Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

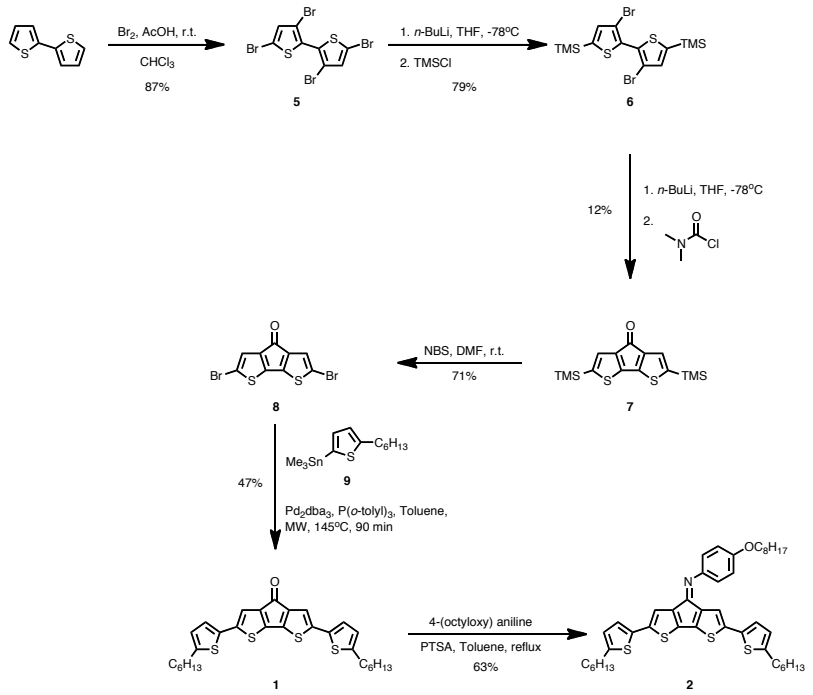
The Effect of Heteroatom Conformation on Optoelectronics Properties of Cyclopentadithiophenes Derivatives

*Sompit Wanwong, Ambata Poe, Ganapathy Balaji, S. Thayumanavan**

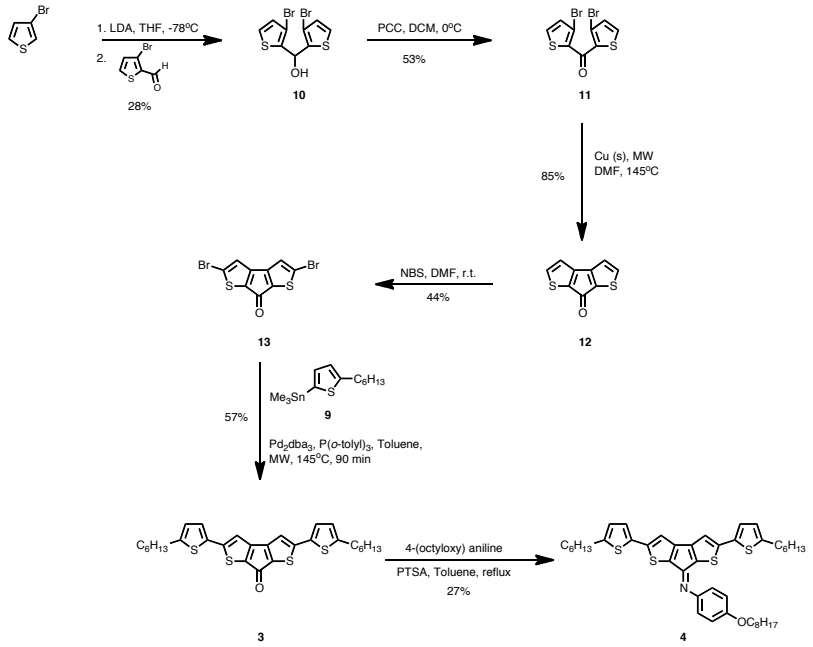
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

thai@chem.umass.edu

Supporting Information



Scheme S1. Synthesis of **CPDT-a-ketone** and **CPDT-a-imine**



Scheme S2. Synthesis of **CPDT-s-ketone** and **CPDT-s-imine**

Experimental Details

General Materials:

2,2′-Bithiophene was purchased from Alfa Aesar and used as received. 3-bromothiophene, 3-bromothiophene-2-carboxaldehyde, 2-hexylthiophene, bromine, chlorotrimethylsilane, *N*, *N*-dimethylcarbamoyl chloride, 4-(octyloxy) aniline, trimethyltin chloride, n-butyl lithium and diisopropylamine were purchased from Aldrich and used as received. *N*-bromosuccinimide was purchased from Aldrich and recrystallized before use. Catalysts and ligand were purchased from Aldrich and used as received. HPLC grade toluene, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), dimethylsulfoxide (DMSO) and methanol were purchased from Fisher and were used as received. Tetrahydrofuran (THF) was purchased from Fisher and dried over sodium and benzophenone. Anhydrous *N*, *N*′-dimethylformamide (DMF) and anhydrous diethyl ether were purchased from Aldrich and used as received.

Instrumentations

^{1}H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer and were reported in ppm using the solvents as the internal standard ($CDCl_3$ at 7.26 ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using the carbon signal of the deuterated solvent as the internal standard. UV-vis absorption spectra were recorded on a Cary 100 scan UV-vis spectrophotometer. Electrochemical measurements were performed on a BASi Epsilon potentiostat in anhydrous dichloromethane. The thermal analysis of small molecule semiconductors was obtained by thermogravimetric analysis (TGA) using Q500 TA instruments. The glass transition

temperatures (T_g) of the CPDT derivatives were determined by differential scanning calorimeter (DSC) using Q200 TA instruments. The optical and electrochemical properties of small molecule semiconductors were recorded. Charge carrier mobility was determined in field effect transistor (FET) mode using Agilent 4165C precision semiconductor parameter analyzer.

Mobility measurements

Field effect transistor (FET) devices were fabricated using pre-patterned n-doped silicon substrate Gold electrodes were deposited on the gate layer to yield the bottom contact FETs. The FET substrates were rinsed with acetone before film deposition. After this, organic thin films were deposited on the surface by spin coating 5 mg/0.5 mL chlorobenzene solution (2000 rpm for 1 minute). The devices were then allowed to dry at r.t. for 30 minutes. The channel width of all transistors was 10 mm and channel length was 20, 10 or 2.5 μm. The capacitance of the insulator is 14.9 nF/cm^2 for 230 nm of SiO_2. All measurements were performed under vacuum at a temperature of 25 °C and again after annealing at 80 °C 10 minute using Agilent 4165C precision semiconductor parameter analyzer.

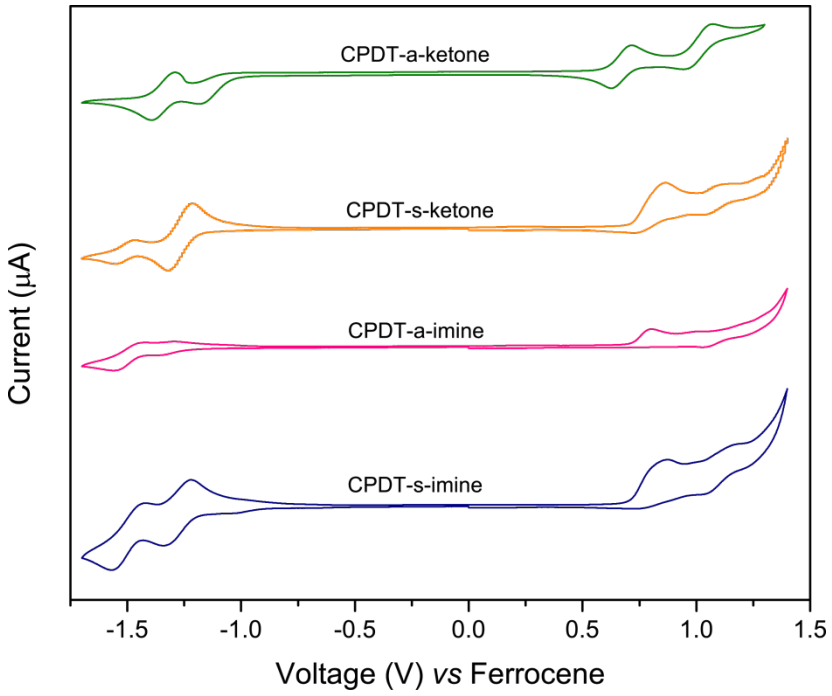


Figure S1. Cyclic voltammograms of CPDT compounds

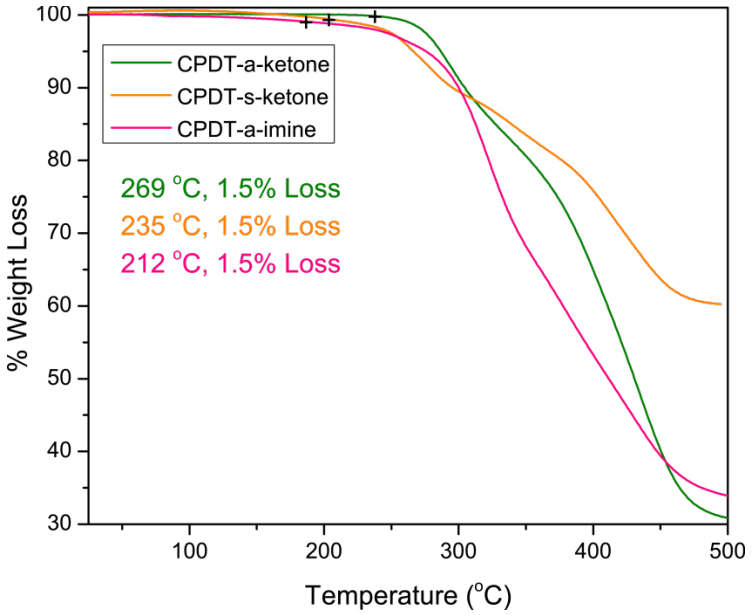


Figure S2. TGA traces of CPDT under nitrogen at 10 °C/min

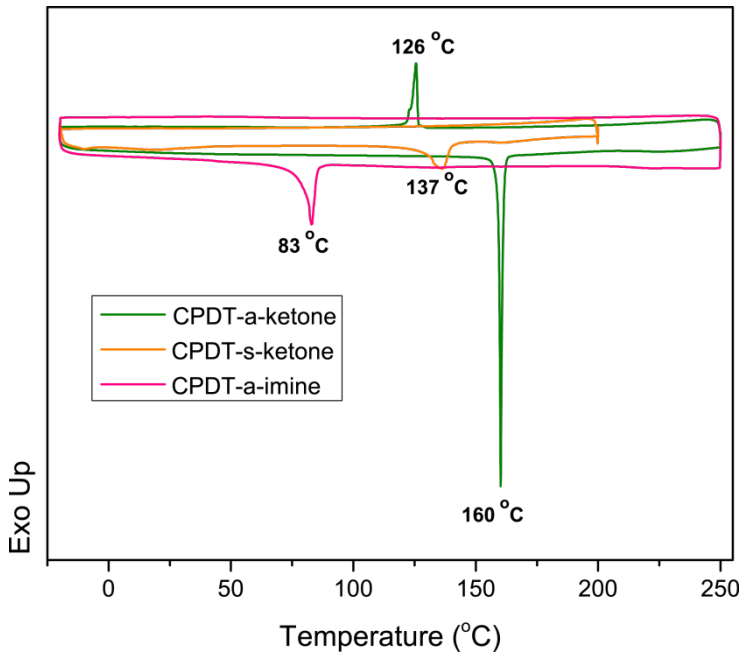
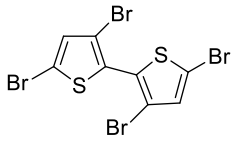


Figure S3. DSC traces of CPDT at a heating rate of 10 °C/min

General procedure for Stille coupling

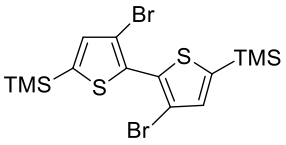
In a quartz microwave vessel, required dibromide (1.00 eq), 2-hexyl-5-trimethylstannyl thiophene (2.50 eq) and tris(*o*-tolyl)phosphine ($P(o\text{-}tol)_3$) (0.05 eq) were taken and dissolved in dry toluene. The reaction mixture was degassed for 20 minutes, followed by adding tris(dibenzylideneacetone) dipalladium(0) (Pd_2dba_3) (0.05 eq). The vessel was sealed and the reaction mixture was stirred in Milestone StartSYNTH microwave reactor. The power was set to 500 W. The temperature was set at 135 °C and monitored by the built-in infrared sensor. The reaction was done in 90 minutes and it was then allowed to cool to room temperature and quenched by water. The product was extracted using dichloromethane. The product was purified by column chromatography. Compound **5-8** and compound **12** were synthesized in accordance to the reported procedures.[1-3]

Synthesis of 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**5**)



2,2′-Bithiophene (5.0 g, 30 mmol) and 25 mL acetic acid were mixed in 50 mL chloroform. The mixture was stirred at 0 °C. A solution of bromine (19.3 g, 120 mmol) in 25 mL chloroform was added dropwise to the reaction mixture over 1 hour. The reaction mixture was allowed to stir for 18 hours. Remaining bromine was removed by air purge. The reaction mixture was then concentrated under reduce pressure. The product **5** was isolated in diethyl ether wash as is green powder (12.6 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 112.1, 114.8, 129.6, 133.0 FAB/MS (*m/z*) calculated for $C_8H_2Br_4S_2$, 481.9; found 481.6.

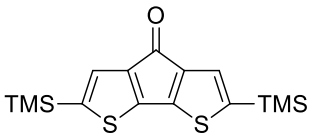
Synthesis of 5,5′-Bis(trimethylsilyl)-3,3′-dibromo,-2,2′-bithiophene (**6**)



n-BuLi (2.5 M solution in hexanes, 31.0 mmol) was added dropwise to a solution of **5** (7.5 g, 15.6 mmol) in 150 mL dry THF at -78 °C. The mixture was stirred for 15 minutes. Chlorotrimethylsilane (4.9 mL, 39.0 mmol) was added to the mixture. The reaction mixture was allowed to warm to room temperature and stirred for 18 hours and quenched with water. Then mixture was extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated using rotary evaporator The crude mixture was then purified by column chromatography over silica to obtain **6** (5.8 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.34

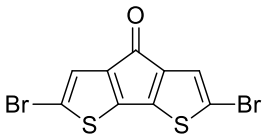
(s, 18H), 7.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): -0.3, 113.0, 134.0, 137.1, 142.9 FAB/MS (*m/z*) calculated for $C_{14}H_{20}O_2S_2Si_2$, 467.8; found 467.8.

Synthesis of 2,6-bis(trimethylsilyl)-4*H*-cyclopenta [2,1-*b*:3,4-*b'*]dithiphen-4-one (**7**)



n-BuLi (2.5 M solution in hexanes, 10 mL) was added dropwise to a solution of **6** (5.8 g, 12.5 mmol) in 60 mL dry THF at -78 °C. The mixture was stirred for 15 minutes. A solution of dimethylcarbamoyl chloride (1.1 mL, 12.5 mmol) in 10 mL dry THF was added dropwise to the reaction mixture. The reaction temperature was raised temperature to 0 °C, stirred for an additional 3 hours and quenched with 50 mL saturated NH_4Cl. The mixture was extracted with diethyl ether and the combined organic layer was dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography over silica to obtain **7** (0.5 g, 12%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.30 (s, 18H), 7.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): -0.2, 127.9, 144.2, 144.9, 154.3, 183.1 FAB/MS (*m/z*) calculated for $C_{15}H_{20}OS_2Si_2$, 336.1; found 337.1 $[M+H]^+$.

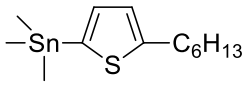
Synthesis of 2,6-dibromo-4*H*-cyclopenta [2,1-*b*:3,4-*b'*]dithiphen-4-one (**8**)



Compound **7** (0.5 g, 1.5 mmol) in 3 mL THF was stirred at 0 °C. A solution of *N*-bromosuccinimide (0.7 g, 3.7 mmol) in 1 mL DMF was added to reaction mixture. The reaction

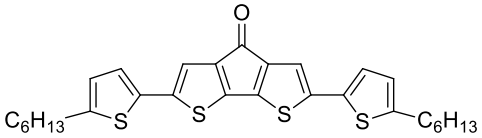
mixture was allowed to warm to room temperature and stirred for 18 hours. The mixture was extracted with dichloromethane and water. The organic layer was dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography over silica to afford **8** as red powder (0.4 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 114.0, 124.4, 140.0, 148.7, 180.5 EI/MS (*m/z*) calculated for $C_9H_2Br_2OS_2$, 350.1; found 349.8.

Synthesis of 2-hexyl-5-thiophenyl-thiophene (**9**)



n-BuLi (2.5 M solution in hexanes, 13.0 mmol) was added dropwise to a solution of 2-hexylthiophen (2.0 g, 12 mmol) in 150 mL dry THF at -78 °C. The mixture was stirred for 1 hour. Trimethyltin chloride (1.0 M solution in THF, 14.0 mmol) was added to the mixture. The reaction mixture was allowed to warm to room temperature and stir for 18 hours and quenched with water. Then mixture was extracted with dichloromethane and water. The organic layers were dried over Na_2SO_4 and concentrated using rotary evaporator. Compound **9** was used for next step without purification.

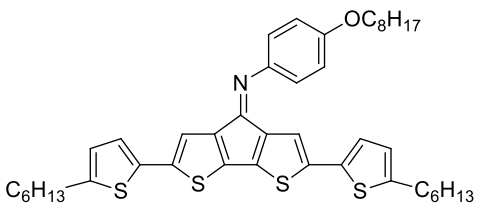
Synthesis of 2,6-bis-(5-hexylthiophene-2-yl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiphen-4-one (**1**)



Following the general procedure, compound **8** (0.100 g, 0. 29 mmol), compound **9** (0.240 g, 0.71 mmol), P(o-tol)$_3$ (0.004 g, 0.01 mmol) and Pd_2dba_3 (0.008 g, 0.01 mmol) were reacted in

the microwave reactor. The crude product was purified by column chromatography to obtain **1** as a green solid (0.070 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm):, 0.88 (t, 6H) 1.31-1.38 (m, 12H), 1.63-1.72 (m, 4H), 2.77 (t, 4H), 6.67(d, 2H, *J* = 3.6 Hz), 6.95 (d, 2H, *J* = 3.6 Hz) 6.97 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm):, 14.1, 22.6, 28.8, 30.8, 31.5, 116.9, 123.5, 133.8, 140.7, 141. 9, 146.2, 146.7, 182.9 EI/HRMS (*m/z*) calculated for $C_{29}H_{32}OS_4$, 524.1336; found 524.1336.

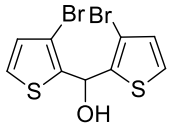
Synthesis of *N*-(2,6-bis(5-hexylthiophen-2-yl)-4*H*-[2,1-*b*:3,4-*b'*]dithiphen-4-ylidene)-4-(octyloxy)aniline (**2**)



Compound **1** (0.07 g, 0.13 mmol), 4-(octyloxy) aniline (0.03 g, 0.14 mmol) and *p*-toluenesulfonic anhydrous (0.01 g, 0.07 mmol) were dissolved in 15 mL toluene. The reaction was refluxed under argon atmosphere for 18 hours. The reaction mixture was then concentrated under reduce pressure and extracted with dichloromethane and water. The organic layers were dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography to yield **2** as orange powder (0.06 g, 63%).^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm):, 0.88 (t, 9H) 1.29-1.33 (m, 20H), 1.46-1.51 (m, 2H), 1.60-1.72 (m, 4H), 1.79-1.87 (m, 2H), 2.72-2.82 (m, 4H), 4.02 (t, 2H), 6.25 (s, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.82 (d, *J* = 3.6 Hz, 1H), 7.03-6.94 (m, 5H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm):, 14.1, 22.6, 26.1, 28.8, 29.3, 30.2, 30.9, 31.6, 68.5, 114.9, 117.0, 119.5,

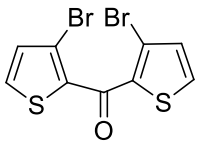
121.9, 123.0, 124.8, 134.3, 134.7, 137.0, 138.1, 139.7, 143.8, 145.3, 145.7, 156.0, 157.2 EI/HRMS (*m/z*) calculated for $C_{43}H_{53}NOS_4$, 727.3010; found 727.3010.

Synthesis of bis(3-bromothiophen-2-yl)methanol (**10**)



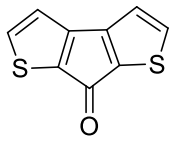
n-BuLi (2.5 M solution in hexanes, 6.3 mL) was added dropwise to a solution of diisopropylamine (2.4 mL, 18 mmol) in 100 mL dry THF at -78 °C. The reaction was stirred for 1 hour and 3-bromothiophene (2.3 g, 14.3 mmol) was added dropwise. The reaction mixture was stirred for an additional 1 hour, and 3-bromothiophene-2-carboxaldehyde (3.0 g, 15.7 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 18 hours and quenched with NH_4Cl. The mixture was extracted with dichloromethane and water. Organic layer was dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography over silica to afford **10** (1.4 g, 28%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.69 (d, 1H, *J* = 3.2Hz), 6.43 (d, 1H, *J* = 3.2 Hz), 6.96 (d, 2H, *J* = 5.2 Hz), 7.29 (d, 2H, *J* = 5.2 Hz) ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 59.0, 67.2, 109.4, 126.0, 130.1, 140.4 EI/HRMS (*m/z*) calculated for $C_9H_6Br_2OS_2$, 353.8206.; found 353.8206.

Synthesis of bis(3-bromothiophene-2-yl)methanone (**11**)



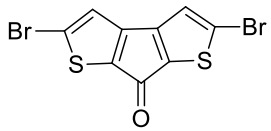
Compound **10** (1.4 g, 4.3 mmol) was dissolved in 15 mL DCM and stirred at 0 °C. Pyridium chlorochromate (1.4 g, 6.5 mmol).was then added to the solution. The mixture was filtered and the solid was washed with dichloromethane several times. The filtrate was then concentrated under reduce pressure and extracted with dichloromethane and water. The organic layers were dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography to obtain **11** (0.8 g, 53%) ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.11 (d, 2H, *J* = 5.3 Hz), 7.55 (d, 2H, *J* = 4.8 Hz) ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 115.8, 131.5, 132.7, 179.5 EI/HRMS (*m/z*) calculated for $C_9H_4Br_2OS_2$, 349.8050; found 351.8049.

Synthesis of 7*H*-cyclopenta [1,2-*b*:4,3-*b'*]dithiphen-7-one (**12**)



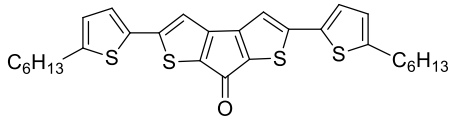
To a quartz microwave vessel, compound **11** (0.62 g, 1.78 mmol) and copper powder (0.56 g, 8.9 mmol) were mixed in 4 mL DMF. The reaction mixture was stirred in microwave reactor at power 500 W, at 145 °C for 3 hours. The reaction mixture was allowed to cool to room temperature. The mixture was filtered and the solid was washed with dichloromethane. The organic layers were extracted with water and dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography to yield **11** (0.3 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.87 (d, 2H, *J* = 5.3 Hz), 7.55 (d, 2H, *J* = 4.8 Hz) ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 119.8, 136.7, 136.9, 152.0, 178.6 EI/HRMS (*m/z*) calculated for $C_9H_4OS_2$, 191.9704; found 191.9704.

Synthesis of 2,5-dibromo-7*H*-cyclopenta [1,2-*b*:4,3-*b'*]dithiphen-7-one (**13**)



Compound **13** (0.15 g, 0.8 mmol) in 3 mL THF was stirred at 0 °C. A solution of *N*-bromosuccinimide (0.08 g, 1.6 mmol) in 0.5 mL DMF was added to reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred for 18 hours. The mixture was extracted with dichloromethane and water. The organic layer was dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography over silica to afford **13** as red powder (0.12 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.91 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 123.0, 125.4, 135.4, 150.4, 176.6 EI/HRMS (*m/z*) calculated for $C_9H_2Br_2OS_2$, 349.7893; found 349.8805.

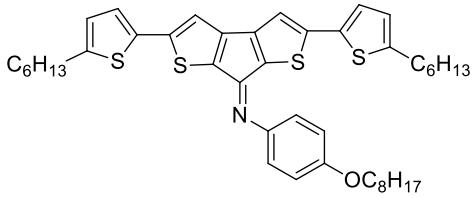
Synthesis of 2,5-bis-(5-hexylthiophene-2-yl)-7*H*-cyclopenta[1,2-*b*:4,3-*b'*]dithiphen-7-one (**3**)



Following the general procedure, compound **13** (0.040 g, 0.11 mmol), compound **9** (0.090 g, 0.29 mmol), P(o-tol)$_3$ (0.002 g, 0.05 mmol) and Pd_2dba_3 (0.003 g, 0.05 mmol) were reacted in the microwave reactor. The crude product was purified by column chromatography to obtain **3** as a red solid (0.030 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm):, 0.88 (t, 6H) 1.31-1.38 (m, 12H), 1.65-1.73 (m, 4H), 2.79 (t, 4H), 6.71 (d, 2H, J = 3.6 Hz), 6.81 (s, 2H), 7.09 (d, 2H, J = 3.6 Hz) ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm):, 14.1, 22.6, 28.7, 29.7, 30.3, 31.5, 115.4,

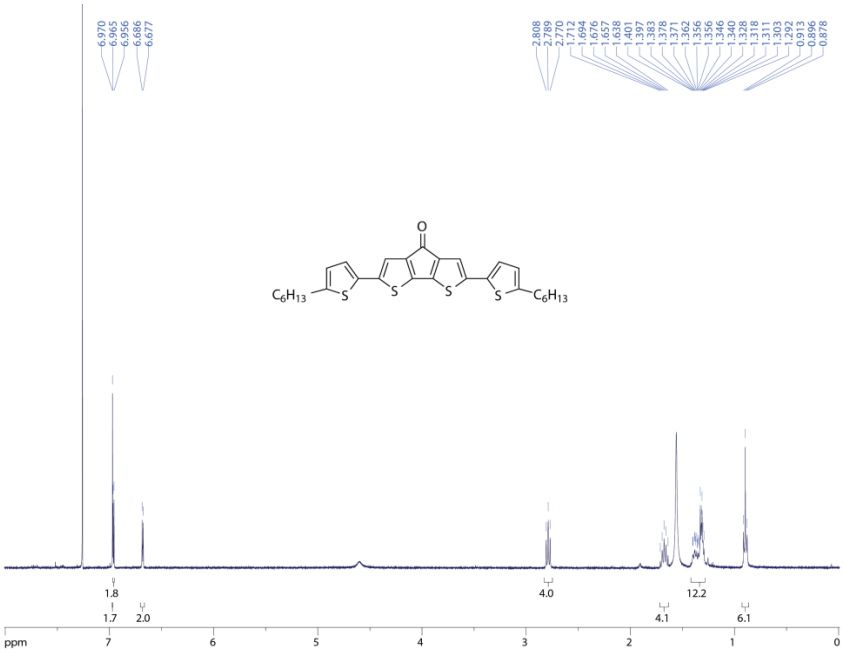
124.8, 125.3 133.3, 133.9, 147.8, 149.9, 151.8, 178.3 EI/HRMS (*m/z*) calculated for $C_{29}H_{32}OS_4$, 524.1336; found 524.1336 [M+H].

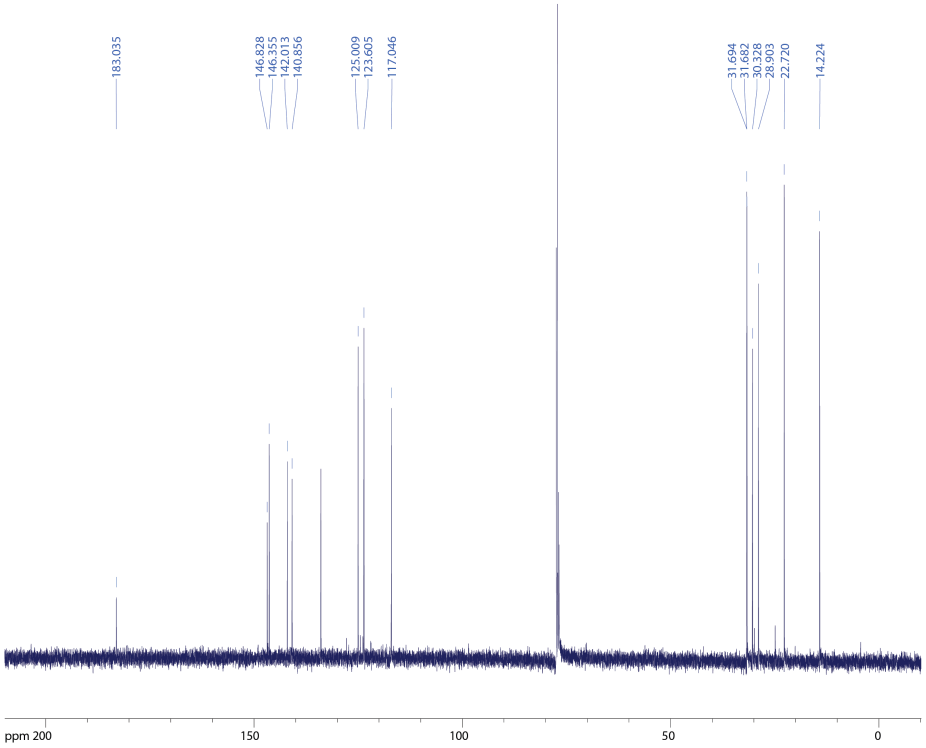
Synthesis of *N*-(2,5-bis(5-hexylthiophen-2-yl)-7*H*-[2,1-*b*:3,4-*b'*]dithiphen-7-ylidene)-4-(octyloxy)aniline (**4**)



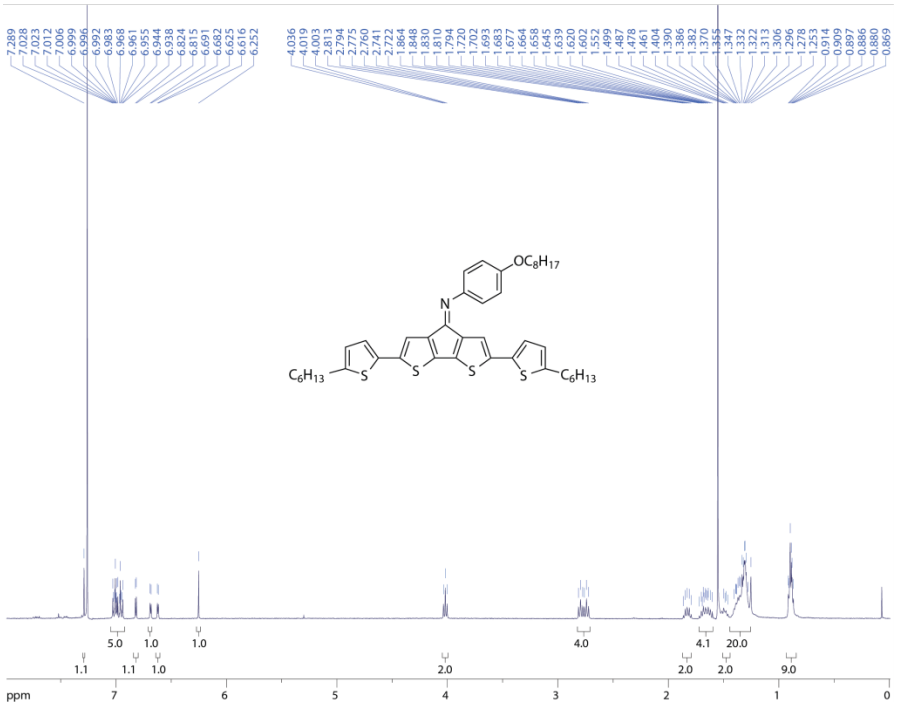
Compound **3** (0.160 g, 0.03 mmol), 4-(octyloxy) aniline (0.008 g, 0.03 mmol) and *p*-toluenesulfonic anhydrous (0.003 g, 0.01 mmol) were dissolved in 15 mL toluene. The reaction was refluxed under argon atmosphere for 18 hours. The reaction mixture was then concentrated under reduce pressure and extracted with dichloromethane and water. The organic layers were dried over Na_2SO_4 and concentrated using rotary evaporator. The crude mixture was then purified by column chromatography to yield **4** as orange powder (0.006 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm):, 0.89 (t, 9H) 1.28-1.41 (m, 20H), 1.46-1.52 (m, 2H), 1.61-1.74 (m, 4H), 1.79-1.87 (m, 2H), 2.74-2.83 (m, 4H), 4.01 (t, 2H) 6.65 (d, *J* = 3.6 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 1H), 6.90-6.93 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 7.01 (s, 1H), 7.04-7.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm):, 14.1, 22.6, 28.7, 29.3, 29.6, 30.2, 31.6, 68.0, 114.4, 115.1, 115.4, 121.5, 123.8. 125.2, 134.1, 134.8, 144.1, 133.8, 145.7, 146.4, 146.7, 149.0, 154.7, 157.2 EI/MS (*m/z*) calculated for $C_{43}H_{53}NOS_4$, 728.2 found 728.3.

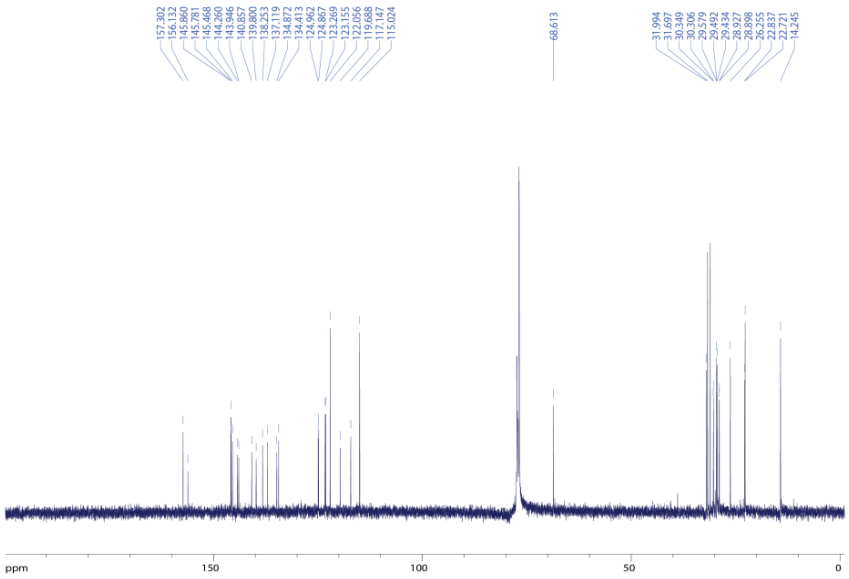
^{1}H and ^{13}C NMR



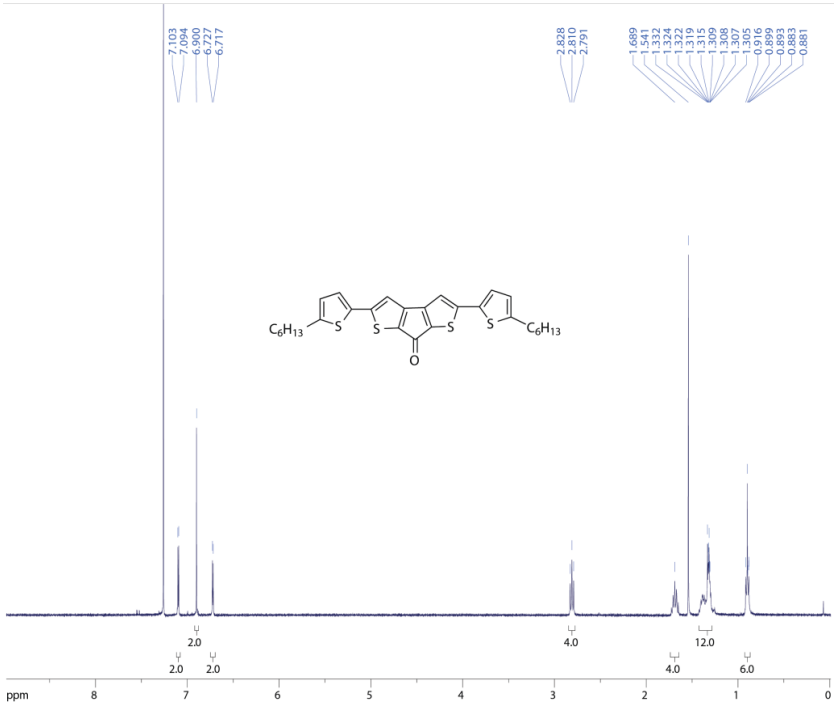


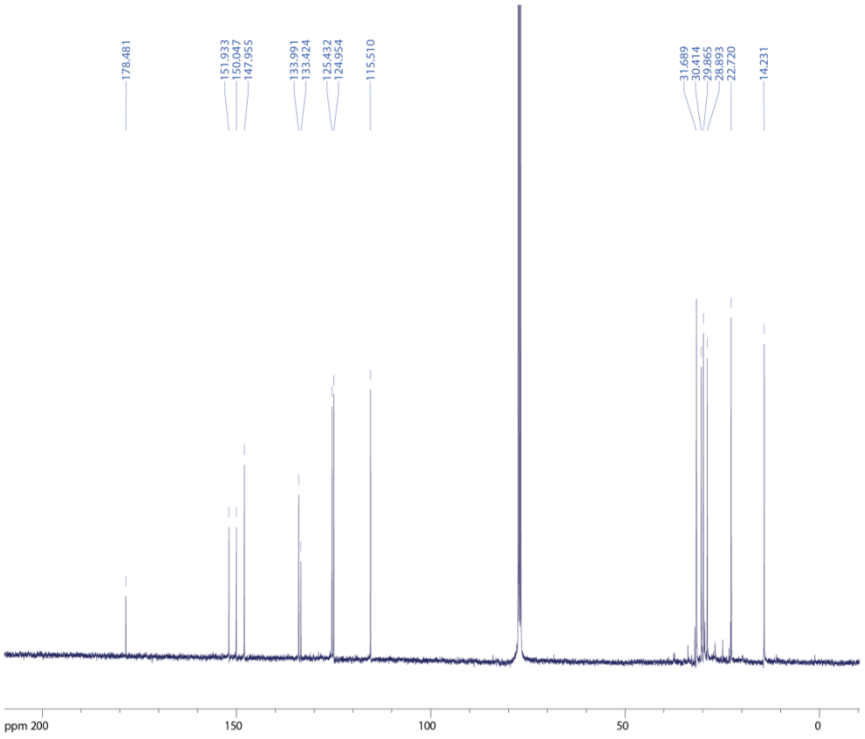
NMR spectra of Compound **1**



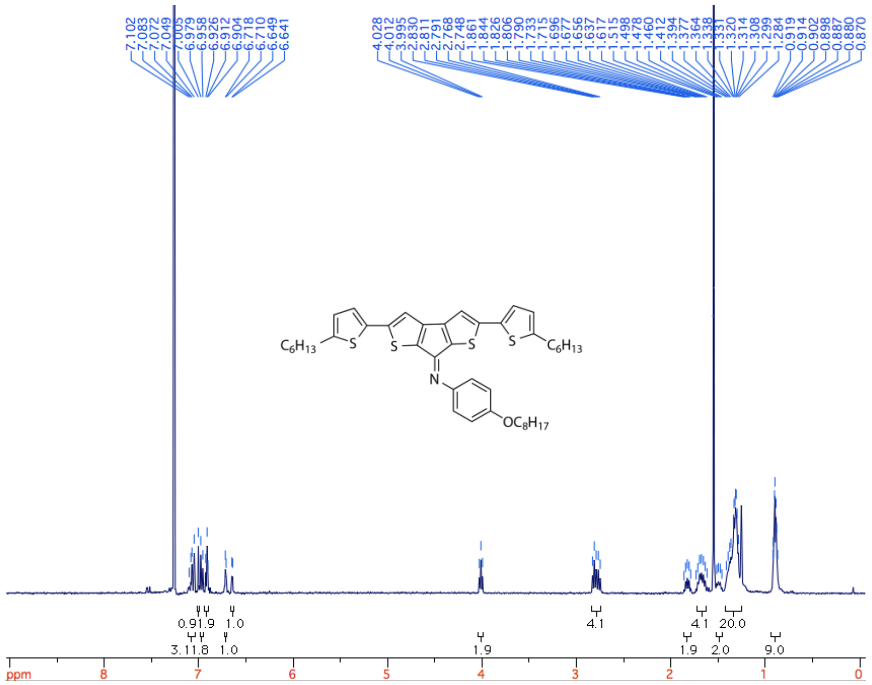


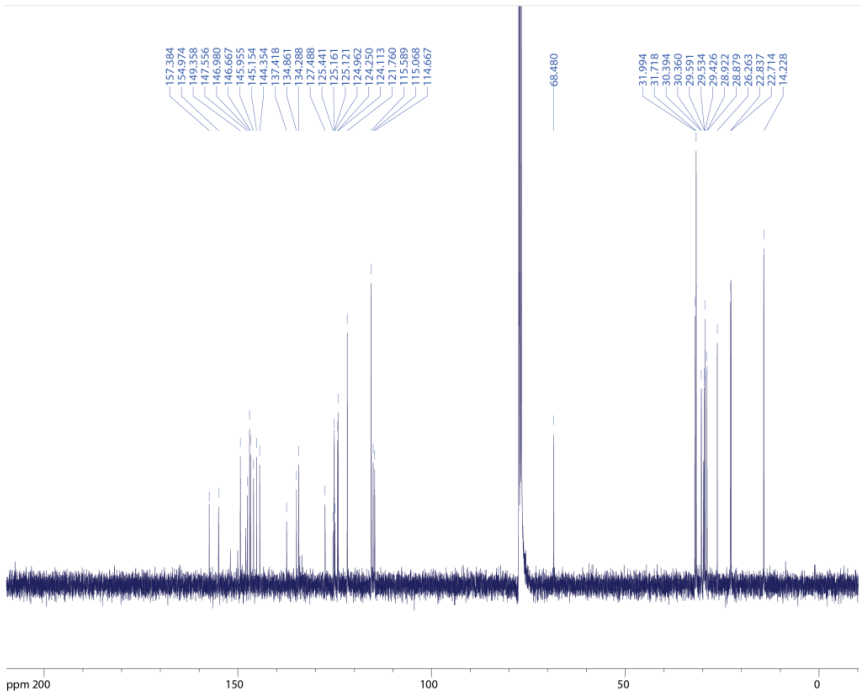
NMR of compound **2**





NMR of compound **3**





NMR of compound **4**

References

(1) Popere, B. C.; Pelle, A. D. M.; Poe, A.; Balaji, G.; Thayumanavan, S., *Chem. Sci* **2012**, 3093-3102.

(2) Li, K. C.; Hsu, Y. C.; Lin, J. T.; Yang, C. C.; Wei, K. H.; Lin, H. C., *J. Polym. Sci. A Polym. Chem.* **2009,** *43*, 2073-2092.

(3) Masatoshi, K.; Shoji, T.; Yoshiro, Y., *Chem. Lett.* **1993,** *3*, 533-536.