Supplementary Information

Synthesis of a Soluble Adenine-Functionalized Polythiophene through Direct Arylation Polymerization and its Fluorescence Responsive Behavior

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Materials and Methods

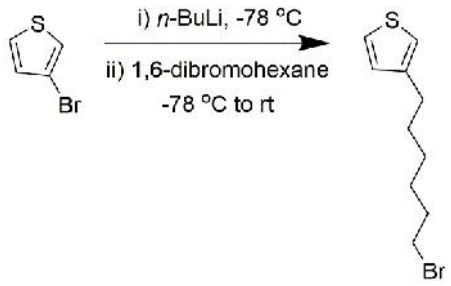
All chemicals and solvents were purchased from Sigma-Aldrich or Fisher Scientific and used as received, unless stated otherwise. Tetrakistriphenylphosphine palladium(0) ($Pd(PPh_3)_4$) was purchased from Strem Chemicals and used without extra purification. Toluene, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were purified using an Innovative Technologies MD-5 Solvent Purification System and degassed prior to use. *N*-Bromosuccinimide (NBS) was recrystallized from hot water prior to use. All synthesized materials were purified via column chromatography using 60 Å silica gel (40-63 μm, Sorbent Technologies).

^{13}C and ^{1}H, gradient-enhanced heteronuclear multiple bond correlation (gHMBC) and gradient-enhanced heteronuclear single quantum coherence (gHSQC) NMR spectra of synthesized molecules or polymers were acquired using a Varian VNMRS 500 MHz NMR or a Varian Mercury Vx 300 MHz at room temperature using 15–20 mg mL^{-1} solutions in deuterated chloroform ($CDCl_3$). Chemical shifts are reported in units of δ (ppm) and referenced to the residual solvent peak. Mass spectrometry measurements used a JEOL AccuTOF DART mass spectrometer with toluene solutions at ~1 mg/mL. The average molecular weight and dispersity of synthesized polymers were determined by gel permeation chromatography (GPC) using universal calibration analysis based on polystyrene (PS) standards (Agilent, EasiVial PS-M, MW 162, 370, 945, 1,230, 3,090, 6,320, 13,000, 27,800, 45,100, 107,000, 217,000, 364,000 g/mol). For this, an Agilent 1260 Infinity II isocratic pump equipped with two Agilent (7.5 × 300 mm) mixed-D type columns in sequence was used. This instrument features a Wyatt Dawn® Helios® 8 Multi-Angle Light Scattering Detector, ViscoStar® III viscometer, and an Optilab® T-rEX™ RI detector. Samples were dissolved in THF at nominal concentrations of 5 mg/mL and passed through a 0.2 μm PTFE filter prior to analysis. The flow rate of the THF mobile phase was set at 1 mL/min. Thermal

stability of the polymers in a nitrogen (N_2) atmosphere was determined using a TA Instruments Q50 Thermogravimetric Analyzer (TGA). The protocol used consisted of ramping from room temperature to 800 °C using a heating rate of 10 °C/min with the analytes in a platinum pan. Thermal transitions were measured by differential scanning calorimetry (DSC) using a TA Instruments Q-2000 DSC. Samples of nominally ~5 mg were sealed standard aluminum pans and subjected to a heat–cool–heat cycle from −40 °C to 270 °C at a heating rate of 10 °C/min and a cooling rate of 10 °C/min under an N_2 atmosphere. Optical absorbance spectra were acquired using a Thermo Scientific Evolution 600 UV-Vis spectrophotometer by scanning from 225–650 nm. The polymer solution concentration was fixed at 0.01 mg/mL. Fluorescence emission spectra were acquired from polymer solutions (at 0.01 mg/mL in $CHCl_3$ and either 0.01 mg/mL or 0.02 mg/mL in THF) using a Cary Eclipse fluorescence spectrophotometer. An excitation wavelength of 360 nm was used, and emission measured by scanning from 370-700 nm.

Synthesis of Small Molecules and Monomers

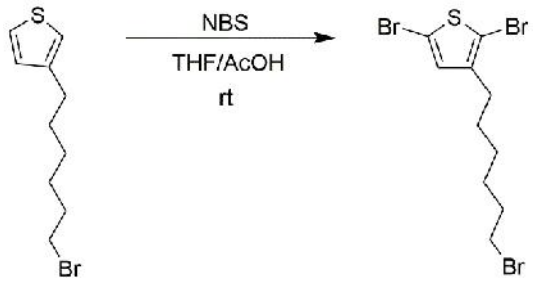
Synthesis of 3-(6-bromohexyl)thiophene:



3-(6-Bromohexyl)thiophene was synthesized following procedures described by McNeil et al.[1] The product was extracted using 100 mL of diethyl ether and the organic phase was dried over $MgSO_4$, filtered, and then concentrated via rotary evaporation. Excess 1,6-dibromohexane was removed by vacuum distillation at 65 °C (at 30 mTorr) and the retained product was purified

by silica gel column chromatography using hexane. The product was recovered as a colorless oil with a 70% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.24 (dd, 1H, *J* = 4.9, 3.0 Hz), 6.94 – 6.90 (m, 2H), 3.41 (t, 2H, *J* = 6.7 Hz), 2.64 (t, 2H, *J* = 7.5 Hz), 1.90 – 1.83 (m, 2H) 1.68 – 1.61 (m, 2H), 1.51 – 1.44 (m, 2H) 1.40 – 1.33 (m, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 142.9, 128.2, 125.2, 119.9, 33.9, 32.7, 30.3, 30.1, 28.4, 28.0. AccuTOF DART: calc'd [M+H$^+$]: 247.0156, found [M+H$^+$] 247.0155.

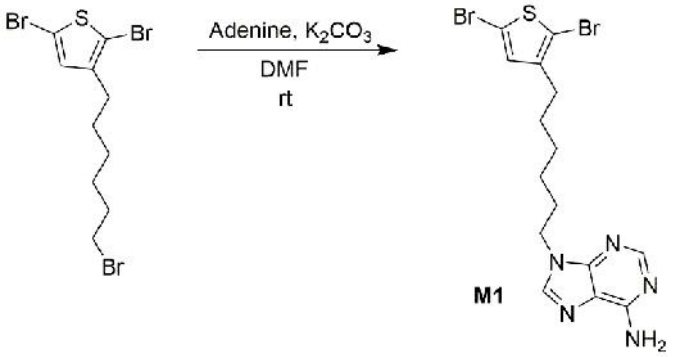
Synthesis of 2,5-dibromo-3-(6-bromohexyl)thiophene:



An oven-dried 3-neck round bottom flask was cooled to room temperature under vacuum. To ensure an inert environment, the flask was evacuated and then refilled 3× with Ar. A solvent mixture consisting of 25 mL of dry and degassed THF and 25 mL of glacial acetic acid (AcOH) was added via syringe. 3-(6-bromohexyl) thiophene (0.985 g, 4 mmol, 1 equiv.) was added to the THF/AcOH mixture and stirred for 30 min at room temperature. Under positive argon pressure, 1.495 g of freshly recrystallized NBS (8.4 mmol, 2.1 equiv.) was added in one portion to the mixture and the flask was covered from light. The resulting mixture was stirred for 3 h at room temperature. After this time, the reaction was quenched by adding a saturated solution of sodium bicarbonate. The product was extracted with 100 mL of diethyl ether and the aqueous phase was discarded. The organic phase was washed with brine, isolated, then dried over $MgSO_4$. The $MgSO_4$

was removed by filtration, and the product was concentrated via rotary evaporation. The product was then purified via silica gel column chromatography using hexane as the mobile phase. The product was subsequently was collected as a colorless oil with a yield of 75%. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 6.77 (s, 1H), 3.40 (t, 2H, *J* = 6.8 Hz), 2.52 (t, 2H, *J* = 7.6 Hz), 1.91 – 1.81 (m, 2H) 1.62 – 1.52 (m, 2H), 1.50 – 1.40 (m, 2H) 1.40 – 1.30 (m, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 142.6, 130.9, 110.5, 108.1, 33.8, 32.6, 29.34, 29.29, 28.2, 27.9. AccuTOF DART: calc'd [M+H$^+$]: 404.8346, found: 404.8312.

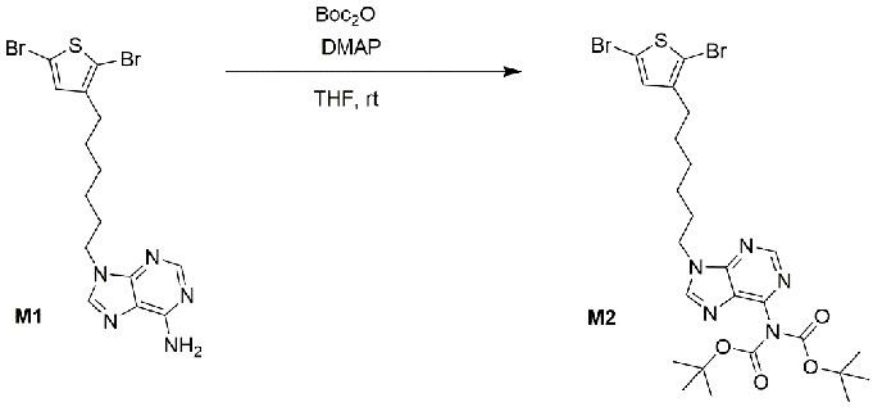
Synthesis of adenine-functionalized dibromothiophene monomer, (9-(6-(2,5-dibromothiophen-3-yl)hexyl)-9H-purine-6-amine), **M1**:



50 mL of dry and degassed DMF was added to a dry 100 mL round bottom flask under positive Ar pressure. Then, 821 mg (2.03 mmol, 1 equiv.) of 2,5-dibromo-3-(6-bromohexyl)thiophene, 547 mg (4.05 mmol, 2 equiv.) of adenine, and 839 mg (6.08 mmol, 3 equiv.) of potassium carbonate (K_2CO_3) were added to the mixture under a stream of Ar. The mixture was stirred at room temperature for 24 h. After this time, the solvent was removed under high vacuum at 50 °C. Then, the product was extracted using 100 mL of CH_2Cl_2 (DCM) and washed with water and a brine solution. Silica gel column chromatography was used to isolate the *N*-9 the product using 5 vol% MeOH in DCM as the mobile phase. The *N*-9 alkylated compound

was collected as the major product as a white solid at 55% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35 (s, 1H, adenine-C2-H), 7.77 (s, 1H, adenine-C8-H), 6.72 (s, 1H, thiophene-C4-H), 6.13 (s, 2H, adenine-NH_2) 4.17 (t, 2H, *J* = 7.2 Hz, adenine-N9-CH_2), 2.46 (t, 2H, *J* = 7.5 Hz, thiophene-C3-CH_2), 1.96 – 1.81 (m, 2H) 1.58 – 1.44 (m, 2H), 1.40 – 1.28 (m, 4H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 155.6 (adenine-C6), 152.9 (adenine-C2), 150.1 (adenine-C4), 142.5 (thiophene-C3), 140.3 (adenine-C8), 130.8 (thiopehen-C4), 119.7 (adenine-C5), 110.5 (thiophene-C5), 108.1 (thiophene-C2), 43.9(adenine-N9-CH_2), 30.0, 29.3, 29.2, 28.4, 26.4. AccuTOF DART: calc'd [M+H^+]: 459.9629, found: 459.9484.

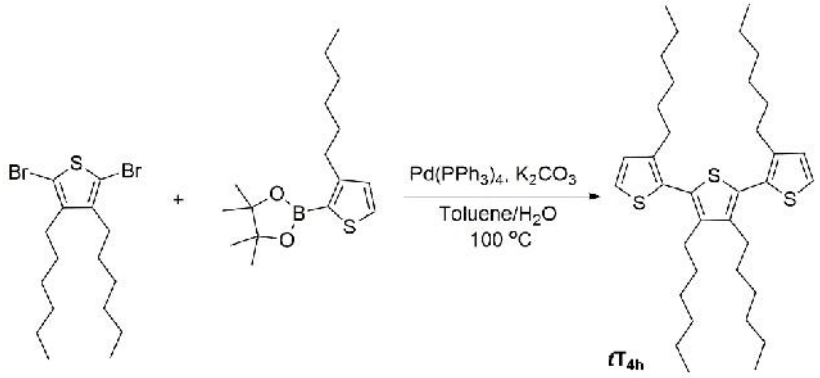
Synthesis of Boc-protected adenine-functionalized monomer, **M2**:



50 mL of dry and degassed THF was added to a dry 100 mL round bottom flask under positive argon pressure. 485.3 mg (1.06 mmol, 1 equiv.) of (9-(6-(2,5-dibromothiophen-3-yl)hexyl)-9H-purine-6-amine) was added to the flask. Then, 38 mg (0.311 mmol, 0.3 equiv.) of 4-dimethylaminopyridine (DMAP) was added to the solution followed by 694 mg of di-*tert*-butyl dicarbonate (Boc_2O, 3.18 mmol, 3 equiv.). (All were added under positive Ar pressure.) The reaction flask was equipped with a mineral oil bubbler to allow carbon dioxide (CO_2) that is produced to be released, and the mixture was stirred for 24 h. After this time, the solvent was

removed by rotary evaporation. Silica gel column chromatography was used to recover the desired product, using 3 vol% MeOH in DCM as the mobile phase. The bis-*N*-Boc protected product was collected as a pale brownish oil in 95% yield.^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.77 (s, 1H, adenine-C2-H), 8.00 (s, 1H, adenine-C8-H), 6.66 (s, 1H, thiophene-C4-H), 4.19 (t, 2H, *J* = 7.2 Hz, adenine-N9-CH_2), 2.39 (t, 2H, *J* = 7.5 Hz, thiophene-C3-CH_2), 1.92 – 1.79 (m, 2H) 1.50 – 1.40 (m, 2H), 1.36 (s, 18H, CH_3), 1.31 – 1.22 (m, 4H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 153.4 (adenine-C4), 151.8 (adenine-C2), 150.4 (Boc-carbonyl), 150.1 (adenine-C6), 144.7 (adenine-C8), 142.4 (thiophene-C3), 130.8 (thiophene-C4), 128.7 (adenine-C5), 110.4 (thiophene-C5), 108.0 (thiophene-C2), 83.5 (Boc-tertiary carbon), 44.1 (adenine-N9-CH_2), 29.7, 29.2, 29.1, 28.3, 27.7 (Boc-methyls), 26.3. AccuTOF DART: calc'd [M+H$^+$]: 660.0678, found: 660.05927.

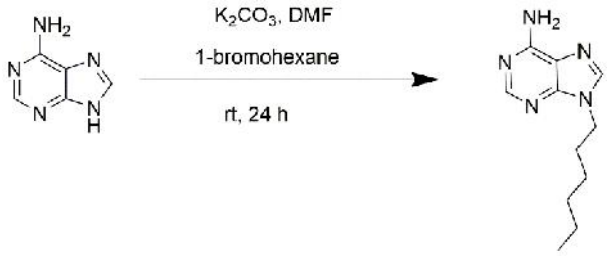
Synthesis of terthiophene comonomer, 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene, ***t*T$_{4h}$**:



30 mL of dry and degassed toluene was added to a dry 100 mL round bottom flask under positive argon pressure. 615.4 mg (483 µL, 1.5 mmol, 1 equiv.) of 2,5-dibromo-3,4-dihexylthiophene was added to the flask. Then, 1103 mg (1.291 mL, 3.75 mmol, 2.5 equiv.) of 3-hexylthiophene-2-boronic acid pinacol ester was added to the solution. While the flask was under positive argon pressure, 86.6 mg (0.075 mmol, 0.05 equiv.) of tetrakis(triphenylphosphine) palladium (0) ($Pd(PPh_3)_4$) and then 30 mL of a 2M aqueous K_2CO_3 solution (20 equiv.) were added

to the reaction mixture. After adding the K_2CO_3, a reflux condenser was attached to the flask and the mixture was stirred for 24 h in an oil bath set to 100 ^oC. After this time, the reaction was quenched by adding 50 mL of water. The reaction mixture was extracted with 100 mL of toluene and the extract was washed with water and a brine solution. Toluene was removed under reduced pressure and the product was purified via column chromatography using hexanes as the mobile phase. The product was collected as a colorless oil in 80% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.28 (d, 2H, *J* = 5.3 Hz, thiophene-C5), 6.96 (d, 2H, *J* = 5.3 Hz, thiophene-C4), 2.58-2.44 (m, 8H, thiophene-CH_2), 1.62-1.50 (m, 4H, thiophene-alkyl) 1.49-1.37 (m, 4H, thiophene-alkyl), 1.30-1.19 (m, 24H, thiophene-alkyl) 0.91-0.82 (m, 12H, thiophene-alkyl-CH_3 ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 142.20 (thiophene-C2), 141.82 (thiophene-C2'), 129.37 (thiophene-C3'), 129.11 (thiophene-C3), 128.51 (thiophene-C4), 125.02 (thiophene-C5), 31.64, 31.49, 30.74, 30.66, 29.42, 29.13, 28.89, 28.00, 22.58, 22.53, 14.07, 14.04. AccuTOF DART: calc'd [M+H$^+$]: 585.3622, found: 585.3527.

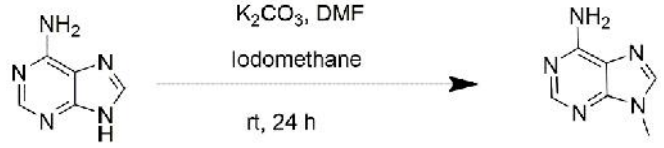
Synthesis of N-hexyl-adenine:



Adenine (540 mg, 4 mmol, 1 equiv.) was dissolved in 50 mL of dry DMF in a 150 mL round bottom flask under an Ar atmosphere. Then, 1-bromohexane (556 µL, 660 mg, 6 mmol, 1.5 equiv.) and K_2CO_3 (1.104 g, 8 mmol, 2 equiv.) were added to the flask under a positive Ar atmosphere. The mixture was stirred for 24 h and then the solvent was removed under vacuum. The remaining solid was washed with water, dissolved in chloroform, and was subsequently

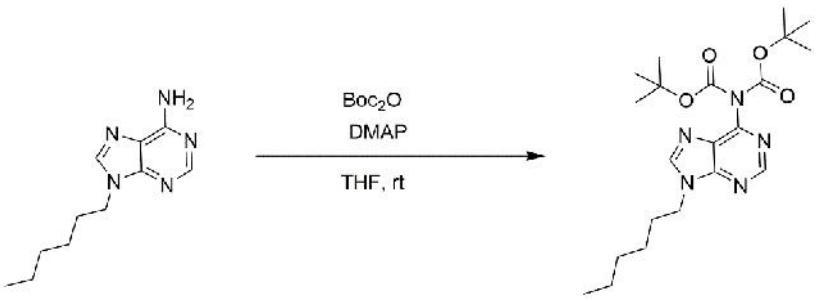
purified via column chromatography with chloroform and MeOH (5 vol%) as the mobile phase. The product was collected and the solvent removed via rotary evaporation, resulting in a white powder (55% yield based on isolated product). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm): 8.30 (s, 1H), 7.74 (s, 1H), 6.65 (s, 2H), 4.12 (t, 2H, *J* = 7.2 Hz), 1.85 – 1.79 (m, 2H) 1.26 – 1.21 (m, 6H), 0.81 – 0.78 (m, 3H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ (ppm): 155.9, 152.8, 149.9, 140.2, 119.5, 43.9, 31.1, 30.0, 26.2, 22.4, 13.9. AccuTOF DART: calc'd [M+H$^+$]: 220.2998, found: 220.3104.

Synthesis of N-methyl-adenine:



50 mL of dry DMF was added to a 150 mL round bottom flask that contained adenine (75.1 mg, 0.56 mmol, 1 equiv.). Then, iodomethane (52.3 µL, 119.2 mg, 0.84 mmol, 1.5 equiv.) and K_2CO_3 (138 mg, 1 mmol, 2 equiv.) were added to the flask under a positive Ar atmosphere. The mixture was stirred for 24 h and then the solvent was removed under vacuum. The remaining solid was washed with water and then purified using silica gel column chromatography with chloroform and added MeOH (5 vol%) as mobile phase to recover the desired product. The product was collected and the solvent removed via rotary evaporation, resulting in a white powder (67% yield based on isolated product). ^{1}H-NMR (300 MHz, $(CD_3)_2SO$), δ (ppm): 8.11 (s, 1H), 8.05 (s, 1H), 7.13 (S, 2H), 3.69 (s, 3H). AccuTOF DART: calc'd [M+H$^+$]: 149.0701, found: 149.0853.

Synthesis of Boc-protected N-hexyl-adenine:



25 mL of dry and degassed THF was added to a dry 50 mL round bottom flask under positive argon pressure. *N*-hexyl-adenine (438.5 mg, 2 mmol, 1 equiv.) was added to the flask and then 76 mg (0.62 mmol, 0.3 equiv.) of DMAP was added to the solution. 1.091 g of di-*tert*-butyl dicarbonate (Boc_2O, 5 mmol, 2.5 equiv.) was added to the mixture under positive argon pressure. Then, the mixture was stirred for 24 h while equipped with bubbler to allow CO_2 gas evolved during the reaction to escape. After this time, the solvent was removed by rotary evaporation. Silica gel column chromatography was used to recover the product, and DCM with 5 vol% MeOH was used as the mobile phase. The bis-*N*-Boc protected product, a pale brownish oil, was collected as the major product in 85% yield. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.84 (S, 1H), 8.04 (S, 1H), 4.26 (t, 2H, J = 7.2), 1.92 – 1.87 (m, 2H), 1.42 (S, 18H), 1.33 – 1.26 (m, 6H), 0.86 – 0.81 (m, 3H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 153.4, 151.9, 150.5, 150.2, 144.7, 128.8, 83.6, 44.2, 31.1, 29.8, 27.8, 26.3, 22.4, 13.9. AccuTOF DART: calc'd [$M+H^+$]: 420.5338, found: 420.5374.

NMR Spectra of Small Molecules and Monomers

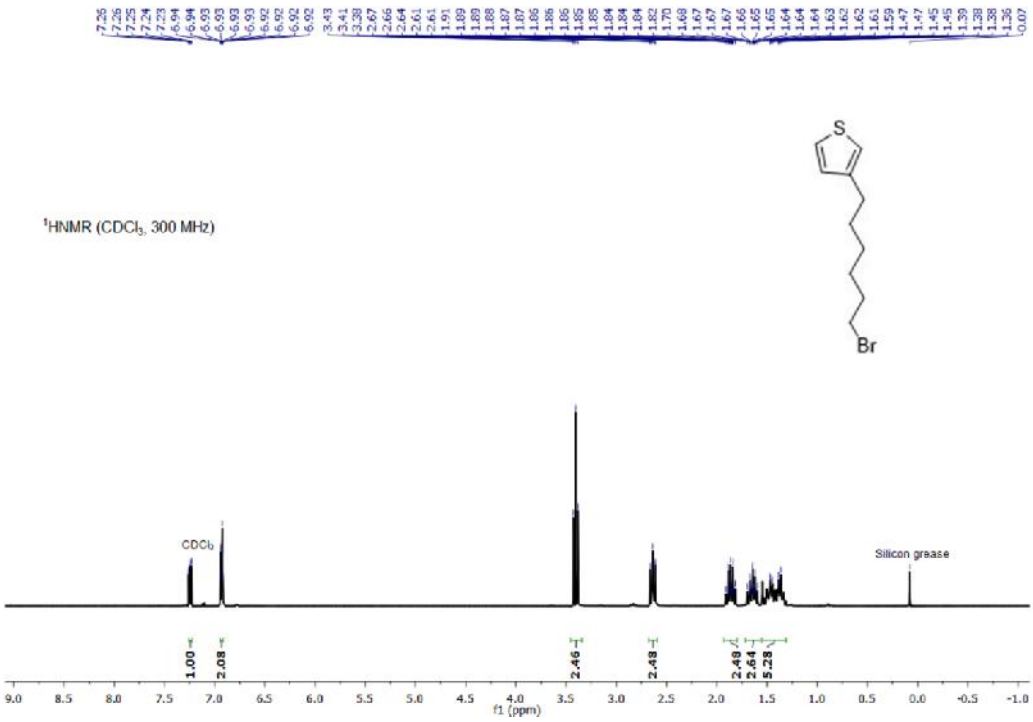


Figure S1. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 3-(6-bromohexyl)thiophene.

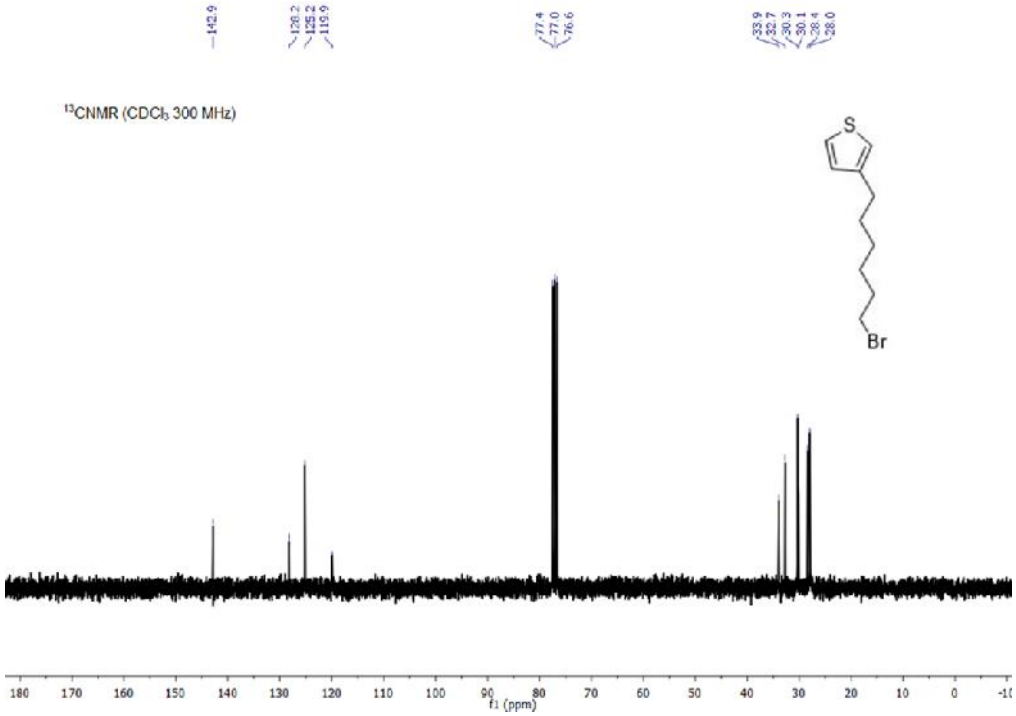


Figure S2. ^{13}C NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 3-(6-bromohexyl)thiophene.

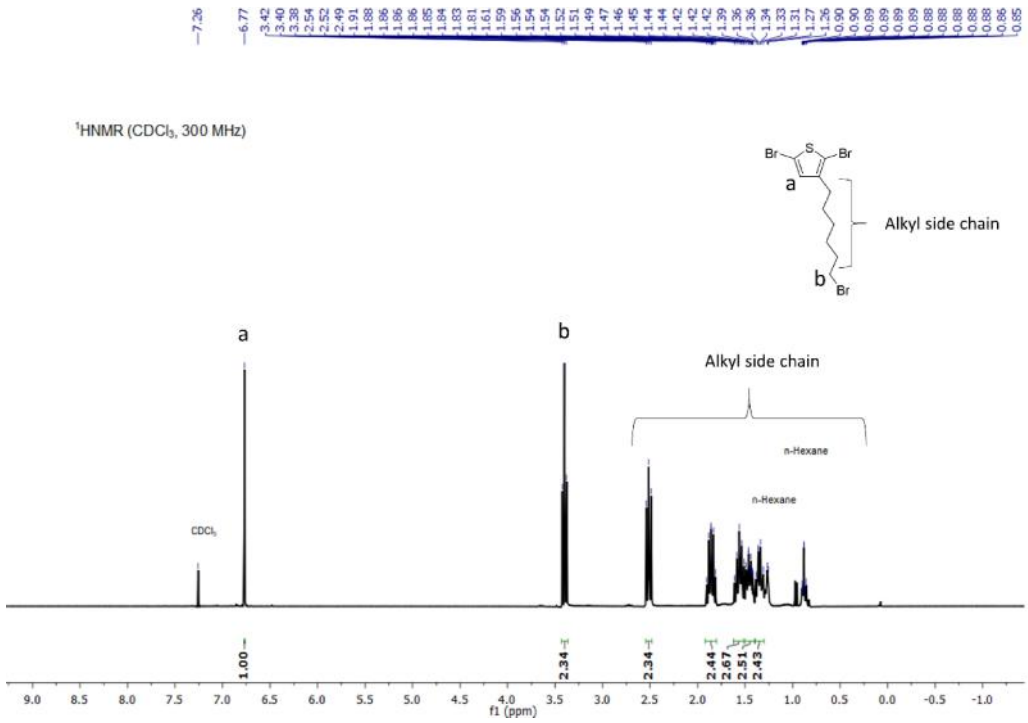


Figure S3. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 2,5-dibromo-3-(6-bromohexyl) thiophene.

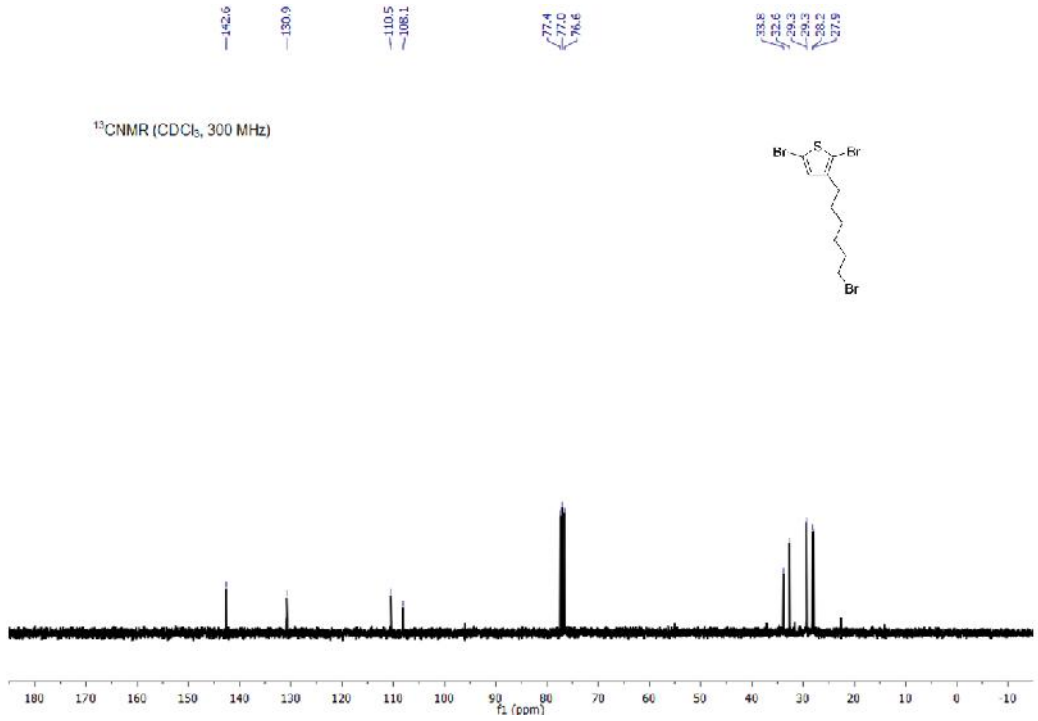


Figure S4. ^{13}C NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 2,5-dibromo-3-(6-bromohexyl) thiophene.

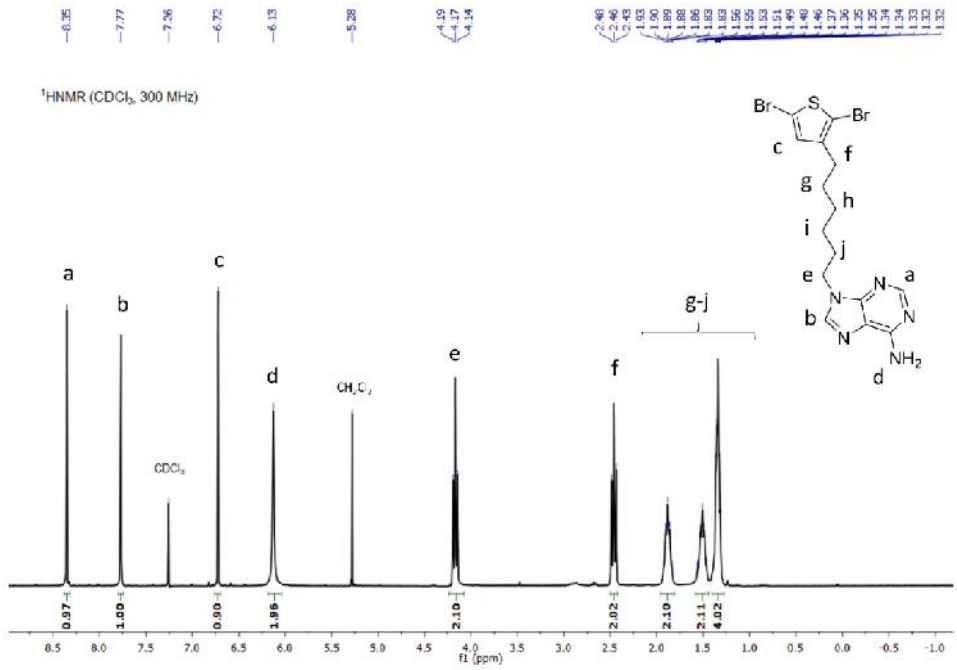


Figure S5. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 9-(6-(2,5-dibromothiophen-3-yl)hexyl)-9H-purine-6-amine) (**M1**).

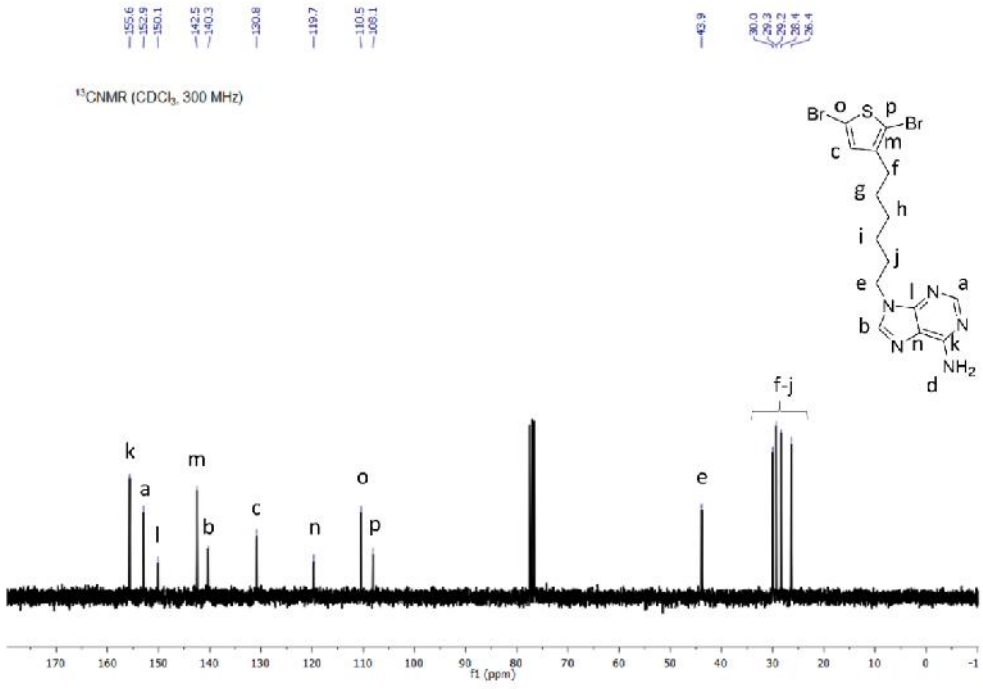


Figure S6. ^{13}C NMR spectrum (300 MHz, 25 °C, CDCl3) of 9-(6-(2,5-dibromothiophen-3-yl)hexyl)-9H-purine-6-amine) (**M1**).

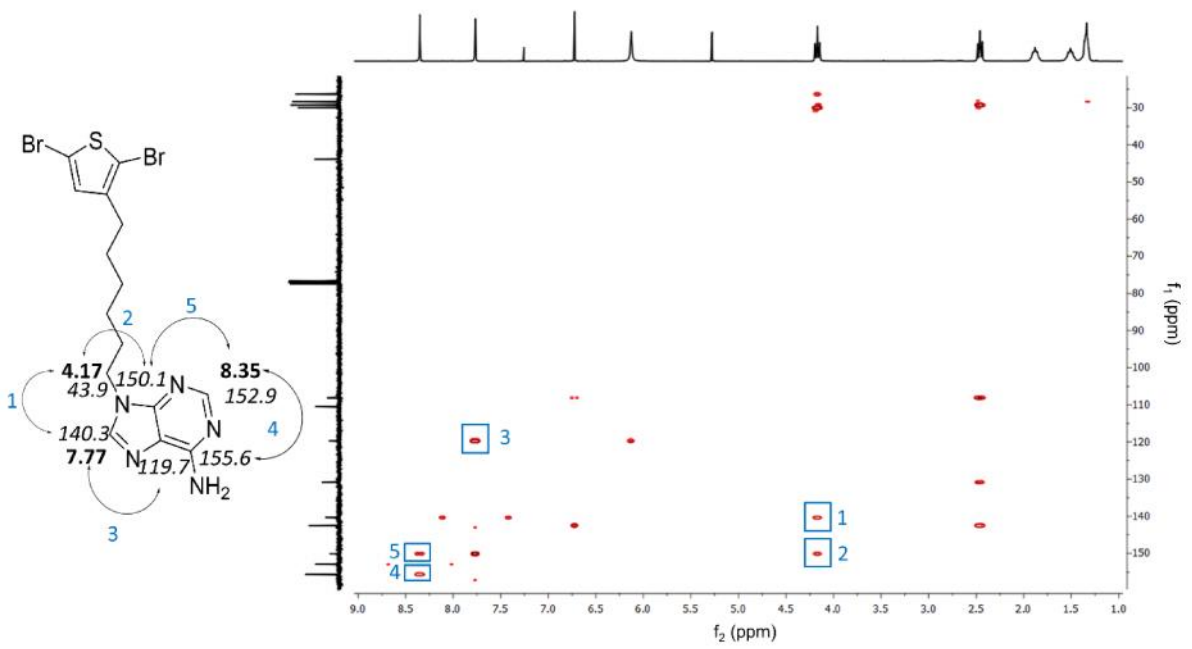


Figure S7. Important multiple bond correlations from 2D gHMBC NMR spectra (500 MHz, 25 °C, $CDCl_3$) of 9-(6-(2,5-dibromothiophen-3-yl)hexyl)-9H-purine-6-amine) (**M1**), which shows corresponding chemical shifts for C-2 and C-8 protons of unprotected adenine and also confirms *N*-9 attachment.

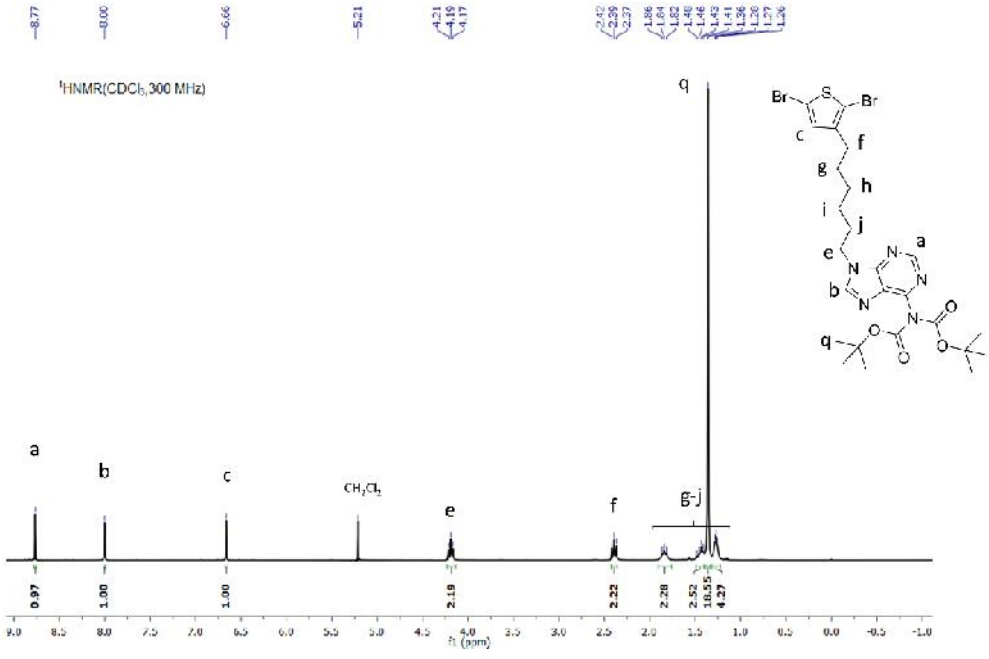


Figure S8. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of Boc-protected dibromo monomer (**M2**).

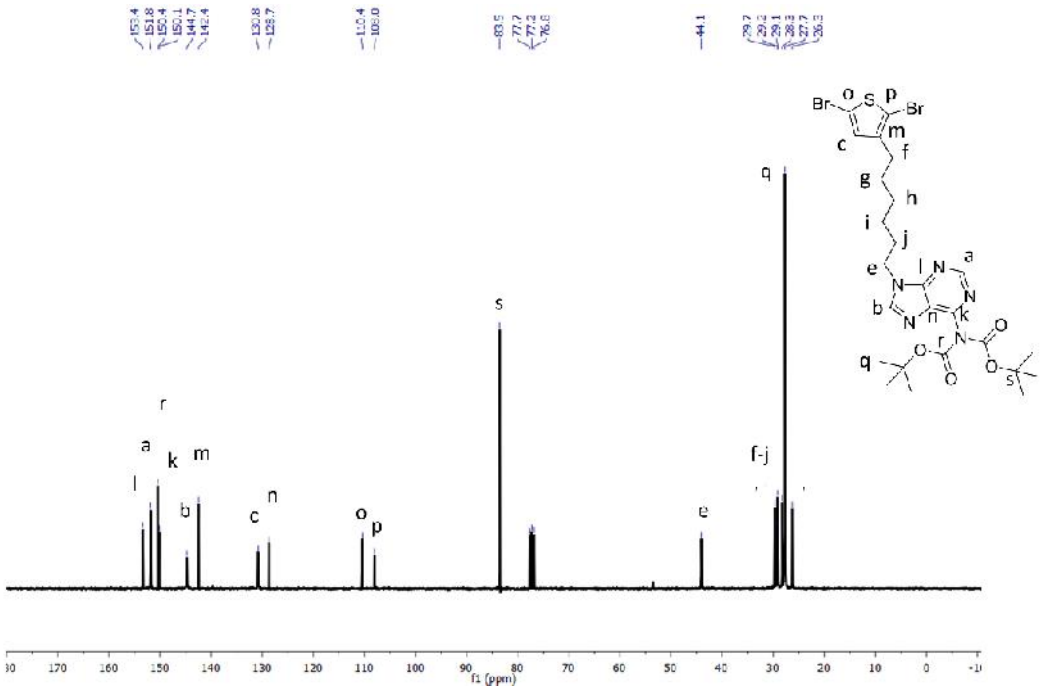


Figure S9. ^{13}C NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of Boc-protected dibromo monomer (**M2**).

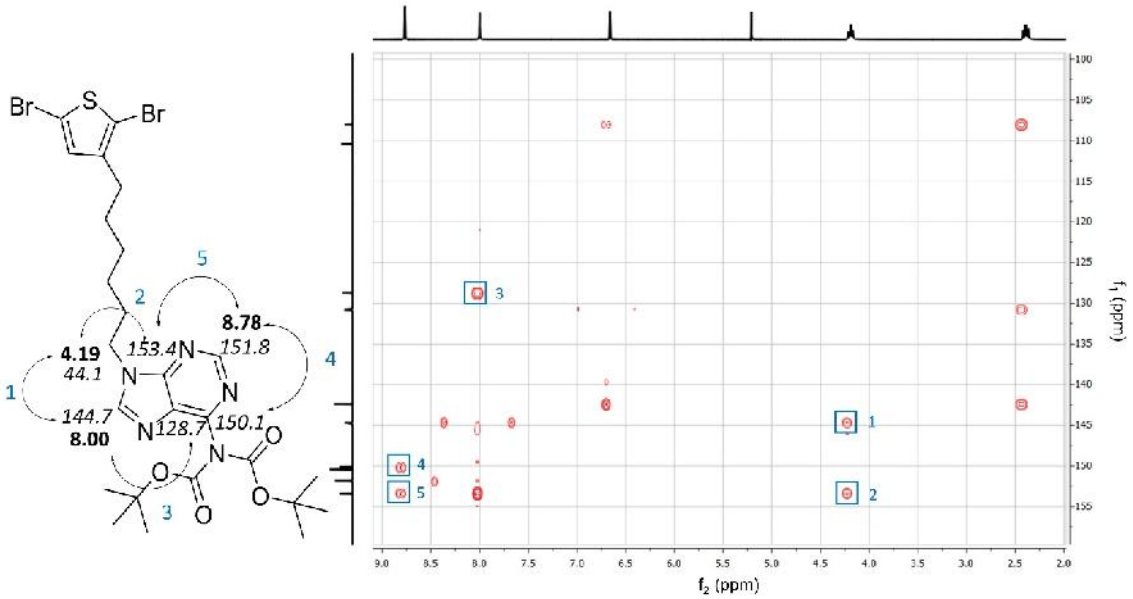


Figure S10. Important multiple bond correlations from 2D gHMBC NMR spectra (500 MHz, 25 °C, $CDCl_3$) of Boc-protected dibromo monomer (**M2**), which shows corresponding chemical shifts for C-2 and C-8 protons of Boc protected adenine.

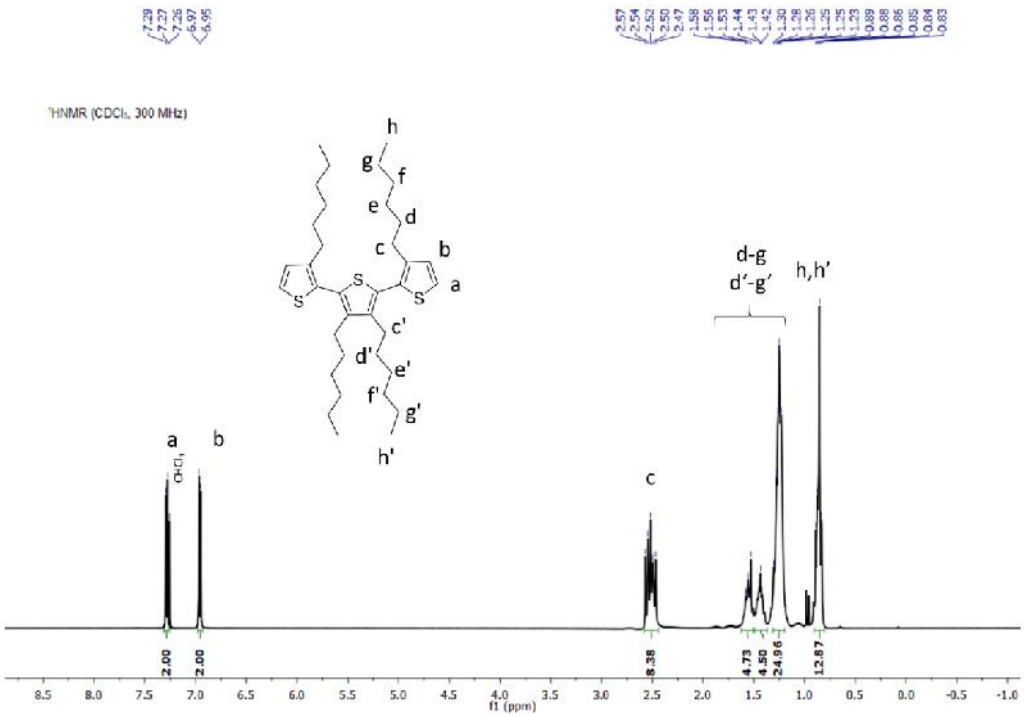


Figure S11. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (**t*T*$_{4h}$**).

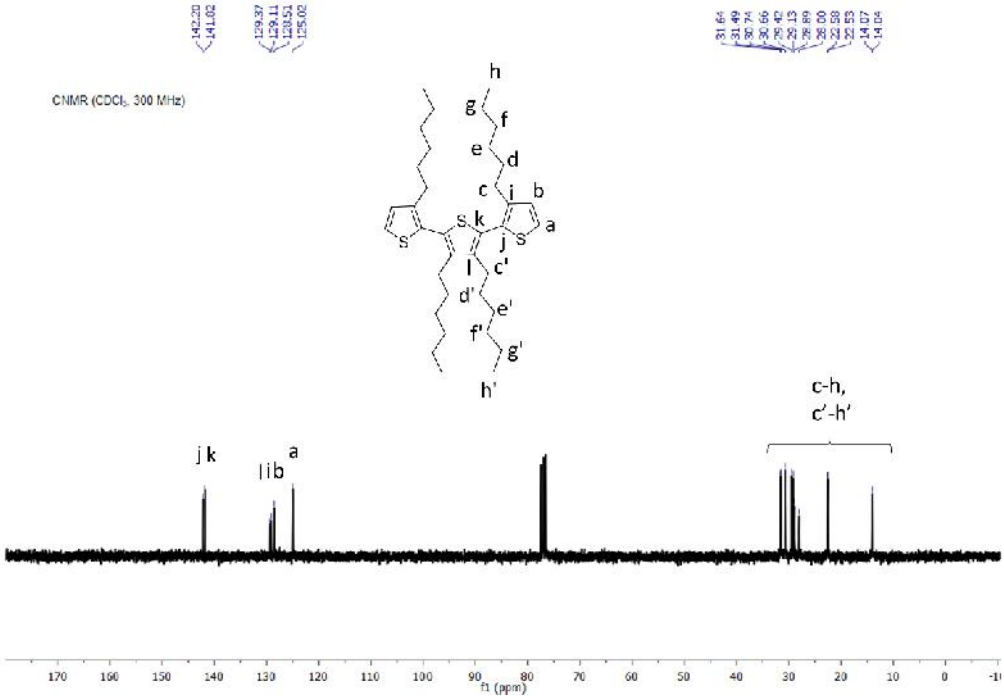


Figure S12. ^{13}C NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (**t*T*$_{4h}$**).

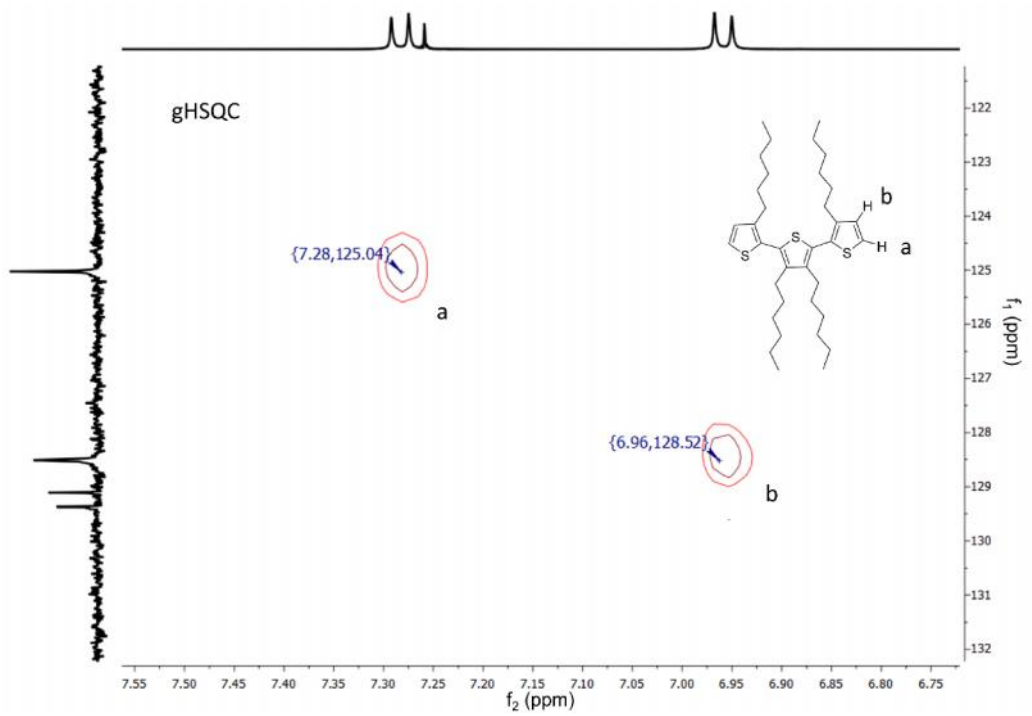


Figure S13. 2D gHSQC NMR spectra (500 MHz, 25 °C, $CDCl_3$) of 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (**t*T*$_{4h}$**) confirms the structure of **t*T*$_{4h}$** monomer.

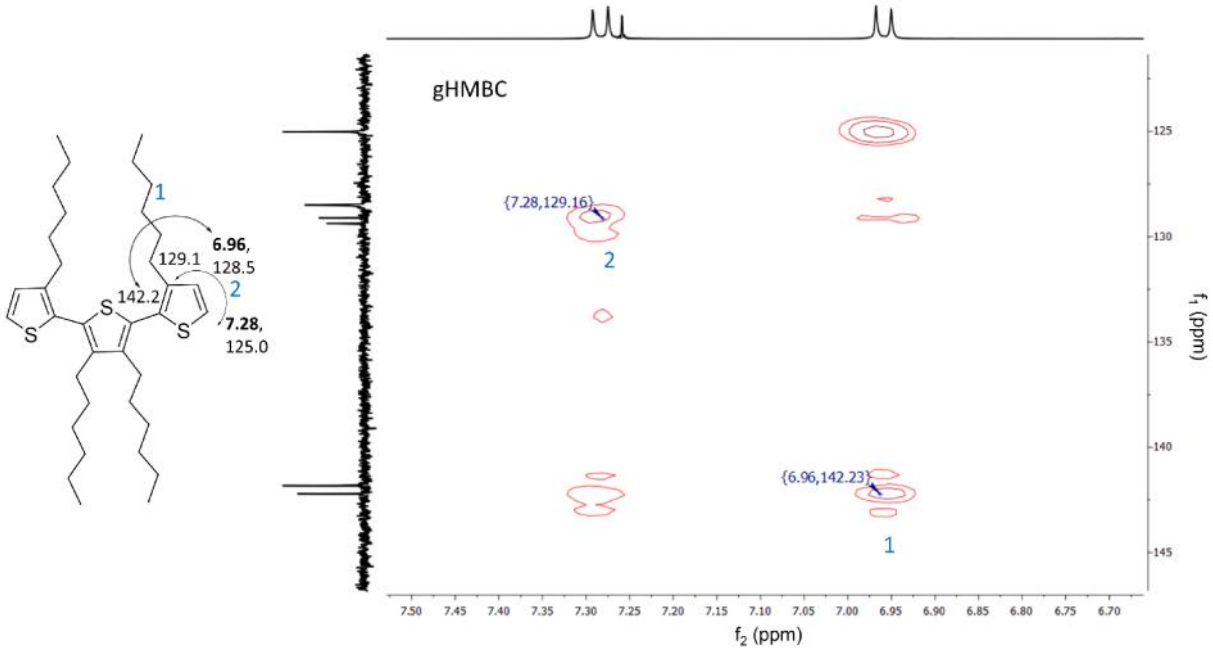


Figure S14. 2D gHMBC NMR spectra (500 MHz, 25 °C, $CDCl_3$) of 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (**t*T*$_{4h}$**) confirms the structure of **t*T*$_{4h}$** monomer.

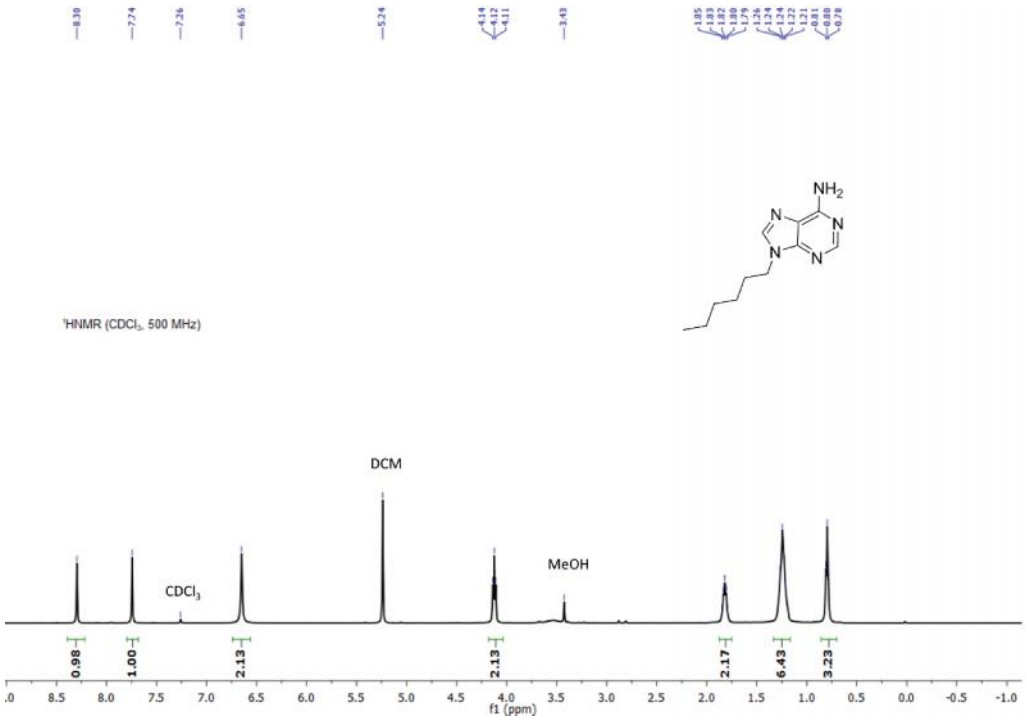


Figure S15. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of *N*-hexyl-adenine.

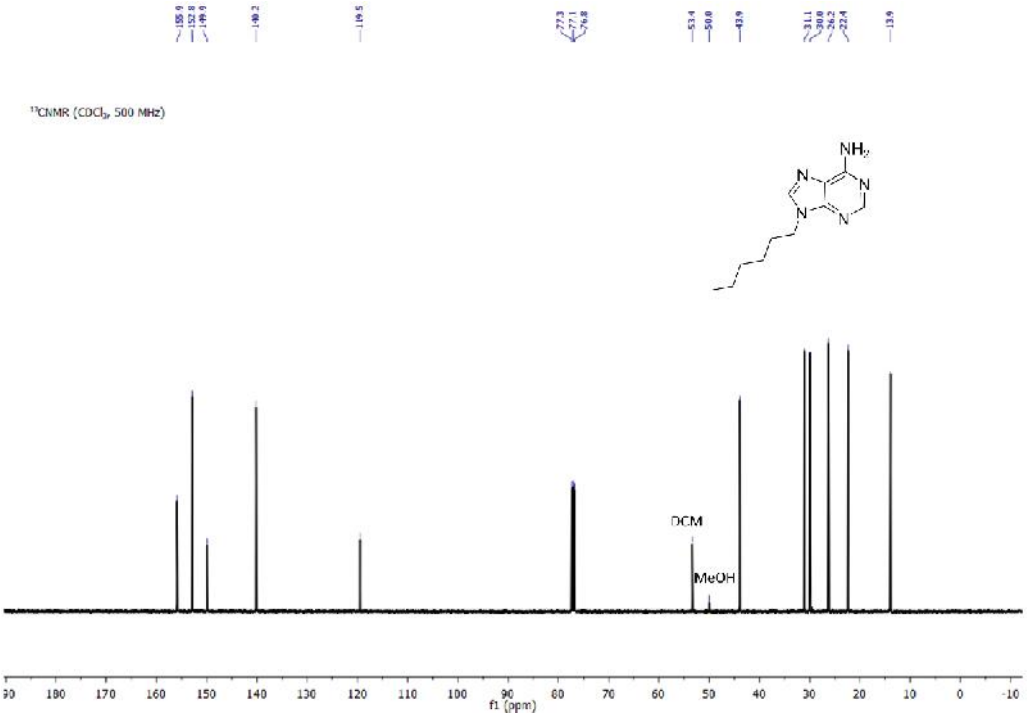


Figure S16. ^{13}C NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of *N*-hexyl-adenine.

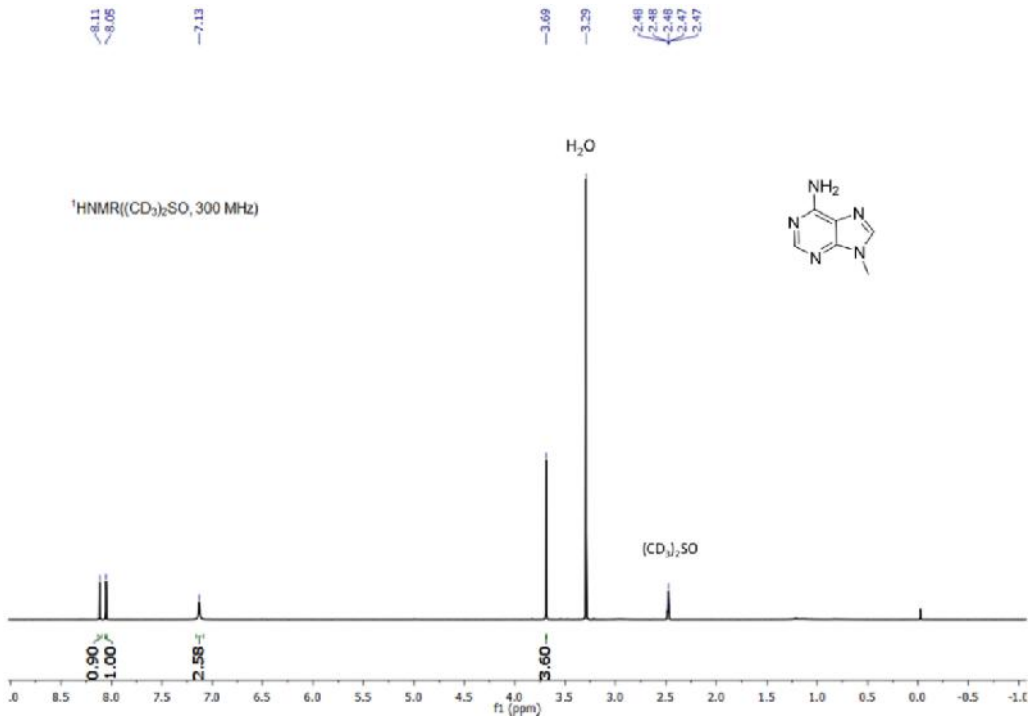


Figure S17. ^{1}H NMR spectrum (300 MHz, 25 °C, $(CD_3)_2SO$) of *N*-methyl-adenine.

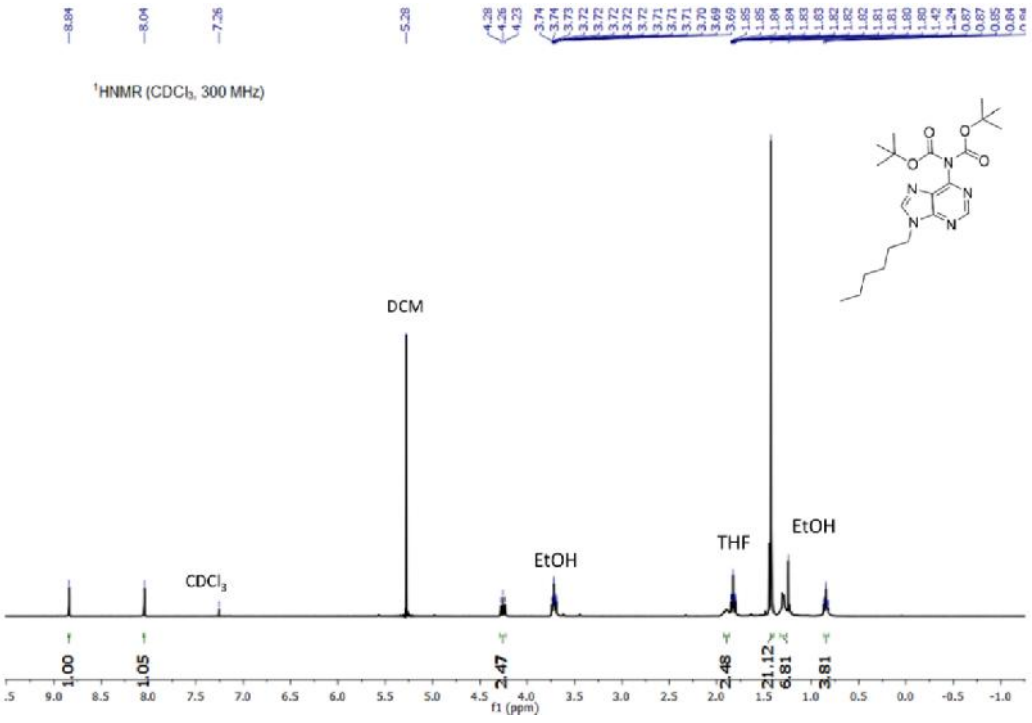


Figure S18. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of Boc-protected *N*-hexyl-adenine.

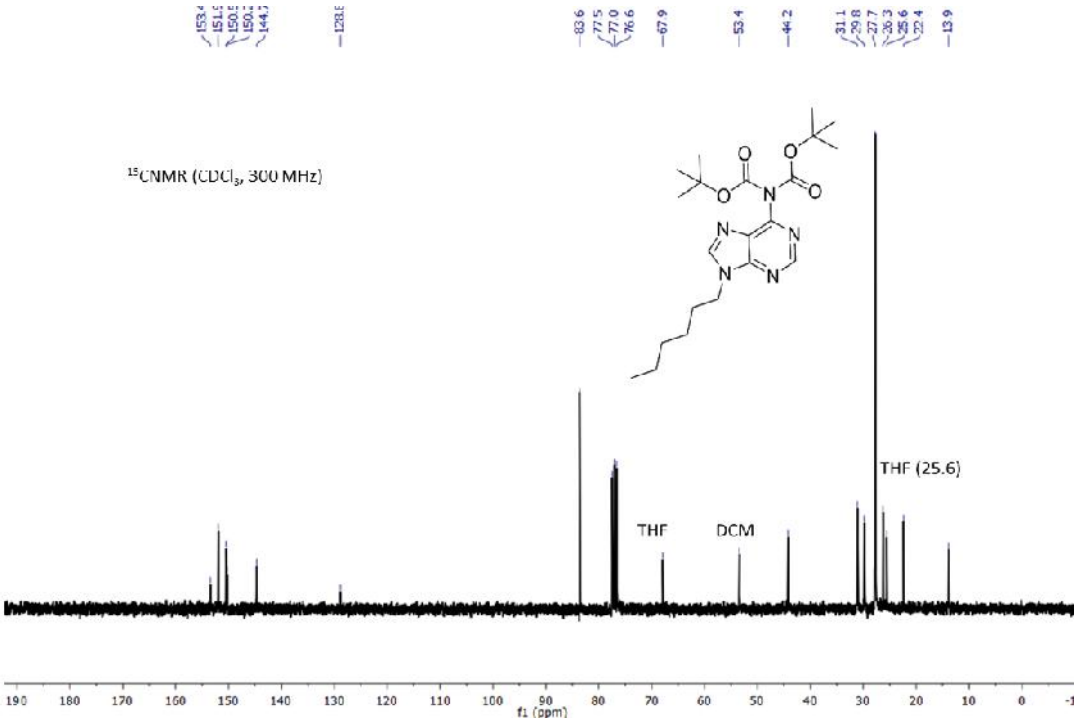


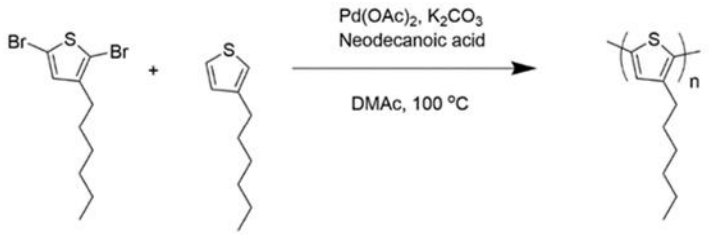
Figure S19. ^{13}C NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of Boc-protected *N*-hexyl-adenine.

Optimization of Conditions for DArP

DArP Test Reaction

Typical test conditions for direct arylation polymerization (DArP) of P3HT following procedures suggested by Thompson et al.[2] are shown in Scheme S1. 15 mL of dry and degassed *N*,*N*-dimethylacetamide (DMAc) was transferred via cannula into a dry 50 mL round bottom flask. Then, 2,5-dibromo-3-hexylthiophene (326 mg, 1 mmol) and 3-hexylthiophene (168 mg, 1 mmol) were added to the flask via syringe. Neodecanoic acid (57 µL, 51 mg, 0.3 mmol), K_2CO_3 (276 mg, 2 mmol) and palladium catalyst ($Pd(OAc)_2$, 13.4 mg, 0.06 mmol) were added to the mixture under positive argon pressure. Then, the mixture was heated in an oil bath set to 100 ^{o}C and stirred for 24 h. At the end of this time, the reaction mixture was precipitated into cold methanol. The precipitate was transferred to a cellulose Soxhlet thimble and subsequently washed with methanol and acetone. The poly(3-hexylthiophene) was extracted from the thimble using chloroform and

then the solution was concentrated via rotary evaporation to obtain the product. This resulting polymer had a number-average molecular weight, M_n, = 35.0 kg/mol and dispersity, $Đ$ = 2.10 at 68% yield. Figure S20 presents the NMR spectrum of the resulting P3HT.



Scheme S1. Optimized DArP conditions used to synthesize poly(3-hexylthiophene) as a test reaction.

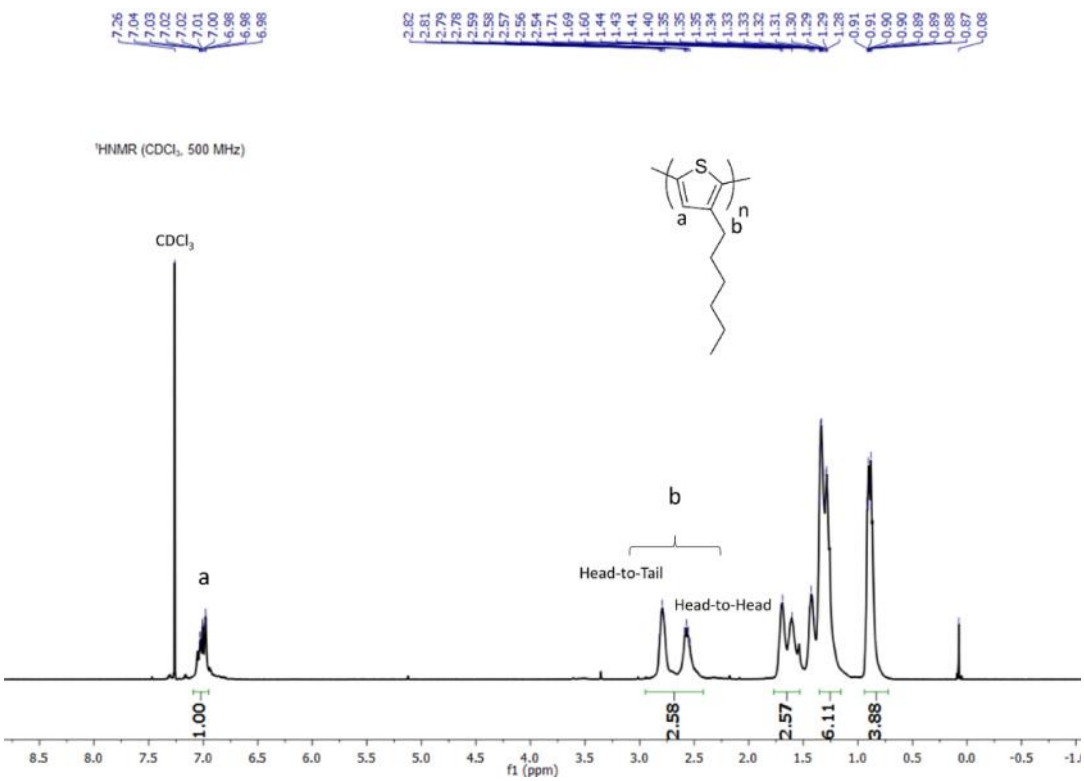
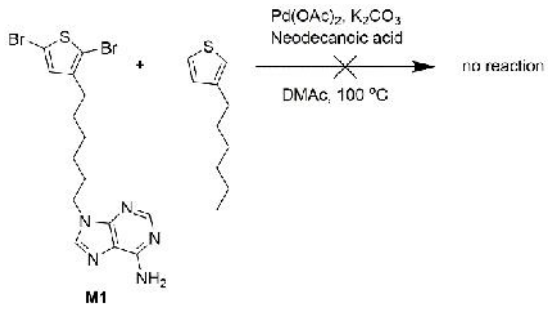


Figure S20. ^{1}H NMR spectrum of P3HT synthesized via optimized DArP conditions in the absence of adenine.

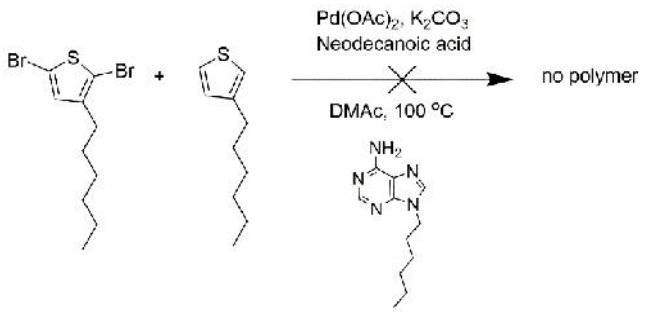
DArP in the Presence of Adenine Functionality

Direct arylation polymerizations of the adenine containing dibromo monomer (**M1**) and 3-hexylthiophene using the optimized reaction conditions were unsuccessful (Scheme S2). The reaction was performed in DMAc at 100 °C with 6 mol% palladium (II) acetate ($Pd(OAc)_2$) as the catalyst, 3 equiv. of potassium carbonate (K_2CO_3) as the base, and 0.3 equiv. of neodecanoic acid as the proton shuttle. The possible effects of adenine functionality on direct arylation polymerization are discussed in the *Article*.



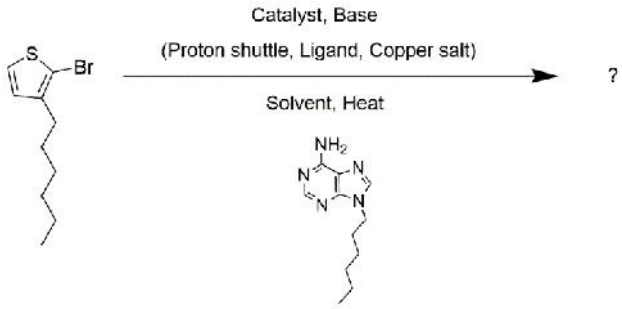
Scheme S2: Attempts to use direct arylation polymerization to copolymerize dibromo adenine-containing monomer, **M1**, and 3-hexylthiophene were unsuccessful.

To test whether adenine interferes with the catalyst, a catalytic amount of *N*-alkylated adenine (0.04 equiv. of *N*-hexyl-adenine) was added to a DArP of 2,5-dibromo-3-hexylthiophene and 3-hexylthiophene, as shown in Scheme S3. Unlike the test reaction performed using optimized conditions described earlier, no P3HT was produced in the presence of the added adenine. This confirms that adenine interacts with and deactivates the palladium catalyst. In the following subsection, we describe a variety of attempts to conduct DArP in the presence of adenine functionality, changing the catalyst, addition of ligand, and auxiliary catalyst as a way to alter the interaction of adenine and Pd catalyst and enable DArP.



Scheme S3. Attempted DArP reaction for synthesis of P3HT in the presence of *N*-hexyl-adenine.

Screening DArP Conditions (with *N*-hexyl-adenine as an Additive)



Scheme S4. General scheme for DArP in presence of *N*-hexyl-adenine.

DArP of 2-bromo-3-hexylthiophene in the presence of *N*-alkylated adenine ("adenine functionality") under a variety of conditions was tested. (See Scheme S4 and Table S1.) Many of the conditions tested as part of the screening study were based on adaptations of polymerization conditions reported in the literature. Daugulis et al. suggested that the addition of bulky, electron-rich phosphine ligands, such as di(1-adamantyl)-*n*-butylphosphine, can stabilize the catalyst for direct arylation of nitrogen containing heteroaromatics.[3] Heterogeneous palladium catalysts like Pd/C and $Pd(OH)_2/C$ also may add functional tolerance to direct arylation, as reported by Alami et al.[4] Another possible method for maintaining the activity of Pd catalyst is to add an excess of a different metal ion that will sacrificially bond with adenine. This method has been used to temper the reactivity of hydrogens on imidazole, thereby enabling direct arylation. Specifically, the

addition of CuI resulted in selective arylation of imidazole at C-2, rather than at C-5.[5, 6] These reports informed out comprehensive screening study that was used to find suitable conditions for DArP of 2-bromo-3-hexylthiophene in presence of adenine functionality, and Table S1 summarizes the results.

Table S1: Screening study used to identify appropriate conditions for synthesis of P3HT in presence of *N*-hexyl-adenine by DArP.

Entry	Catalyst	Ligand	Solvent, Temperature	Base/Acid[a]	Other additives[b]	Results and M_n
1	$Pd(OAc)_2$	-	DMAc,100°C	K_2CO_3/ Neodecanoic acid	-	No polymer
2	$Pd(OAc)_2$	-	DMAc,100°C	K_2CO_3/PivOH	-	No polymer
3	$Pd(OAc)_2$	dppe, 12 mole%	DMAc,100°C	K_2CO_3/PivOH	-	No polymer
4	$Pd(OAc)_2$	-	DMF, 100°C	K_2CO_3/ Neodecanoic acid	-	No polymer
5	$Pd(OAc)_2$	PAd_2Bu 6 mol%	DMAc,100°C	K_2CO_3/ Neodecanoic acid	-	No polymer
6	$Pd(OAc)_2$	dppe	DMAc,100°C	K_2CO_3/ PivOH	-	No polymer
7	$Pd(OAc)_2$	XantPhos	DMAc,100°C	K_2CO_3/ PivOH	-	No polymer
8	Herrmann's, 2 mole%	NSC 4 mol%	THF, 100°C	Cs_2CO_3	-	No polymer
9	Herrmann's, 2 mole %	NSC 4 mol%	Toluene, 100°C	Cs_2CO_3	-	No polymer
10	Herrmann's, 2 mole%	dppe	DMAc,100°C	K_2CO_3/ Neodecanoic acid	-	No polymer
11	$Pd_2(dba)_3$, 2 mole %	NSC, 6 mol%	Toluene, 100°C	Cs_2CO_3/PivOH	-	No polymer
12	$Pd_2(dba)_3$, 2 mole%	(n-Bu)$PHBF_4$, 6 mol%	Toluene, 100°C	Cs_2CO_3/PivOH	-	No polymer
13	$Pd(PPh_3)_4$	NSC, 4 mol%	Toluene, 100°C	Cs_2CO_3/PivOH	-	No polymer
14	$Pd(OH)_2$/C	-	DMAc,100°C	K_2CO_3/ PivOH	-	No polymer
15	$Pd(OAc)_2$	-	DMAc,100°C	Cs_2CO_3/PivOH	CuI	No polymer
16	$Pd(OAc)_2$	PAd_2Bu 6 mol%	DMAc,100°C	K_2CO_3/ PivOH	CuI	Polymer 15% yield M_n ~ 2 kg/mol

a: PivOH = pivalic acid
b: molar ratio of CuI:*N*-hexyl-adenine= 3:1

Among these possibilities, only the addition of CuI and a bulky phosphine ligand (together) allowed P3HT to be produced when *N*-hexyl-adenine was present. Applying the same reaction

conditions – added CuI and bulky phosphine ligand – to DArP of monomer **M1** did not afford any polymer. This may be due to limited solubility of the polymer in the reaction solvent DMAc. In total, the results of these screening studies suggest that binding of adenine to the Pd catalyst plays significant role in deactivation of the catalyst or interference in the catalytic cycle.

Interaction of Pd ion with Adenine

Metal ions, including platinum ions, can bind to nucleobases, and these interactions have been studied to explain the activity of platinum compounds as drugs or the effects of metal ions on the activity of metalloenzymes.[7-11] Adenine can bind with cations through its primary amine as well as through nitrogen atoms in the fused ring heterocycle, forming various bidentate or multidentate complexes. N-7 has greatest propensity for chelating Pt and Pd ions.[9, 10] To gain insight into complex formation of adenine with Pd ions, N-methyl-adenine was synthesized and used. An equimolar mixture of $Pd(OAc)_2$ (30.1 mg, 0.134 mmol) and N-methyl-adenine (20.3 mg, 0.134 mmol) was prepared in DMSO. Changes in chemical shifts of C-2 and C-8 are interpreted as indicating formation of Pd^{2+}/adenine complexes. At least five different complexes can be observed from coordination of Pd^{2+} with adenine, as shown in Figure S21. This finding is in general agreement with previous reports[9, 10] and highlights the strong interaction between adenine and Pd^{2+} ions.

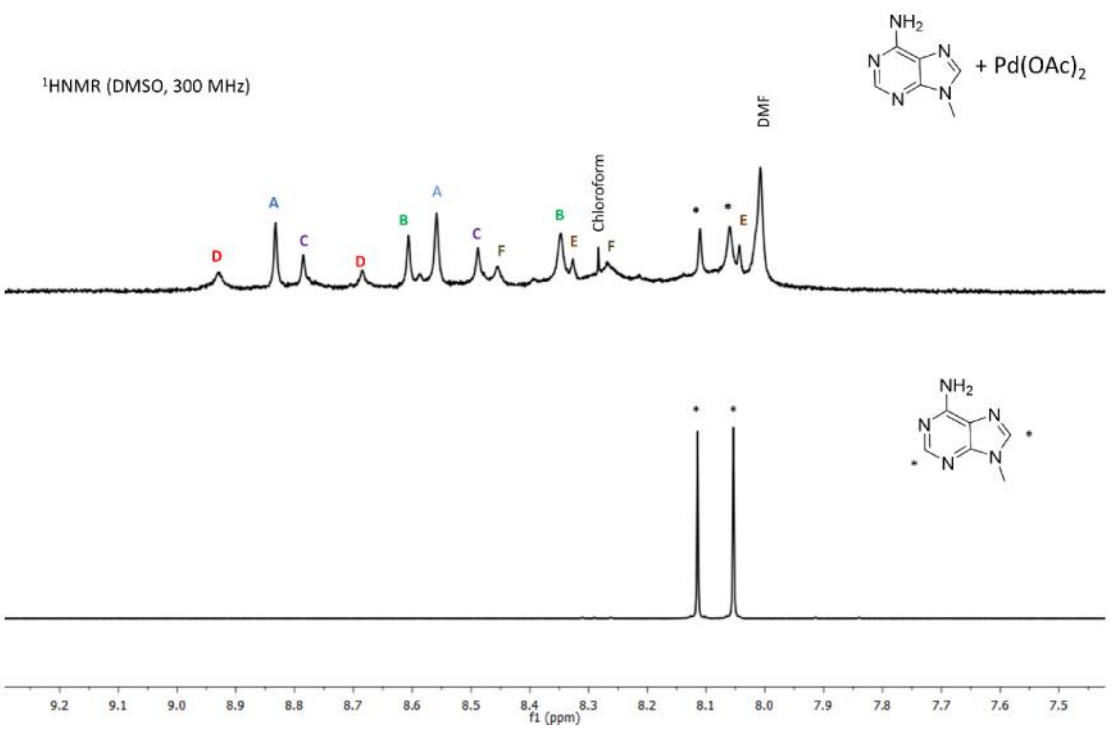
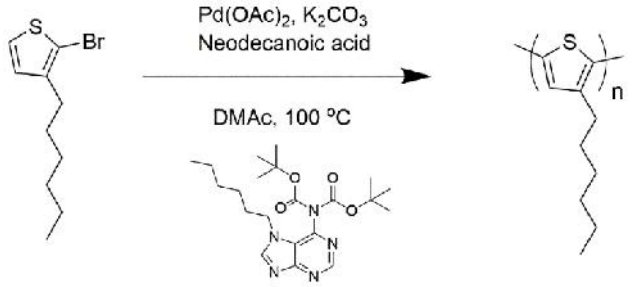


Figure S21. Aromatic region of (bottom) *N*-methyl-adenine and (top) an equimolar mixture of *N*-methyl adenine and Pd^{2+} in DMSO-d_6. A, B, C, D, E, and F refer to different Pd^{2+}/adenine complexes.

Amine-protected Adenine

Protecting the primary amine functionality of the adenine may weaken its interaction with palladium ions, thereby enabling DArP in the presence of the protected adenine. To test this, *tert*-butyloxycarbonyl (Boc) protecting groups were utilized. DArP of 2-bromo-3-hexylthiophene in presence of bis-Boc protected *N*-hexyl-adenine (0.04 equiv.) was conducted using the same optimized conditions proven for DArP of 2-bromo-3-hexylthiophene. Under these conditions (see Scheme S5), the direct arylation polymerization was successful, resulting in a 45% yield of P3HT having M_n = 5.90 kg/mol and $Đ$ =1.68. Thus, we conclude that amine protection is necessary to prevent interference due to complex formation between the adenine and the Pd catalyst. Figure S22 shows the ^{1}H NMR spectrum of the P3HT produced by DArP in the presence of Boc-protected

adenine. Based on this result, a Boc-protected, adenine containing monomer (**M2**) was synthesized.



Scheme S5. DArP conditions for successful polymerization in presence of Boc-protected *N*-hexyl-adenine.

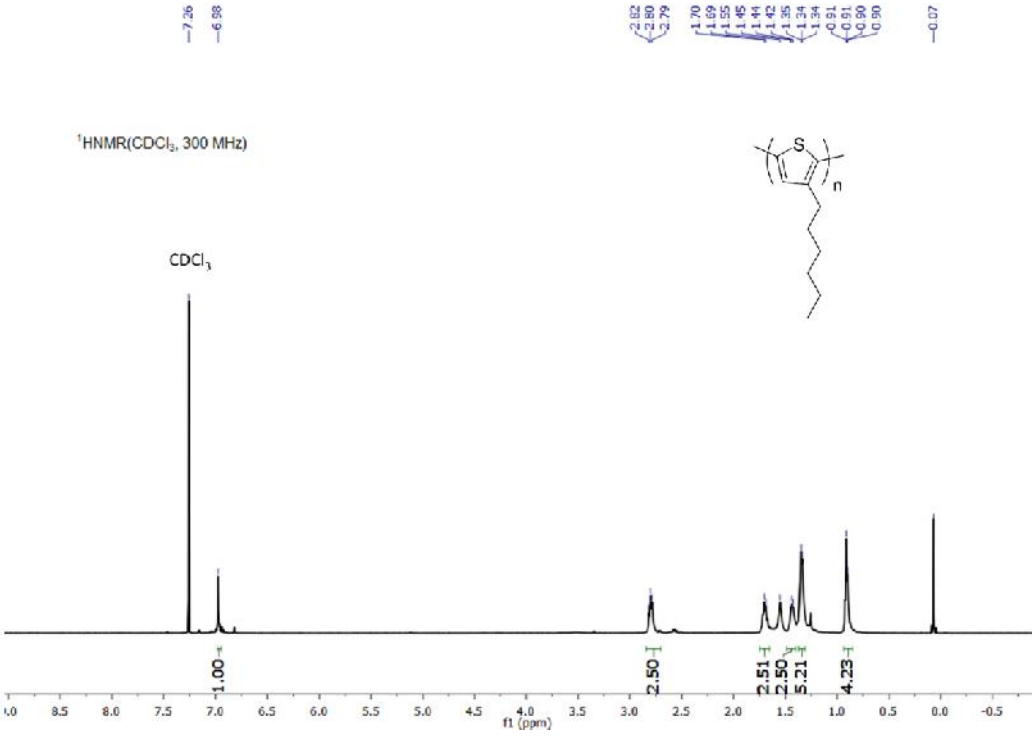
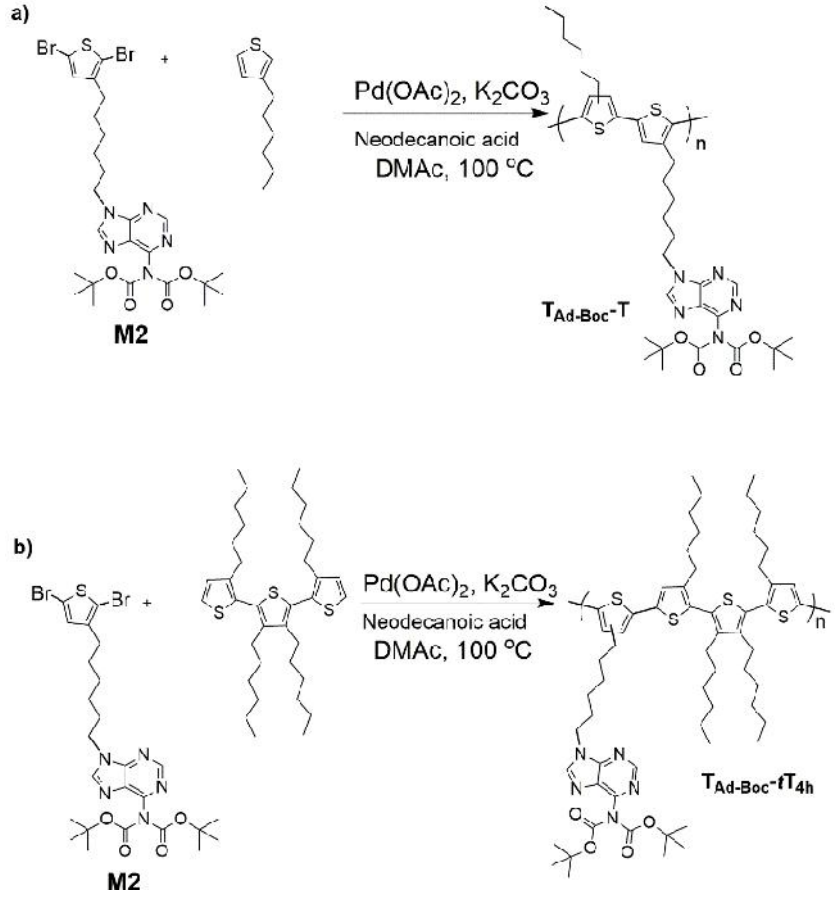


Figure S22. ^{1}H NMR spectrum of P3HT produced by DArP of 2-bromo-3-hexylthiophene in the presence of a catalytic amount of Boc protected *N*-hexyl-adenine.

DArP Synthesis of $T_{Ad\text{-}Boc}$-T and $T_{Ad\text{-}Boc}$-*t*T_{4h}

Two alternating copolymers, **$T_{Ad\text{-}Boc}$-T** and **$T_{Ad\text{-}Boc}$-*t*T_{4h}**, were synthesized in similar DArP conditions, as shown in Scheme S6.



Scheme S6. Scheme for polymerization of Boc-protected monomers via DArP to produce a) **$T_{Ad\text{-}Boc}$-T** and b) **$T_{Ad\text{-}Boc}$-*t*T_{4h}.**

8 mL of dry and degassed DMAc was transferred via cannula to a dry 50 mL round bottom flask. Then, amine-protected dibromo monomer, **M2**, (329 mg, 0.5 mmol, 1 equiv.) was added to the flask. The other comonomer, either 3-hexylthiophene, **T**, (84mg, 0.5 mmol, 1 equiv.) or 3,3',3",4'-tetrahexyl-2,2':5',2"-terthiophene, ***t*T$_{4h}$** (292.5 mg, 0.5 mmol), was added to the solution, which would yield either **$T_{Ad\text{-}Boc}$-T** or **$T_{Ad\text{-}Boc}$-*t*T_{4h}**, respectively. Then, neodecanoic acid (29 µL, 26 mg, 0.15 mmol, 0.3 equiv.) and K_2CO_3 (138 mg, 1 mmol, 2 equiv.) were added to the mixture

while it was maintained under a positive argon atmosphere. After the additions, the flask was sealed with a septum and the mixture was heated to 100 °C and stirred for 24 h. At the end of this time, the reaction mixture was precipitated into cold methanol. The precipitate was washed with methanol and transferred to a cellulose thimble. The final product was extracted from the Soxhlet thimble by dissolving the soluble components in chloroform. **$T_{Ad\text{-}Boc}$-T** and **$T_{Ad\text{-}Boc}$-*t*T_{4h}** were isolated in 56% and 72% yield, respectively. ^{1}H NMR spectra and GPC traces of these fully conjugated, alternating copolymers are shown in Figures S23 – S26.

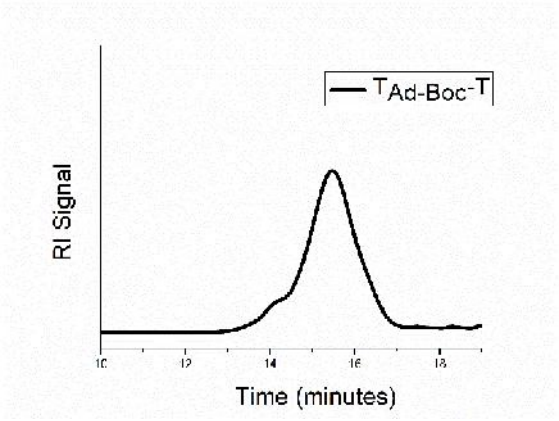


Figure S23. GPC trace of **$T_{Ad\text{-}Boc}$-T** synthesized via DArP using the amine-protected dibromo monomer (**M2**). Relative to PS standards, this copolymer has an M_n = 6.9 kg/mol and $Đ$ = 1.37. As described in the following section, the deprotected copolymer was insoluble.

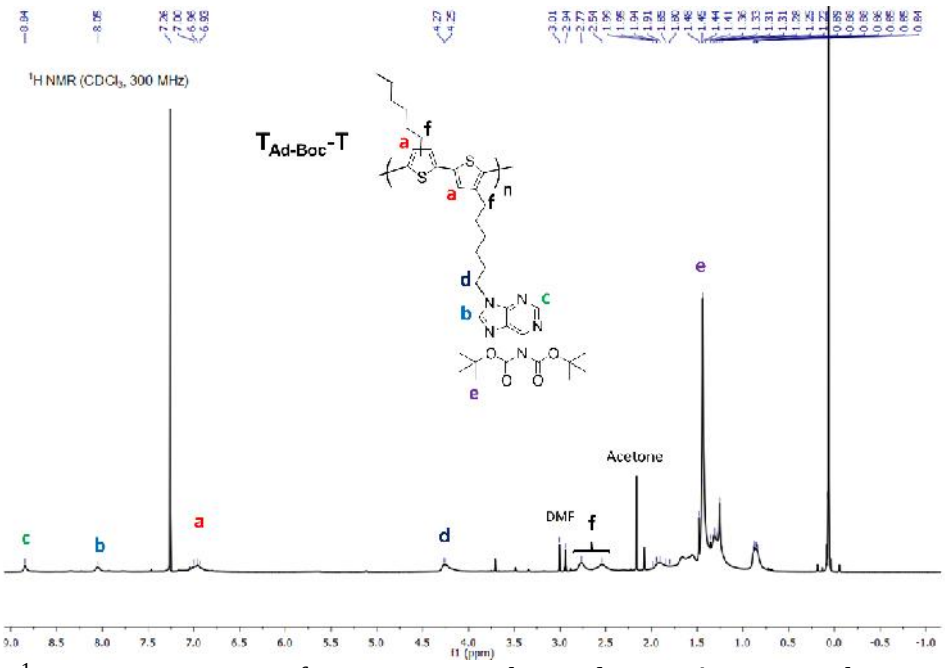


Figure S24. ^{1}H NMR spectrum of $\mathbf{T_{Ad\text{-}Boc}\text{-}T}$ synthesized via DArP using the amine-protected dibromo monomer (**M2**).

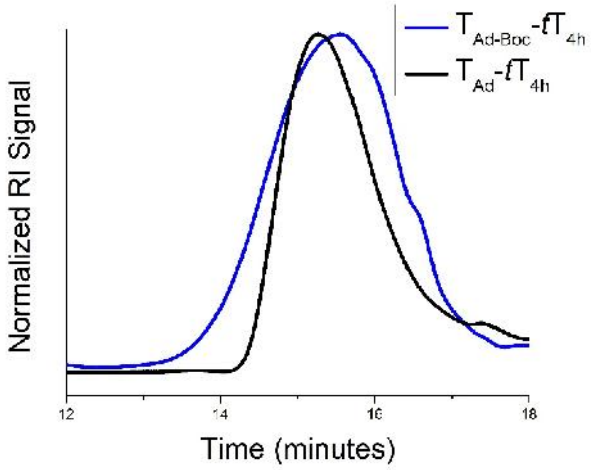


Figure S25. Overlay of GPC traces of $\mathbf{T_{Ad\text{-}Boc}\text{-}\textit{t}T_{4h}}$ (M_n =7.0 and $Đ$ = 2.01, blue trace) and $\mathbf{T_{Ad}\text{-}\textit{t}T_{4h}}$ (M_n = 7.0 kg/mol and $Đ$ = 1.82, black trace). (These are the Boc-protected and deprotected copolymers, respectively.)

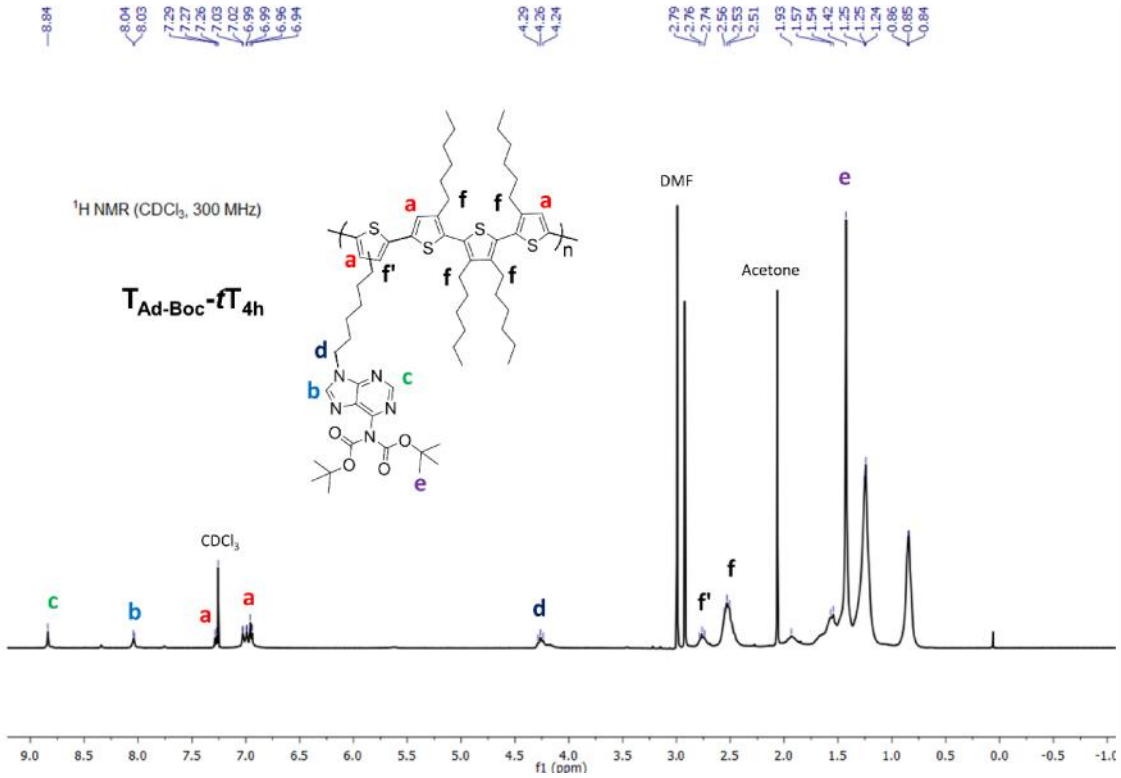
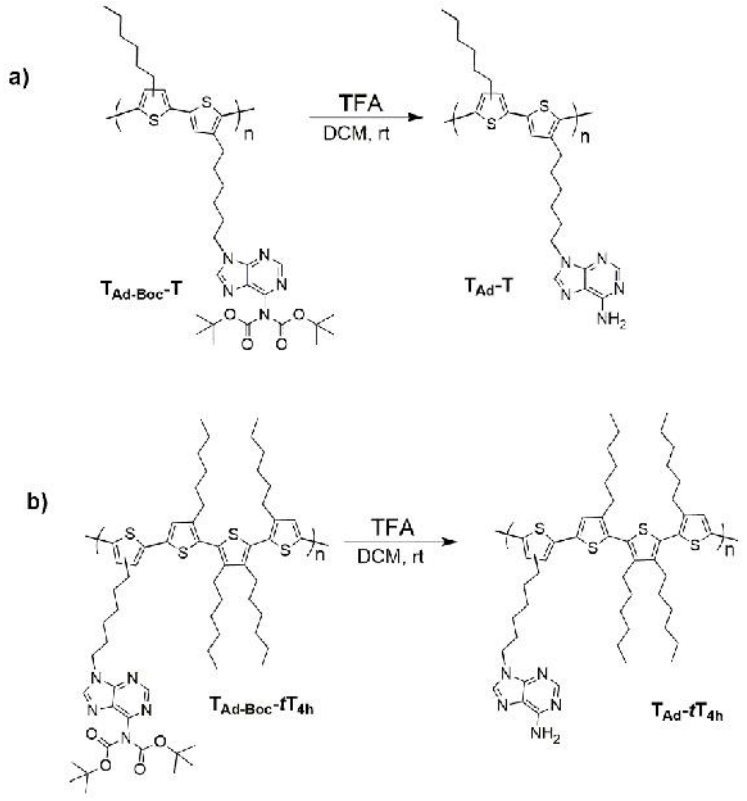


Figure S26. ^{1}H NMR spectrum of $\mathbf{T_{Ad\text{-}Boc}}$-$\mathbf{tT_{4h}}$ synthesized via DArP using the amine-protected dibromo monomer (**M2**).

General Procedure for Acid Catalyzed Deprotection of $T_{Ad\text{-}Boc}$-T or $T_{Ad\text{-}Boc}$-tT_{4h}



Scheme S7. Acid catalyzed deprotection of a) **$T_{Ad\text{-}Boc}$-T** and b) **$T_{Ad\text{-}Boc}$-*t*T$_{4h}$.**

Boc groups were removed by acid catalysis, as shown in Scheme S7. The Boc-protected polymer (either **$T_{Ad\text{-}Boc}$-T** or **$T_{Ad\text{-}Boc}$-*t*T$_{4h}$**) was added to a 100 mL dry round bottom flask. Then, 50 mL of a solution compared of trifluoroacetic acid (TFA) and dichloromethane (DCM) at a 1:1 volumetric ratio was added to the flask. The flask was connected to a bubbler to allow the gas produced (CO_2) to escape. The mixture was stirred for 24 h at room temperature. At the end of this time, the volatiles were removed under reduced pressure and then the rest of the mixture was precipitated into cold methanol. The precipitate was washed with methanol and acetone via subsequent Soxhlet washes and then extracted from the cellulose Soxhlet thimble using chloroform. The deprotected product of **$T_{Ad\text{-}Boc}$-T** was insoluble in various organic solvents and further characterization was impossible due to this solubility issue. On the other hand, **$T_{Ad\text{-}Boc}$-*t*T$_{4h}$**

showed quantitative and complete deprotection and the resulting polymer, **T_{Ad}-*t*T_{4h}**, was soluble in most organic solvents, including chloroform, THF, and DCM. Figure S25 and Figure S28 present GPC trace and ^{1}H NMR data of **T_{Ad}-*t*T_{4h}**, with the GPC results comparing the protected and deprotected polymers.

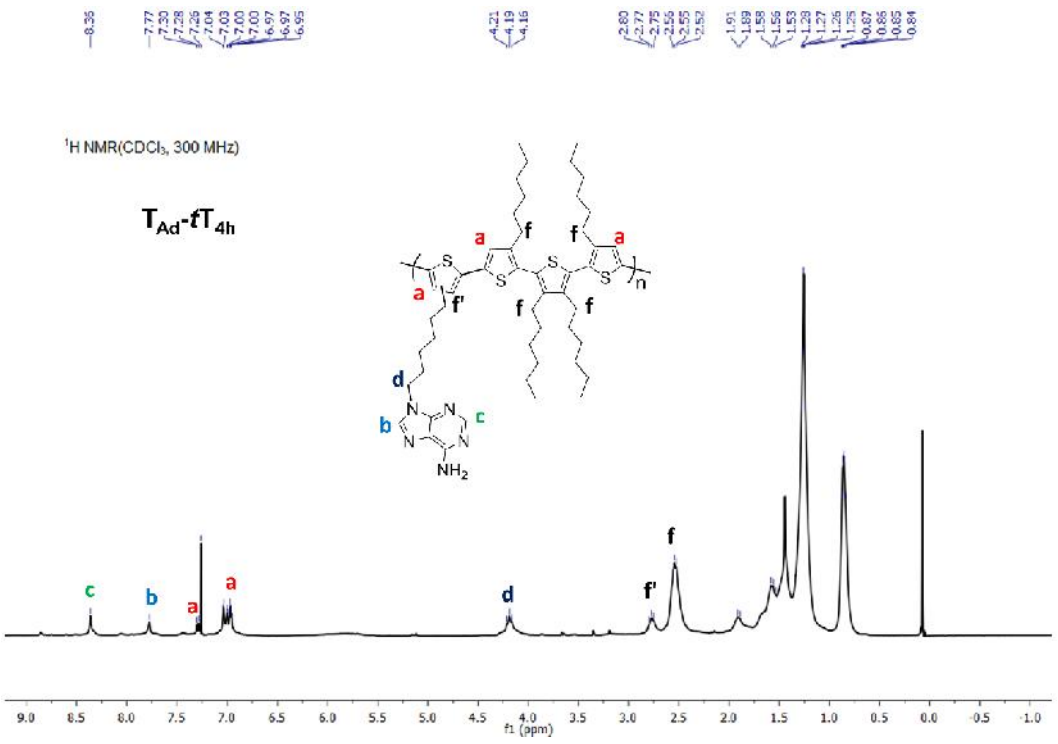
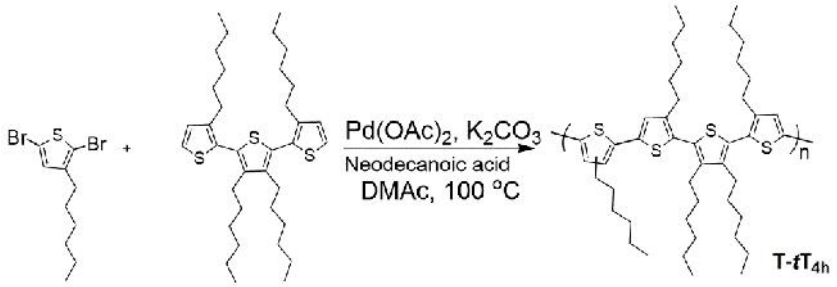


Figure S27. ^{1}H NMR spectrum of **T_{Ad}-*t*T_{4h}** after acid-catalyzed deprotection of the adenine functionality.

Synthesis of T-*t*T_{4h} (homologue of T_{Ad}-*t*T_{4h} without adenine)



Scheme S8. Synthesis of non-adenine containing homologue polymer, **T-*t*T_{4h}** via DArP.

A homologue without adenine was synthesized using the same DArP conditions. Specifically, 25 mL of dry and degassed DMAc was cannula transferred to a dry 50 mL round bottom flask. Then, 2,5-dibromo-3-hexylthiophene (163 mg, 0.5 mmol, 1 equiv.) and 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (***t*T$_{4h}$**) (292.5 mg, 0.5 mmol, 1 equiv.) were added to the flask. Neodecanoic acid (29 μL, 26 mg, 0.15 mmol, 0.3 equiv.) and K_2CO_3 (138 mg, 1 mmol, 2 equiv.) were added to the mixture while it was purging under argon. The mixture was heated to 100 ^oC and stirred for 24 h. Then, the reaction mixture was precipitated into cold methanol. The precipitate was washed with methanol and acetone. The precipitate was transferred to a cellulose thimble and then collected from the soluble material after Soxhlet extraction using chloroform. These reaction conditions resulted in a copolymer having a M_n = 8.5 kg/mol and $Đ$ = 1.64 at 71% yield. Figure S28 and Figure S29 show the GPC trace and ^{1}H NMR spectrum, respectively, of the resulting polymer, **T-*t*T$_{4h}$**.

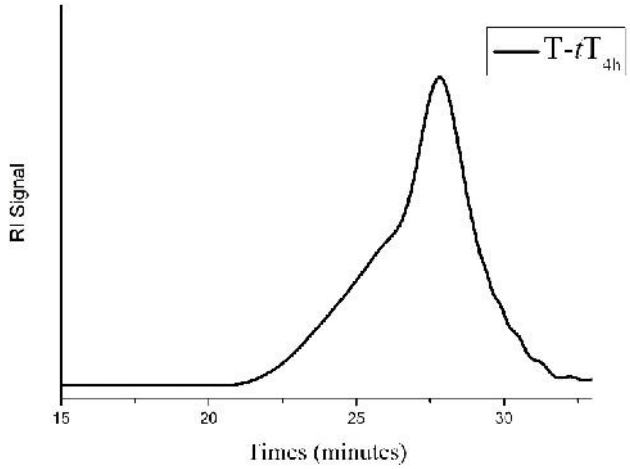


Figure S28. GPC trace of **T-*t*T$_{4h}$** synthesized using optimized DArP conditions. Relative to PS standards, this copolymer has a M_n =8.5 kg/mol and $Đ$ = 1.64.

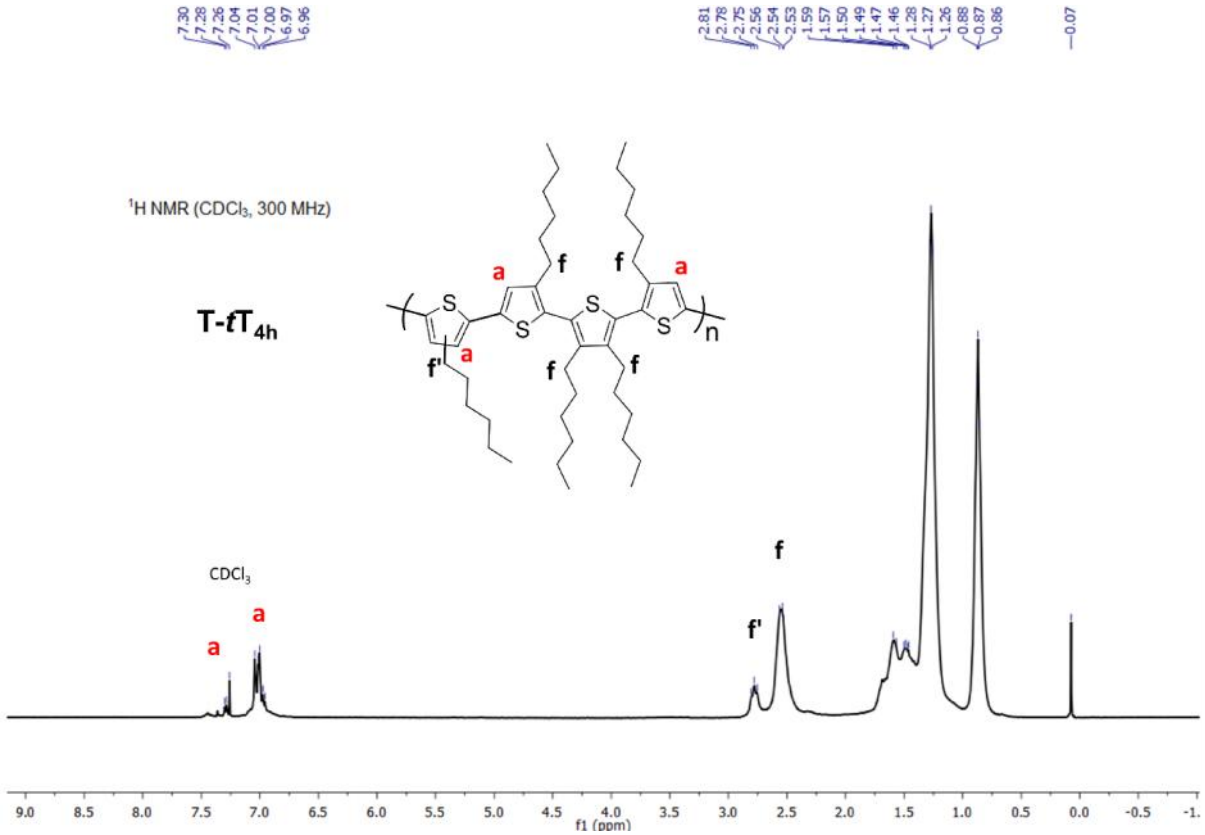


Figure S29. ^{1}H NMR spectrum of **T-*t*T$_{4h}$** synthesized using optimized DArP conditions.

Thermal Properties of Alternating Copolymers

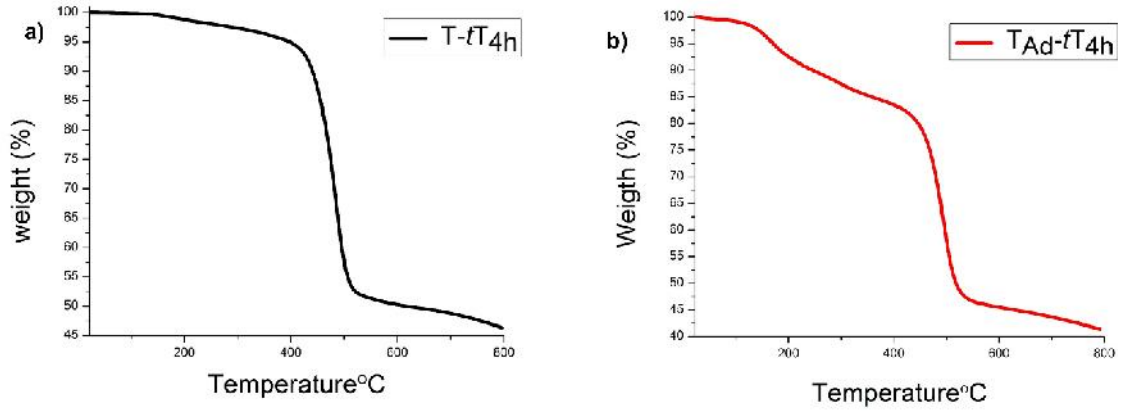


Figure S30. Mass loss measured by thermogravimetric analysis of a) **T-*t*T$_{4h}$** and b) **T$_{Ad}$-*t*T$_{4h}$.** Data were acquired by ramping from 20 °C to 800 °C at a rate of 10 °C/min.

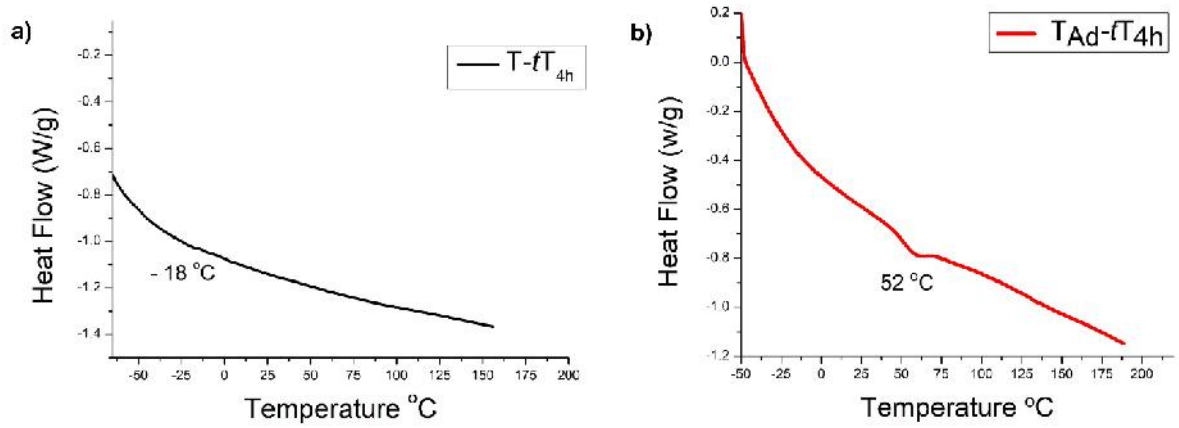


Figure S31. Results of differential scanning calorimetry measurements of a) **T-*t*T$_{4h}$** ($T_g \approx -18$ °C) and b) **T$_{Ad}$-*t*T$_{4h}$** ($T_g \approx 52$ °C). Experiments were performed using heating and cooling rates of 10 °C/min, with T_g's determined from the second heating ramp.

Optical Properties of Alternating Copolymers

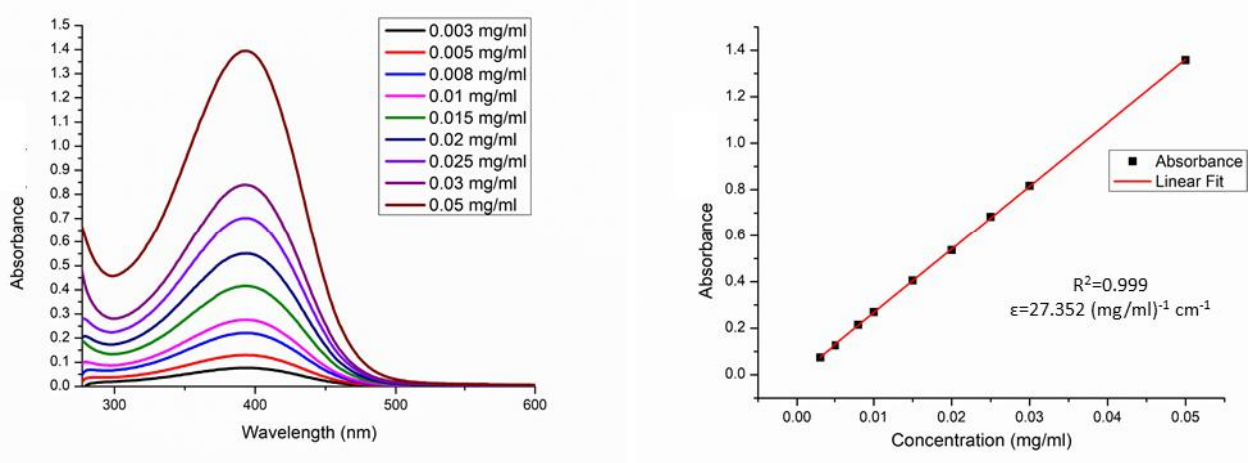


Figure S32. UV-Vis spectra of the non-adenine containing copolymer, **T-*t*T$_{4h}$,** at various concentrations in chloroform (left) and the Beer-Lambert plot (right).

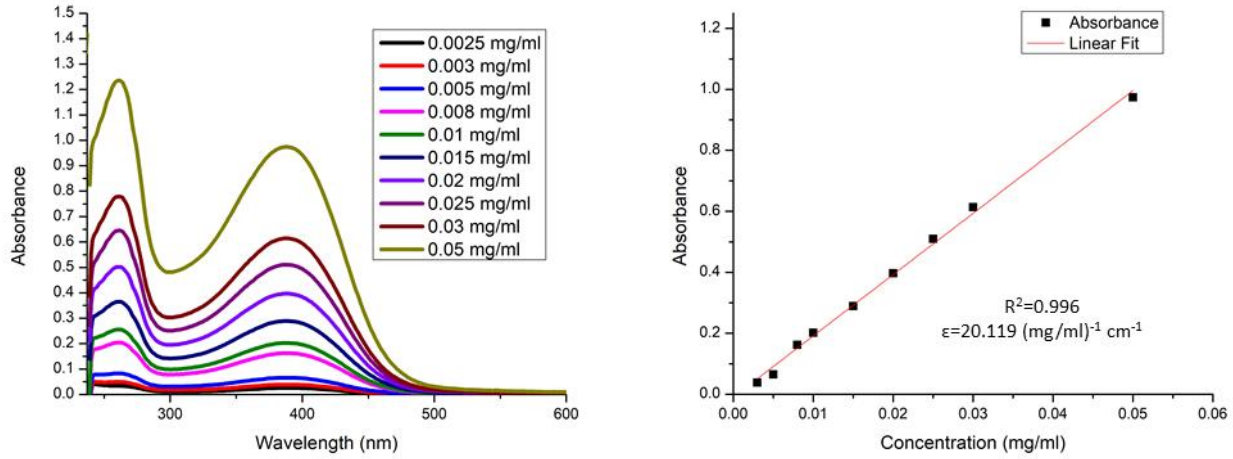


Figure S33. UV-Vis spectra of the adenine-containing copolymer, **T$_{Ad}$-*t*T$_{4h}$,** at various concentrations in chloroform (left) and the Beer-Lambert plot based on the absorbance mode attributed to the polythiophene backbone (right).

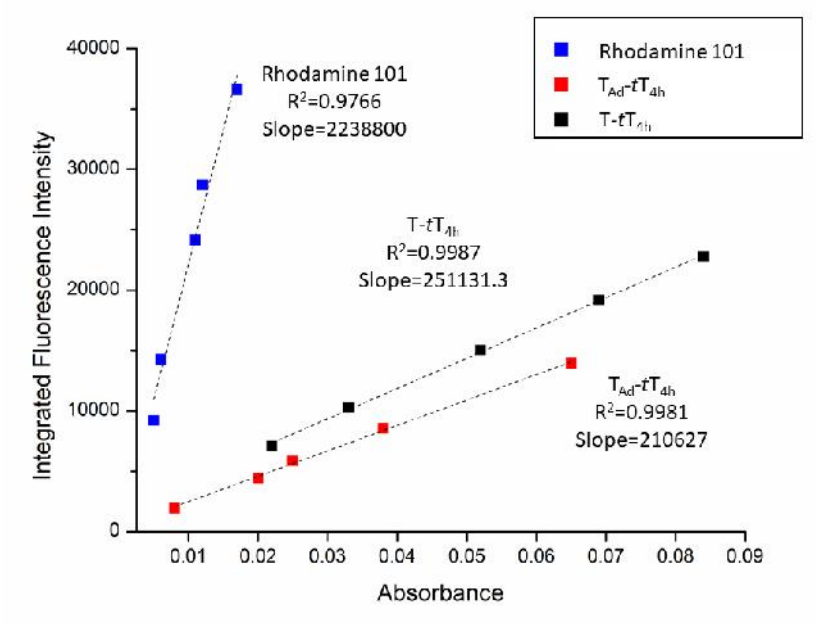


Figure S34. Integrated fluorescence intensity as a function of absorbance intensity maximum (of the polythiophene backbone) used for measurements of quantum yield by the comparative method (relative to Rhodamine 101).

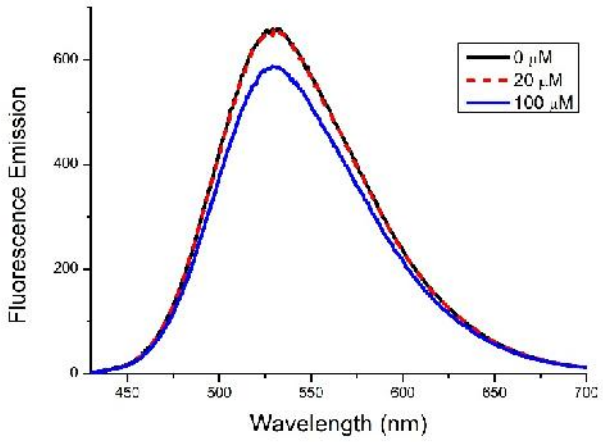


Figure S35. Fluorescence quenching response of **T-*t*T$_{4h}$** (at 0.01 mg/mL) upon addition of Cu^{2+}. No detectable change in fluorescence emission is observed for at 20 μM Cu^{2+}. A 10% quenching efficiency is observed for **T-*t*T$_{4h}$** at 100 μM Cu^{2+}, while **T$_{Ad}$-*t*T$_{4h}$** shows a 54% quenching efficiency at the same Cu^{2+} concentration.

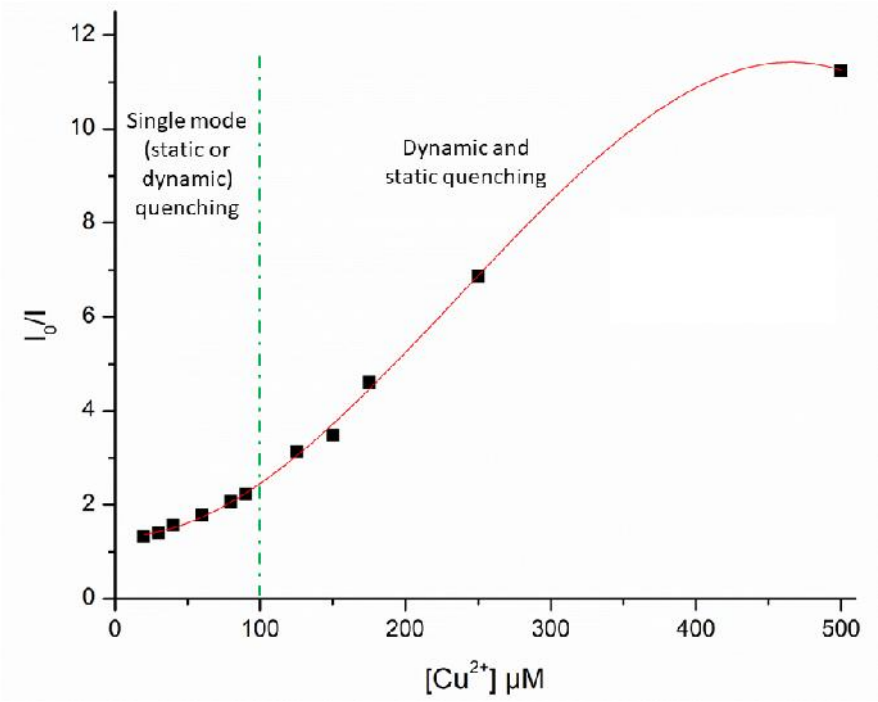


Figure S36. Fluorescence quenching response of **T_{Ad}-*t*T_{4h}**. As indicated in the figure, a single mechanism is present at low concentration, while the change in slope, nominally demarcated by the dashed green line, suggests both static and dynamic quenching occurs at higher concentration. The red line corresponds to a polynomial fit (R^2 = 0.9986).

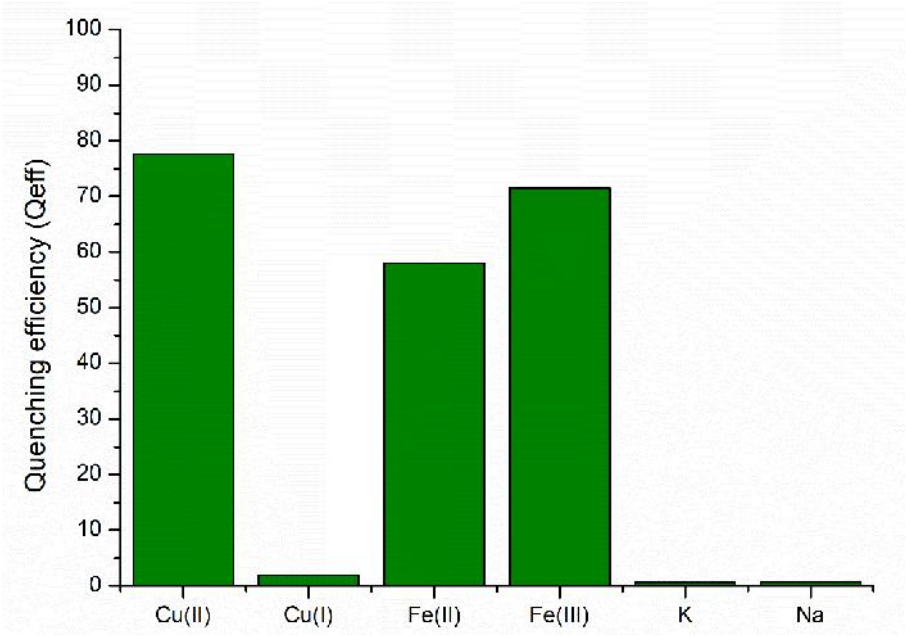


Figure S37. Fluorescence quenching response of **T_{Ad}-*t*T_{4h}** in presence of different ions (0.01 mg/mL in THF and 400 μM metal ion).

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