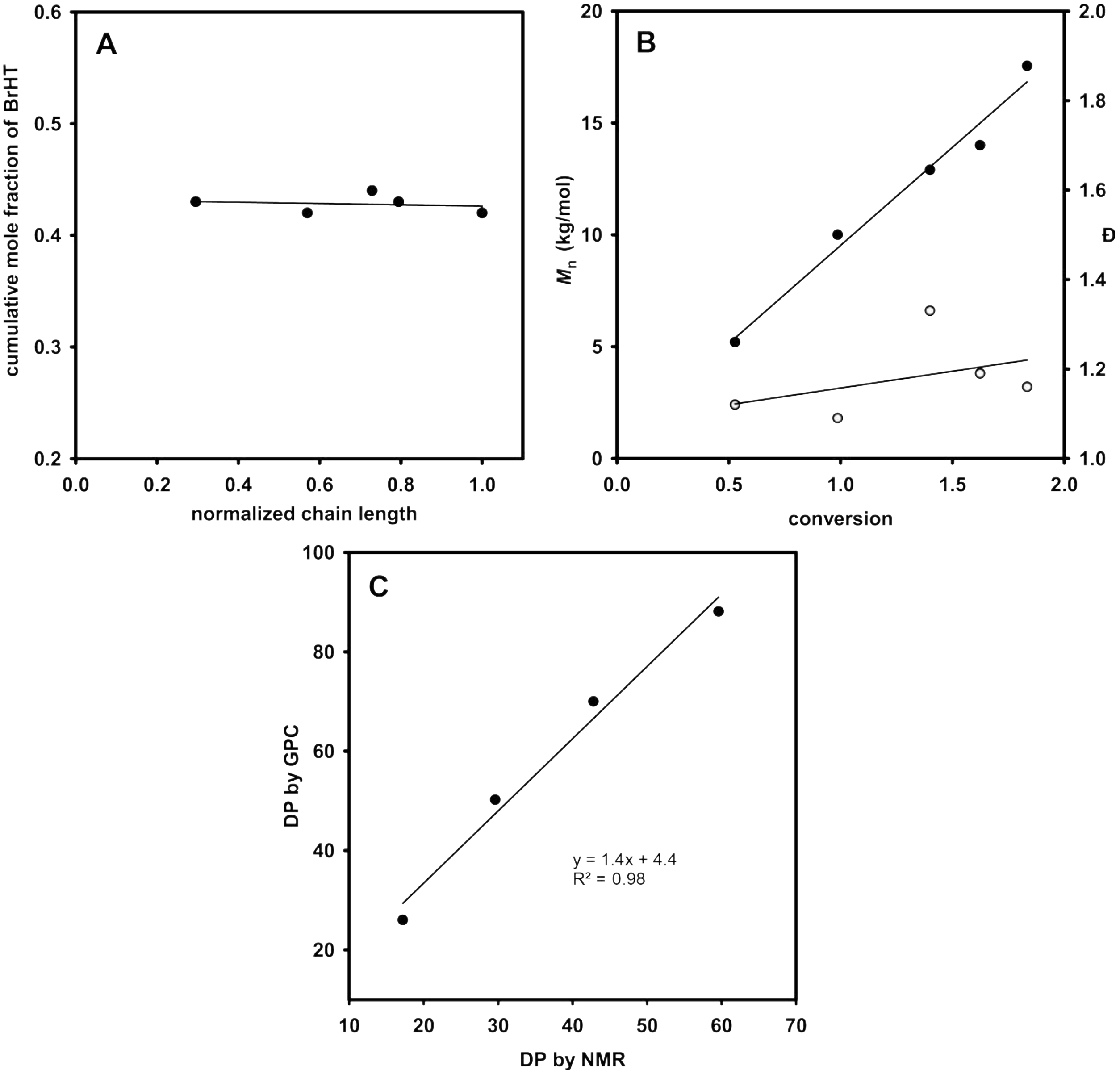
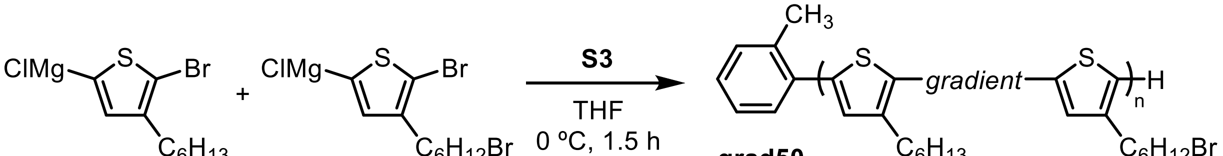


Figure S19. (A) Plot of the cumulative mole fraction of monomer **BrHT** in **ran40**$_{\mathbf{Br}}$ as a function of normalized chain length, (B) M_n (filled circles, ●) and Đ (open circles, ○) versus % conversion, and (C) comparison of the degree of polymerization (DP) obtained by GPC and ^{1}H NMR spectroscopic analysis of end groups. DP = M_n/ average repeat unit MW. Comparing the results of these two methods, it appears that GPC overestimates the DP of these copolymers by a factor of approximately 1.4, in reasonable agreement with a previous report.[6]

Copolymers for further studies



HT **BrHT**

grad50$_{Br}$
grad35$_{Br}$
grad20$_{Br}$

poly(3-hexylthiophene-*grad*-3-(6-bromohexyl)thiophene) (grad50$_{Br}$). In the glovebox, to an oven-dried 25 mL Schlenk flask, a 0.0810 M solution of **HT** (2.80 mL, 0.227 mmol, 40.0 equiv) in THF was added and diluted with THF (15 mL). The Schlenk flask was capped and removed from the glovebox, put under N_2 and cooled to 0 °C. In a 20 mL vial, a 0.0810 M solution of **BrHT** (2.80 mL, 0.227 mmol, 40.0 equiv) in THF was added and diluted with THF (0.2 mL). The solution of **BrHT** was taken out of the glovebox in a syringe and affixed to a syringe pump. A 0.010 M solution of pre-catalyst **S3** (0.56 mL, 5.6 µmol, 1.0 equiv) in THF was taken out of the glovebox in a plastic syringe and injected to the solution of **3HT**. Then the syringe pump was activated to inject **BrHT** at a rate of 0.1 mL/min. After 90 min, the polymerization was quenched with 6 M aq HCl (15 mL), extracted with $CHCl_3$ (3 x 20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a reddish purple solid. The solid was then dissolved in a minimal amount of $CHCl_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The mixture was centrifuged and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and was collected by centrifugation, decanting, and drying the pellet under vacuum, affording a purple solid (79.1 mg, 85%). Gel permeation chromatography (GPC) after purification: M_n = 20.7 kg/mol, Đ = 1.15.

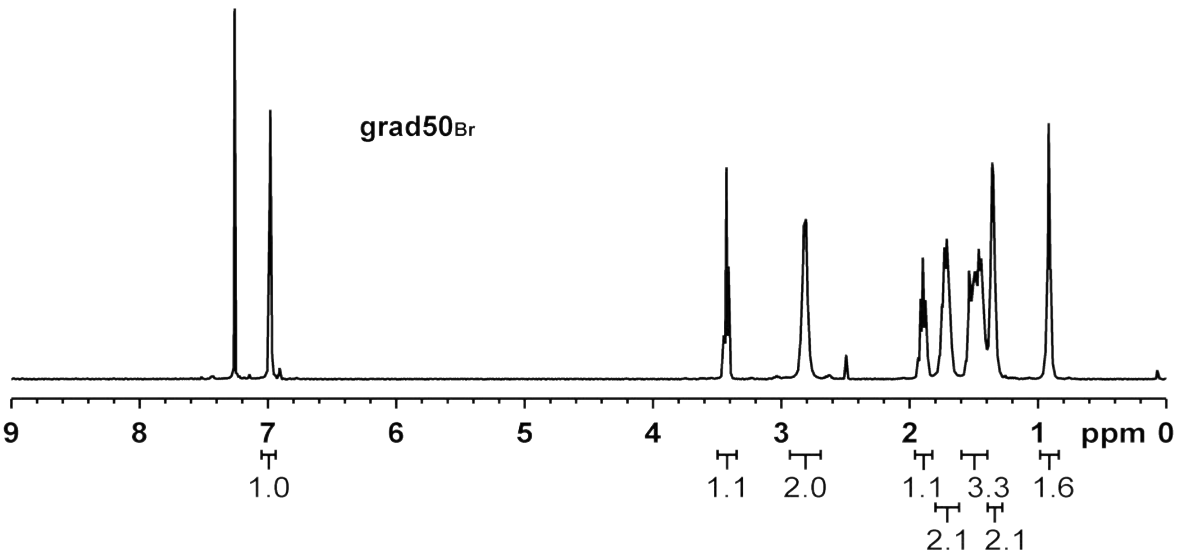


Figure S20. NMR spectrum for **grad50$_{\mathbf{Br}}$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.43 (t, 1H), 2.82 (bs, 2H), 1.90 (m, 1H), 1.70 (m, 2H), 1.49 (m, 3H), 1.35(m, 2H), 0.92 (bs, 1.5H).

poly(3-hexylthiophene-*grad*-3-(6-bromohexyl)thiophene) (grad35$_{\mathbf{Br}}$). In the glovebox, to an oven-dried 25 mL Schlenk flask, a 0.0953 M solution of **HT** (2.80 mL, 0.267 mmol, 52.0 equiv) in THF was added and diluted with THF (15 mL). The Schlenk flask was capped and removed from glovebox, put under N_2 and cooled to 0 °C. In a 20 mL vial, a 0.0762 M solution of **BrHT** (1.90 mL, 0.145 mmol, 28.0 equiv) in THF was added and diluted with THF (1.1 mL). The solution of **BrHT** was taken out of the glovebox with a syringe affixed to a syringe pump. A 0.010 M solution of precatalyst **S3** (0.51 mL, 5.1 μmol, 1.0 equiv) in THF was taken out of the glovebox in a plastic syringe and injected to the solution of **3HT**. After 2 min, the syringe pump was activated to inject **BrHT** at a rate of 0.1 mL/min. After 90 min, the polymerization was quenched with 6 M aq. HCl (15 mL), extracted with $CHCl_3$ (3 x 20 mL) and dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a reddish purple solid. The solid was then dissolved in minimal amount of $CHCl_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The mixture was centrifuged and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and was collected by centrifugation, decanting, and drying the pellet under vacuum, affording a purple solid (65.1 mg, 82%). Gel permeation chromatography (GPC) after purification: M_n = 22.1 kg/mol, Đ = 1.11.

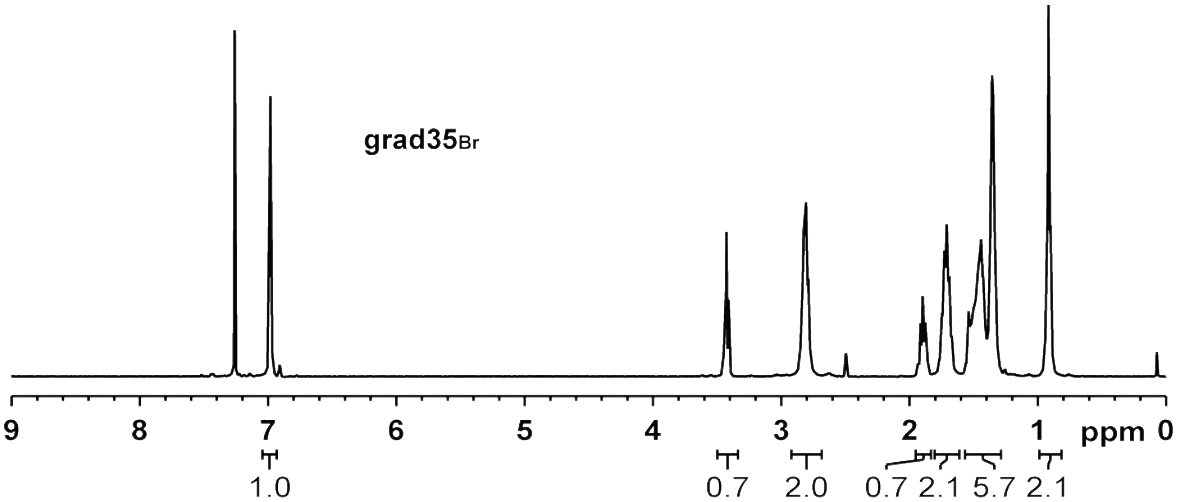


Figure S21. NMR spectra for **grad35$_{\mathbf{Br}}$**. ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.43 (m, 0.7H), 2.81 (m, 2H), 1.90 (q, 0.7H), 1.70 (m, 2H), 1.42 (m, 5.7H), 0.92 (t, 2H).

poly(3-hexylthiophene-*grad*-3-(6-bromohexyl)thiophene): grad20$_{\mathbf{Br}}$ In the glovebox, to an oven-dried 25 mL Schlenk flask, a 0.112 M solution of **HT** (3.80 mL, 0.424 mmol, 65.0 equiv) in THF was added and diluted with THF (20 mL). The Schlenk flask was capped and removed from the glovebox, put under N_2 and cooled to 0 °C. In a 20 mL vial, a 0.0689 M solution of **BrHT** (1.50 mL, 0.103 mmol, 16.0 equiv) in THF was added and diluted with THF (1.5 mL). The solution of **BrHT** was taken out of the glovebox in a syringe and affixed to a syringe pump. A 0.010 M solution of precatalsyt **S3** (0.65 mL, 6.5 μmol, 1.0 equiv) in THF was taken out of the glovebox in a plastic syringe and injected to the solution of **HT**. After 5 min, the syringe pump was activated to inject **BrHT** at a rate of 0.1 mL/min. After 90 min, the polymerization was quenched with 6 M aq. HCl (15 mL), extracted with $CHCl_3$ (3 x 20 mL) and dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a reddish purple solid. The solid was then dissolved in minimal amount of $CHCl_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with acetone, MeOH, hexane, CH_2Cl_2 and $CHCl_3$. The $CHCl_3$ fraction was dried *in vacuo* to afford a purple solid (72.7 mg, 76%). Gel permeation chromatography (GPC) after purification: M_n = 19.0 kg/mol, Đ = 1.18.

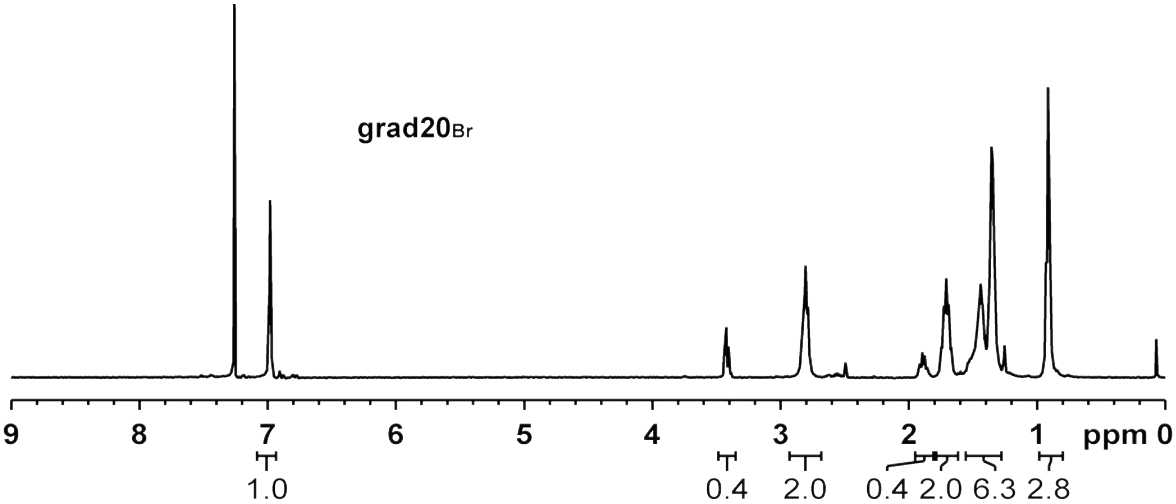
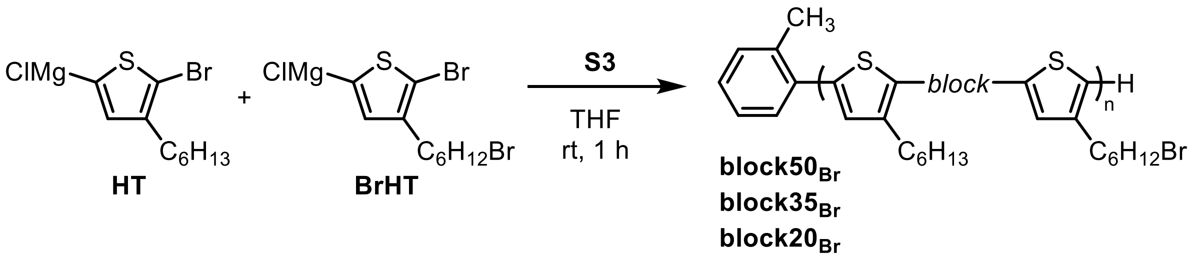


Figure S22. NMR spectra for **grad20$_{\mathbf{Br}}$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.42 (t, 0.4H), 2.81 (t, 2H), 1.89 (m, 0.4H), 1.71 (t, 2H), 1.39 (m, 6H), 0.92 (t, 2.4H).



poly(3-hexylthiophene-*block*-3-(6-bromohexyl)thiophene) (block50$_{Br}$). In the glovebox, to a 20 mL vial, a 0.103 M solution of **HT** (1.50 mL, 0.154 mmol, 40.0 equiv) in THF was added and diluted with THF (12 mL). A 0.010 M solution of precatalyst **S3** (0.38 mL, 3.8 μmol, 1.0 equiv) in THF was added and stirred at r.t. for 30 min. Then a 0.0823 M solution of **BrHT** (1.87 mL, 0.154 mmol, 40.0 equiv) in THF was added and the solution stirred for 30 min. The polymerization was quenched with 6 M aq. HCl (5 mL) and precipitated into cold MeOH (50 mL). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with acetone, MeOH, hexane, CH_2Cl_2 and $CHCl_3$. The $CHCl_3$ fraction was dried *in vacuo* to afford a purple solid (50.0 mg, 79%). Gel permeation chromatography (GPC) after purification: M_n = 18.8 kg/mol, Đ = 1.19.

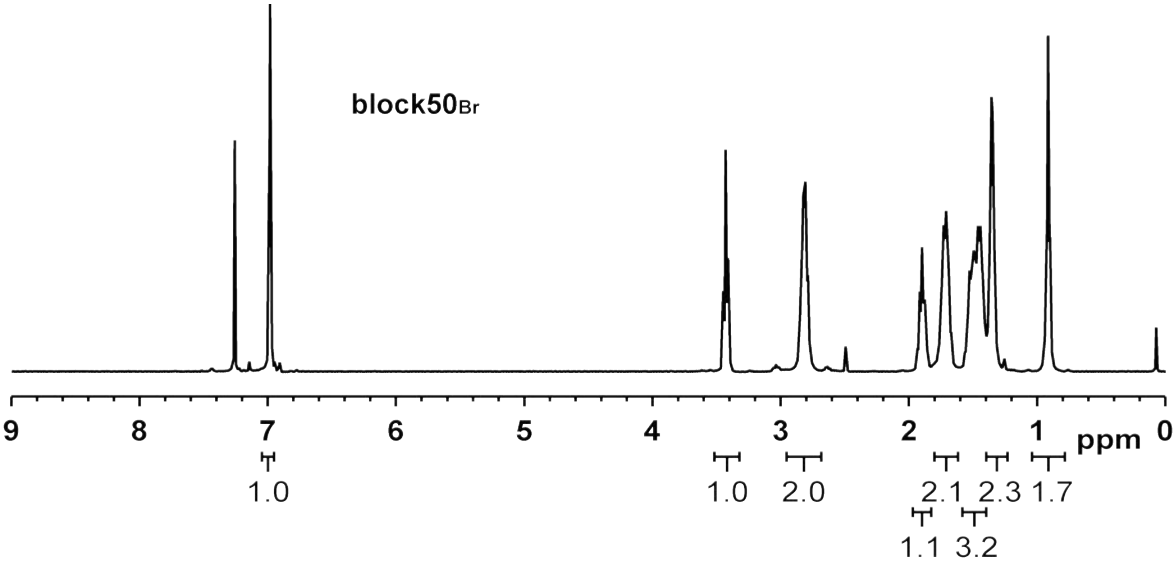


Figure S23. NMR spectra for **block50$_{Br}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 3.43 (t, 1H), 2.81 (t, 2H), 1.90 (q, 1H), 1.70 (m, 2H), 1.48 (m, 3H), 1.35 (m, 2H), 0.92 (t, 1.5H).

poly(3-hexylthiophene-*block*-3-(6-bromohexyl)thiophene): block35$_{Br}$

In the glovebox, to a 20 mL vial, a 0.103 M solution of **HT** (2.00 mL, 0.206 mmol, 53.0 equiv) in THF was added and diluted with THF (12 mL). A 0.010 M solution of precatalyst **S3** (0.39 mL, 3.9 μmol, 1.0 equiv) in THF was added and stirred at r.t. for 30 min. Then a 0.0823 M solution of **BrHT** (1.34 mL, 0.110 mmol, 28.0 equiv) in THF was added and the solution stirred for 30 min. The polymerization was quenched with 6 M aq. HCl (5 mL) and precipitated into cold MeOH (50 mL). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with acetone, MeOH, hexane, CH_2Cl_2 and $CHCl_3$. The $CHCl_3$ fraction was dried *in vacuo* to afford a purple solid (49.2 mg, 80%). Gel permeation chromatography (GPC) after purification: M_n = 19.1 kg/mol, Đ = 1.17.

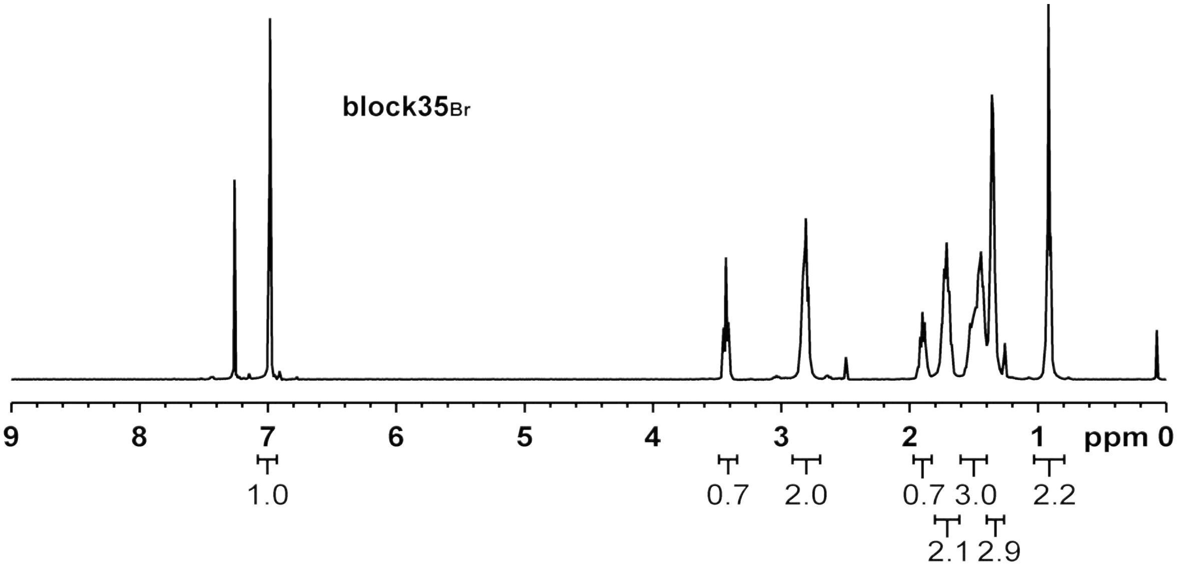


Figure S24. NMR spectra for **block35$_{Br}$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.43 (t, 0.7H), 2.81 (t, 2H), 1.90 (q, 0.7H), 1.70 (m, 2H), 1.47 (m, 3H), 1.35 (m, 3H), 0.92 (t, 2H).

poly(3-hexylthiophene-*block*-3-(6-bromohexyl)thiophene) (block20$_{Br}$). In the glovebox, to a 20 mL vial, a 0.103 M solution of **HT** (2.40 mL, 0.247 mmol, 65.0 equiv) in THF was added and diluted with THF (12 mL). A 0.010 M solution of precatalyst **S3** (0.38 mL, 3.8 μmol, 1.0 equiv) in THF was added and stirred at r.t. for 30 min. Then a 0.083 M solution of **BrHT** (0.75 mL, 0.062 mmol, 16.0 equiv) in THF was added and the solution stirred for 30 min. The polymerization was quenched with 6 M aq. HCl (5 mL) and precipitated into cold MeOH (50 mL). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with acetone, MeOH, hexane, CH_2Cl_2 and $CHCl_3$. The $CHCl_3$ fraction was dried *in vacuo* to afford a purple solid (48.4 mg, 86%). Gel permeation chromatography (GPC) after purification: M_n = 19.5 kg/mol, Đ = 1.15.

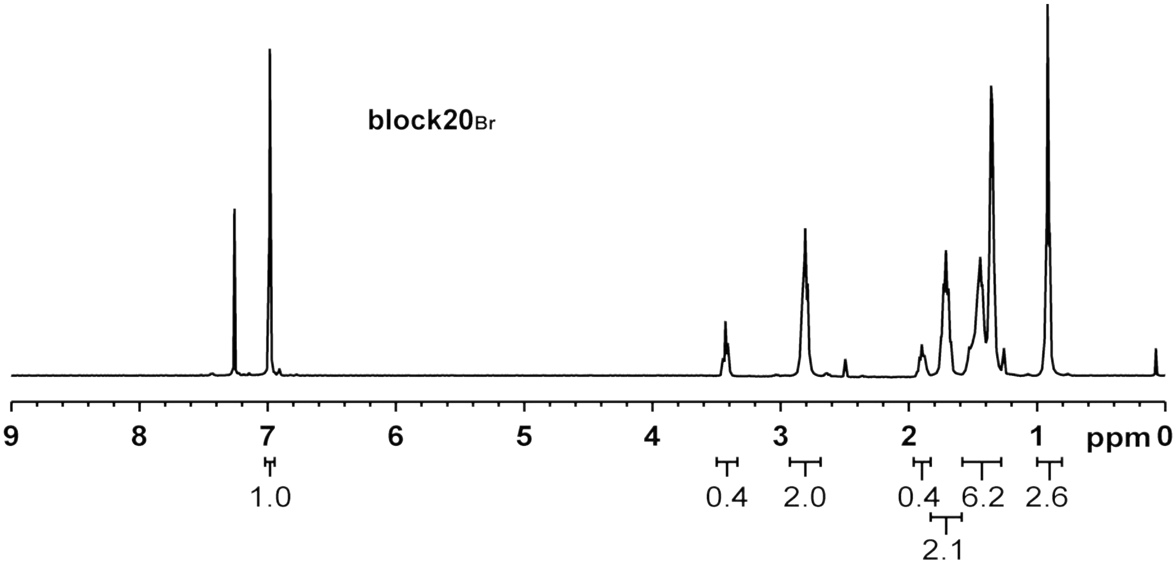
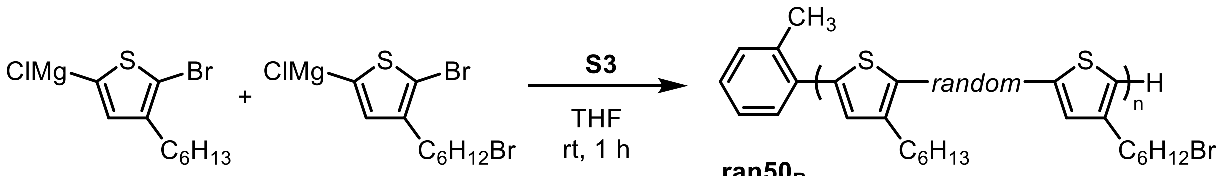


Figure S25. NMR spectra for **block20$_{Br}$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.43 (t, 0.4H), 2.81 (t, 2H), 1.90 (q, 0.4H), 1.71 (t, 2H), 1.39 (m, 6H), 0.92 (t, 2.4H).



HT **BrHT**

ran50$_{Br}$
ran35$_{Br}$
ran20$_{Br}$

poly(3-hexylthiophene-*random*-3-(6-bromohexyl)thiophene) (ran50$_{Br}$). In the glovebox, to a 20 mL vial, was added a 0.110 M solution of **HT** (1.50 mL, 0.165 mmol, 40.0 equiv) in THF and a 0.142 M solution of **BrHT** (1.16 mL, 0.164 mmol, 40.0 equiv) in THF and diluted with THF (12 mL). A 0.010 M solution of precatalyst **S3** (0.41 mL, 4.1 μmol, 1 equiv) in THF was then added and the solution was stirred at r.t. for 1 h. The polymerization was quenched with 6 M aq. HCl (5 mL), extracted with CHCl$_3$ (3 x 5 mL) and dried *in vacuo* to afford the crude polymer as a dark purple solid. The solid was then dissolved in minimal amount of CHCl$_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The mixture was centrifuged and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and was collected by centrifugation, decanting, and drying the pellet under vacuum, affording a purple solid (64.7 mg, 96%). Gel permeation chromatography (GPC) after purification: M_n = 21.1 kg/mol, Đ = 1.24.

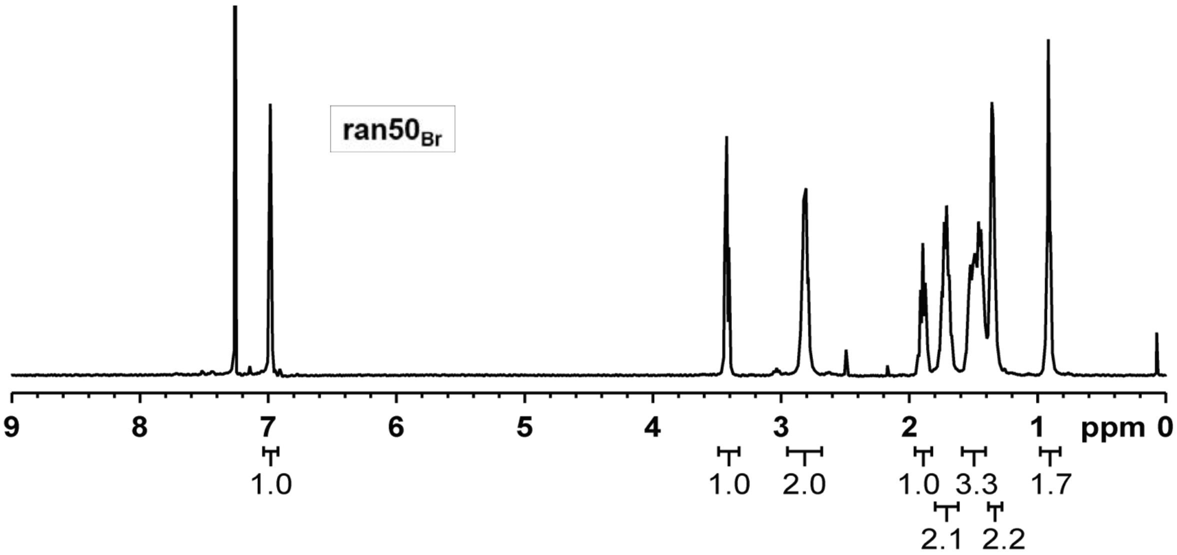


Figure S26. NMR spectra for **ran50$_{Br}$**. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.42 (t, 1H), 2.81 (m, 2H), 1.90 (q, 1H), 1.70 (m, 2H), 1.47 (m, 3H), 1.35 (m, 2H), 0.92 (t, 1.5H).

poly(3-hexylthiophene-*random*-3-(6-bromohexyl)thiophene) (ran35$_{Br}$). In the glovebox, to a 20 mL vial, was added a 0.110 M solution of **HT** (1.60 mL, 0.176 mmol, 52.0 equiv) in THF and a 0.142 M solution of **BrHT** (0.670 mL, 0.095 mmol, 28.0 equiv) in THF and diluted with THF (12 mL). A stock solution of **S3** (10 mM in THF, 0.41 mL, 4.1 μmol, 1 equiv) was then added and the solution was stirred at r.t. for 1 h. The polymerization was quenched with 6 M aq. HCl (5 mL), extracted with $CHCl_3$ (3 x 5 mL) and dried *in vacuo* to afford the crude polymer as a dark purple solid. The solid was then dissolved in minimal amount of $CHCl_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The mixture was centrifuged and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and was collected by centrifugation, decanting, and drying the pellet under vacuum, affording a purple solid (53.6 mg, 93%). Gel permeation chromatography (GPC) after purification: M_n = 21.4 kg/mol, Đ = 1.23.

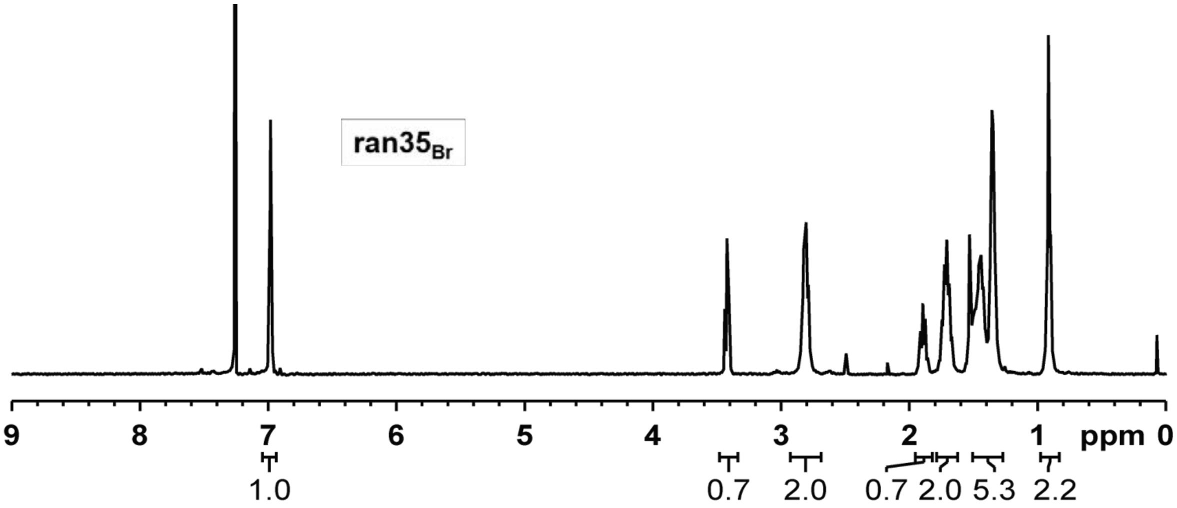


Figure S27. NMR spectra for **ran35$_{Br}$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.42 (t, 0.7H), 2.81 (q, 2H), 1.89 (q, 0.7H), 1.70 (m, 2H), 1.39 (m, 5.3H), 0.92 (t, 2H).

poly(3-hexylthiophene-*random*-3-(6-bromohexyl)thiophene) (ran20$_{Br}$). In the glovebox, to a 20 mL vial, was added a 0.110 M solution of **HT** (2.00 mL, 0.220 mmol, 65.0 equiv) in THF and a 0.142 M solution of **BrHT** (0.390 mL, 0.055 mmol, 16.0 equiv) in THF and diluted with THF (12 mL). A stock solution of **S3** (10 mM in THF, 0.41 mL, 4.1 μmol, 1 equiv) was then added and the solution was stirred at r.t. for 1 h. The polymerization was quenched with 6 M aq. HCl (5 mL), extracted with $CHCl_3$ (3 x 5 mL) and dried *in vacuo* to afford the crude polymer as a dark purple solid. The solid was then dissolved in minimal amount of $CHCl_3$ (1.5 mL) and precipitated into cold MeOH (50 mL). The mixture was centrifuged and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and was collected by centrifugation, decanting, and drying the pellet under vacuum, affording a purple solid (49.4 mg, 89%). Gel permeation chromatography (GPC) after purification: M_n = 21.7 kg/mol, Đ = 1.22.

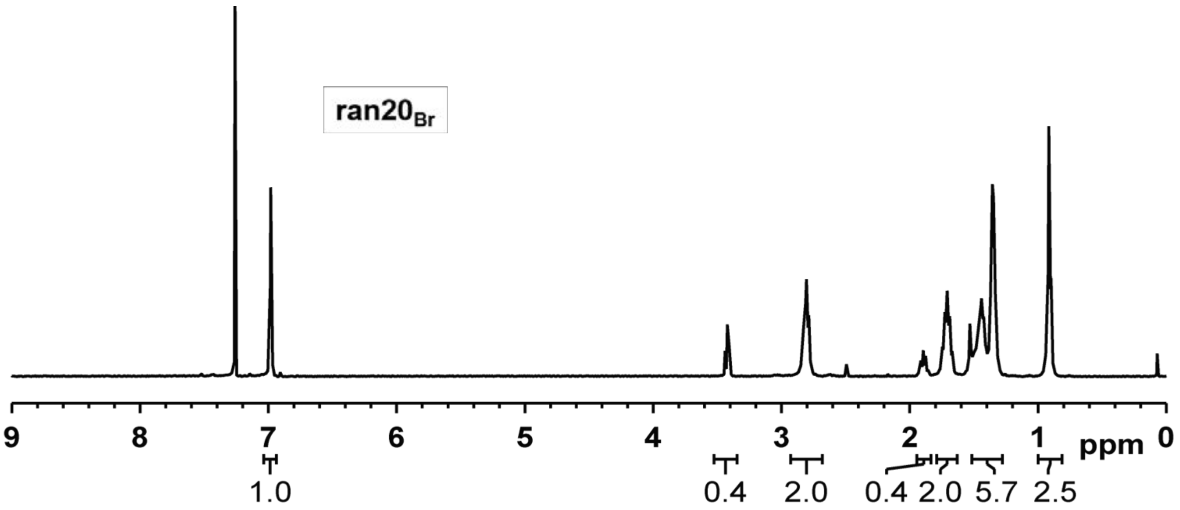
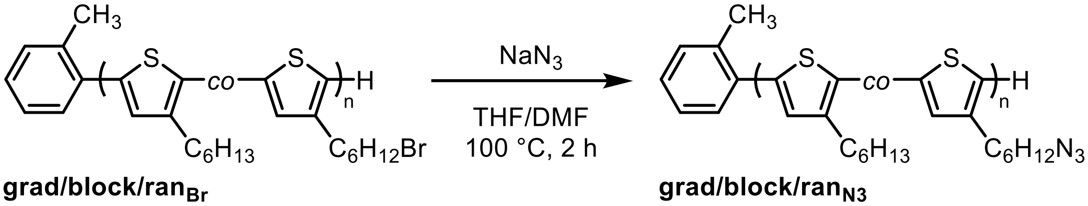


Figure S28. NMR spectra for **ran20$_{Br}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.42 (t, 0.4H), 2.81 (t, 2H), 1.89 (q, 0.4H), 1.71 (m, 2H), 1.39 (m, 5.6H), 0.92 (t, 2.4H).

VI. Post-polymerization Procedures and Data



General procedure: The precursor polymer (~40 mg, 1.0 equiv) was dissolved in THF (30 mL) in a 100 mL round bottom flask equipped with a reflux condenser. The solution was heated to 60 °C for 5 min to give a bright orange solution. A solution of sodium azide (~80 mg, 10 equiv) in DMF (15 mL) was added dropwise over 1 min. Then the flask was protected from light using aluminum foil, the temperature was increased to 100 °C and the mixture was stirred for 2 h. After removing THF by rotary evaporation, the resulting suspension was precipitated in cold MeOH (100 mL), centrifuged, and the supernatant was decanted. Then, the precipitate was suspended in MeOH (30 mL) with sonication and separated by centrifugation, decanting, and drying the pellet under vacuum for 18 h at r.t. in the dark, affording a purple solid (yields: 93% – 99%).

poly(3-hexylthiophene-*grad*-3-(6-azidohexyl)thiophene)

grad50$_{N3}$: **grad50$_{Br}$** (30.3 mg) was used to afford purple solid (27.3 mg, 99%). GPC after purification: M_n = 21.3 kg/mol, Đ = 1.15.

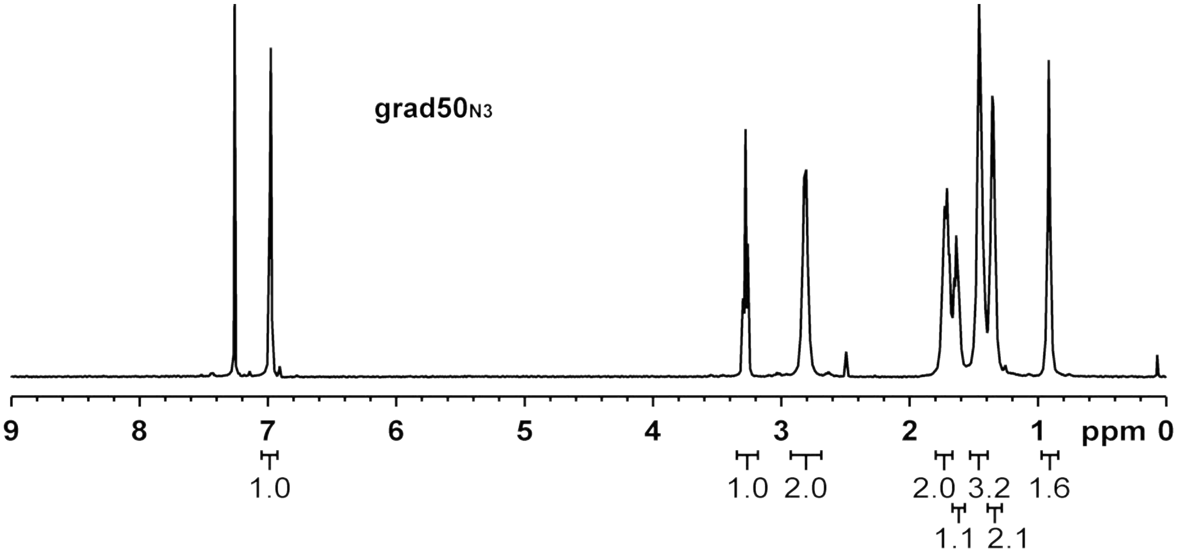


Figure S29. NMR spectra for **grad50$_{N3}$**. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 1H), 2.81 (q, 2H), 1.70 (m, 2H), 1.64 (m, 1H), 1.46 (m, 3H), 1.35 (m, 2H), 0.92 (t, 1.5H).

grad35$_{N3}$: **grad35$_{Br}$** (33.9 mg) was used to afford purple solid (31.3 mg, 99%). GPC after purification: M_n = 22.1 kg/mol, Đ = 1.12.

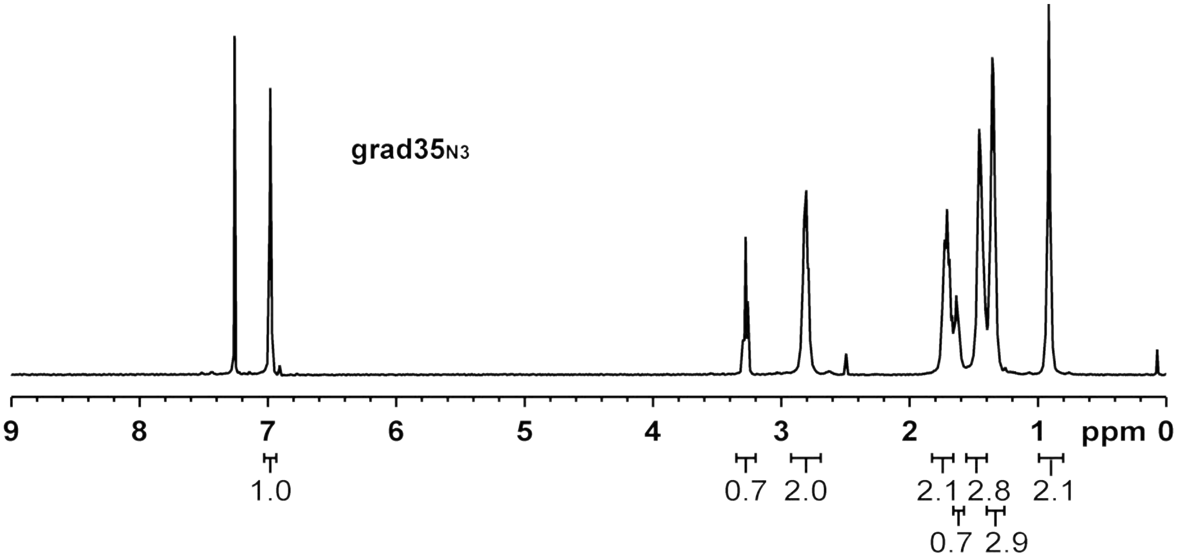


Figure S30. NMR spectra for **grad35$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 0.7H), 2.81 (t, 2H), 1.71 (q, 2H), 1.63 (m, 0.7H), 1.45 (m, 3H), 1.35 (m, 3H), 0.91 (m, 2H).

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grad20$_{N3}$: **grad20$_{Br}$** (46.8 mg) was used to afford purple solid (44.1 mg, 99%). GPC after purification: M_n = 18.8 kg/mol, Đ = 1.21.

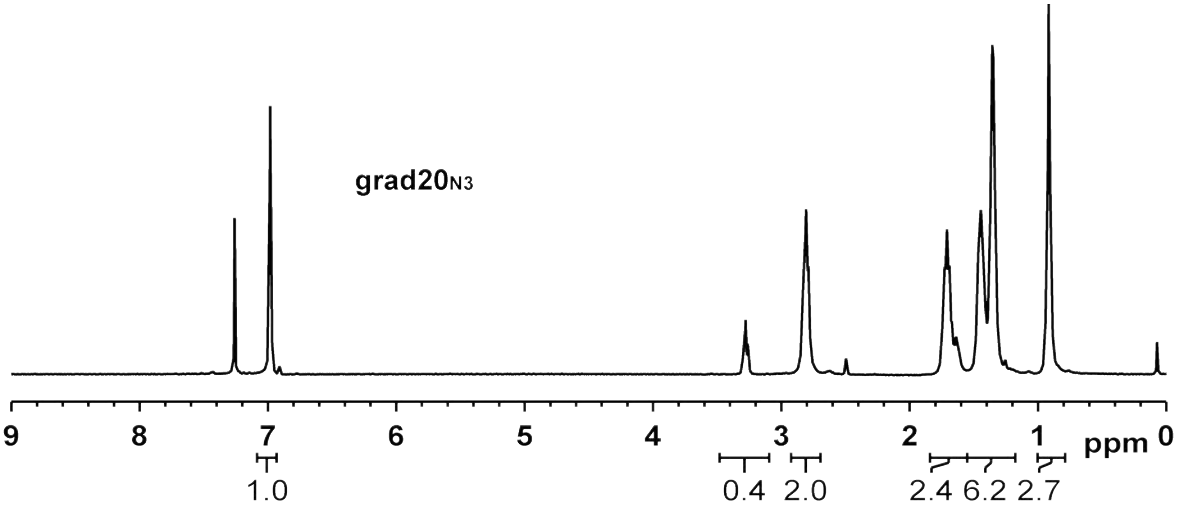

Figure S31. NMR spectra for **grad20$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 0.4H), 2.81 (t, 2H), 1.67 (m, 2H), 1.40 (m, 6H), 0.92 (t, 2.4H).

poly(3-hexylthiophene-*block*-3-(6-azidohexyl)thiophene)

block50$_{N3}$: **block50$_{Br}$** (33.6 mg) was used to afford purple solid (30.1 mg, 99%). GPC after purification: M_n = 19.8 kg/mol, Đ = 1.19.

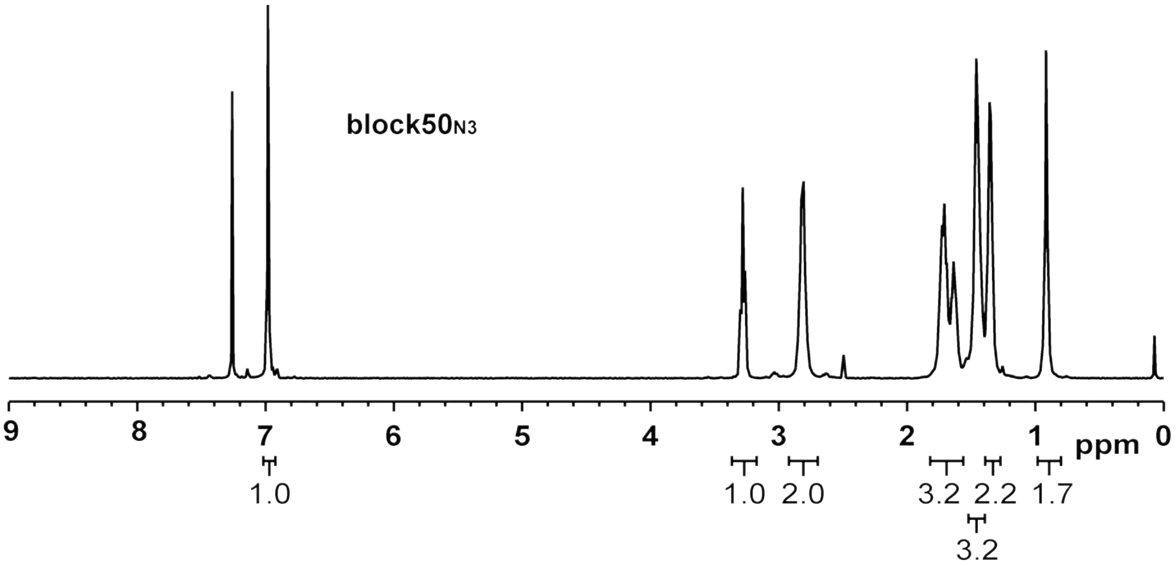

Figure S32. NMR spectra for **block50$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 1H), 2.81 (t, 2H), 1.67 (m, 3H), 1.46 (m, 3H), 1.35 (m, 2H), 0.92 (t, 1.5H).

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block35$_{N3}$: **block35$_{Br}$** (31.5 mg) was used to afford purple solid (29.1 mg, 99%). GPC after purification: M_n = 19.6 kg/mol, Đ = 1.17.

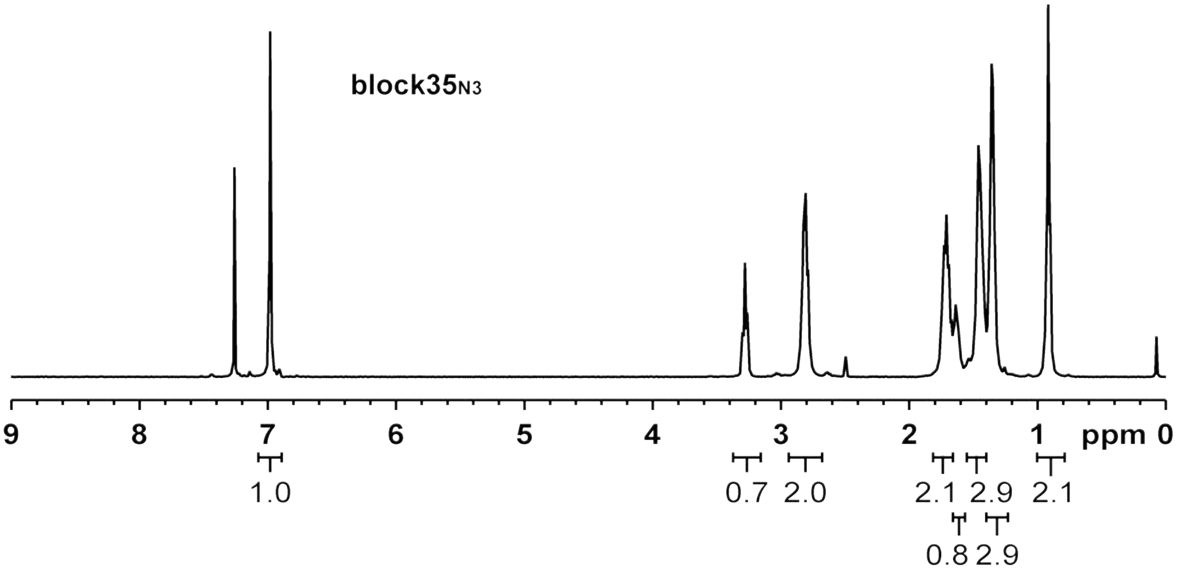

Figure S33. NMR spectra for **block35$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 0.7H), 2.81 (t, 2H), 1.70 (m, 2H), 1.64(m, 0.8H), 1.46 (m, 3H), 1.35 (m, 3H), 0.92 (t, 2H).

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block20$_{\mathrm{N3}}$: **block20$_{\mathrm{Br}}$** (38.1 mg) was used to afford purple solid (36.0 mg, 99%). GPC after purification: M_n = 20.5 kg/mol, Đ = 1.14.

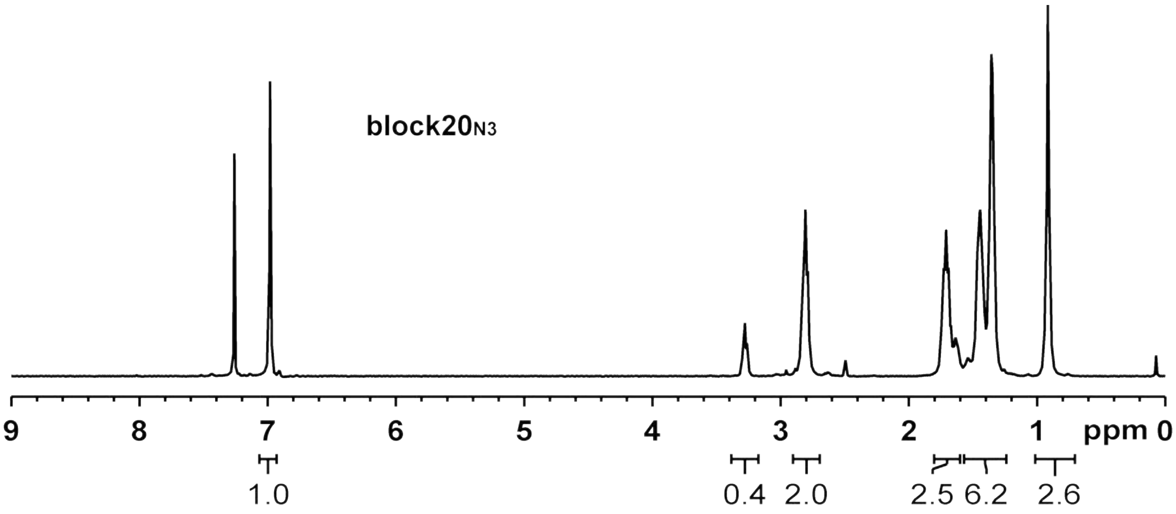

Figure S34. NMR spectra for **block20$_{\mathrm{N3}}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.28 (t, 0.4H), 2.81 (t, 2H), 1.71 (m, 2H), 1.40 (m, 6H), 0.92 (t, 2.4H).

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poly(3-hexylthiophene-*random*-3-(6-azidohexyl)thiophene)

ran50$_{\mathrm{N3}}$: **ran50$_{\mathrm{Br}}$** (49.9 mg) was used to afford purple solid (42.2 mg, 93%). GPC after purification: M_n = 21.5 kg/mol, Đ = 1.26.

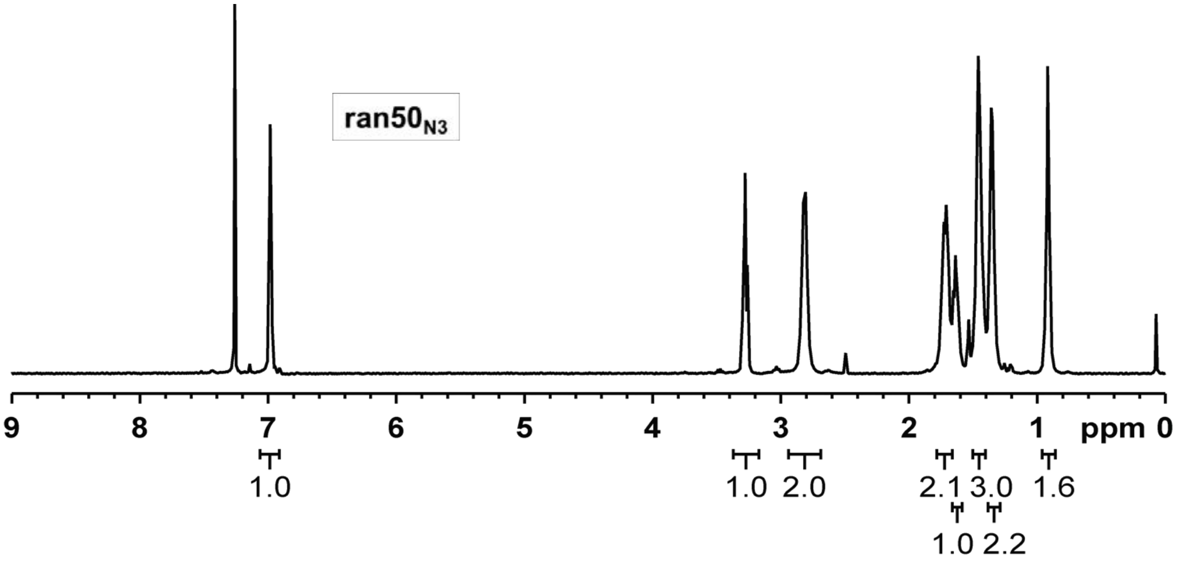


Figure S35. NMR spectra for **ran50$_{\mathrm{N3}}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 3.28 (t, 1H), 2.82 (q, 2H), 1.71 (q, 2H), 1.64 (m, 1H), 1.46 (m, 3H), 1.35 (m, 2H), 0.92 (t, 1.5H).

ran35$_{N3}$: **ran35$_{Br}$** (42.7 mg) was used to afford purple solid (37.3 mg, 93%). GPC after purification: M_n = 21.8 kg/mol, Đ = 1.24.

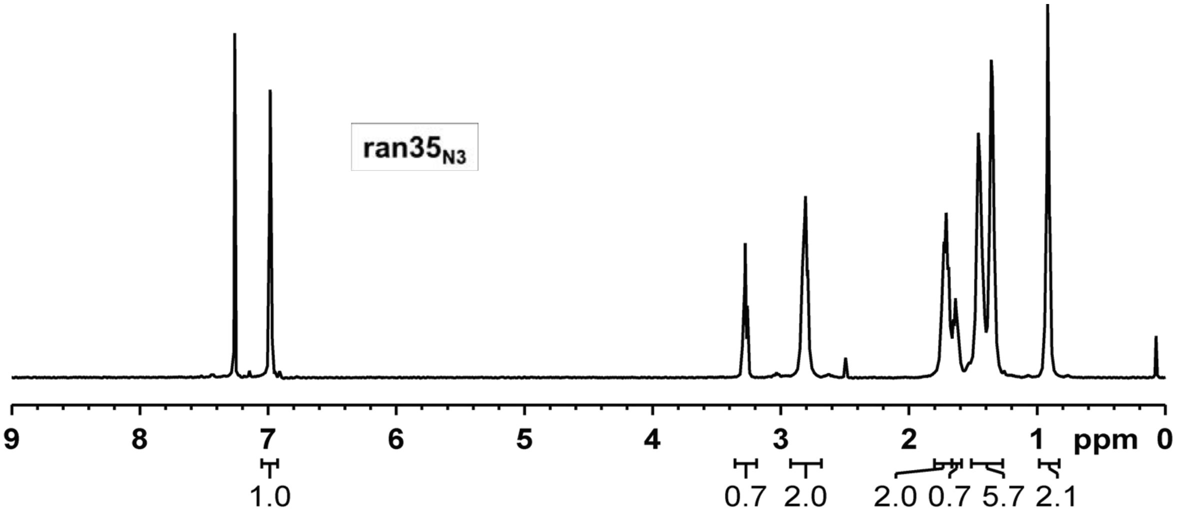


Figure S36. NMR spectra for **ran35$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 0.7H), 2.81 (t, 2H), 1.71 (q, 2H), 1.64 (m, 0.7H), 1.40 (m, 5.3H), 0.92 (t, 2H).

ran20$_{N3}$: **ran20$_{Br}$** (35.8 mg) was used to afford purple solid (33.1 mg, 97%). GPC after purification: M_n = 22.7 kg/mol, Đ = 1.18.

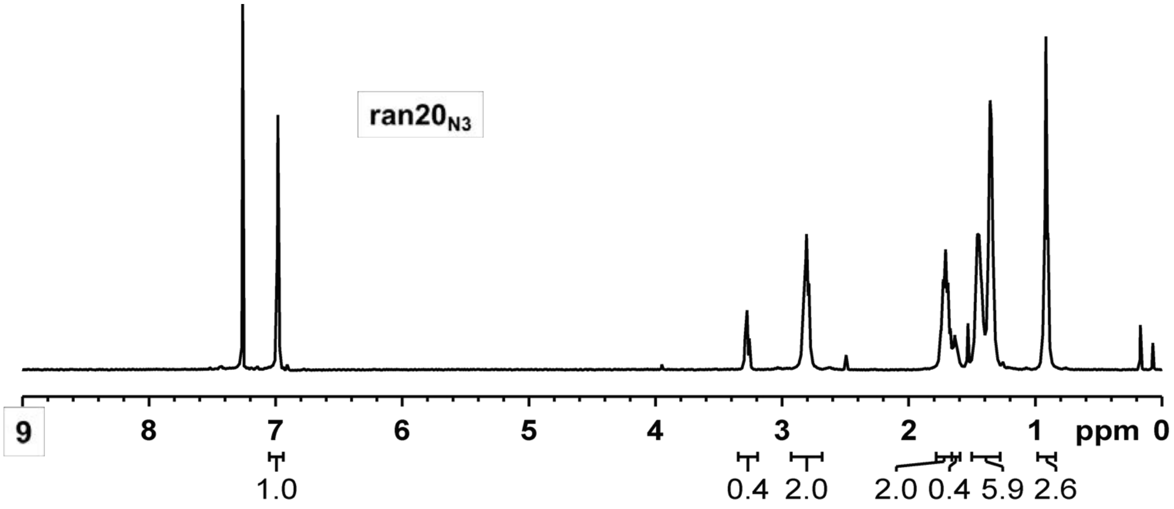


Figure S37. NMR spectra for **ran20$_{N3}$**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 3.28 (t, 0.4H), 2.81 (t, 2H), 1.71 (q, 2H), 1.64 (m, 0.4H), 1.40 (m, 5.9H), 0.92 (t, 2.6H).

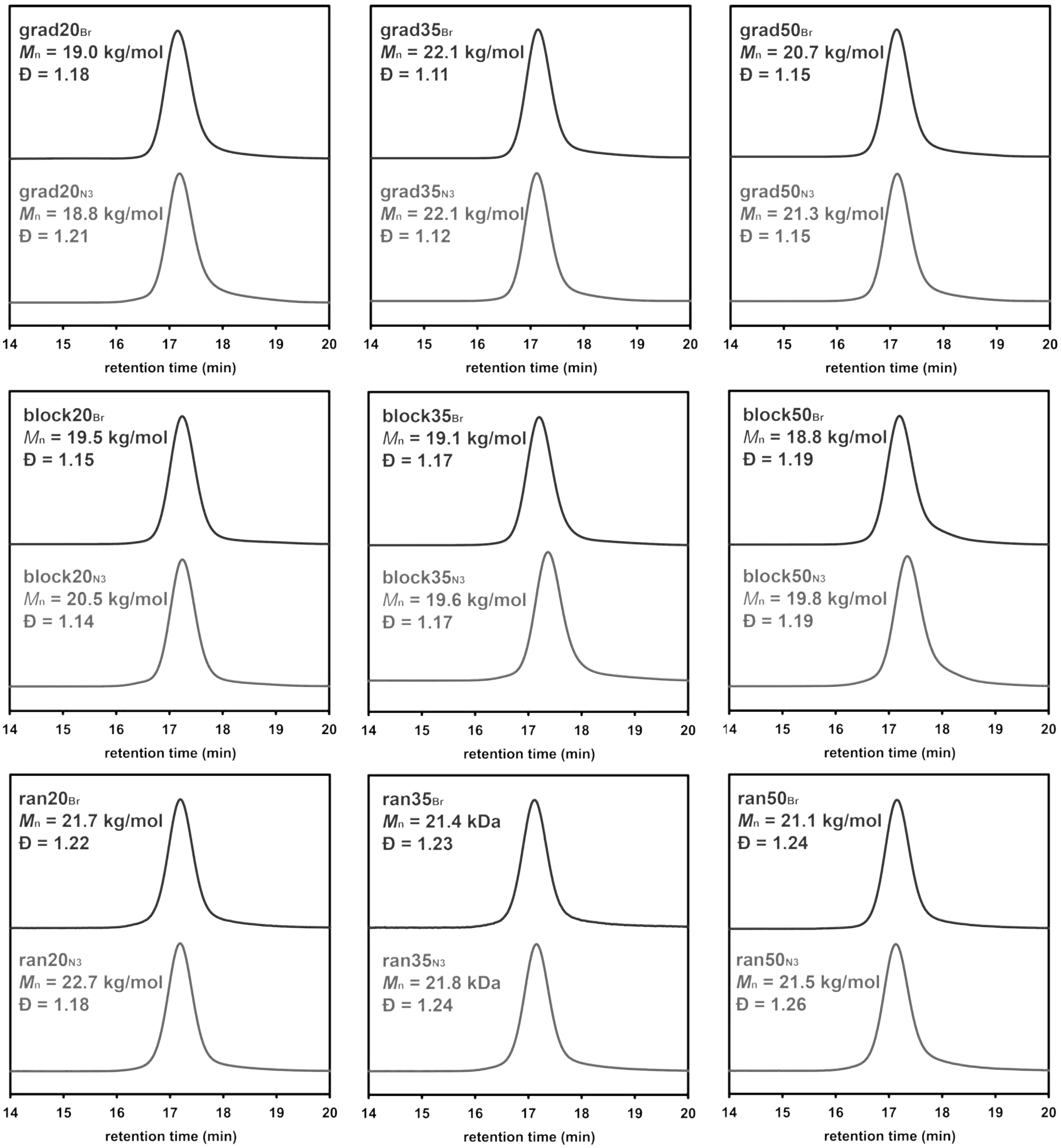
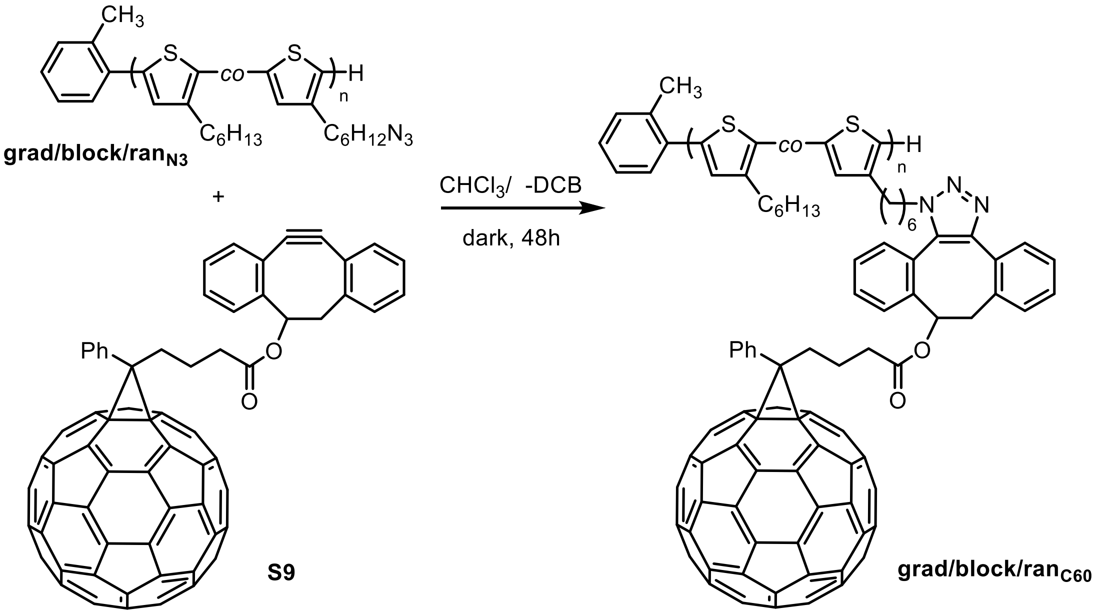


Figure S38. GPC traces of copolymers before (**grad/block/ran$_{\mathrm{Br}}$)** and after conversion to **grad/block/ran$_{\mathrm{N3}}$**.



General Procedure: In a 20 mL vial, copolymer **grad/block/ran$_{\mathbf{N3}}$** (~10-20 mg, 1.0 equiv of N_3) and **S9** (~30-50 mg, 1.5 equiv) were dissolved in $CHCl_3$ (15 mL) and *o*-DCB (1 mL) and stirred at r.t. in the dark for 48 h. Then the solution was concentrated, redissolved in a minimal amount of $CHCl_3$ and precipitated in a mixture of DCM/MeOH (30 mL v/v 1/1). The precipitate was collected on filter paper and purified by Soxhlet extraction sequentially with CH_2Cl_2 and $CHCl_3/CS_2$. The $CHCl_3/CS_2$ fraction was condensed *in vacuo* to afford a brown solid (80–90%).

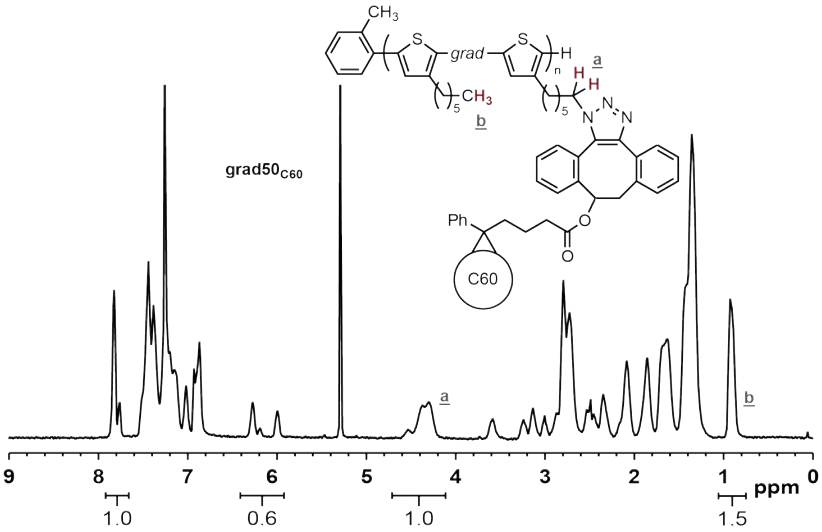


Figure S39. ^{1}H NMR spectrum for **grad50$_{C60}$**.

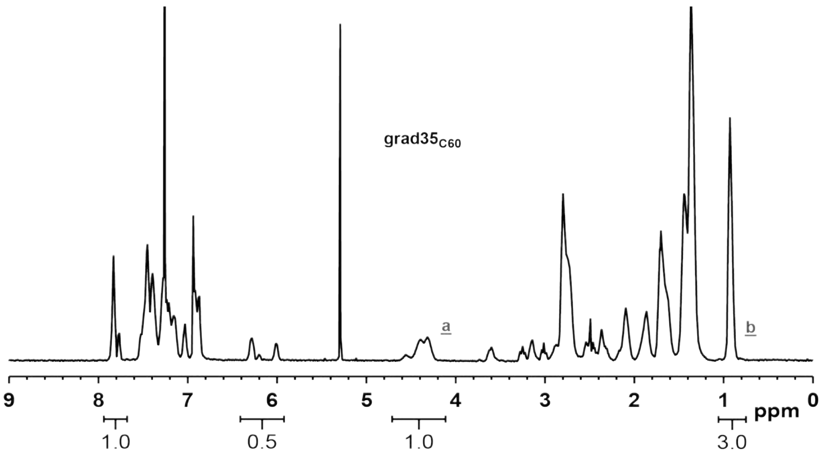


Figure S40. ^{1}H NMR spectrum for **grad35$_{C60}$**.

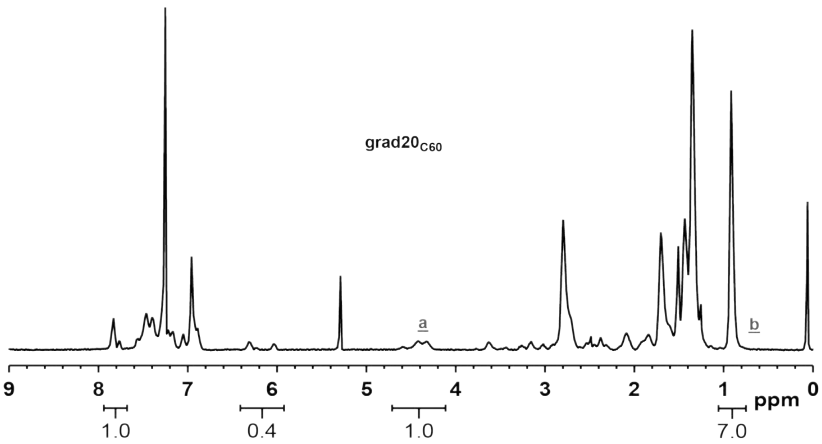


Figure S41. ^{1}H NMR spectrum for **grad20$_{C60}$**.

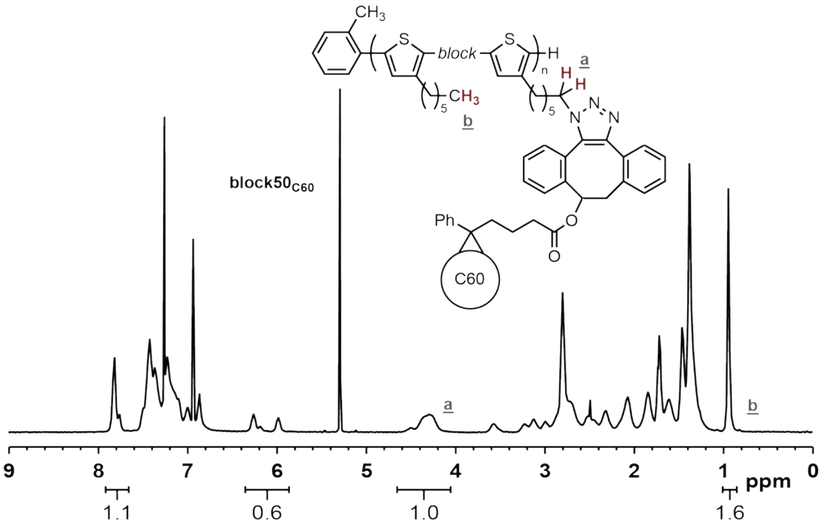


Figure S42. ^{1}H NMR spectrum for **block50$_{C60}$**.

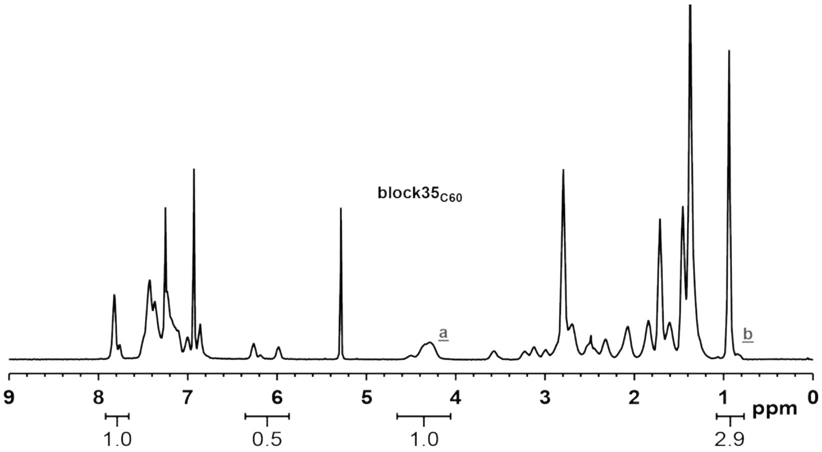


Figure S43. ^{1}H NMR spectrum for **block35$_{C60}$**.

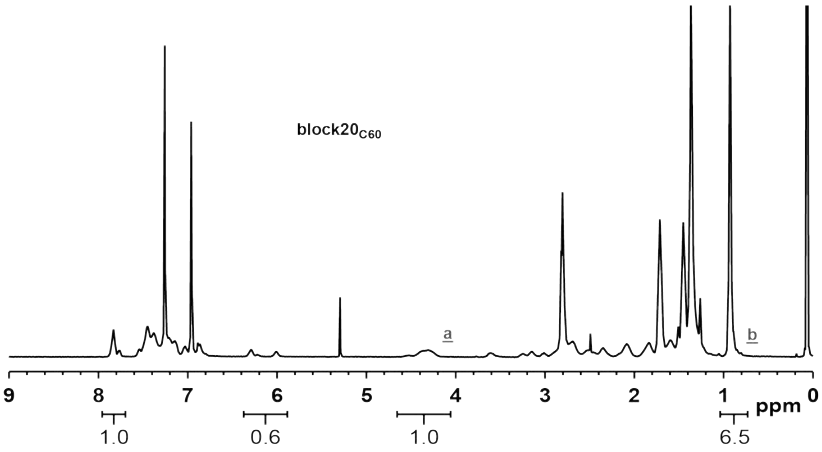


Figure S44. ^{1}H NMR spectrum for **block20$_{C60}$**.

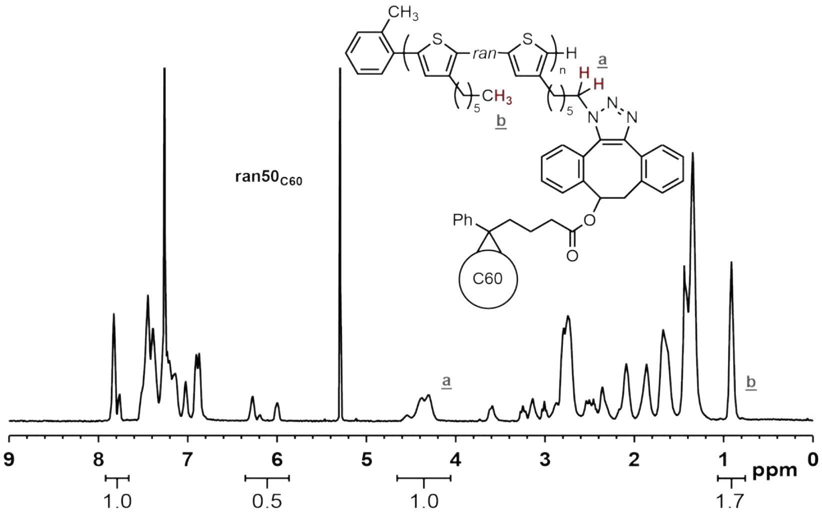


Figure S45. ^{1}H NMR spectrum for **ran50$_{C60}$**.

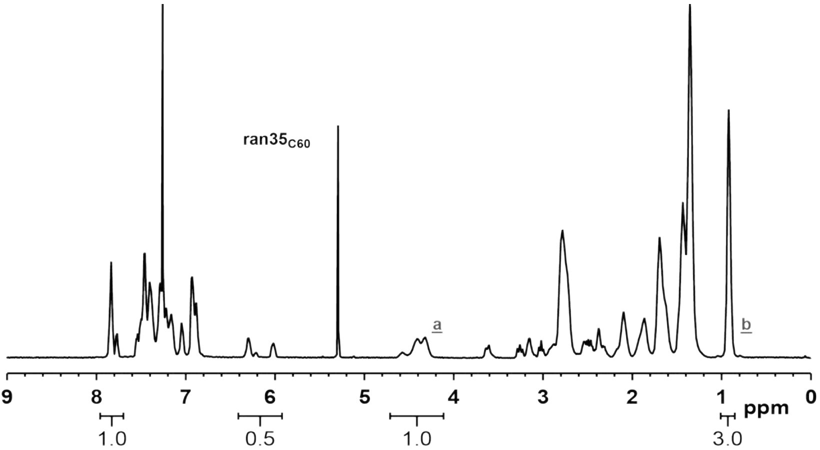


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Figure S46. ^{1}H NMR spectrum for **ran35$_{C60}$**.

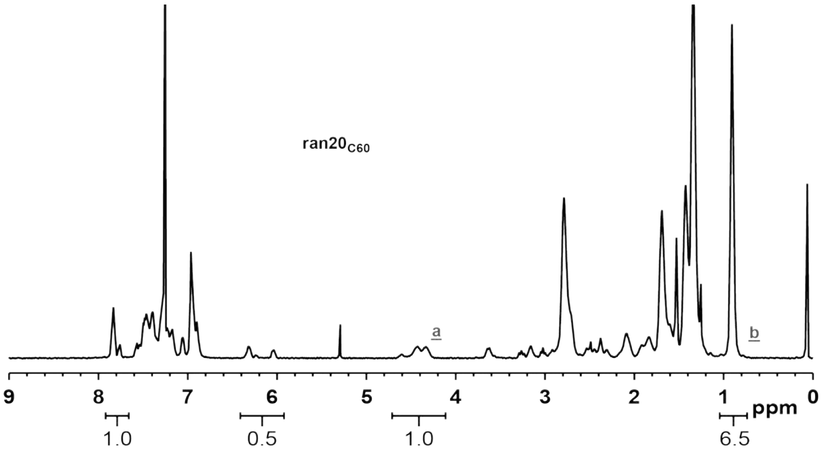

Figure S47. ^{1}H NMR spectrum for **ran20$_{C60}$**.

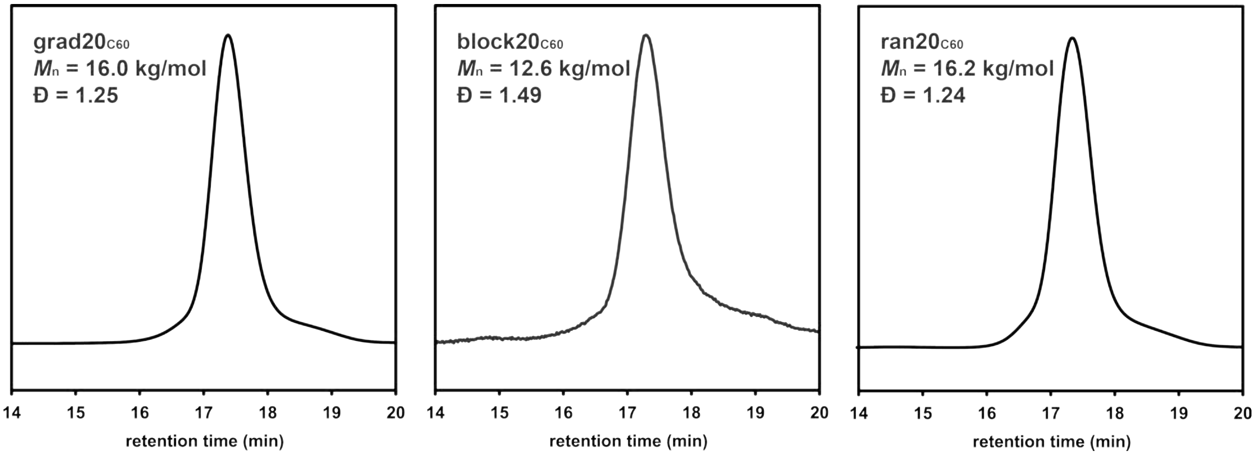

Figure S48. GPC trace of copolymers **grad20$_{\mathbf{C60}}$**, **block20$_{\mathbf{C60}}$**, and **ran20$_{\mathbf{C60}}$**.

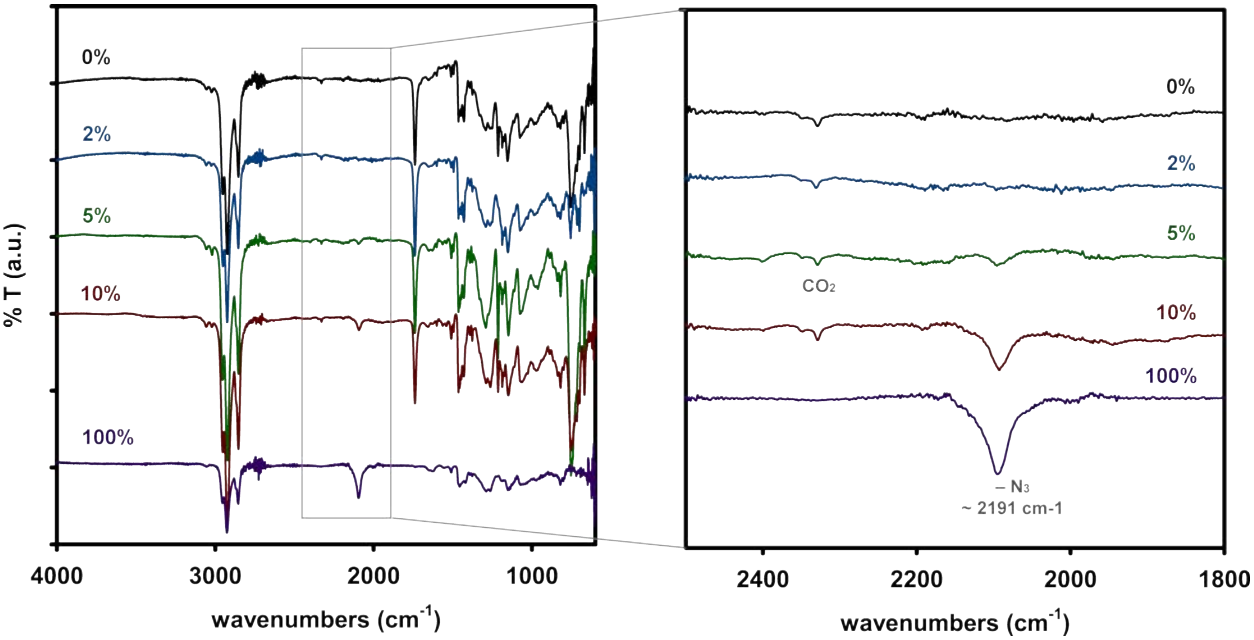

Figure S49. IR spectrum data for a solution of P3HT and PCBM (3.5 mg/mL in $CHCl_3$, 1:1 wt:wt) with **block20$_{N3}$** at indicated wt%.

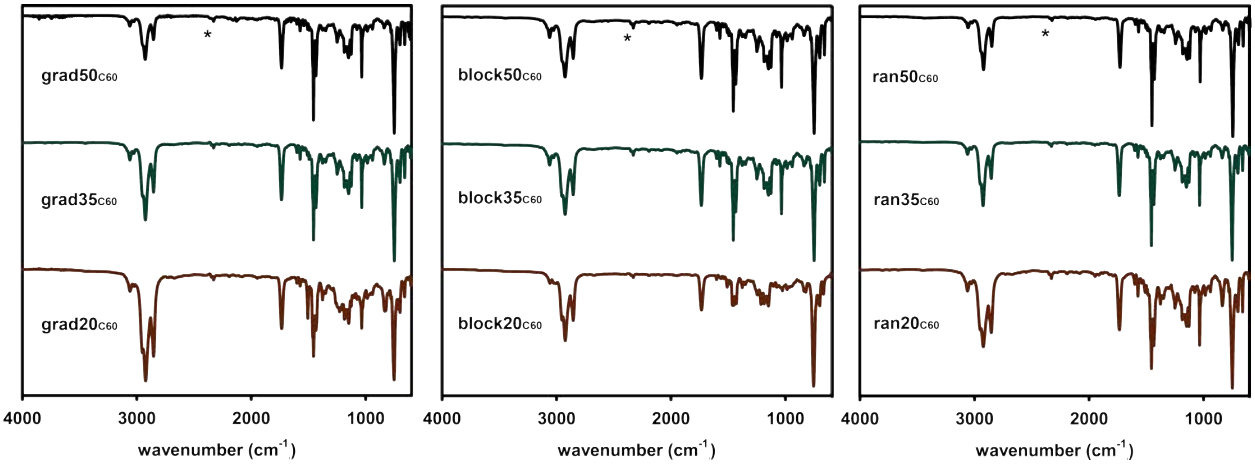

Figure S50. IR spectrum data for completed SPAAC reaction containing **grad/block/ran$_{C60}$** and unreacted PCB-DIBO**.** *CO_2

VII. Optical Microscopy Images

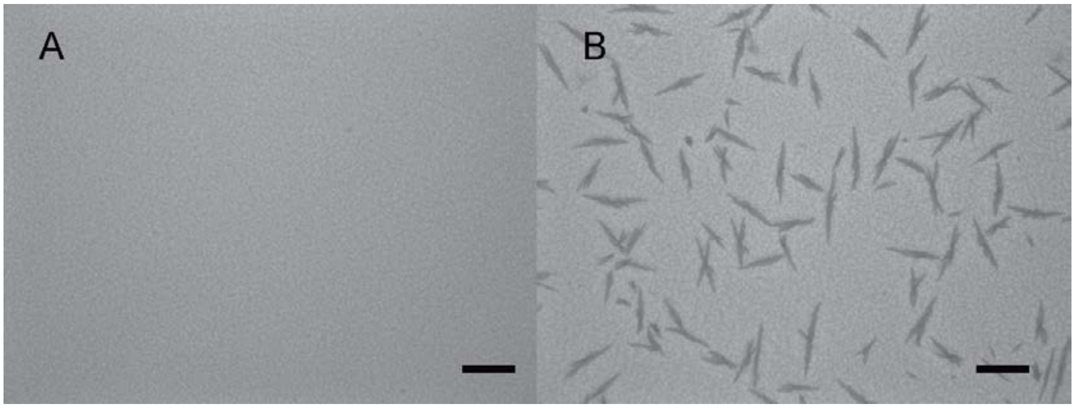

Figure S51. Optical microscopy images of P3HT/PCBM thin films (A) before and (B) after annealing for 60 min at 150 °C. Scale bar represents 30 μm.

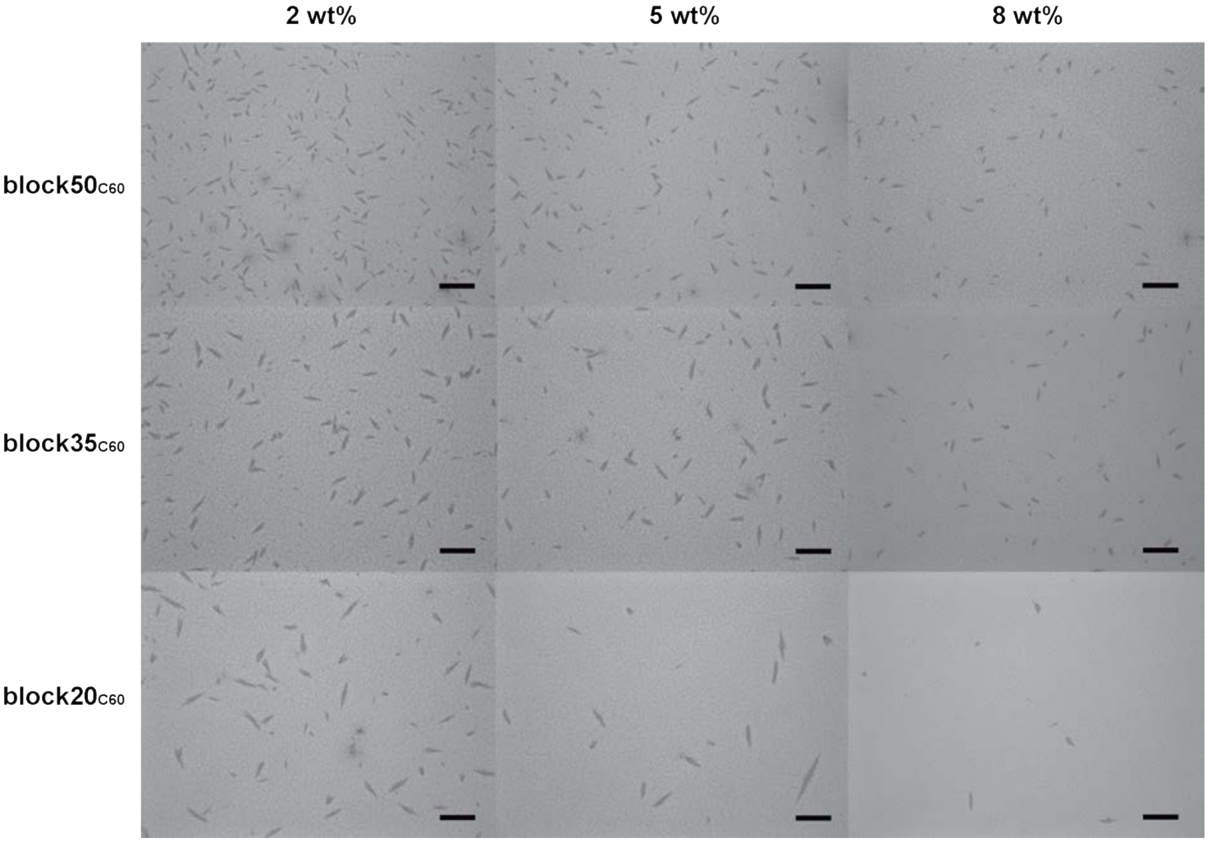

Figure S52. Optical microscopy images of P3HT:PC$_{61}$BM thin films with 2 wt%, 5 wt%, and 8 wt% of **block20$_{C60}$, block35$_{C60}$**, or **block50$_{C60}$** after annealing for 60 min at 150 °C. Scale bar represents 30 μm.

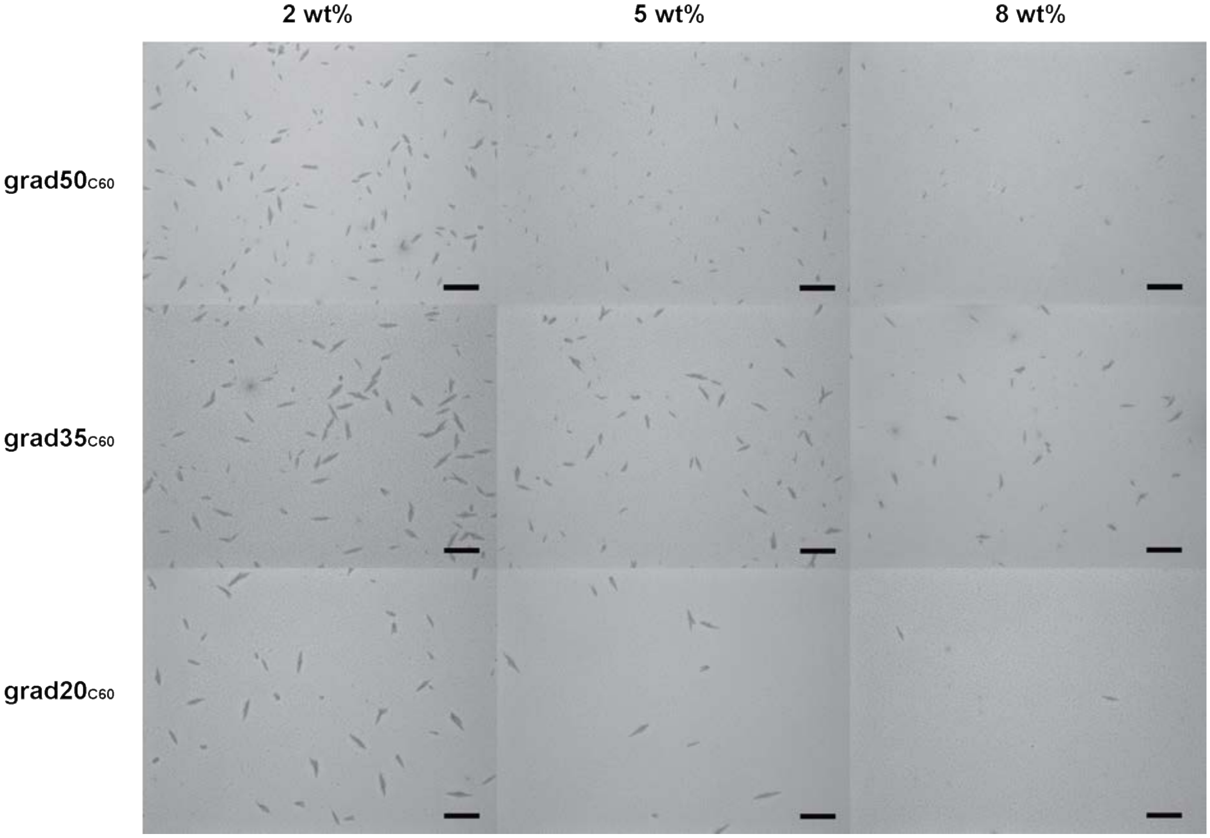

Figure S53. Optical microscopy images of P3HT:PC$_{61}$BM thin films with 2 wt%, 5 wt%, and 8 wt% of **grad20$_{C60}$, grad35$_{C60}$**, or **grad50$_{C60}$** after annealing for 60 min at 150 °C. Scale bar represents 30 μm.

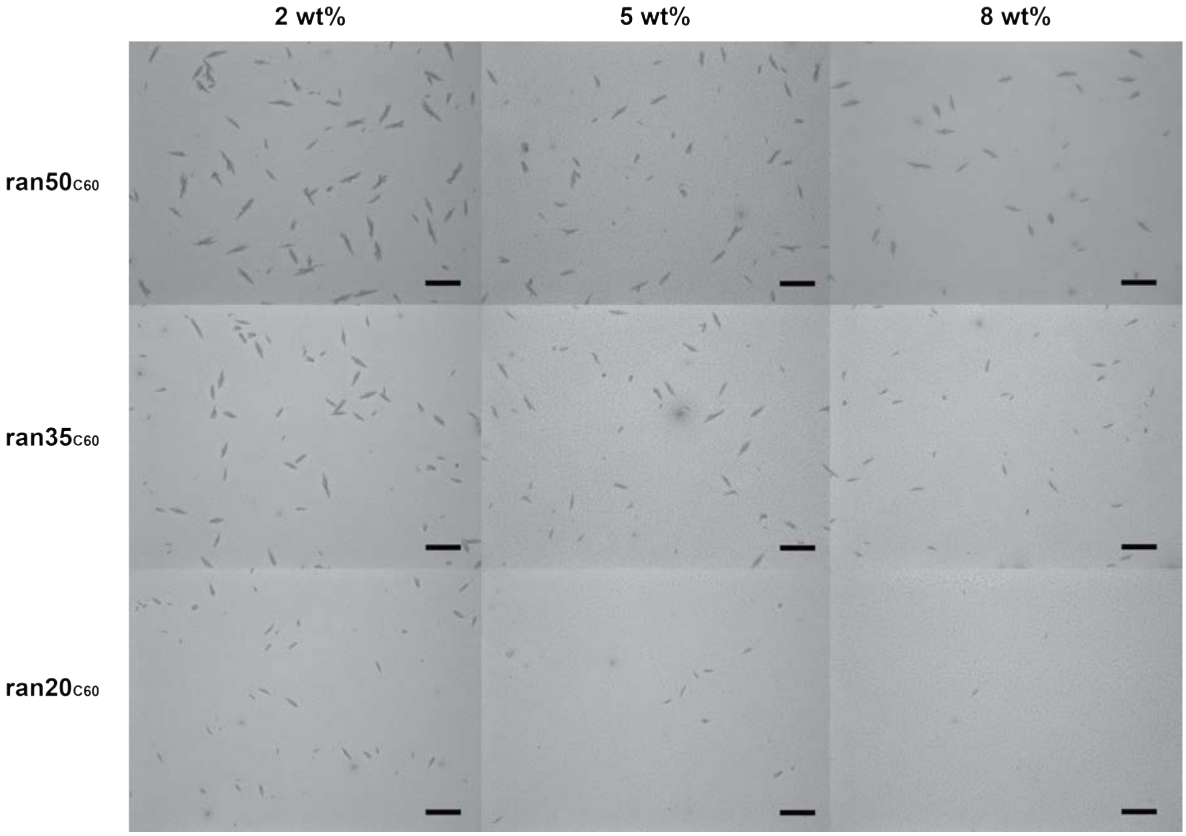

Figure S54. Optical microscopy images of P3HT:PC$_{61}$BM thin films with 2 wt%, 5 wt%, and 8 wt% of **ran20$_{C60}$, ran35$_{C60}$**, or **ran50$_{C60}$** after annealing for 60 min at 150 °C. Scale bar represents 30 μm.

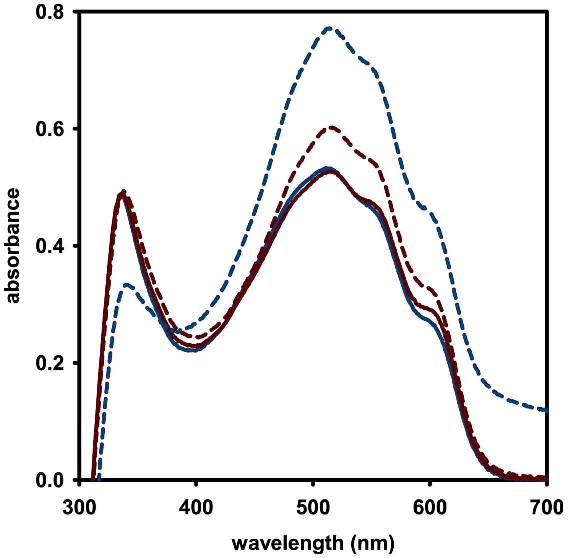

Figure S55. UV-Vis spectra of P3HT:PC$_{61}$BM thin films on quartz with 0 (blue) or 8 (red) wt% **ran20$_{C60}$** after 0 (solid) or 60 (dashed) min of annealing at 150 °C.

Concentration influence

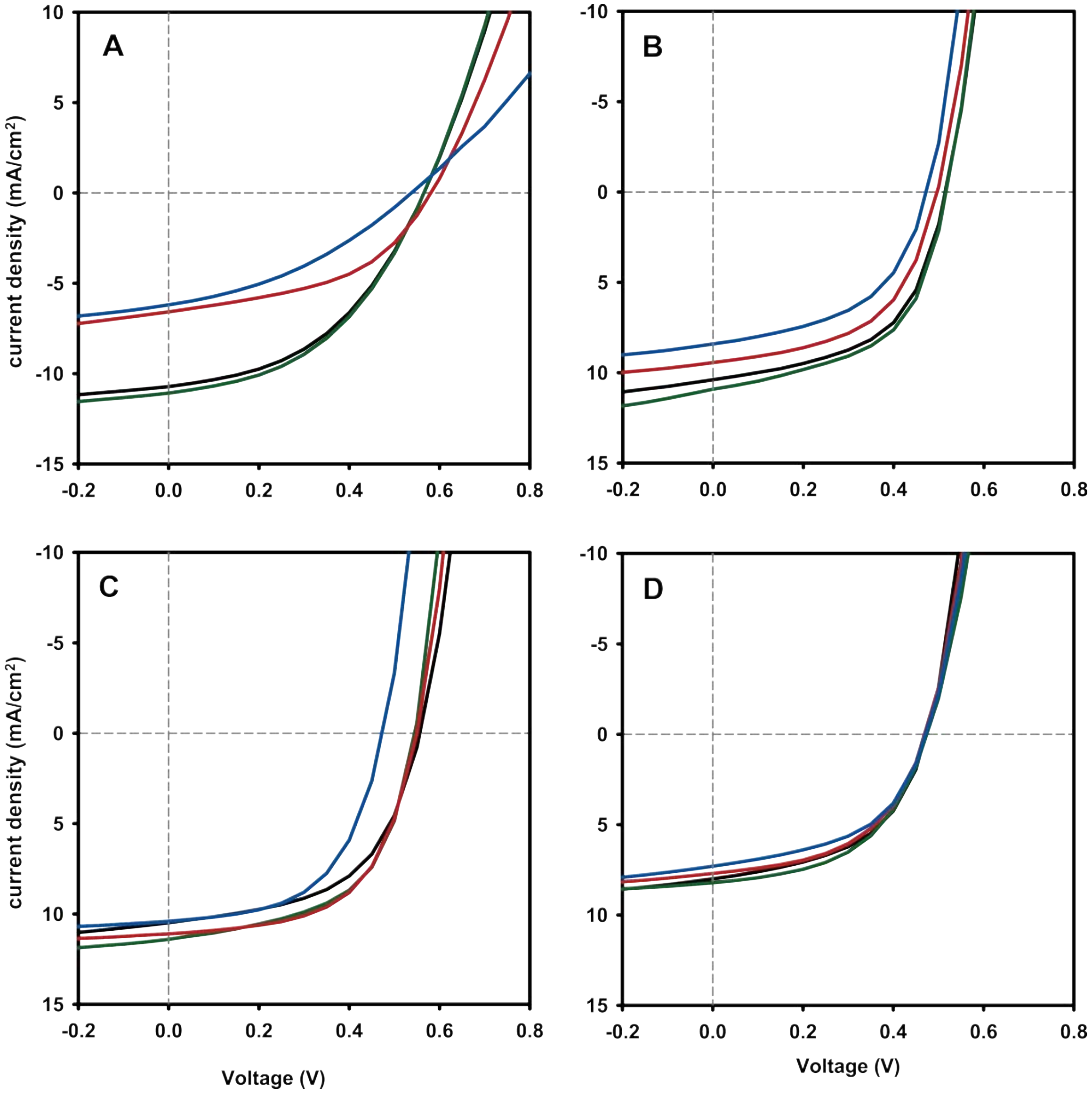

Figure S56. Current-voltage characteristics for the bulk heterojunction devices. The device active layer is composed of P3HT:PC$_{61}$BM blend with (A) 0 wt%, (B) 2 wt%, (C) 8 wt%, (D) 12 wt% **ran20$_{\mathbf{C60}}$** copolymer additive. Thermal annealing at 150 °C for 0 min (black), 15 min (green), 45 min (red), 60 min (blue).

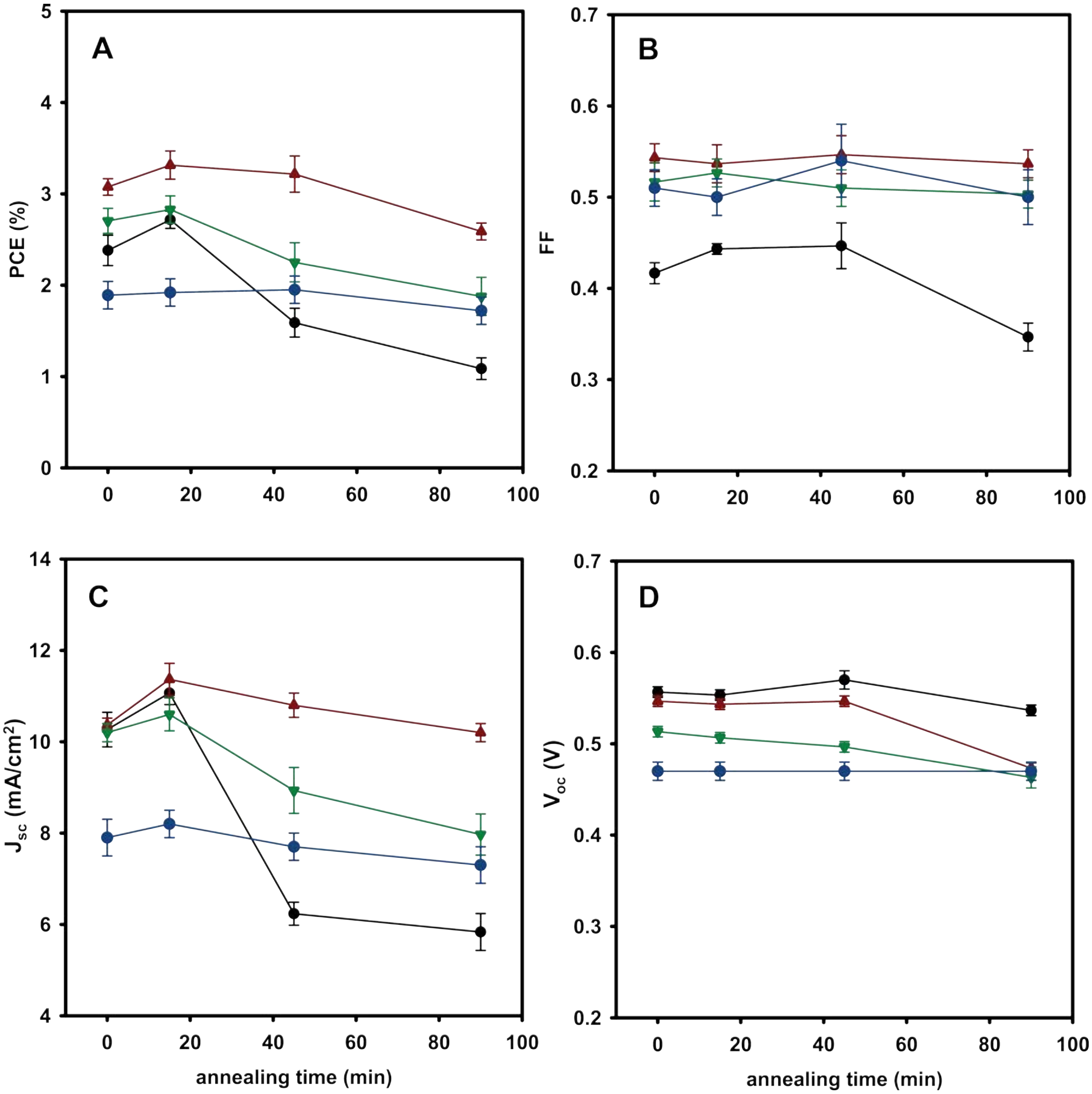

Figure S57. Performance data for bulk heterojunction devices with active layers composed P3HT:PC$_{61}$BM blend with 0 (black circles ●), 2 (green triangles ▼), 8 (red triangles ▲), and 12 (blue circles ●) wt% **ran20$_{C60}$**. (A) PCE, (B) FF, (C) J_{sc}, and (D) V_{oc} as a function of annealing time at 150 °C.

Composition influence

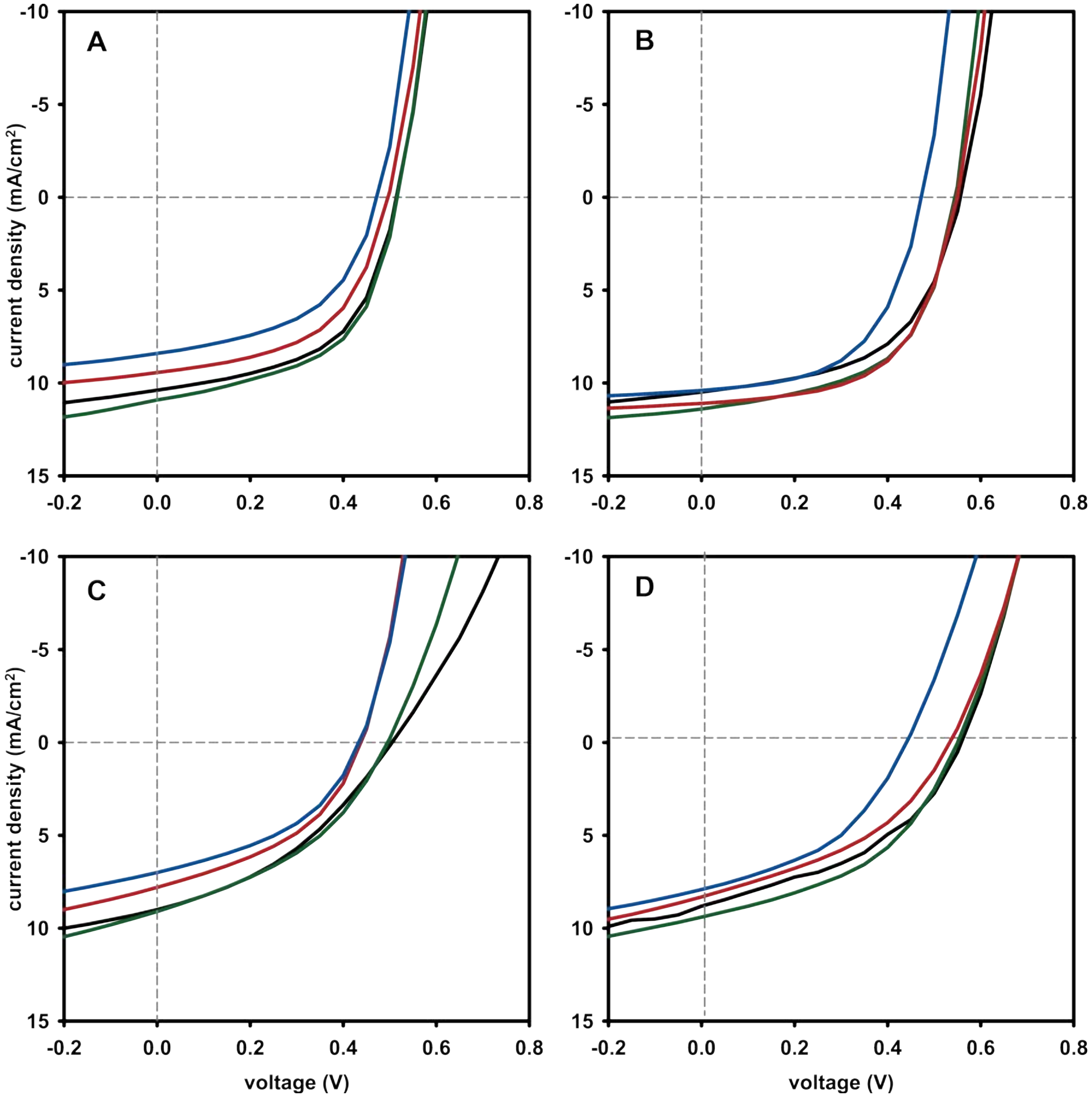

Figure S58. Current-voltage characteristics for the bulk heterojunction devices. The device active layer is composed of P3HT:PC$_{61}$BM blend with (A) 2 wt%, (B) 8 wt% **ran20$_{C60}$**, or (C) 2 wt%, (D) 8 wt% **ran50$_{C60}$** copolymer additive. Thermal annealing is at 150 °C for 0 min (black), 15 min (green), 45 min (red), 60 min (blue).

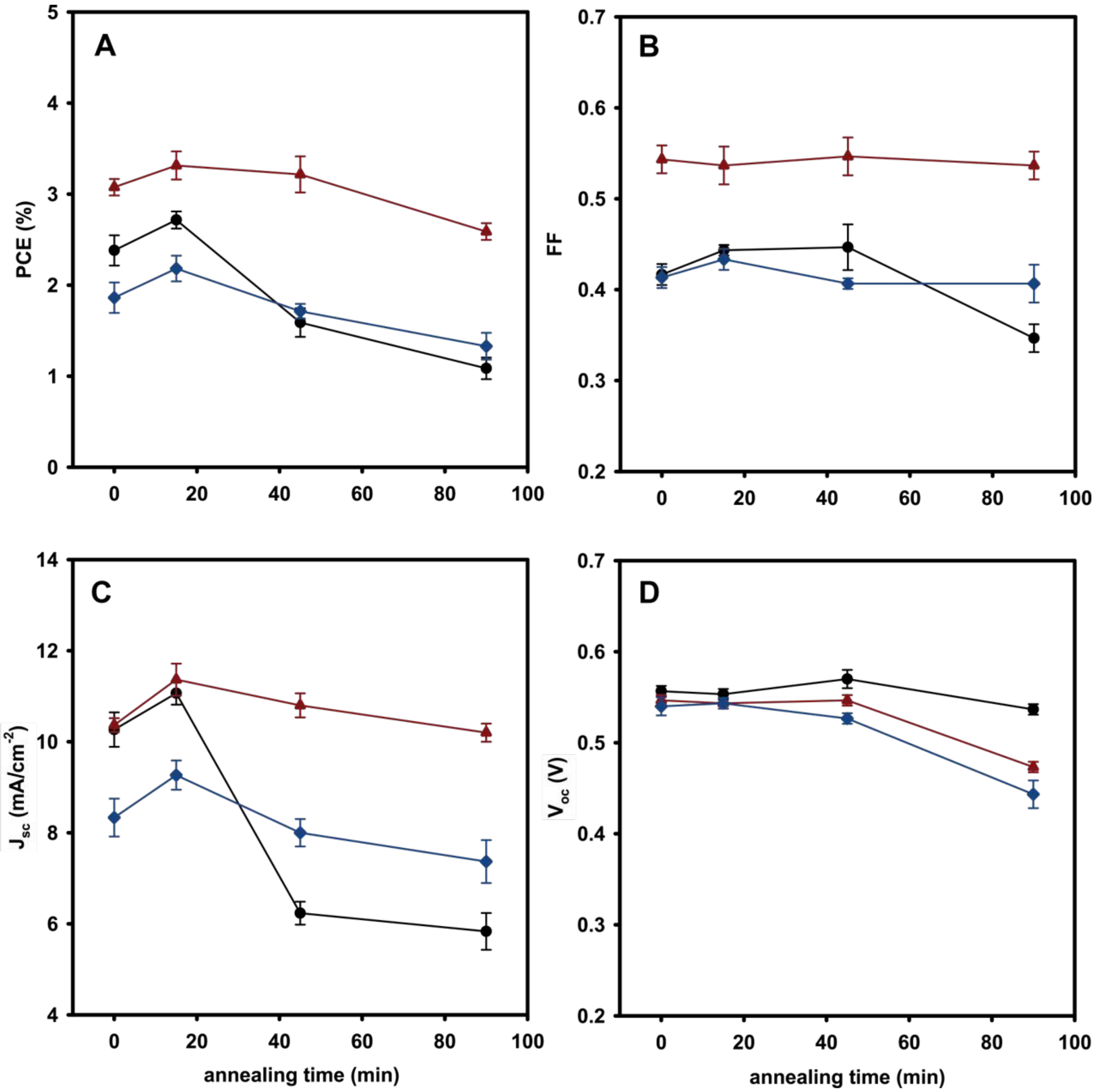

Figure S59. Performance data for bulk heterojunction devices with active layers composed P3HT:PC$_{61}$BM with 0 (black circles ●), 8 wt% **ran20**$_{\mathbf{C60}}$ (red triangles ▲), or 8 wt% **ran50**$_{\mathbf{C60}}$ (blue diamonds ◆) copolymer additive. (A) PCE, (B) FF, (C) J_{sc}, and (D) V_{oc} as a function of annealing time at 150 °C.

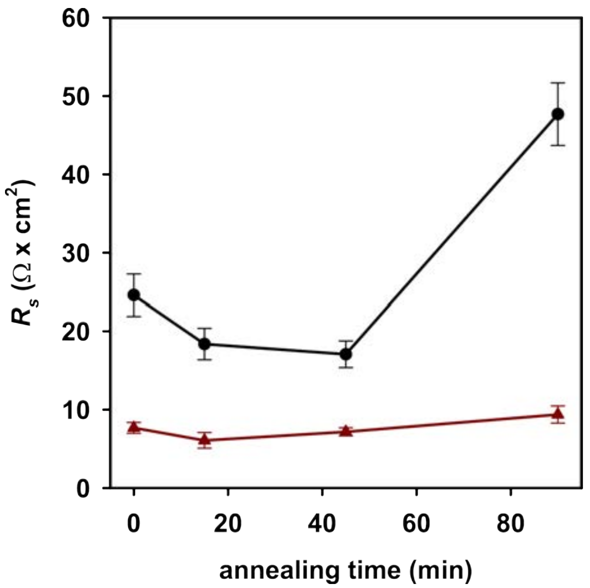

Figure S60. Series resistance (R_s) for bulk heterojunction solar cells as a function of annealing time at 150 °C containing 0 (black circles ●) or 8 wt% (red circles ●) **ran20**$_{\mathbf{C60}}$ in the P3HT:PC$_{61}$BM blend.

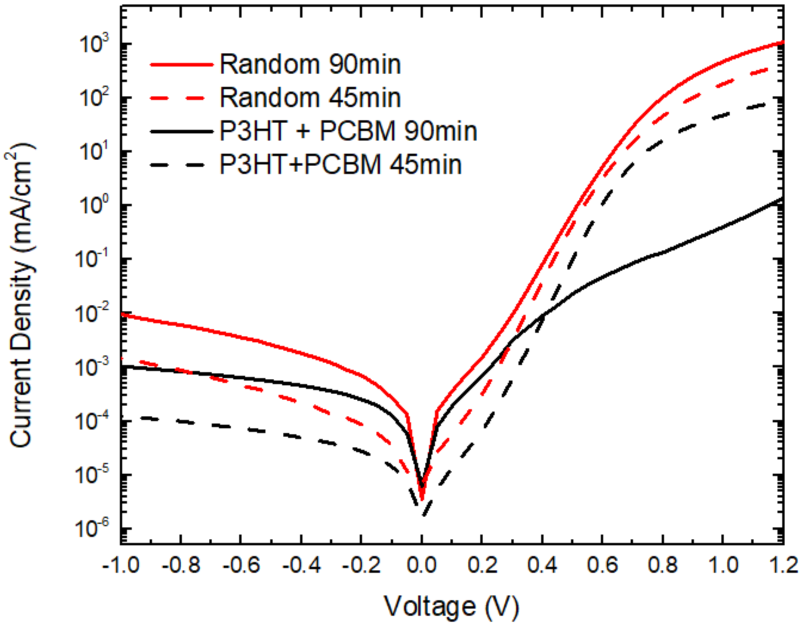

Figure S61. The *J-V* characteristics in the dark for solar cell devices with P3HT:PC$_{61}$BM blends containing 0 (black) or 8 (red) wt% **ran20**$_{C60}$ after annealing at 150 °C for 45 (dashed) and 90 (solid) mins.

Derivation and calculation for change in *V_{oc}* from change in *J_o*:

The V_{oc} for **ran20$_{\mathbf{C60}}$** is given in equation S1,[7]

$$V_{\mathrm{oc}_1} = \Delta E_{HL} - nk_B T \ln\left(\frac{J_{\mathrm{o}_1}}{J_{\mathrm{sc}_1}}\right) \tag{S1}$$

The V_{oc} for P3HT:PC$_{61}$BM is given in equation S2

$$V_{\mathrm{oc}_2} = \Delta E_{HL} - nk_B T \ln\left(\frac{J_{\mathrm{o}_2}}{J_{\mathrm{sc}_2}}\right) \tag{S2}$$

The reverse bias saturation current for the device with **ran20$_{\mathbf{C60}}$** is approximately 1 order of magnitude greater than that of the P3HT:PC$_{61}$BM device.

$$\mathrm{J}_{\mathrm{o}_1} \cong 10\left(\mathrm{J}_{\mathrm{o}_2}\right) \tag{S3}$$

The difference in V_{oc} between the **ran20$_{\mathbf{C60}}$** and P3HT:PC$_{61}$BM devices can be calculated by subtracting equation S2 from S1.

$$\Delta V_{oc} = nk_B T \left[\ln\left(\frac{J_{o_1}}{J_{sc_1}}\right) - \ln\left(\frac{J_{o_2}}{J_{sc_2}}\right)\right] \tag{S4}$$

Using the relationship in equation S3 and simplifying gives equation S5.

$$\Delta V_{oc} = nk_B T \ln\left(\frac{10 J_{sc_2}}{J_{sc_1}}\right) \tag{S5}$$

Substituting measured values for J_{sc_1} and J_{sc_2}, and approximating $n \cong 1.5$ (where n is the diode ideality factor approximated for P3HT: PC$_{61}$BM after annealing)[8] gives the approximate difference in V_{oc} between the **ran20$_{\mathbf{C60}}$** and P3HT:PC$_{61}$BM devices:

$$\Delta \mathrm{V}_{\mathrm{oc}} \cong 0.07\ \mathrm{V}$$

IX. HOMO/LUMO Determination

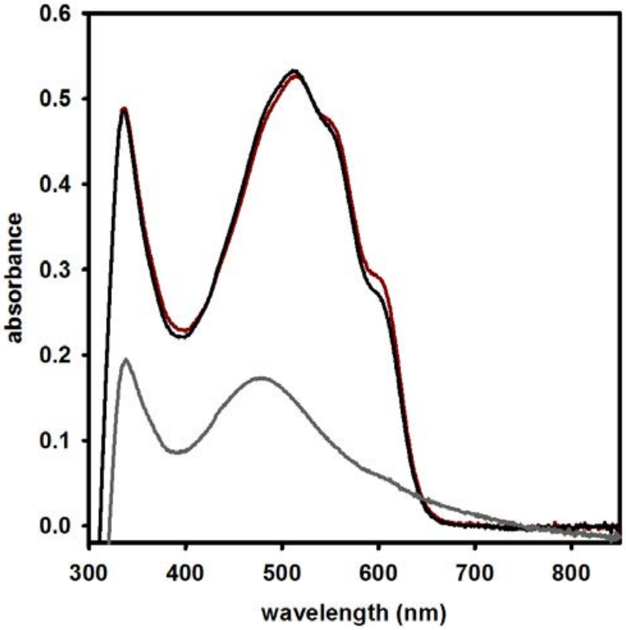

Figure S62. UV-Vis spectra of neat **ran20$_{C60}$** (grey) and P3HT:PC$_{61}$BM thin films on quartz with 0 (black) and 8 (red) wt% **ran20$_{C60}$**. The spectrum of neat **ran20$_{C60}$** was used to calculate the optical bandgap (E_g^{opt}) (see page S67).

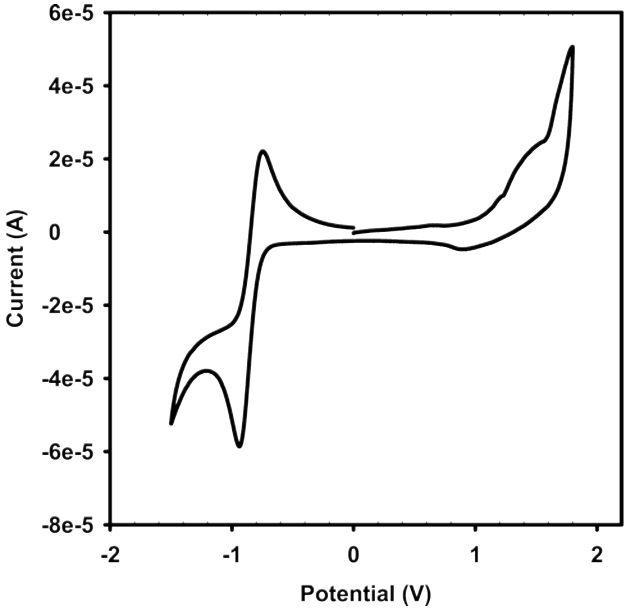

Figure S63. Cyclic voltammogram of **ran20$_{C60}$** (1 mg/mL in $CHCl_3$) which was used to determine the HOMO of the copolymer (see page S67).

Calculation of the HOMO/LUMO

P3HT:

Values for the HOMO (-4.76 eV) and E_g^{opt} (1.80 eV) of P3HT were obtained from reference 9. The LUMO (-2.96 eV) was then calculated by adding the E_g^{opt} to the HOMO:

$$-4.76 \text{ eV} + 1.80 \text{ eV} = -2.96\text{eV} \tag{S6}$$

PC$_{61}$BM:

The value for the HOMO (-5.93 eV) was obtained from reference 10. The E_g^{opt} (1.87 eV) of PC$_{61}$BM was calculated from the approximate optical absorption edge (~660 nm) in reference 10. The LUMO (-4.06 eV) was then calculated by adding the E_g^{opt} to the HOMO:

$$-5.93 \text{ eV} + 1.87 \text{ eV} = -4.06 \text{ eV} \tag{S7}$$

ran20$_{C60}$:

The HOMO (-5.5 eV) was calculated from the electrochemical onset potential. The E_g^{opt} (1.6 eV) was calculated from the optical absorption edge. The LUMO (-3.9 eV) was then calculated by adding the E_g^{opt} to the HOMO:

$$-5.5 \text{ eV} + 1.6 \text{ eV} = -3.9 \text{ eV} \tag{S8}$$

X. Atomic force microscopy (AFM) Data

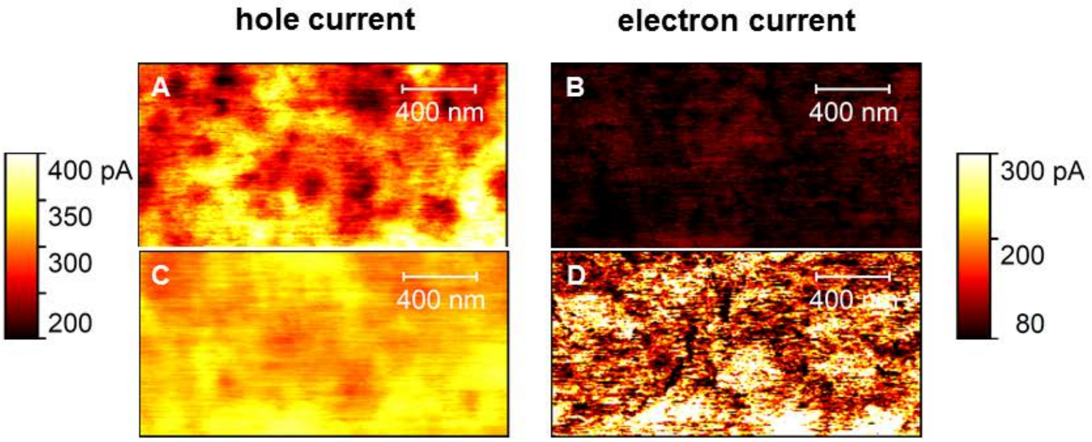

Figure S64. conductive-Atomic Force Microscopy (c-AFM) phase images of the active layer blend. The hole current was measured for P3HT:PC_{61}BM blends with (A) 0, or (C) 8 wt% **ran20$_{C60}$** spin-casted onto ITO/MoO_3 (scale bar at left corresponds to images A, C). The electron current was measured for active layer blends with (B) 0, or (D) 8 wt% **ran20$_{C60}$** spin-casted onto ITO/ZnO (scale bar at right corresponds to images B, D).

Table S1. Hole and electron current data from c-AFM of P3HT:PC_{61}BM blends with 0 or 8 wt% **ran20$_{C60}$**.

wt% ran20$_{C60}$	hole current (pA/μm^2)	electron current (pA/μm^2)
0	292 ± 37	88 ± 11
8	319 ± 15	202 ± 47

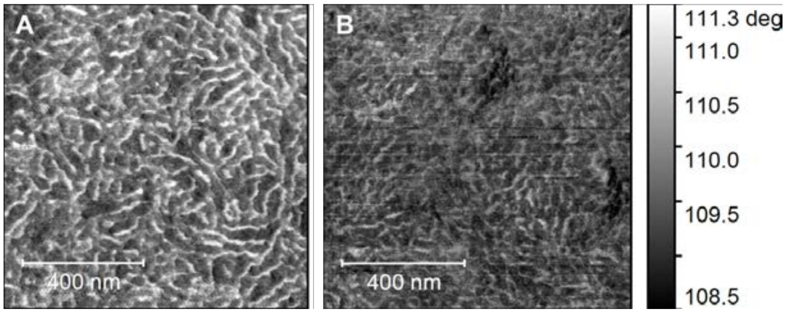

Figure S65. Atomic force microscopy phase images depicting surface morphology of P3HT:PC_{61}BM blends with (A) 0 and (B) 8 wt% **ran20$_{C60}$**.

XI. Differential Scanning Calorimetry (DSC) Data

The glass transition temperature (T_g) can be difficult to observe in semicrystalline materials like P3HT, $PC_{61}BM$, and blends of both, because only a small fraction of each material is amorphous.[11] Nevertheless, a variety of DSC conditions were screened in an effort to measure the glass transition temperatures (T_g) of the fullerene-functionalized copolymers and blends.

Optimizing Standard DSC Conditions

- Pan and lid type (Tzero and Tzero Low-Mass pans, Tzero and Tzero Hermetic lids)
- Sample mass (1–8 mg)
- Scan rate (5, 10, 20 °C/min)
- Initial temperature (anneal at -60 °C or 150 °C before beginning scan cycles)
- Minimum temperature (-80, -60, -40, 0 °C)
- Maximum temperature (150, 295 °C)
- Isotherm length at minimum/maximum temperatures (1, 5 min)

Optimizing Modulated Temperature DSC (MDSC) Conditions

- Pan and lid type (Tzero and Tzero Low-Mass pans, Tzero Hermetic lids)
- Sample mass (1–8 mg)
- Period (60 s)
- Amplitude (0.398, 0.400, 0.500, 0.738)
- Minimum temperature (-80, -60 °C)
- Maximum temperature (150, 295 °C)
- Ramp rate (2.0, 2.5 °C/min)

Copolymer crosslinking at high temperatures

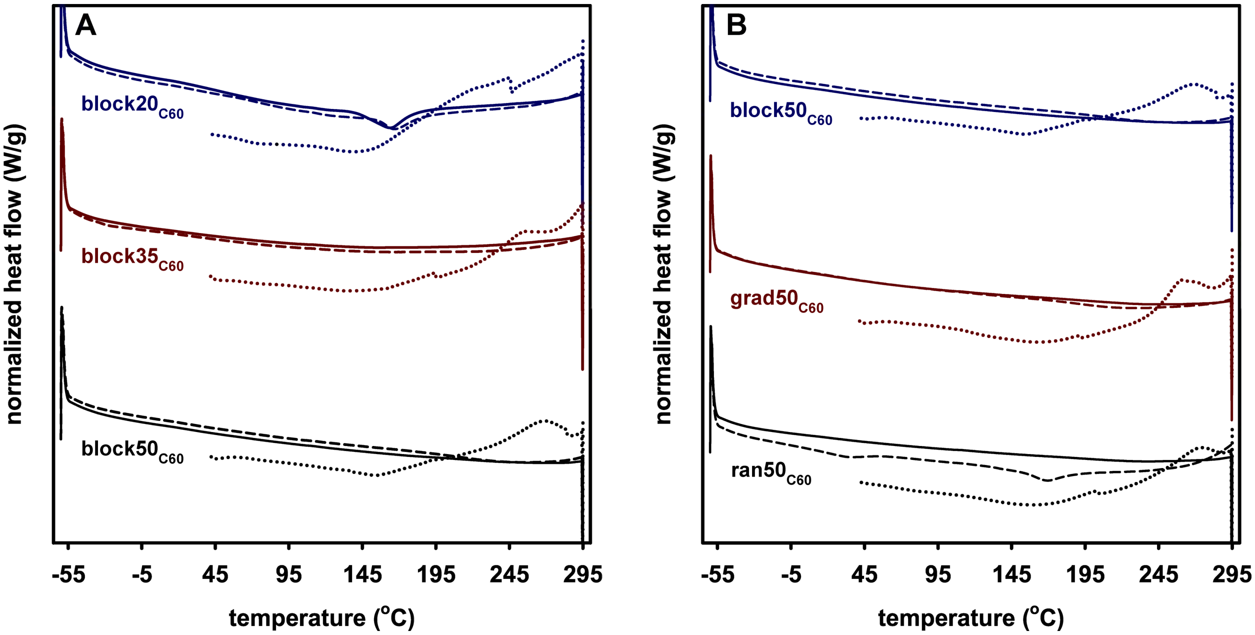

Figure S66. Standard DSC heating thermograms for fullerene-functionalized copolymers with (A) varying composition and (B) varying sequence. The initial (dotted) heating ramp shows crosslinking at temperatures >150 °C as a broad exothermic peak. The second (dashed) and third (solid) heating ramps show minimal to no thermal transitions, as would be expected for crosslinked material.

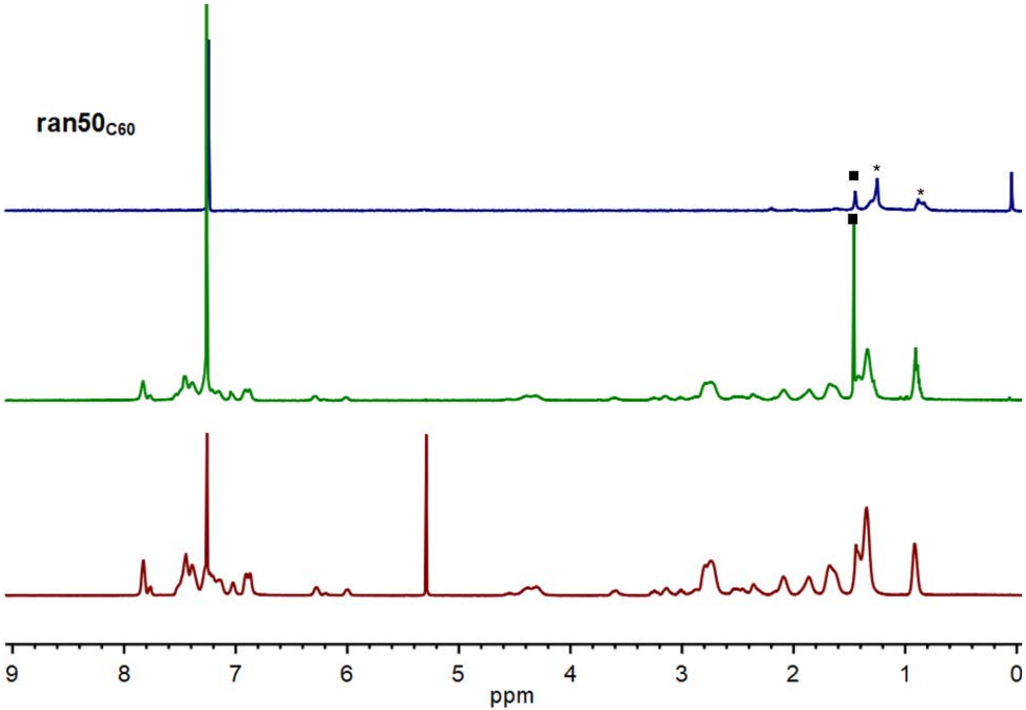

Figure S67. ^{1}H NMR spectra depicting ran50$_{C60}$ copolymer before (red) and after DSC scans with maximum temperatures of 150 °C (green), and 295 °C (blue). ■ H_2O, *grease

Fullerene-functionalized copolymers and blends

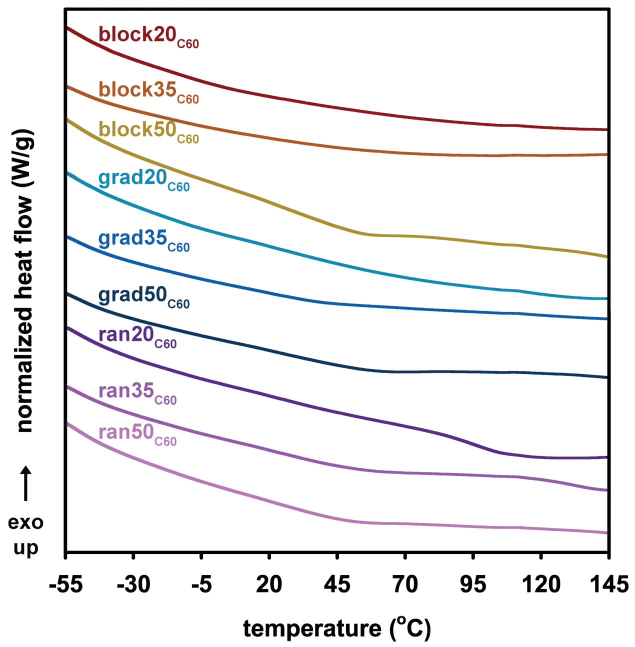

Figure S68. Standard DSC thermograms of all fullerene-functionalized copolymers showing the 3rd heating ramp. Most copolymers did not display a thermal glass transition temperature (T_g). The T_g for ran20$_{\mathrm{C60}}$ is 99 °C.

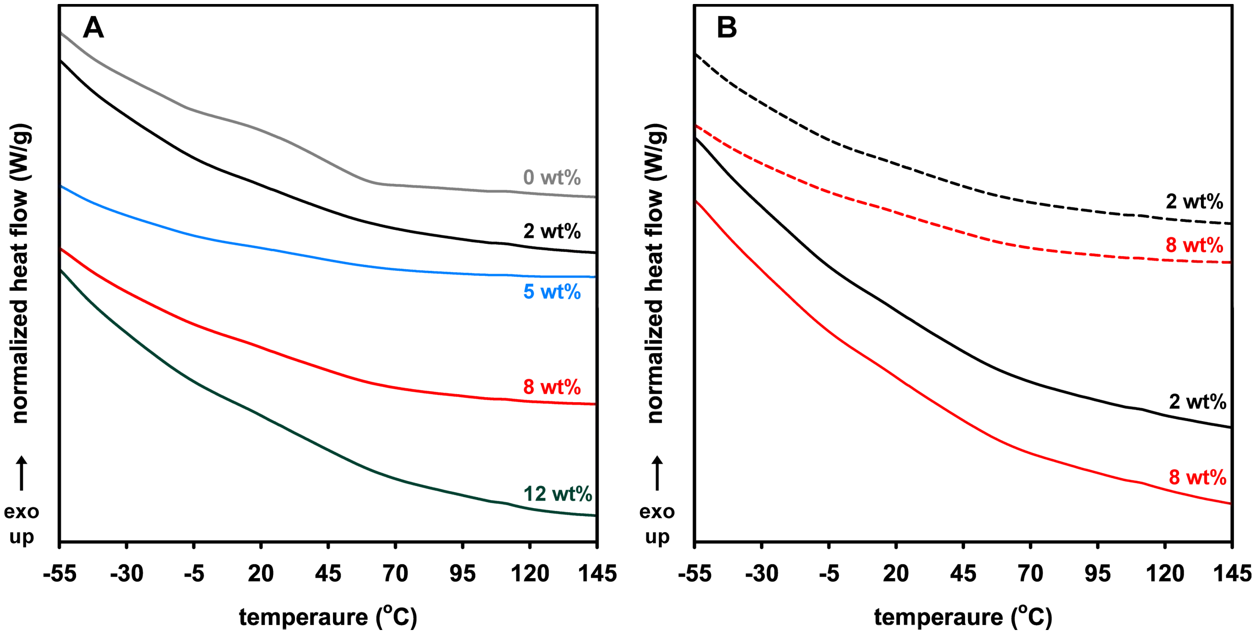

Figure S69. Standard DSC thermograms of 1:1 P3HT:PC$_{61}$BM (wt:wt) blends with (A) varying concentration for ran20$_{\mathrm{C60}}$ and (B) varying composition (ran20$_{\mathrm{C60}}$ (dashed) and ran50$_{\mathrm{C60}}$ (solid)).

XII. References

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