Electronic Supplementary Information

for

π-Conjugated Gradient Copolymers Suppress Phase Separation and Improve Stability in Bulk Heterojunction Solar Cells

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I. Materials

Flash chromatography was performed on SiliCycle silica gel (40−63 µm) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254. iPrMgCl (2 M in THF) was purchased in 100 mL quantities from Aldrich. Ni(cod)$_2$ and 1,2-bis(diphenylphosphino)ethane (dppe) were purchased from Strem. 1,6-Dibromohexane, 3-bromothiophene, 2-bromotoluene, N-bromosuccinimide (NBS), CS_2, sodium azide, phenyl-C_{61}-butyric acid methyl ester (PCBM), CuBr, and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich. NBS was purified by recrystallization from water, PMDETA was distilled from sodium, o-xylene was distilled from sodium, and CS_2 was purified by stirring with Br_2, shaking with KOH, then shaking with copper, filtered and then distilled from $CaCl_2$. All reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, or Fisher and used without further purification unless otherwise noted. THF was dried and deoxygenated using an Innovative Technology (IT) solvent purification system composed of activated alumina, copper catalyst, and molecular sieves. All glassware was oven-dried at 150 °C for at least 1 h before use.

II. General Experimental

NMR Spectroscopy: ^{1}H, ^{31}P and ^{13}C NMR spectra for all compounds were acquired in $CDCl_3$ or CD_2Cl_2 as noted on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 162 and 100 MHz, respectively. For ^{1}H and ^{13}C NMR spectra the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced to residual solvent. ^{31}P NMR spectra are referenced to external H_3PO_4. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonance (br). All NMR spectra were recorded at rt.

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

Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580−377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm) at 40 °C in THF. Samples were dissolved in THF (with mild heating) and passed through a 0.2 µm PTFE filter prior to analysis.

MALDI-TOF-MS: Spectra were recorded using Waters Tofspec-2E in reflectron mode at a unit mass resolution of 5000. The matrix dithranol was prepared at a concentration of 0.1 M in $CHCl_3$. A polymer solution in $CHCl_3$ (10 µL, 10^{-4} M) was mixed with the matrix solution (10 µL) and 1 µL of this mixture was spotted on the target plate and then air-dried. The spectra were calibrated to a mixture of standard peptides.

UV-vis Spectroscopy: UV-vis spectra were acquired using a Perkin Elmer Lambda 850 UV-vis spectrometer. ITO-coated glass slides were cleaned with Liquinox surfactant, rinsed with DI water, and sonicated in water, acetone, and isopropanol for 15 min each. The slides were dried for 15 min in a convection oven at 70 °C and then treated with UV-ozone for an additional 15 min. Then, a suspension of PEDOT/PSS in water (1.3 wt%) was spin coated onto the ITO layer at 1500 rpm for 1 min. The slides were taken into a glovebox and dried for 15 min at 150 °C on a hotplate. A solution of P3HT/PCBM (17 mg/mL, 60/40 w/w) in 1,2-dichlorobenzene (*o*-DCB), with 0 or 10 wt% gradient copolymer added, was stirred at 60 °C for 18 h and then spin cast onto the PEDOT/PSS surface at 1000 rpm for 1 min, followed by thermal annealing on a hotplate at 150 °C for 10 or 60 min.

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) column.

Photoluminescence: ITO-coated glass slides were cleaned with Liquinox surfactant, rinsed with DI water, and sonicated in water, acetone, and isopropanol for 15 min each. The slides were dried for 15 min in a convection oven at 70 °C and then treated with UV-ozone for an additional 15 min. Then, a suspension of

PEDOT/PSS in water (1.3 wt%) was spin coated onto the ITO layer at 1500 rpm for 1 min. The slides were taken into a glovebox and dried for 15 min at 150 °C on a hotplate. A solution of P3HT/PCBM (17 mg/mL, 60/40 w/w) in 1,2-dichlorobenzene (*o*-DCB), with 0 or 10 wt% gradient copolymer added, was stirred at 60 °C for 18 h and then spin cast onto the PEDOT/PSS surface at 1000 rpm for 1 min, followed by thermal annealing on a hotplate at 150 °C for 10 or 60 min. The substrates were affixed to a sample holder in a Horiba Fluorimeter and PL intensity was recorded using a CCD detector for excitation wavelengths ranging from 500 to 700 nm (4 nm increments, 2 nm bandwidth) using 600 x 500 gratings and emission wavelengths centered on 550 nm (2 nm bandwidth) with 100 x 450 gratings.

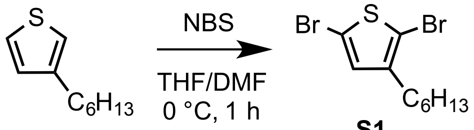
Optical Microscopy: The same samples used in the PL intensity measurements were examined using a Leica DMCB optical microscope with a 40x objective lens. Images were recorded with an attached QICAM Fast 1394 digital video camera.

Bulk Heterojunction Solar Cell Fabrication and Testing: Thin films of P3HT/PCBM bulk heterojunctions on PEDOT/PSS/ITO/glass substrates were prepared using the same procedure as described above for the PL intensity measurements. Subsequently, a narrow region of the films was wiped off using a cotton swab wetted with acetone to partially expose the ITO surface for further deposition. The films were then placed in a holder with a mask and positioned in a metal deposition chamber. After evacuation to 10^{-6} torr for 18 h, Ca (20 nm, 0.2 nm/sec) and Al (100 nm, 0.7 nm/sec) were deposited on the films to form the top electrode. The solar cells were tested under AM 1.5 illumination using a solar simulator under a flow of nitrogen. Voltage sweeps from -0.2 to 1.0 V in the dark and under illumination were collected and the sample active area was 0.049 cm^2.

X-ray Diffraction: Polymer solutions (10 mg/mL) in $CHCl_3$ were drop-cast onto glass slides and dried on a hot plate at 50 °C for 2 min. Samples were analyzed using a Bruker AXS in the 2-theta geometry. Samples were scanned at a rate of 1 sec/step from $2\theta = 4$ to 30° with a step size of 0.04°.

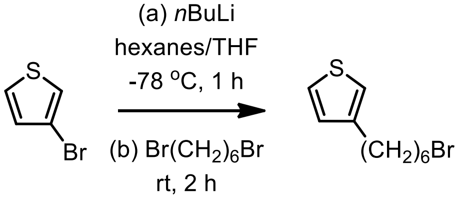
Differential Scanning Calorimetry: Polymer solutions (10 mg/mL) in $CHCl_3$ were drop-cast onto glass slides and dried on a hot plate at 50 °C for 2 min. DSC was performed on a TA Instruments DSC Q2000. Samples (~5 mg) were sealed in aluminum pans (Tzero Hermetic) and sealed using a TA Instruments crimper. Heating and cooling scans were run at linear ramp rates of 10 and 5 °C/min, respectively.

III. Synthetic Procedures



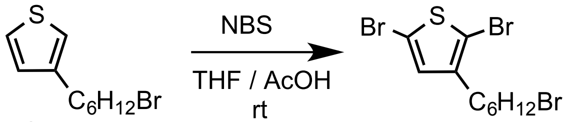
S1

2,5-dibromo-3-hexylthiophene (S1): We used the method of McCullough[1] with minor modifications. To a 100 mL oven-dried Schlenk flask, cooled to 0 °C under positive N_2 pressure, were added 3-hexylthiophene (5.00 g, 29.7 mmol, 1.00 equiv), THF (25 mL) and DMF (25 mL). Freshly recrystallized NBS (10.8 g, 74.3 mmol, 2.50 equiv) was added in a single portion and the mixture was stirred for 1 h in the dark. The reaction was then warmed to rt, stirred for an additional 1 h, and quenched using saturated aq $NaHCO_3$ (50 mL), and diluted 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 an orange oil. This crude oil was purified by vacuum distillation (85 °C, 0.031 torr) to afford the title compound as a clear, colorless oil (6.53 g, 67%). HRMS (EI): Calcd. for $C_{10}H_{14}Br_2S$ [M^+] 323.9183; found, 323.9176.



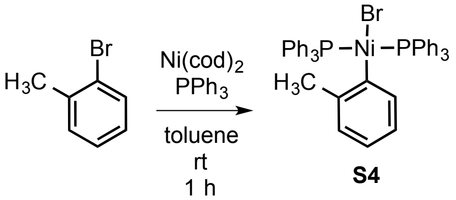
S2

3-(6-bromohexyl)thiophene (S2): To a 200 mL oven-dried Schlenk flask, 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 under N_2. A solution of n-butyllithium in hexanes (1.6 M, 12.7 mL, 20.0 mmol, 0.95 equiv) was added dropwise and the mixture was stirred for 10 min. THF (5 mL) was injected dropwise over 15 minutes and the mixture stirred for an additional 1 h to produce a white precipitate and a transparent, colorless supernatant. The supernatant liquid was then removed via cannula transfer and replaced with hexanes/THF (10:1 v/v, 55 mL). 1,6-Dibromohexane (32.7 mL, 213 mmol, 10.0 equiv) was added and the slurry was then warmed to rt and stirred for another 2 h. The reaction was quenched using saturated aq $NaHCO_3$ (50 mL), diluted with Et_2O (100 mL), 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 (0.04 torr, 55 °C) and the remaining oil was purified by silica gel column chromatography (ethyl acetate/hexane gradient from 1/99 to 5/95 v/v) to obtain a clear, colorless oil (2.74 g, 55%). HRMS (EI): Calcd. for $C_{10}H_{15}SBr$ [M^+] 246.0078; found, 246.0073.

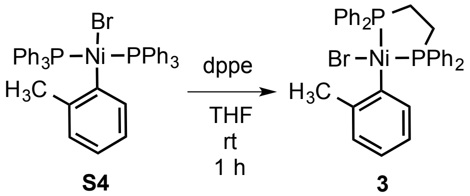


S2 **S3**

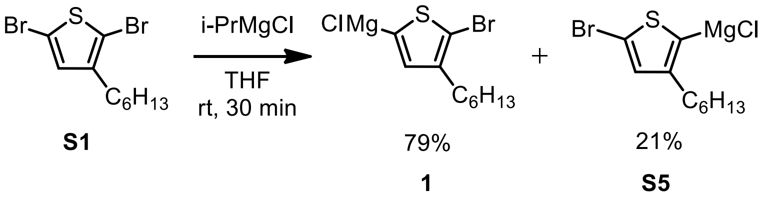
2,5-dibromo-3-(6-bromohexyl)thiophene (S3): To a 100 mL oven-dried Schlenk flask under positive N_2 pressure, were added **S2** (2.50 g, 1.01 mmol, 1.00 equiv), THF (25 mL) and acetic acid (25 mL). Freshly recrystallized NBS (3.80 g, 2.12 mmol, 2.10 equiv) was added in one portion and the mixture was stirred at rt for 2 h. The reaction was then quenched using saturated aq $NaHCO_3$ (50 mL), diluted 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 an orange oil. This crude oil was purified by silica gel column chromatography (ethyl acetate/hexane, 1/10 v/v) to obtain a clear, colorless oil (2.63 g, 64%). HRMS (EI): Calcd. for $C_{10}H_{13}SBr_3$ [M^+] 401.8288; found, 401.8302.



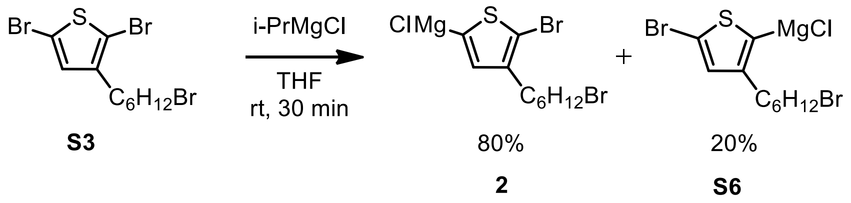
(*o*-tolyl)bis(triphenylphosphino)nickel bromide (S4): Following literature precedents,[2] $Ni(cod)_2$ (517 mg, 1.88 mmol, 1.00 equiv) and PPh_3 (986 mg, 3.76 mmol, 2.00 equiv) were dissolved in toluene (10 mL) in an oven-dried 25 mL round-bottom flask equipped with a stir bar under N_2. 2-Bromotoluene (354 mg, 2.07 mmol, 1.10 equiv) was added in a single portion and the mixture was stirred at rt for 1 h. Hexanes (20 mL) were added and the resulting precipitate was collected by filtration inside a glovebox. The solids were purified by recrystallization from THF/hexanes at -35 °C to afford the title compound as an orange powder (345 mg, 24%).



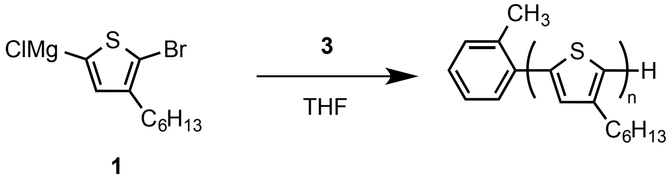
(*o*-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (3): Following literature precedents,[2] in a 25 mL oven-dried round-bottom flask equipped with a stir bar, under N_2, **S4** (340 mg, 0.45 mmol, 1.00 equiv) was dissolved in THF (5 mL). Then, dppe (198 mg, 0.50 mmol, 1.10 equiv) was added and the mixture was stirred at rt for 1 h. The volume of THF was reduced to ~1 mL under reduced pressure and hexanes (10 mL) were added. The resultant precipitate was isolated by filtration inside a glovebox, washed with hexanes (10 mL) and Et_2O (10 mL), and recrystallized from THF/hexanes (20 mL) at -35 °C to afford the title compound as a fine yellow powder (215 mg, 76%). HRMS (EI): Calcd. for $C_{33}H_{31}BrNiP_2$ [M^+] 626.0438, found, 626.0428.



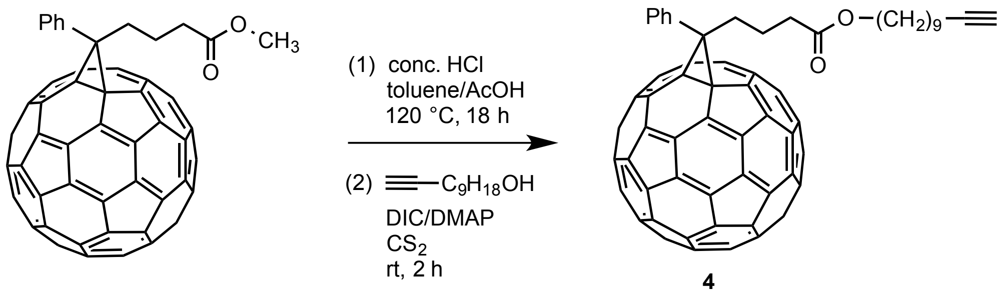
1: According to the procedure of McCullough,[3] **S1** (195 mg, 0.597 mmol, 1.00 equiv) was dissolved in THF (5 mL) under N_2, in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (270 µL, 0.537 mmol, 0.90 equiv) was added and the reaction stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with $CHCl_3$ (2 x 1 mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 79:21. Note that only the 2-bromo isomer (**1**) undergoes polymerization in the presence of catalyst **3**, giving highly regioregular materials.



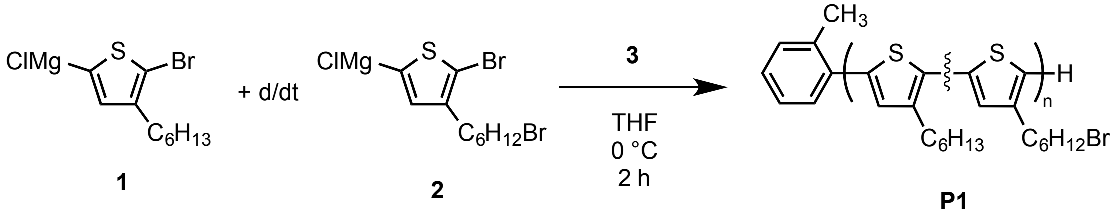
2: Under N_2, **S3** (242 mg, 0.597 mmol, 1.00 equiv) was dissolved in THF (5 mL) in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (270 μL, 0.429 mmol, 0.90 equiv) was added and the reaction was stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with $CHCl_3$ (2 x 1 mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 80:20. Note that only the 2-bromo isomer (**2**) undergoes polymerization in the presence of catalyst **3**, giving highly regioregular materials.



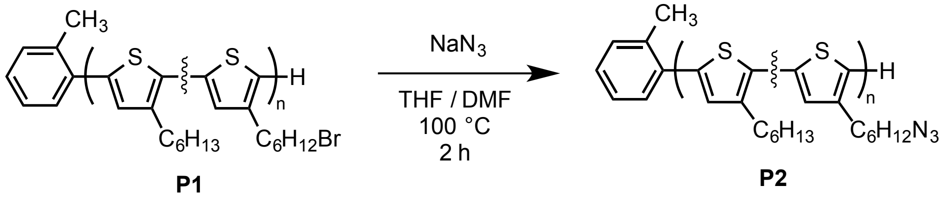
poly(3-hexylthiophene) (P3HT): To a 50 mL oven-dried Schlenk flask, a solution of **1** in THF (5 mL, 0.5 mmol, 0.1 M) was injected via syringe and diluted with THF (25 mL). A stock solution of **3** in THF (1 mL, 5 μmol, 5 mM) was then injected and the mixture was stirred at rt for 1 h. Hence, the monomer:catalyst ratio was initially 100:1, and the expected value of M_n is therefore 16.6 kDa. The polymerization was quenched with 5 M aq HCl (5 mL), extracted with $CHCl_3$ (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of $CHCl_3$ (~2 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, dichloromethane, and $CHCl_3$ respectively. The $CHCl_3$ fraction was dried in vacuo to afford the polymer as a purple solid (76 mg, 85%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C) after purification: M_n = 32.4 kDa, Đ = 1.12.



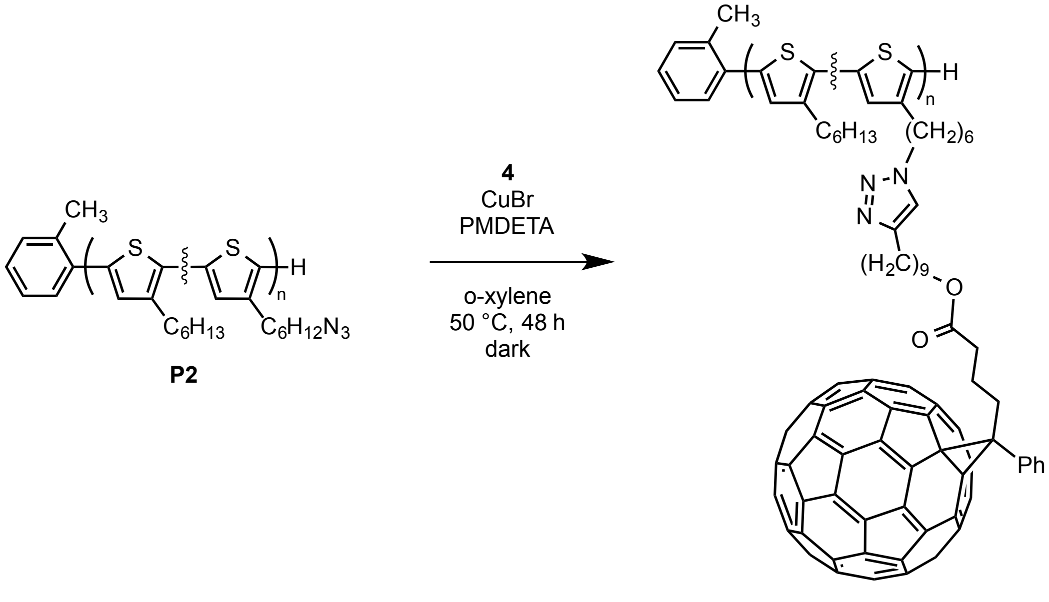
Phenyl-C_{61}- butyric acid undec-10-ynyl ester (4): Using a modified literature procedure,[4] phenyl-C_{61}-butyric acid methyl ester (PCBM, 135 mg, 0.148 mmol) was dissolved in toluene (20 mL) and acetic acid (10 mL) in a 100 mL bomb flask. To this mixture, conc. HCl (5 mL) was added. The flask was sealed and heated to 120 °C for 18 h with vigorous stirring. The mixture was then cooled to rt and an insoluble brown powder, presumably phenyl-C_{61}-butyric acid (PCBA), was isolated by filtration. This powder was washed with MeOH, acetone, toluene, and diethyl ether (30 mL each) and carried to the next step without further purification or characterization. The PCBA was dried under vacuum at 70 °C for 18 h and then suspended in dry CS_2 (10 mL) under N_2. Then, 10-undecyn-1-ol (49 μL, 0.25 mmol) and DMAP (18 mg, 0.15 mmol) were added, followed by diisopropylcarbodiimide (DIC, 39 μL, 0.25 mmol). The reaction was stirred at rt for 1 h and quenched with MeOH (1 mL). The solvent was evaporated and the residue dissolved in toluene (3 mL), and purified by silica gel column chromatography using toluene as the eluent. Pure fractions were concentrated by rotary evaporation and dried at 70 °C for 18 h under vacuum. The title compound was obtained as a black powder (126 mg, 81% for two steps). MALDI-TOF-MS: Calcd. for $C_{82}H_{30}O_2$ [M^+] 1046.2; found, 1046.0.



poly(3-hexylthiophene-*grad*-3-(6-bromohexyl)thiophene) (**P1**): Under a N_2 atmosphere, a solution of **1** (15 mL, 0.27 mmol) was transferred to an oven-dried 25 mL Schlenk flask and cooled to 0 °C. A solution of **2** (3 mL, 0.053 mmol) was loaded into a 5 mL plastic syringe and attached to a syringe pump apparatus. With constant stirring, a stock solution of **3** in THF (5.0 mM, 0.60 mL, 3.0 μmol) was transferred to the flask via syringe, and the syringe pump was activated to deliver **2** at a rate of 0.05 mL/min. Hence, the total monomer to catalyst ratio was 100:1 after complete syringe pump addition and the theoretical value of M_n is therefore 20.6 kDa. Aliquots were withdrawn periodically and analyzed by ^1H NMR spectroscopy and GPC to give the cumulative mole fraction of **2** in the copolymer and the normalized chain length, respectively. After 2 h at 0 °C, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with $CHCl_3$ (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of $CHCl_3$ (~1 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, CH_2Cl_2, and $CHCl_3$. The $CHCl_3$ fraction was dried in vacuo to afford the polymer as a purple solid (43 mg, 70%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C) after purification: M_n = 23 kDa, Đ = 1.17.



poly(3-hexylthiophene-*grad*-3-(6-azidohexyl)thiophene) (**P2**): The precursor polymer **P1** (40 mg, 0.023 mmol bromine side chains) was dissolved in THF (40 mL) in a 100 mL round bottom flask equipped with a reflux condenser and the solution was heated to 60 °C to give a bright orange solution. Sodium azide (15 mg, 0.23 mmol, 10 equiv) was added and DMF (20 mL) was injected dropwise over 1 min. Then the flask was protected from light, the temperature was increased to 100 °C and the solution was stirred for 2 h. The resulting polymer was precipitated in cold MeOH (100 mL), centrifuged, the supernatant decanted. Then, the pellet was suspended in MeOH with sonication and then isolated by centrifugation, decanting, and drying the pellet under vacuum for 18 h at rt in the dark. The title compound was obtained as a purple powder (32 mg, 78%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C), after purification: M_n = 24 kDa, Đ = 1.20.



poly(3-hexylthiophene-*grad*-3-(9-(1-hexyl-1*H*-1,2,3-triazol-4-yl)phenyl-C_{61}-butyric acid nonyl ester) thiophene) (**P3**): The azide precursor polymer **P2** (32 mg, 0.02 mmol azide side chains) and fullerene derivative **4** (63 mg, 0.06 mmol) were separately dissolved in rigorously dried and degassed *o*-xylenes (10 mL each), heated to 50 °C, and stirred for 18 h in the dark. The polymer and fullerene solutions were filtered through 0.2 µm PTFE membranes and transferred to a 50 mL flask and stirred at 50 °C for 10 min. CuBr (10 mg) and PMEDTA (100 µL) were dissolved in 9.9 mL o-xylenes (9.9 mL) and 1 mL of this stock solution was injected. The mixture was further stirred for 48 h at 50 °C in the dark, under strictly air-free conditions. The resulting brownish orange solution was poured into MeOH (200 mL, 0 °C) to produce a purple solid after standing for several minutes. The solids were rinsed with acetone (3 x 50 mL), hexanes (3 x 50 mL) and DCM (1 x 50 mL) and dried under vacuum. Residual unreacted fullerene was then removed by a preparative GPC column using BioBeads SX-10 gel in THF. The pure fractions were concentrated to ~ 5 mL and precipitated into MeOH (20 mL), centrifuged, and dried under vacuum for 18 h at 40 °C. The title compound was obtained as a purple powder (42 mg, 82 %). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C) after purification: M_n = 20 kDa, Đ = 1.24.

IV. NMR Spectra

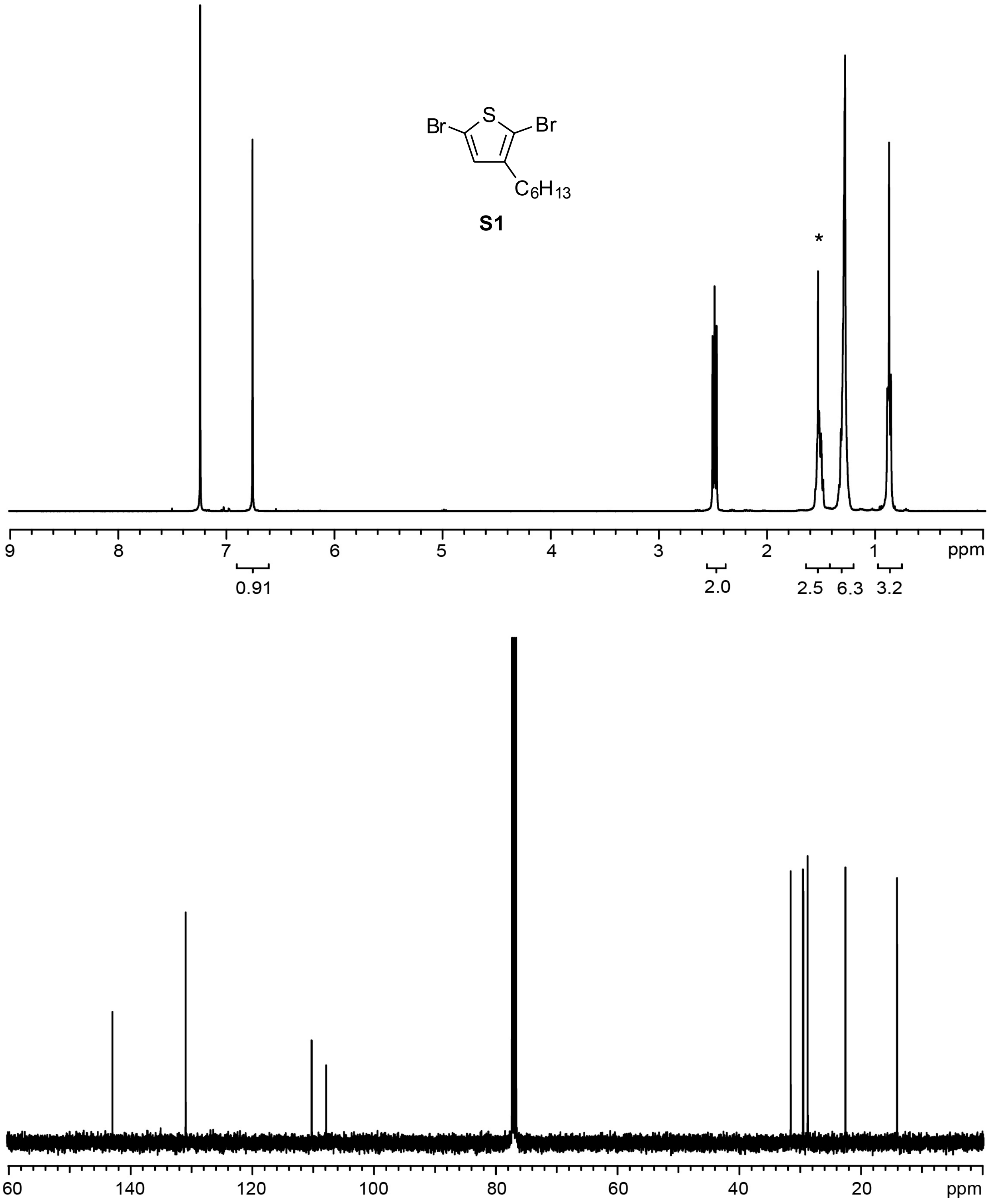


Figure S1. NMR spectra for **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.52 (m, 2H), 1.28 (br m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). The symbol * denotes residual water in the $CDCl_3$. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.98, 130.94, 110.26, 107.89, 31.54, 29.53, 29.46, 28.76, 22.55, 14.06.

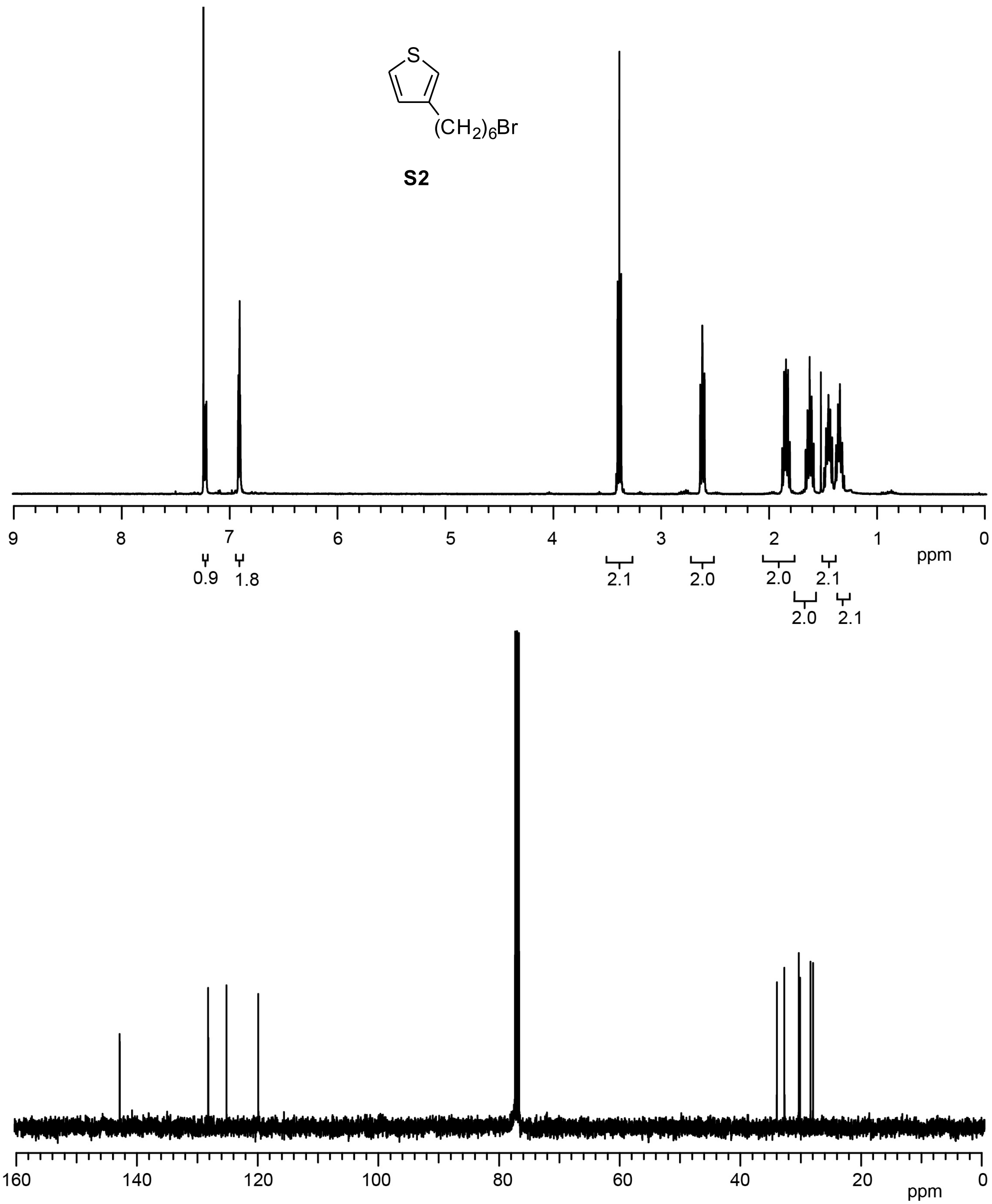


Figure S2. NMR spectra for **S2**. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 (m, 1H), 6.92 (m, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.84 (m, 2H), 1.62 (m, 2H), 1.45 (m, 2H), 1.34 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.98, 128.22, 125.19, 119.92, 33.99, 32.72, 30.33, 30.12, 28.39, 27.97.

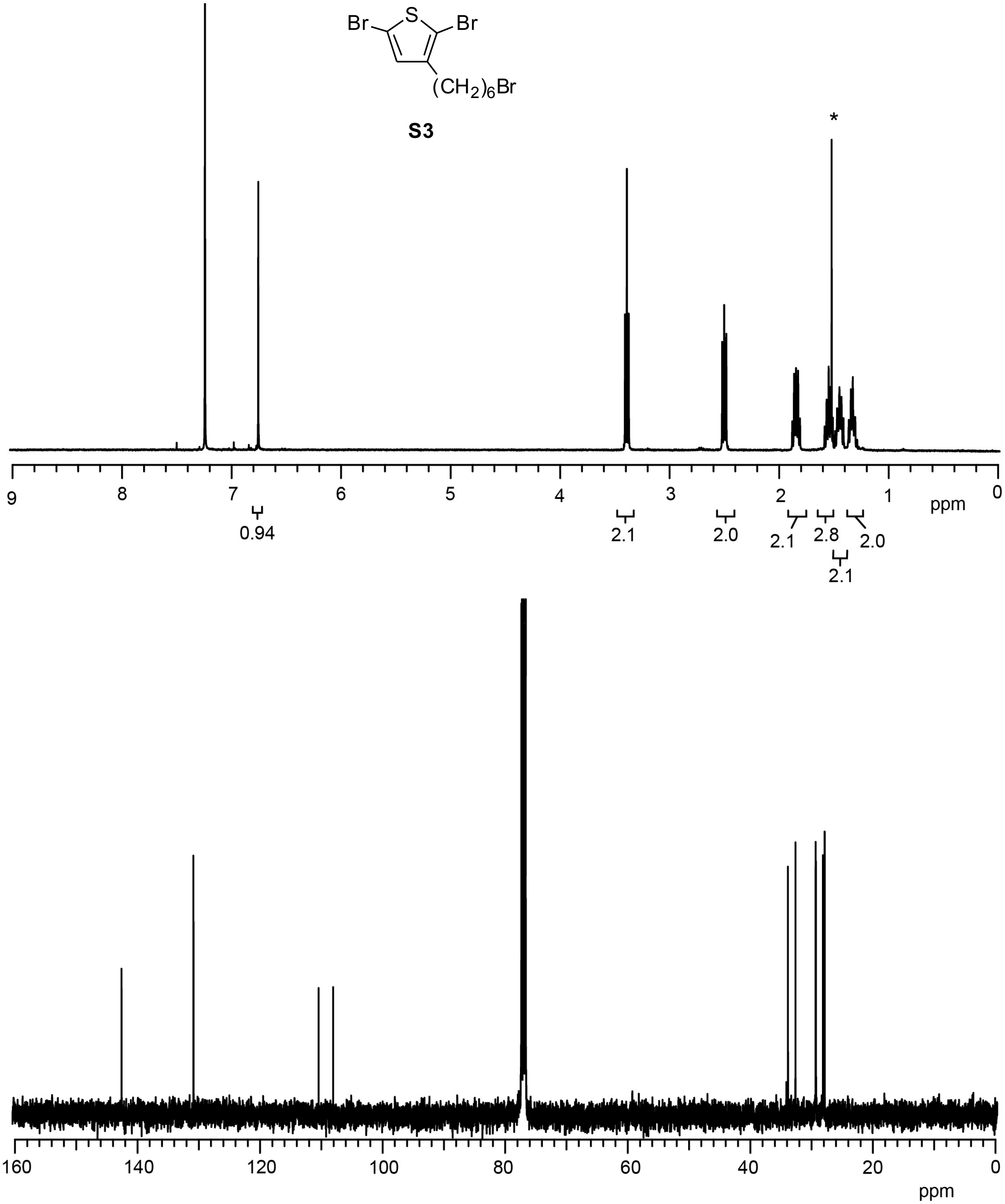


Figure S3. NMR spectra for **S3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 3.39 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.84 (m, 2H), 1.55 (m, 2H), 1.45 (m, 2H), 1.34 (m, 2H). The symbol * denotes residual water in the $CDCl_3$. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.59, 130.86, 110.43, 108.06, 33.85, 32.62, 29.33, 29.27, 29.13, 28.86.

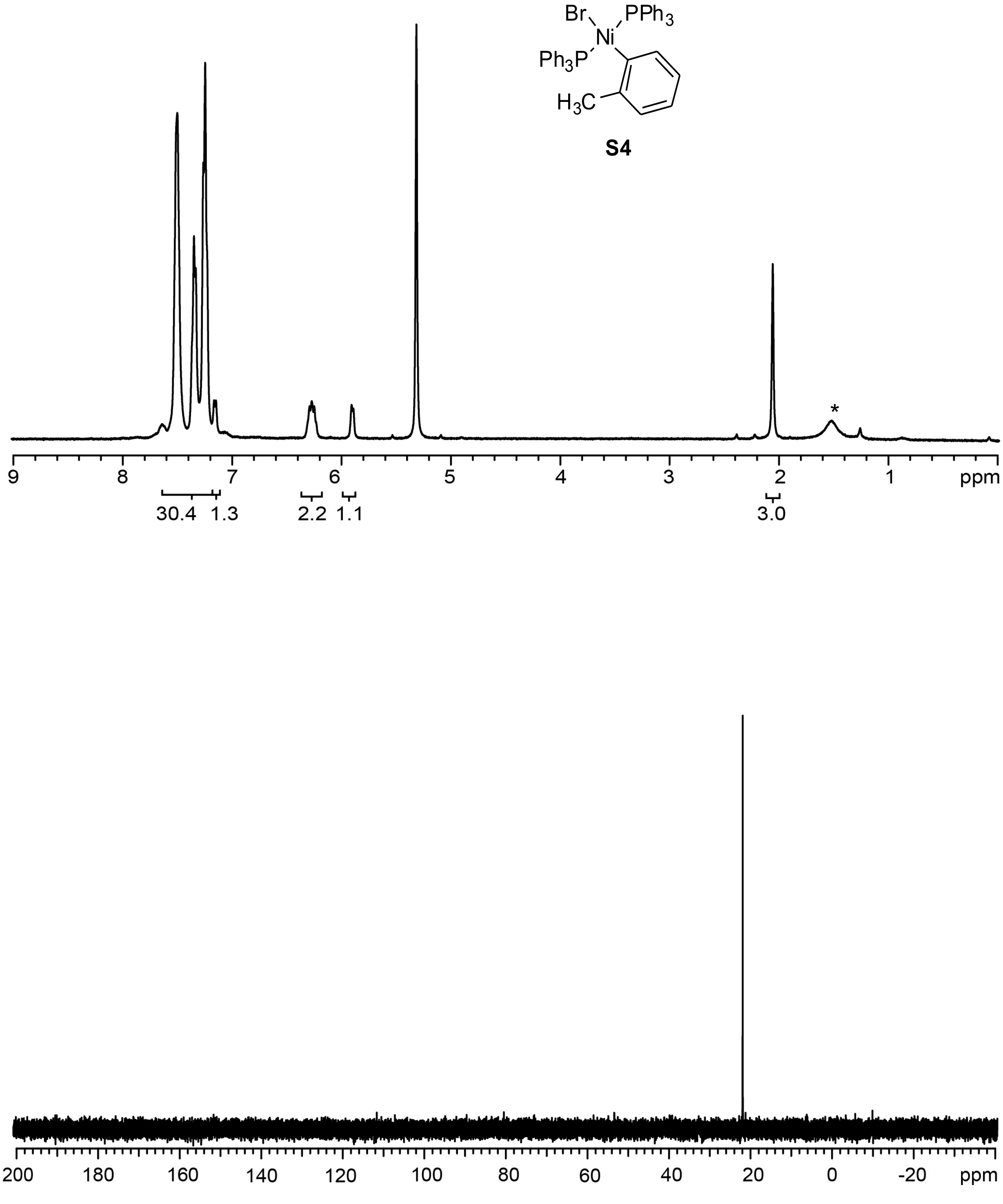


Figure S4. NMR spectra for **S4.** ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50-7.20 (m, 30H), 7.15 (m, 1H), 6.27 (m, 2H), 5.91 (m, 1H), 2.06 (br, 3H). The symbol * denotes residual water in the CD_2Cl_2. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 21.9 (s).

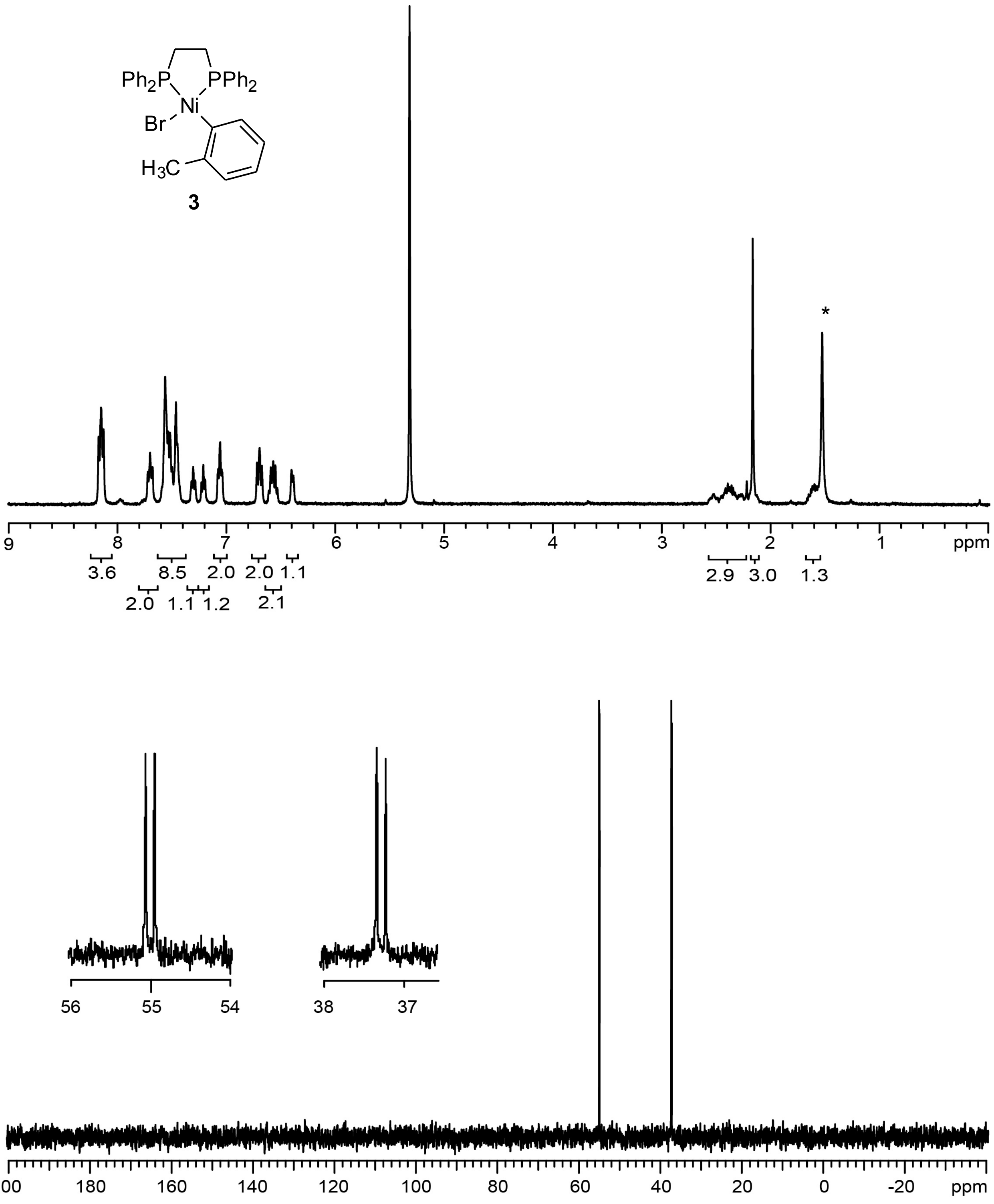


Figure S5. NMR spectra for **3**. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.15 (m, 4H), 7.70 (m, 2H), 7.55-7.46 (m, 9H), 7.30 (t, 1H), 7.21 (t, 1H), 7.06 (m, 2H), 6.69 (m, 2H), 6.57 (m, 2H), 6.39 (m, 1H), 2.5-2.2 (m, 3H), 2.18 (s, 3H), 1.7-1.5 (m, 1H). The symbol * denotes residual water in the CD_2Cl_2. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 55.01 (d, *J* = 18.5 Hz), 37.25 (d, *J* = 18.3 Hz).

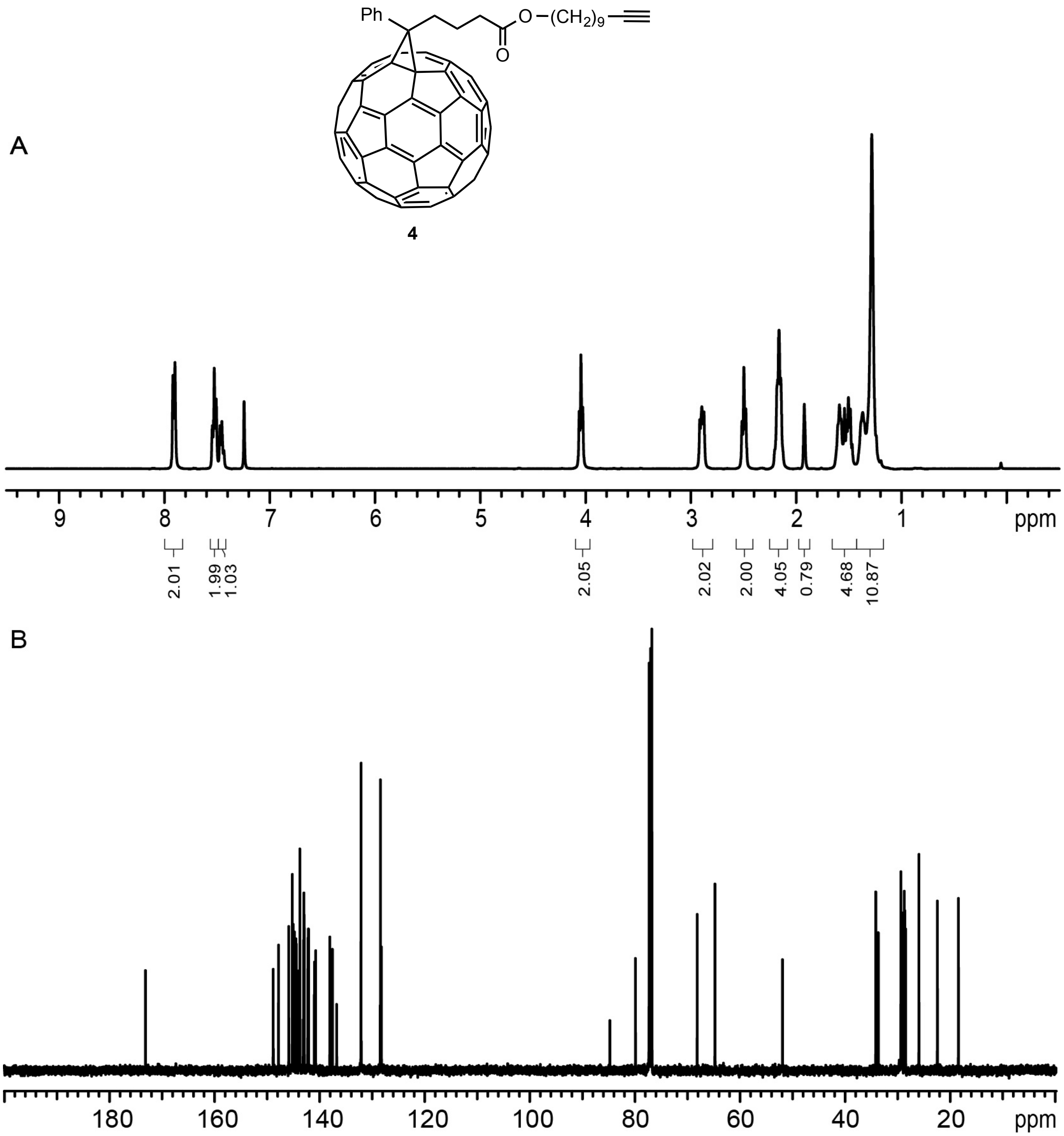


Figure S6. NMR spectra for **4**. (A) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.50 (t, *J* = 6.8 Hz, 2H), 2.16 (t, *J* = 6.0 Hz, 4H), 1.92 (s, 1H), 1.58-1.49 (m, 4H), 1.36-1.28 (m, 10H). (B) ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.13, 148.83, 147.82, 145.86, 145.19, 145.14, 145.09, 145.03, 144.79, 144.78, 144.69, 144.67, 144.51, 144.42, 144.01, 143.76, 143.12, 143.03, 142.99, 142.94, 142.92, 142.24, 142.18, 142.13, 142.11, 140.98, 140.75, 138.05, 137.56, 136.75, 132.11, 128.43, 128. 24, 84.75, 79.90, 77. 28, 77.01, 76.76, 68.14, 64.75, 51.9, 34.15, 33.67, 29.38, 29.22, 29.03, 28.72, 28.63, 28.47, 25.93, 22.43, 18.41.

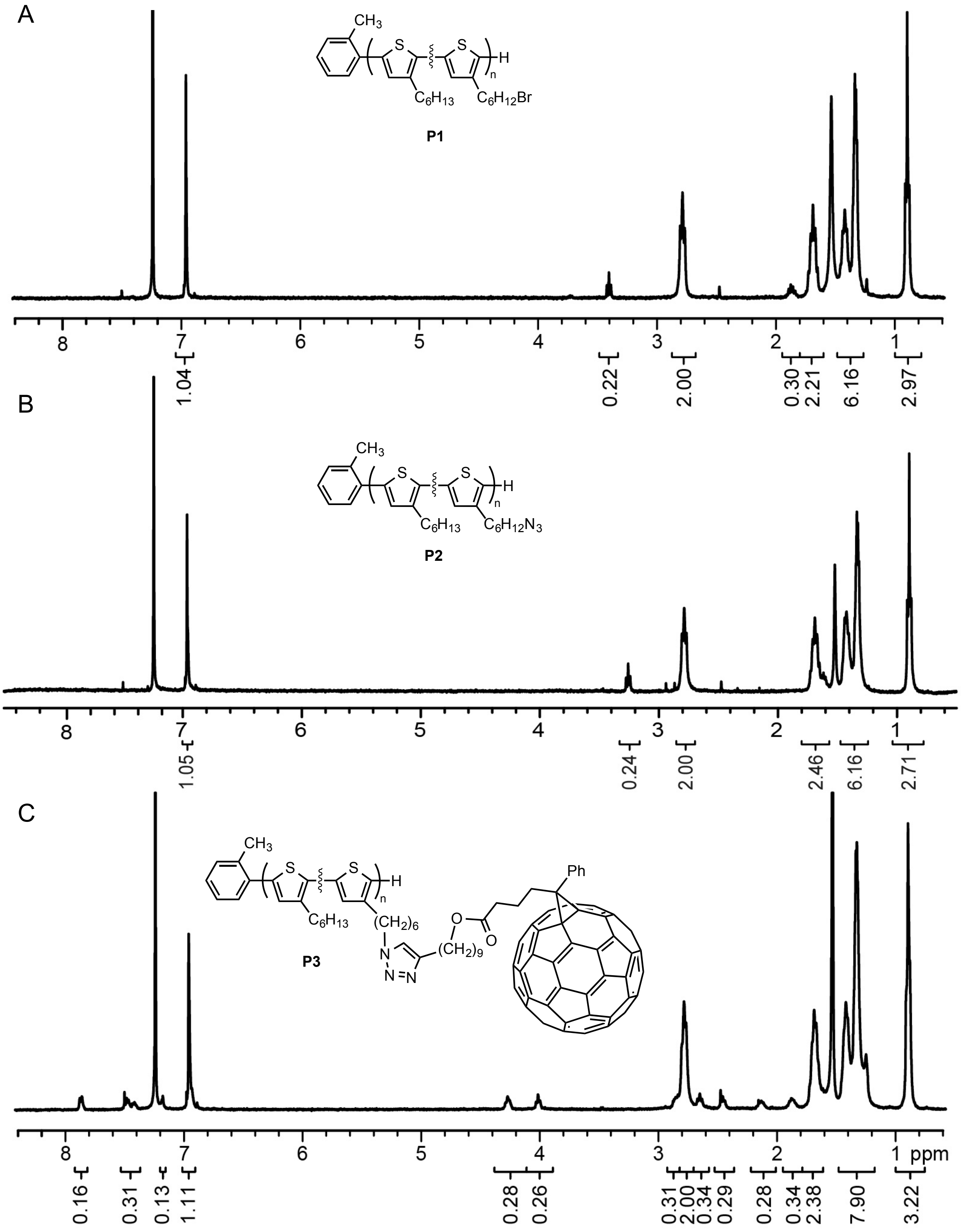


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) for (A) **P1:** δ 6.98 (s, 1H), 3.42 (t, 0.2H), 2.81 (t, 2H), 1.90 (q, 0.2H), 1.71 (m, 2H), 1.48-1.33 (br, 6H), 0.90 (br, 2.8H), (B) **P2:** 6.98 (s, 1H), 3.22 (t, 0.2H), 2.81 (t, 2H), 1.62 (q, 0.2H), 1.71 (m, 2H), 1.48-1.33 (br, 6H), 0.90 (br, 2.8H), (C) **P3**: δ 7.91 (br, 0.2H), 7.52-7.45 (br, 0.4H), 6.98 (s, 1H), 4.24 (br, 0.2H), 4.04 (t, 0.2H), 2.90-2.75 (br, 2H), 2.63 (br, 0.2H), 2.42 (br, 0.2H), 2.17 (br, 0.2H), 1.83 (br, 0.2H), 1.71 (m, 2.2H), 1.48-1.33 (br, 7.2H), 0.90 (br, 2.8H).

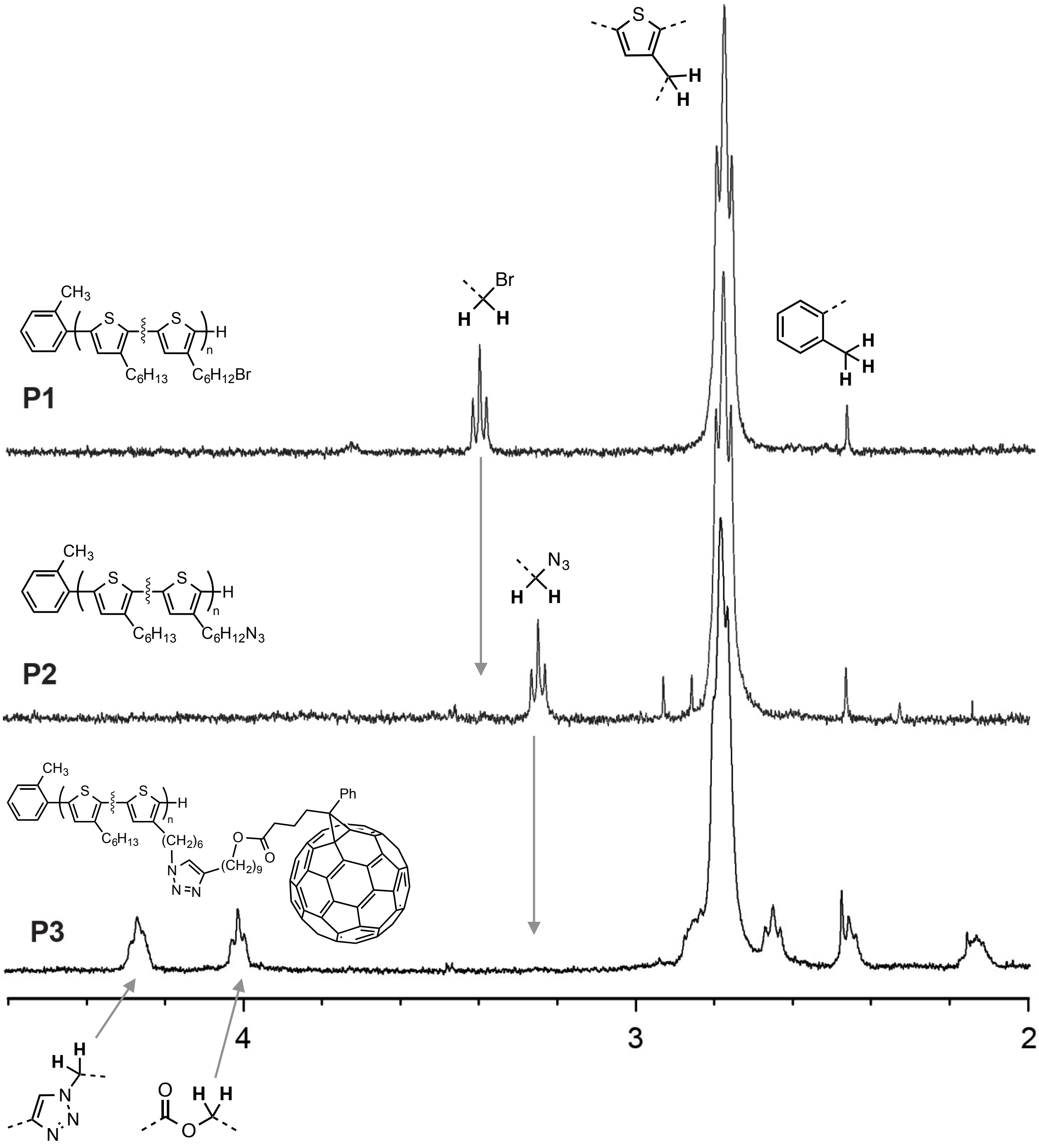


Figure S8. Inset of the NMR spectra in Figure S7, showing the quantitative conversion of bromoalkyl side chains in **P1** to the organoazides in **P2** and finally the triazole linkages in **P3**.

V. Semi-batch Copolymerization Data

Semi-batch copolymerization data for compound **P1**. For a detailed procedure, see page S7.

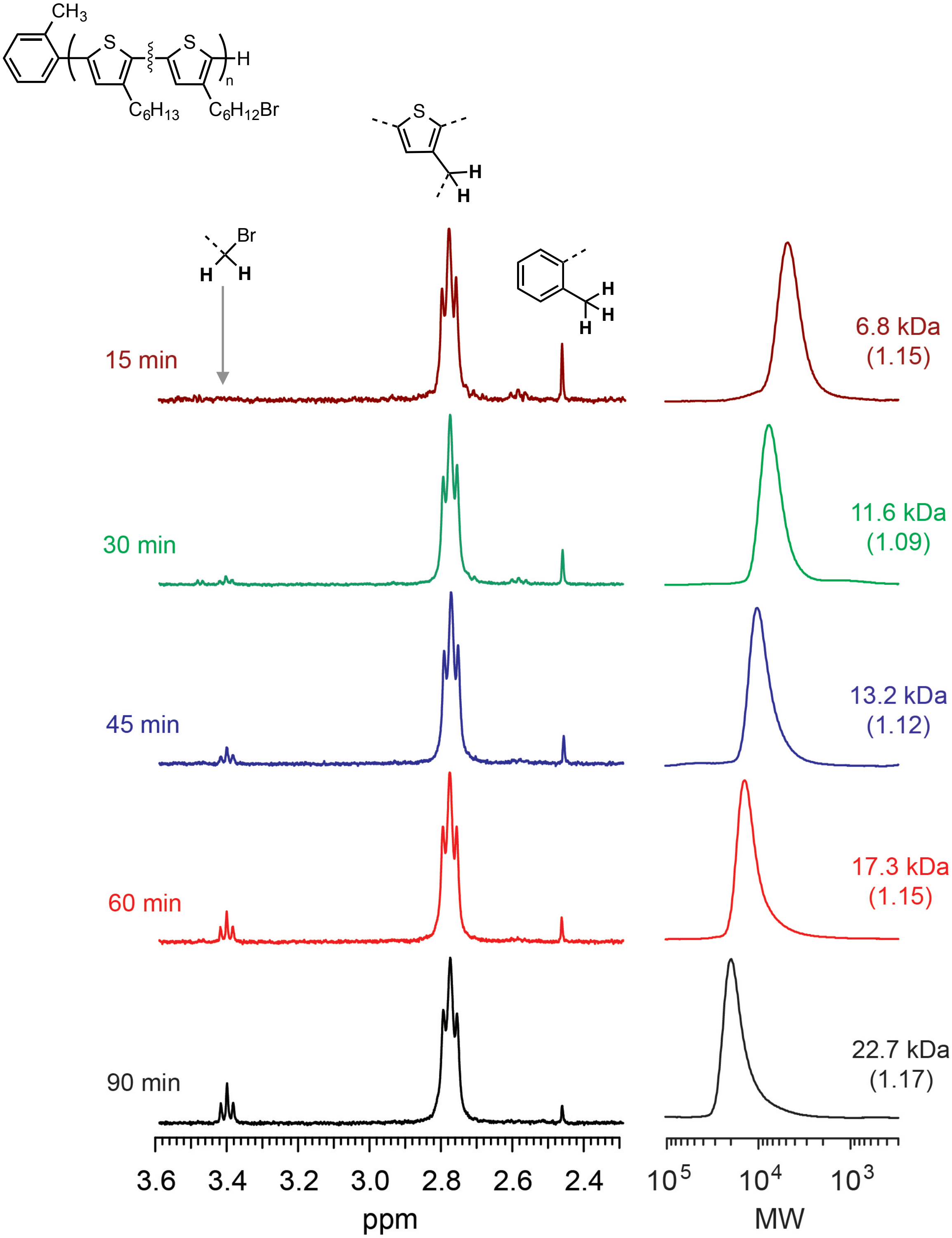


Figure S9. ^{1}H NMR spectra and GPC curves for aliquots drawn during the semi-batch copolymerization, at the times indicated.

Aliquots from the semi-batch copolymerization were analyzed by GPC and NMR (see Figure S9). A plot of cumulative mole fraction of **2** in the copolymer, based on ^{1}H NMR integrations, versus the normalized chain length determined by GPC, reveal a linear relationship indicative of a gradient copolymer (Figure S10A). The Mn rises linearly with time because the syringe pump delivers monomer 2 at the same rate that 1 is being consumed, keeping the monomer concentration roughly constant (Figure S10B). The degree of polymerization (DP) may be calculated based on GPC, relative to PS standards, or based on the absolute measurement by ^{1}H NMR end group analysis. Comparing the results of these two methods, it appears that GPC overestimates the DP of these copolymers by a factor of approximately 1.5 (Figure S10C), in reasonable agreement with a previous report.[5]

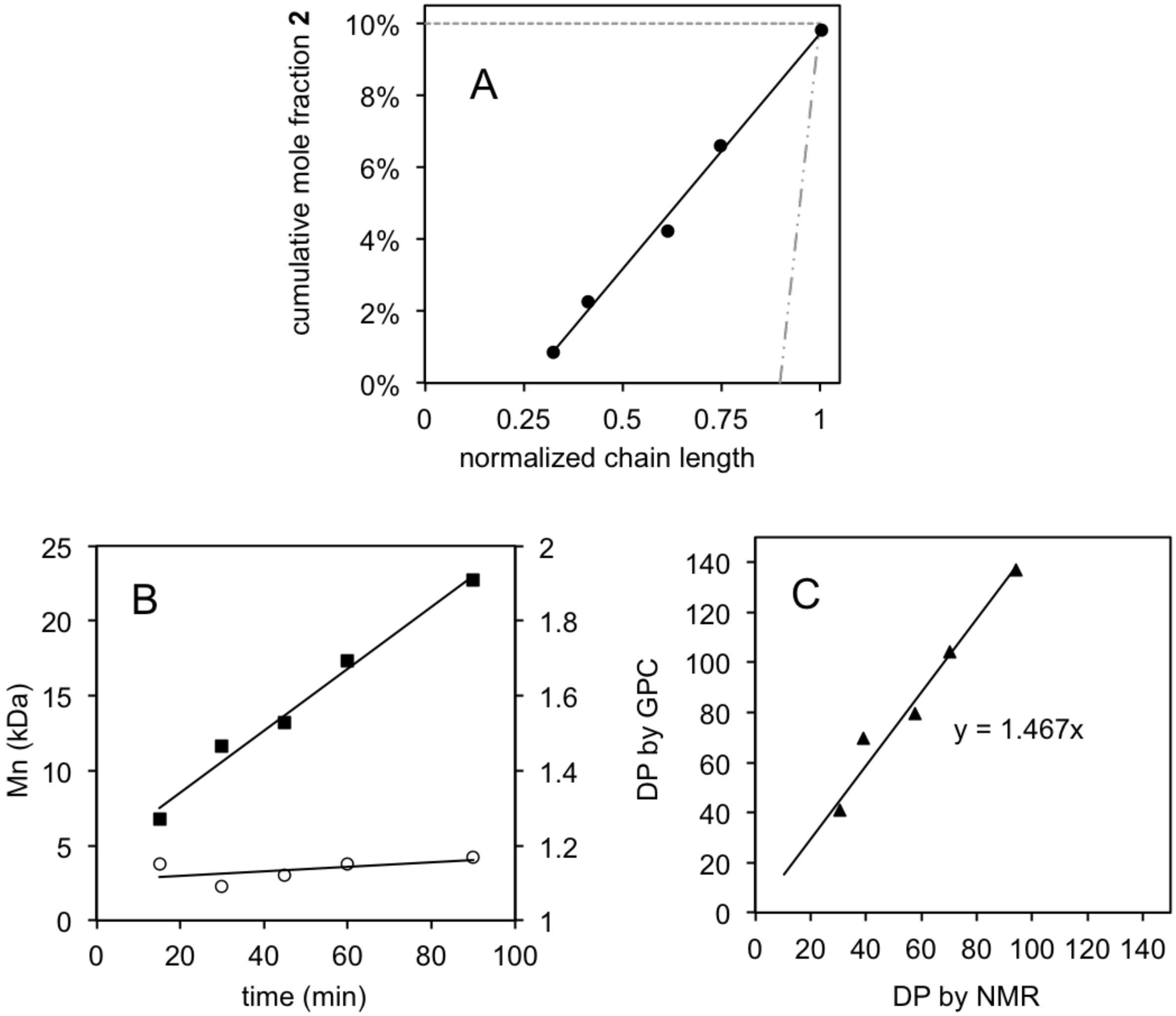


Figure S10. (A) Cumulative mole fraction of comonomer **2** in the copolymer **P1** as a function of normalized chain length, (B) Mn and Đ versus time, and (C) comparison of the degree of polymerization (DP) obtained GPC and 1H NMR end group analysis.

VI. Optimization of Copolymer Composition for CuAAC

A copolymer of **1** and **2** was prepared according to the procedure on page S7 except that the feed molar ratio of **1**:**2** was 80:20 instead of 90:10. This copolymer was converted to the azide functional analogue according to the procedure on page S7 and then reacted with **4** via CuAAC according to the procedure on page S8. GPC raw data for this crude copolymer are given below (Figure S10A) as well as the raw data for the 90:10 copolymers **P1**, **P2**, and **P3** (Figure S10B) for comparison. Clearly, the 80:20 copolymers showed broadening of the molecular weight distribution after the CuAAC step, which is likely due to some cross-linking side reactions. In contrast, the GPC curve for the 90:10 copolymer remains narrow in all three samples.

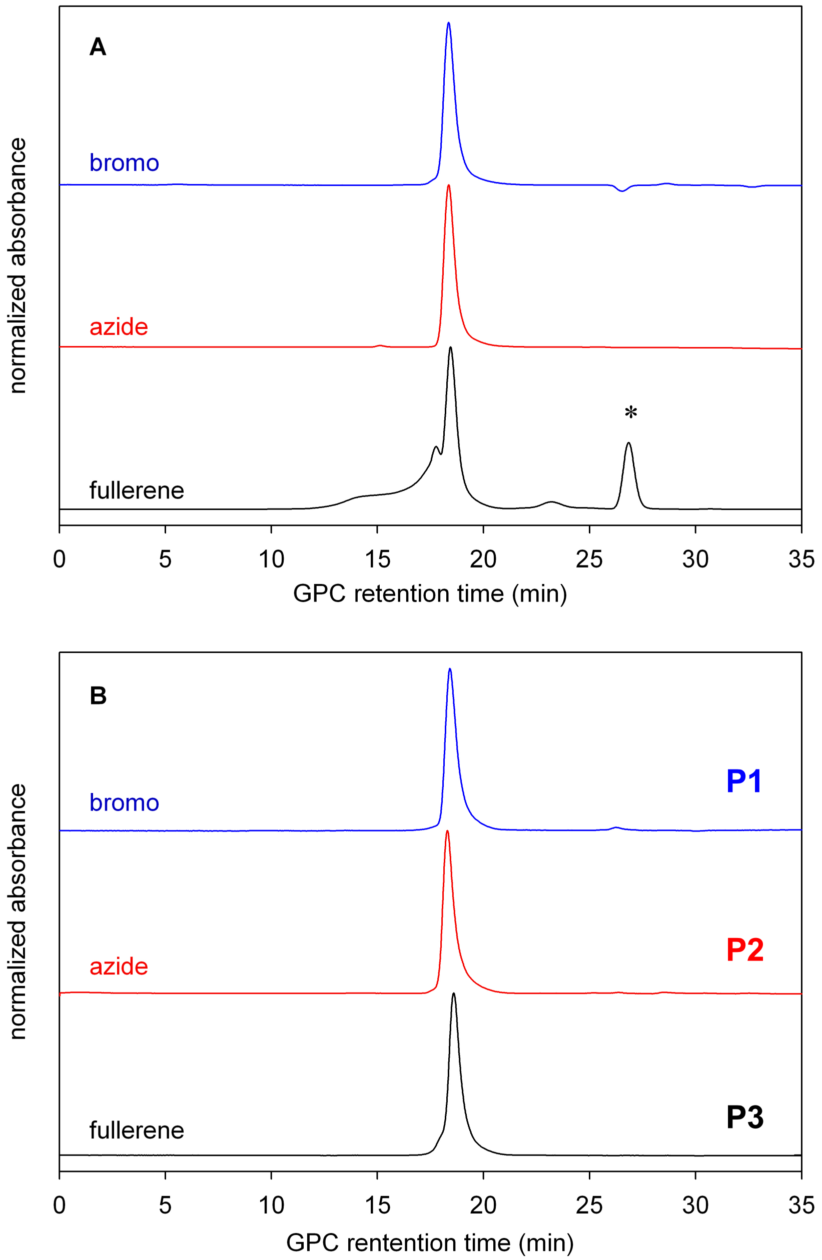


Figure S14. GPC raw data for the bromo, azide, and fullerene functionalized copolymers in (A) 80:20 and (B) 90:10 molar ratios of comonomer **1** to **2**. The * denotes unreacted **4** in the crude product.

VII. UV/Vis Absorbance Spectra

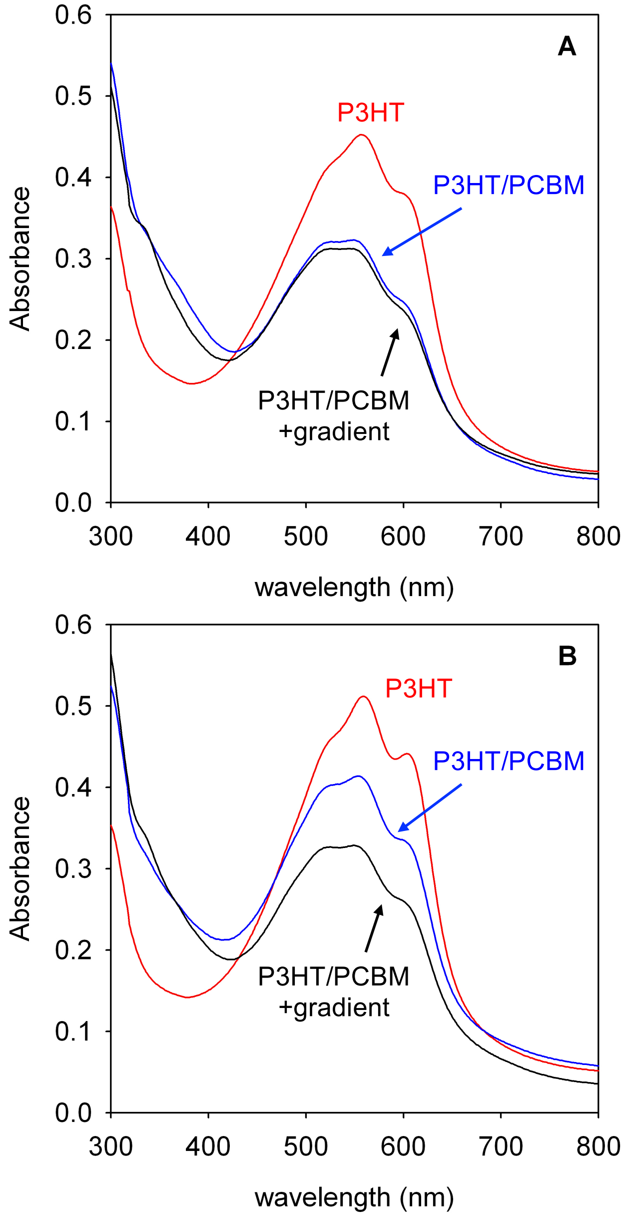


Figure S15. UV-Vis absorbance spectra for thin films of P3HT, P3HT/PCBM blend, and P3HT/PCBM blend containing 10 w% gradient copolymer additive, after thermal annealing at 150 °C for (A) 10 min and (B) 60 min. Procedure for thin film preparation is given on page S2.

VIII. Optical Microscopy Images

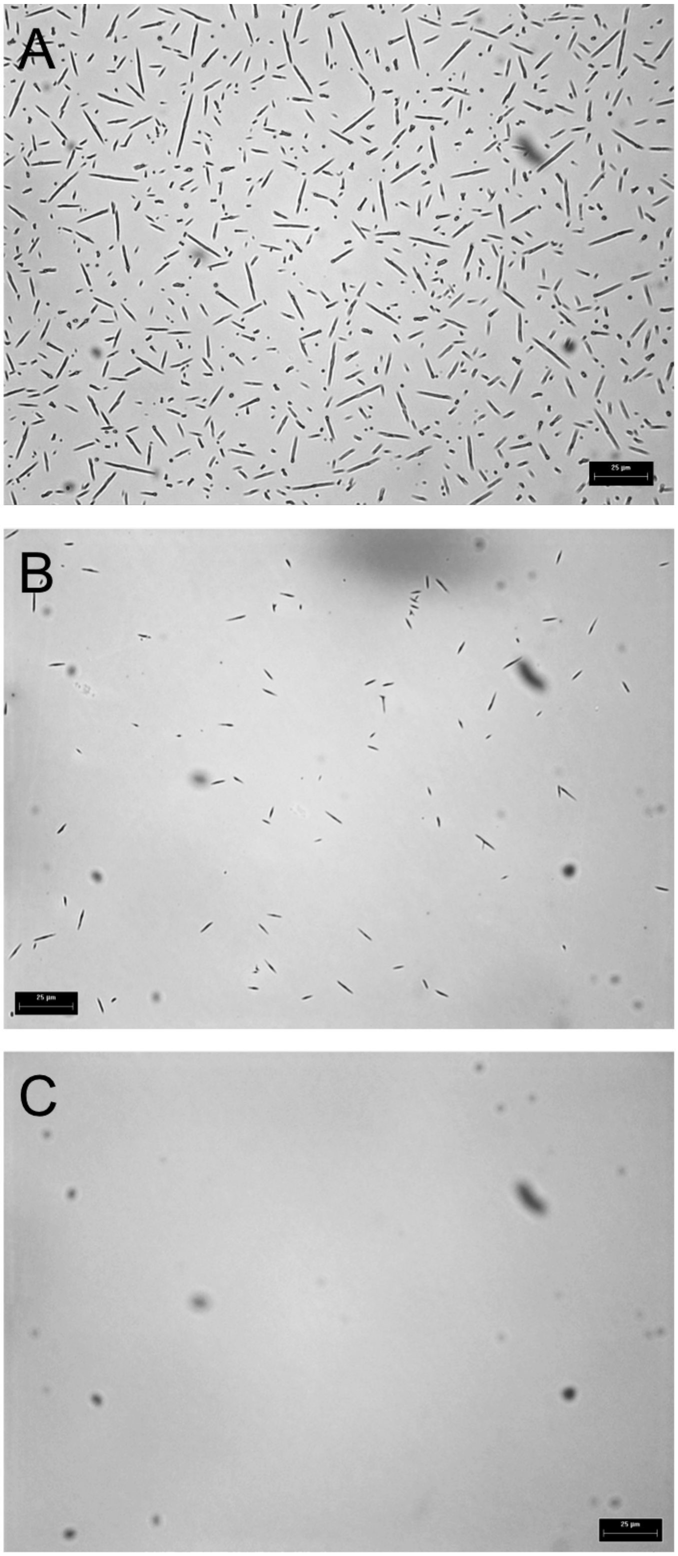


Figure S16. Optical Microscopy Images of P3HT/PCBM thin films after 60 min annealing with (A) 0, (B) 1, and (C) 10 wt% gradient copolymer additive.

IX. Photoluminescence Data

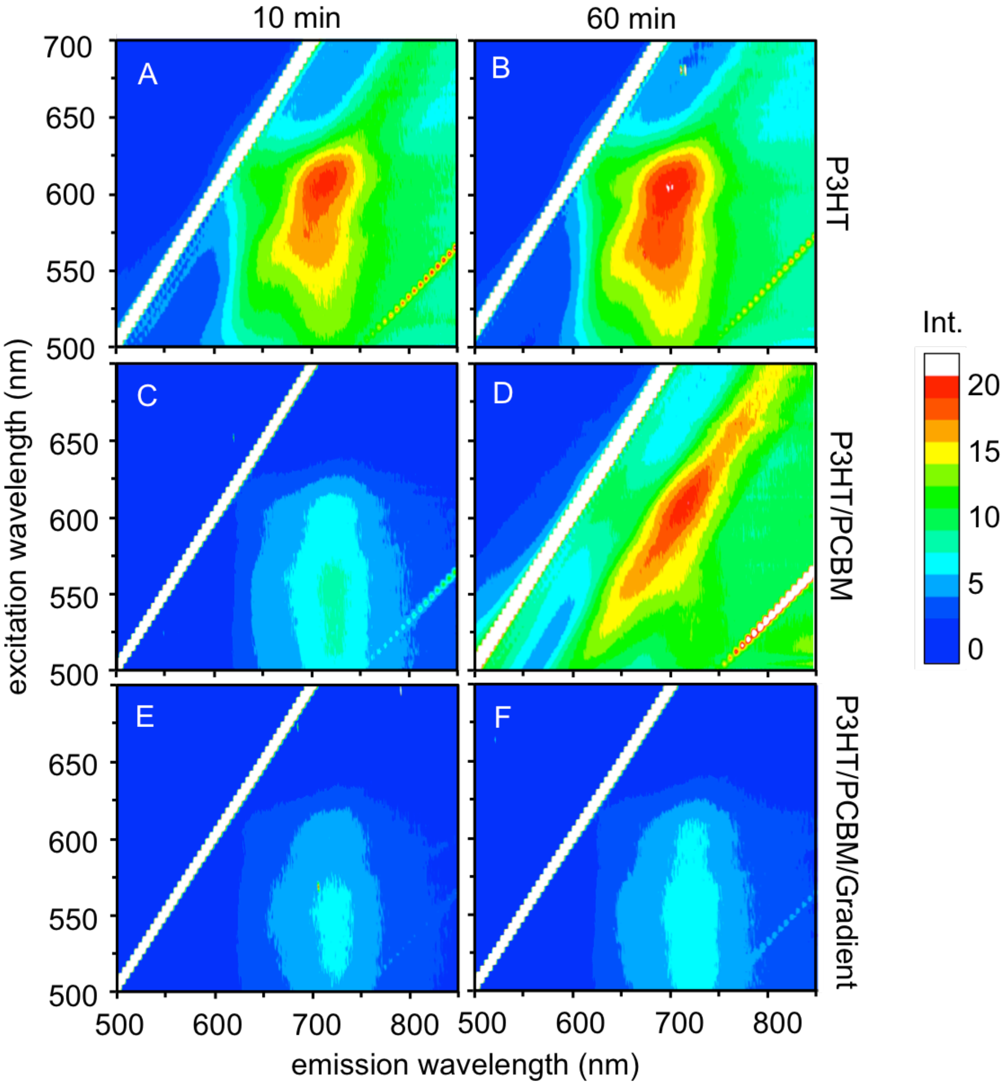


Figure S17. Photoluminescence intensity for P3HT, P3HT/PCBM, and P3HT/PCBM + 10 wt% gradient copolymer additive after annealing at 150 °C for 10 or 60 min, as indicated.

Table S1. PL maxima wavelengths and intensities from Figure S17.

Sample	**Anneal time (min)**	**PL λ_{max} (nm)**		**PL Intensity (arb)**	**PL Intensity (rel)**
		Excitation	**Excitation**		
P3HT	10	703	604	24423	1.0
P3HT/PCBM	10	724	552	6730	0.28
P3HT/PCBM/gradient	10	725	552	5442	0.22
P3HT	60	713	604	20457	1.0
P3HT/PCBM	60	715	608	19643	0.96
P3HT/PCBM/gradient	60	723	556	6008	0.29

X. Dark Current and Photocurrent Data

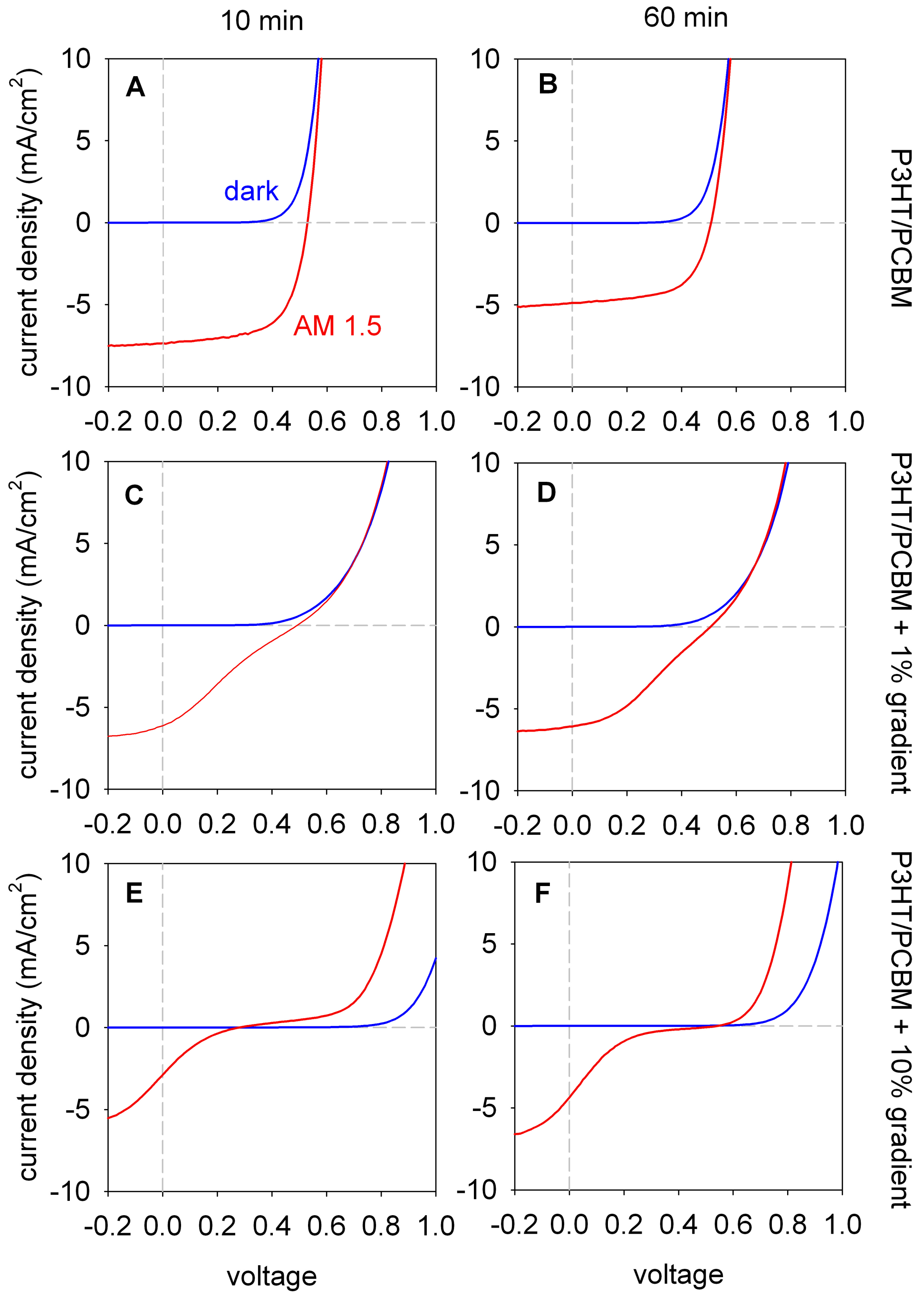


Figure S18. Current-voltage characteristics for the bulk heterojunction devices with the lamp off (blue curves) and lamp on (red curves). The device active layer was composed of P3HT/PCBM blend with (A,B) 0, (C,D) 1, and (E,F) 10 wt% gradient copolymer additive. Thermal annealing at 150 °C for (A,C,E) 10 min or (E,D,F) 60 min. Procedure for BHJ device fabrication is given on page S3.

XI. Solar Cell Performance Data

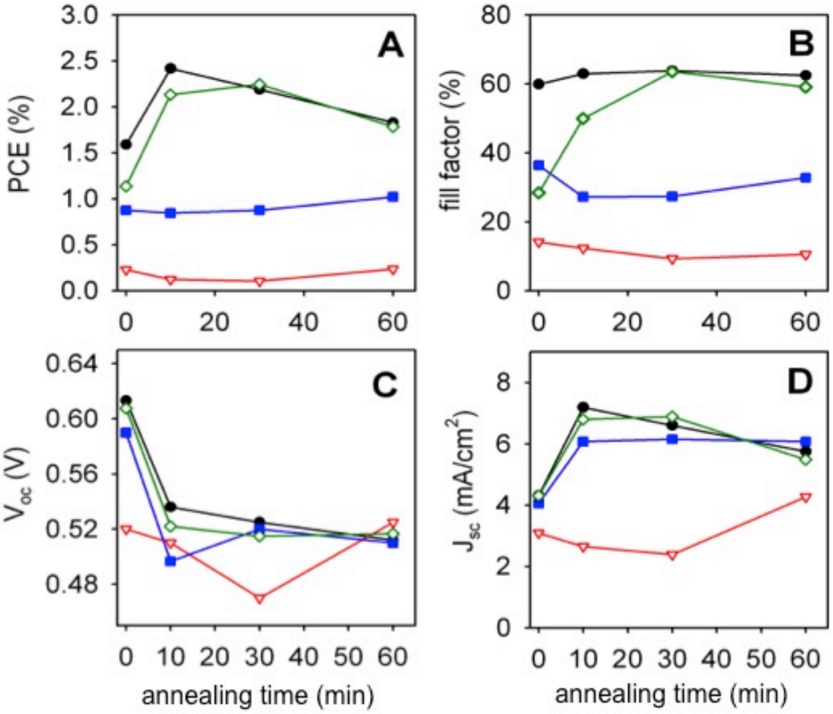


Figure S19. Solar cell performance data for bulk heterojunction solar cells based on P3HT/PCBM active layers with or without gradient copolymer additive. (A) PCE, (B) FF, (C) V_{oc}, and (D) J_{sc} as a function of annealing time at 150 °C containing 0 (black circles), 0.1 (green diamonds), 1 (blue squares), or 10 (red triangles) wt% gradient copolymer additive in the P3HT/PCBM blend.

XII. Powder X-ray Diffraction Data

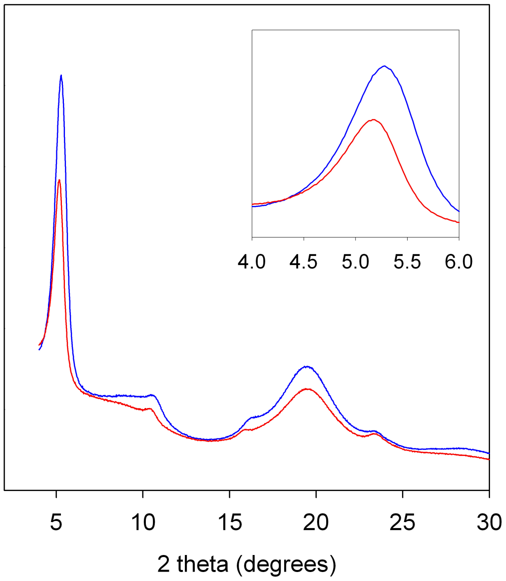


Figure S20. Powder X-ray Diffraction pattern for P3HT/PCBM blends without (blue) and with (red) 10 wt % gradient copolymer additive. Solutions were drop-cast from $CHCl_3$ onto glass slides held at 50 °C for 2 min.

XIII. Differential Scanning Calorimetry Data

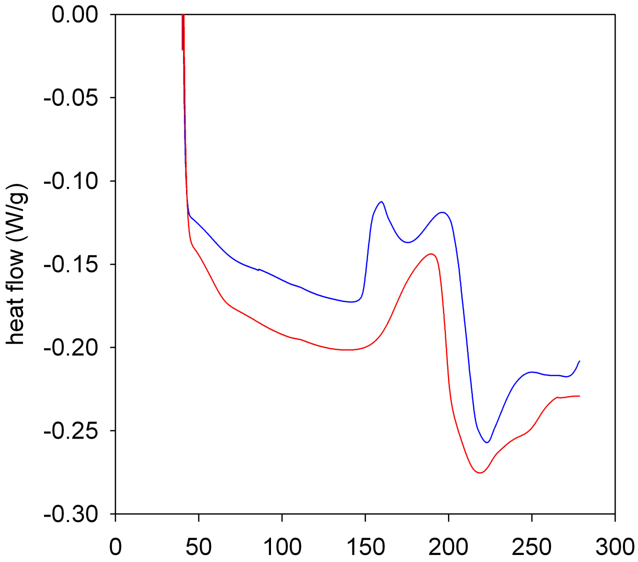


Figure S21. Differential Scanning Calorimetry data for P3HT/PCBM blends without (blue) and with (red) 10 wt % gradient copolymer additive. Solutions were drop-cast from $CHCl_3$ onto glass slides held at 50 °C for 2 min.

XIV. References

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[1] L. Zhai, R. L. Pilston, K. L. Zaiger, K. K. Stokes and R. D. McCullough, *Macromolecules*, 2003, **36**, 61-64.

[2] (a) E. L. Lanni and A. J. McNeil, *Macromolecules*, 2010, **43**, 8039-8044; (b) S. R. Lee, J. W. G. Bloom, S. E. Wheeler and A. J. McNeil, *Dalton Trans*, 2013, **42**, 4218-4222; (c) S. R. Lee, Z. J. Bryan, A. M. Wagner and A. J. McNeil, *Chem Sci*, 2012, **3**, 1562-1566.

[3] R. S. Loewe, P. C. Ewbank, J. S. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001,**34**, 4324-4333.

[4] S. Miyanishi, Y. Zhang, K. Hashimoto and K. Tajima, *Macromolecules*, 2012, **45**, 6424-6437.

[5] M. Wong, J. Hollinger, L. M. Kozycz, T. M. McCormick, Y. J. Lu, D. C. Burns and D. S. Seferos, *ACS Macro Lett*, 2012, **1**, 1266-1269.