

Phthalimide-Thiophene-based Conjugated Organic Small Molecules with High Electron Mobility

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Supporting Information

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O₂-free N₂ via Schlenk line techniques and/or an Innovative Technology inc. N₂ atmosphere glove box.

Materials: 4-bromo-phthalic anhydride (**1**), N,N'-Dimethylacetamide (DMF), and Pivalic acid (PivOH) were purchased from TCI America and were used without further purification. N-Octylamine, 2-tributylstannylthiophene (SnBu₃-T), and 2,5 bis-tributylstannylthiophene ((SnBu₃)₂-T), were purchased from Sigma-Aldrich and were used without further purification. Pd(PPh₃)₄ and Pd(OAc)₂ were purchased from Strem Chemicals. Anhydrous Potassium Carbonate (K₂CO₃) was purchased from ACP Chemicals, and after initial usage, was stored in a Gallenkamp Hotbox oven at 100°C. Glacial Acetic Acid (CH₃COOH) was purchased from Fisherbrand and used without further purification. All solvents were purchased from the Dalhousie solvent exchange program and used without further purification, unless otherwise noted.

Nuclear Magnetic Resonance (NMR): ¹H and {¹H}¹³C (NMR) spectroscopy spectra were recorded on either a Bruker Avance-500 MHz spectrometer or a Bruker Avance-300 MHz spectrometer at 300K. Chemical shifts (in ppm) were referenced to SiMe₄. All experiments were performed in deuterated chloroform (CDCl₃).

Mass Spectrometry: Mass spectrometry measurements were performed courtesy of Xiao Feng in the Dalhousie University Analytical Laboratory. A Bruker-Daltronics Micro TOF Mass Spectrometer was used. Electrospray ionization was used to ionize the samples with a spray voltage of 45kV and a sample introduction rate of 2uL/min.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a NETZSCH Tarsus-TG 203 F3 instrument with Nitrogen as the purging gas. Samples were heated to 600°C at 15°C/minute under a N₂ atmosphere.

Synthesis of 5,5'-bis-(2-octyl)isoindoline-1,3-dione)-bithiophene (1): Was synthesized as previously reported.^[37]

Synthesis of 5,5'-bis-(2-hexyl)isoindoline-1,3-dione)-bithiophene (2): was synthesized in a similar manner to compound **1**, substituting N-Hexyl phthalimide in place of N-Octyl phthalimide. Yield: 70mg (35%). ¹H NMR (Chloroform-d, TMS/ppm) δ 8.06 (m, 2H), 7.90 (m,

Hz, 2H), 7.84 (m, Hz, 2H), 7.44 (d, $^3J=0.01$ Hz, 2H), 7.27 (d, $^3J=0.01$ Hz, 2H), 3.69 (t, $^3J=0.05$ Hz, 4H), 1.75-1.63 (m, 4H), 1.44-1.24 (m, 20H), 0.94-0.83(m, 6H). ^{13}C NMR (Chloroform-d, TMS/ppm) δ 186.06, 167.96, 141.36, 139.6, 138.33, 133.9, 130.35, 130.17, 126.15, 125.57, 123.92, 119.75, 38.23, 31.36, 28.55, 26.53, 22.50, 13.99. LRMS: M+ m/z expected: 625.2 found 625.2

Synthesis of 5,5'-bis-(2-butyl)isoindoline-1,3-dione)-bithiophene (3): was synthesized in a similar manner to compound 1, substituting N-Butyl phthalimide in place of N-Octyl phthalimide. Yield: 62mg (31%). ^1H NMR(Chloroform-d, TMS/ppm). ^1H NMR (Chloroform-d, TMS/ppm) δ 8.05 (m, 2H), 7.90 (m, Hz, 2H), 7.84 (m, Hz, 2H), 7.45 (m, $^3J=0.03$ Hz, 2H), 7.28 (m, $^3J=0.03$ Hz, 2H), 3.71 (t, $^3J=0.05$ Hz, 4H).), 1.72-1.65 (m, 4H), 1.42-1.34 (m, 4H), 0.99-0.93(m, 6H). LRMS: M+ m/z expected: 569.1 found 569.1. Due to the extremely low solubility of this compound no ^{13}C nmr data was obtained.

Synthesis of 5,5'-bis-(2-octyl)isoindoline-1,3-dione)-trithiophene (4): In a 2-5 mL microwave tube with a stir bar, 5-bis-(trimethylstannyl)-thiophene (214 mg, 0.668 mmol, 1eq) was combined with 5-(5-bromothiophen-2-yl)-2-octylisoindoline-1,3-dione (441 mg, 1.05 mmol, 2eq) and $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.01 eq). Toluene (3mL) was added as a solvent and the microwave tube was heated to 200 °C for 20 minutes using microwave irradiation. At the end of the reaction an orange colour had developed and a suspension of yellow solid was present in the reaction tube. The contents were stirred into chloroform (~200mL) and the solvent was removed to yield a crude orange solid. The crude solid was dissolved in dichloromethane and loaded onto silica and purified via column chromatography. A three solvent system was used to purify the product. First a gradient from Pentane (100%) to ethyl acetate (100%) was run and a band was collected at 100% ethyl acetate. Next a gradient was run from ethyl acetate (100%) to chloroform (100%) and the product was eluted at 100% Chloroform. Removal of the volatiles from the product fraction gave the product as a bright orange solid. Iso-propanol/water (1:9) was used to slurry the material prior to filtration in a Buchner funnel. The product was washed with iso-propanol/water (1:9) and dried in a vac oven overnight to give the product as a pure orange solid. Yield: 33mg (8.3%). ^1H NMR(Chloroform-d, TMS/ppm) δ 8.06 (m, 2H), 7.90 (m, Hz, 2H), 7.85 (m, Hz, 2H), 7.45 (m, $^3J=0.03$ Hz, 2H),7.28-7.26 (m,4H), 3.70 (t, $^3J=0.05$ Hz, 4H).), 1.73-1.65 (m, 4H), 1.38-1.22 (m, 20H), 0.90-0.84(m, 6H). ^{13}C NMR(Chloroform-d, TMS/ppm) δ 168.11, 168.01,140.93, 139.69, 138.62, 136.29, 133.41, 130.25, 130.11, 126.25, 125.205, 125.173, 123.93, 119.7, 38.26, 31.79, 29.17, 28.62, 26.90 .LRMS: M+ m/z expected: 763.1 found 763.1

Synthesis of 2,5-bis-(2-octyl)isoindoline-1,3-dione)-thiophene (5): In a 2-5mL microwave tube with a stir bar, 2,5-bis-(trimethylstannyl)-thiophene (274mg, 0.668 mmol, 1eq) was combined with 5-bromo-2-octylisoindoline-1,2-dione (452mg, 1.34 mmol, 2eq) and $\text{Pd}(\text{PPh}_3)_4$ (60mg, 0.01 eq). Toluene (3mL) was added as a solvent and the microwave tube was heated to 200 °C for 20 minutes using microwave irradiation. At the end of the reaction a yellow colour had developed and a suspension of yellow solid was present in the reaction tube. The contents were stirred into chloroform (~150mL) and the solvent was removed from the filtrate to yield a crude yellow solid. The crude solid was dissolved in dichloromethane and loaded onto silica and purified via column chromatography. The product was eluted using a pentane/ CHCl_3 gradient. An impurity is washed off at 80% CHCl_3 The product fraction eluted at 100% CHCl_3 . Removal of solvent from the product fraction using a rotary evaporator gave the product compound as a bright yellow solid. Iso-propanol/water (1:9) was used to slurry the material prior to filtration in a Buchner funnel. The product was washed with iso-propanol/water (1:9) and dried in a vac oven overnight to give the product as a pure yellow solid. Yield: 374 mg (93.5%) ^1H NMR (Chloroform-d, TMS/ppm) δ 8.05 (m, 2H), 7.90

(m, Hz, 2H), 7.87 (m, Hz, 2H), 7.53 (m, $^3J=0.03$ Hz, 2H), 3.70 (t, $^3J=0.05$ Hz, 4H.), 1.73-1.66 (m, 4H), 1.38-1.22 (m, 20H), 0.89-0.86 (m, 6H). ^{13}C NMR(Chloroform-d, TMS/ppm) δ 168.07, 167.96, 141.35, 139.57, 138.33, 133.40, 130.35, 130.17, 126.26, 125.67, 123.92, 119.75, 38.23, 31.36, 28.55, 26.53, 22.50, 13.99 LRMS: M+ m/z expected: 599.2 found 599.2

¹H NMR Spectra:

(1)

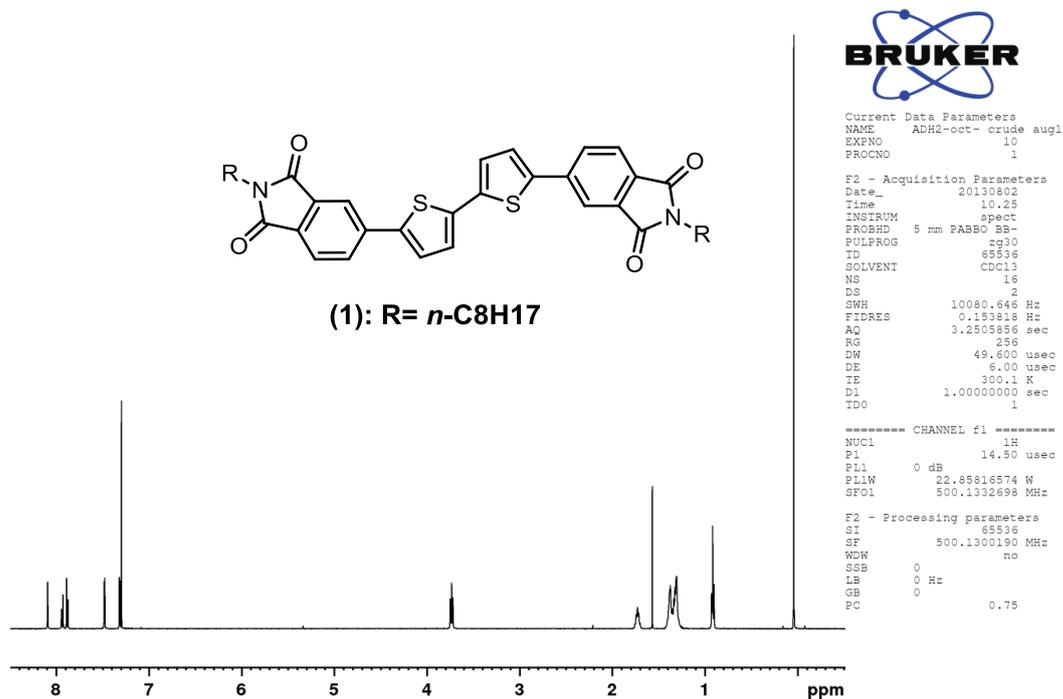


Figure S1: ¹H NMR spectra of (1) in CDCl₃ (peak at 7.27 is CHCl₃)

(2)

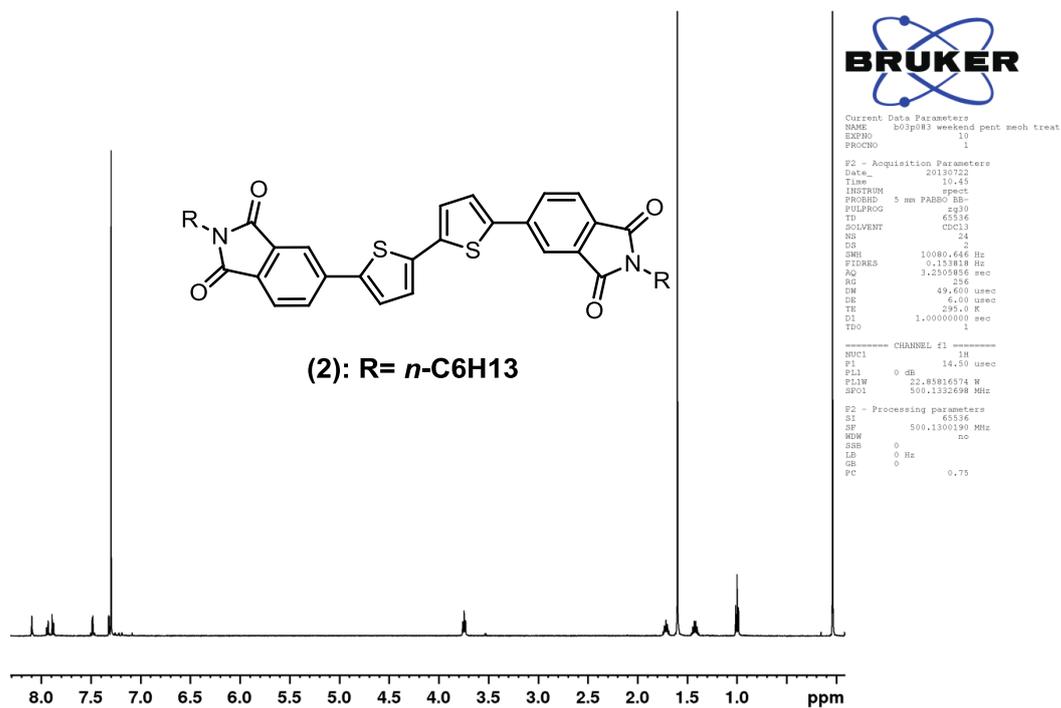


Figure S2: ^1H NMR spectra of (2) in CDCl_3 (peak at 7.27 is CHCl_3)

(3)

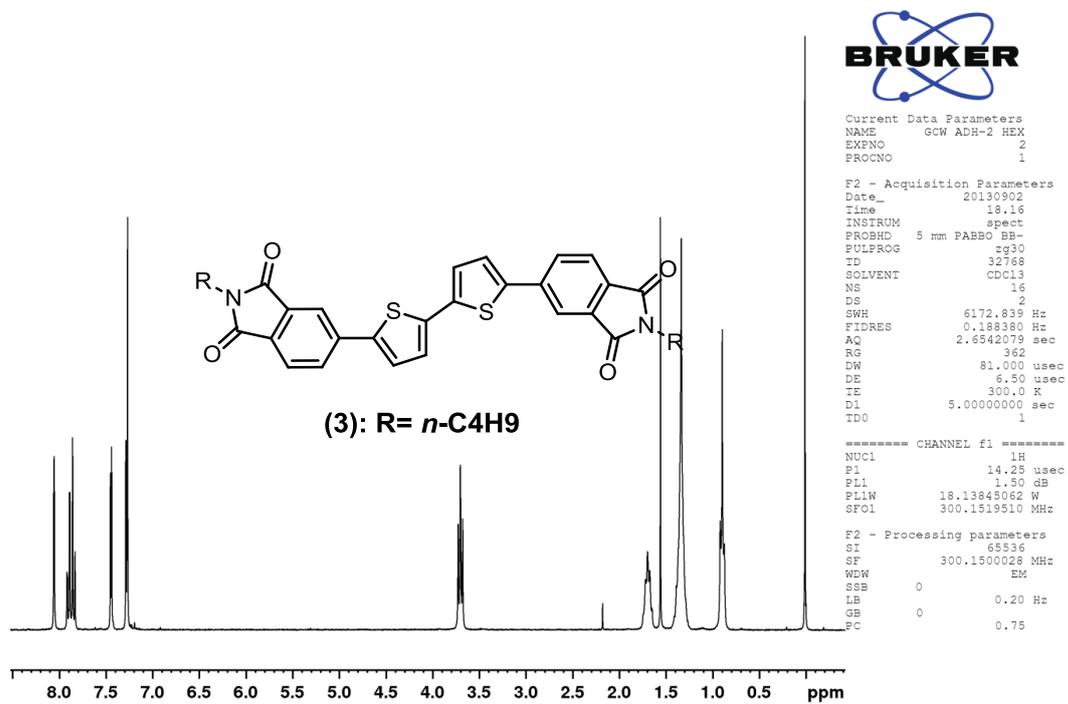


Figure S3: ¹H NMR spectra of (3) in CDCl₃ (peak at 7.27 is CHCl₃)

(4)

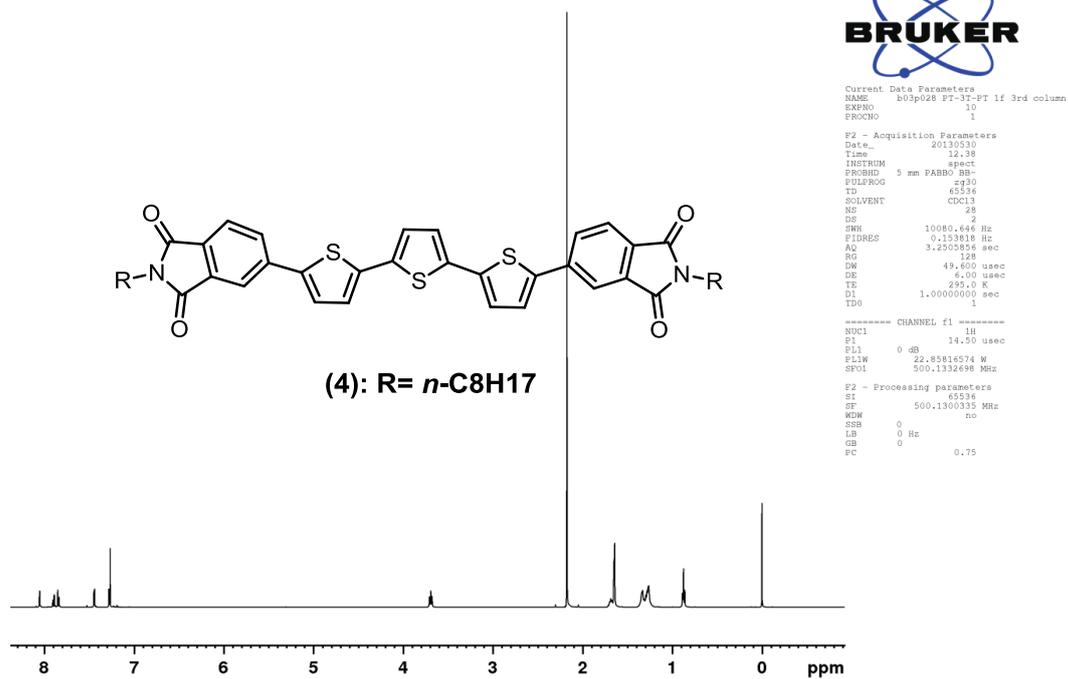


Figure S4: ¹H NMR spectra of (4) in CDCl₃ (peak at 7.27 is CHCl₃)

(5)

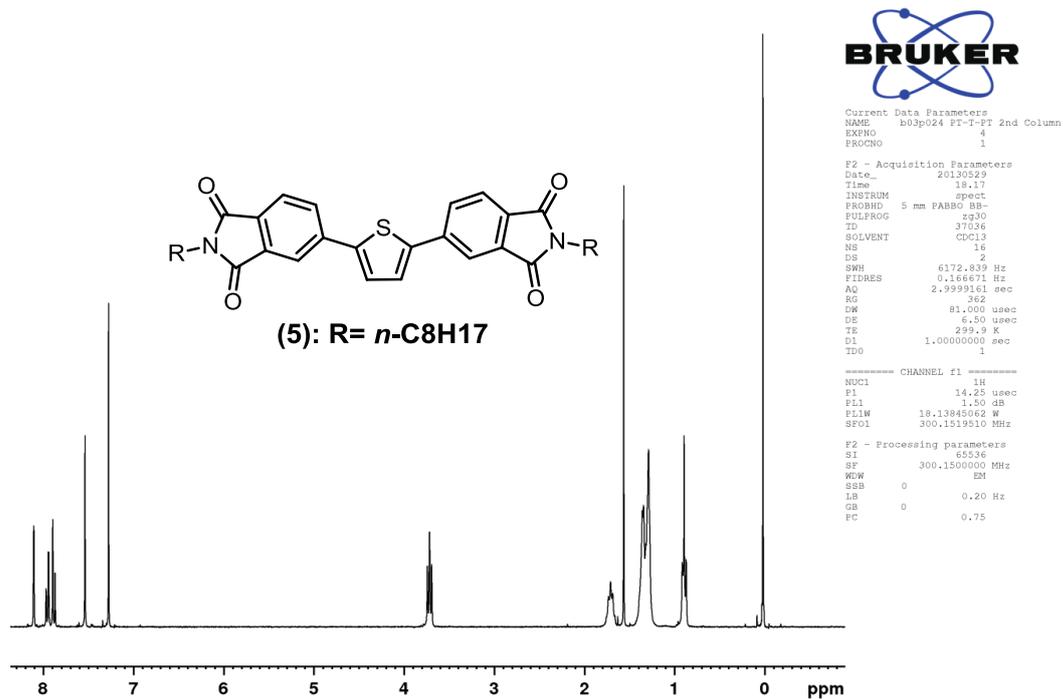


Figure S5: ¹H NMR spectra of (5) in CDCl₃ (peak at 7.27 is CHCl₃)

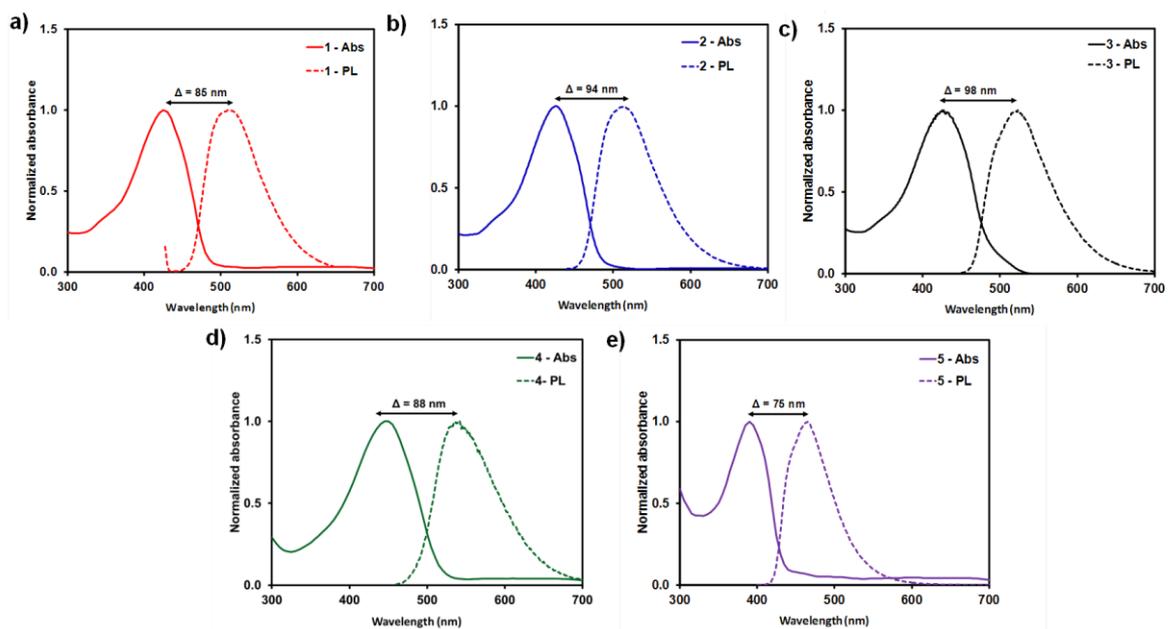
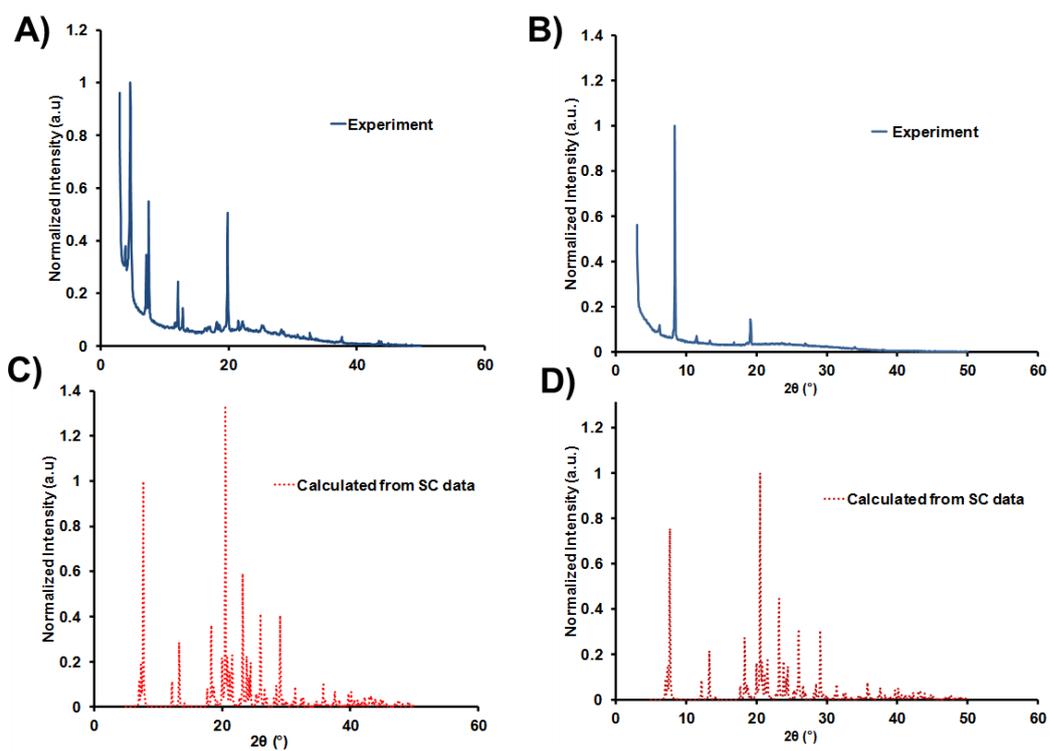
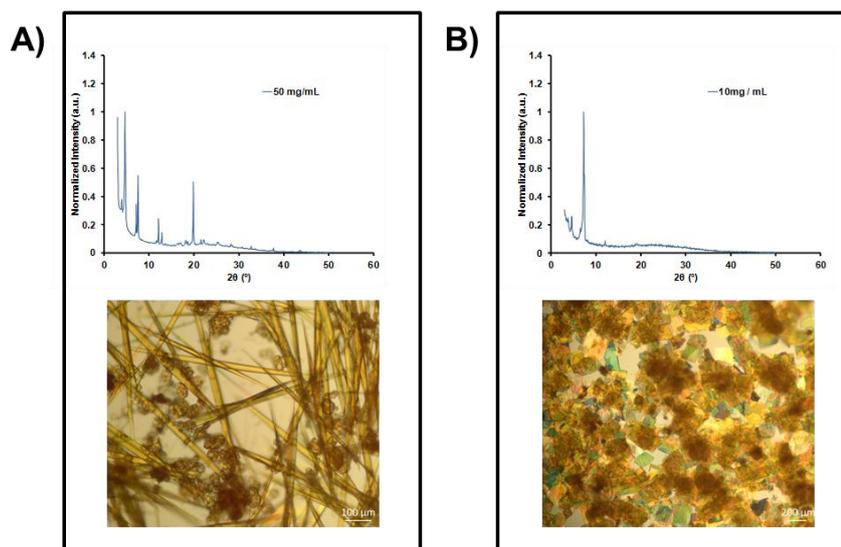


Figure S6. UV-Vis absorption spectra of compounds **1-5** in chloroform solution (solid lines) and photoluminescence (dotted lines).



- A) Compound (1) drop cast from 50mg/mL CHCl₃ at 58°C
 B) Compound (2) drop cast from 13.2mg/mL CHCl₃ at 58°C
 C) Diffraction pattern of compound (1) calculated from single crystal data
 D) Diffraction pattern of compound (2) calculated from single crystal data

Figure S7: Comparison of experimental thin-film XRD pattern to the computed XRD pattern obtained from the single crystal structures for **1** and **2**.



- A) Experimental X-ray pattern (top) and optical microscope image (bottom) for compound (1) drop cast from 50 mg/mL CHCl₃ at 58°C
- B) Experimental X-ray pattern (top) and optical microscope image (bottom) for compound (1) drop cast from 10 mg/mL CHCl₃ at 58°C

Figure S8. XRD and Optical images for films of **1** cast from different solution concentrations

Table S1. Selected crystallographic data for compound (**2**).

Compound	(2)	Space Group	P-1
Formula	C ₃₆ H ₃₆ N ₂ O ₄ S ₂	V(Å)³	760.8(4)
Formula Weight	624.81	Z	1
a(Å)	5.021(5)	Abs Coeff, μ, mm⁻¹	0.219
b(Å)	11.022(12)	Data Collected	3592
c(Å)	14.579(15)	Data F_o² > 2σ(F_o²)	566
α(°)	107.556(12)	Restraints	198
β(°)	94.166(13)	R	0.1595
γ(°)	95.760(12)	R_w	0.2515
Crystal System	Triclinic	GOF	1.084

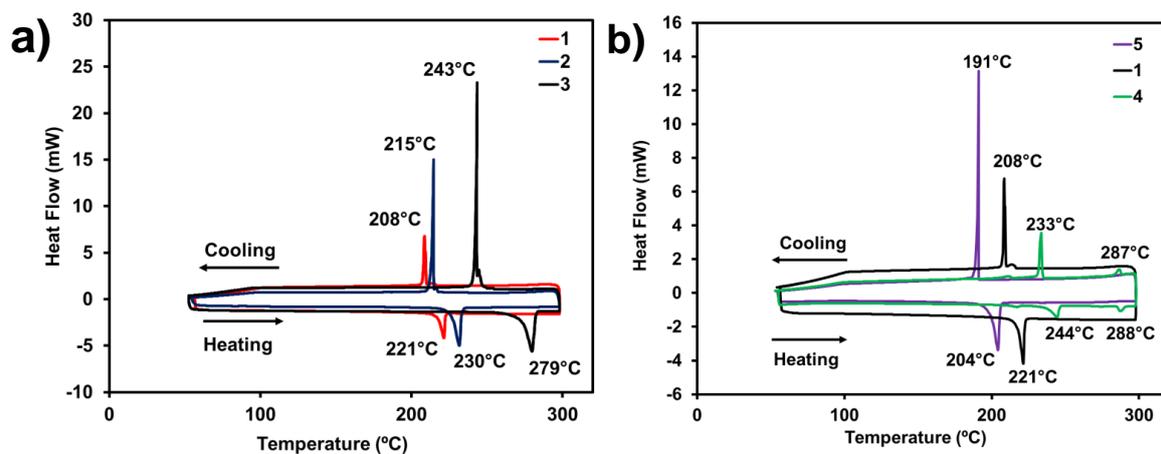


Figure S9. Differential scanning calorimetry plots for, a) compounds **1**, **2** and **3** (differing in the alkyl chain length) and b) compounds **5**, **1** and **4** comparing the effect of increasing the number of thienyl spacers.

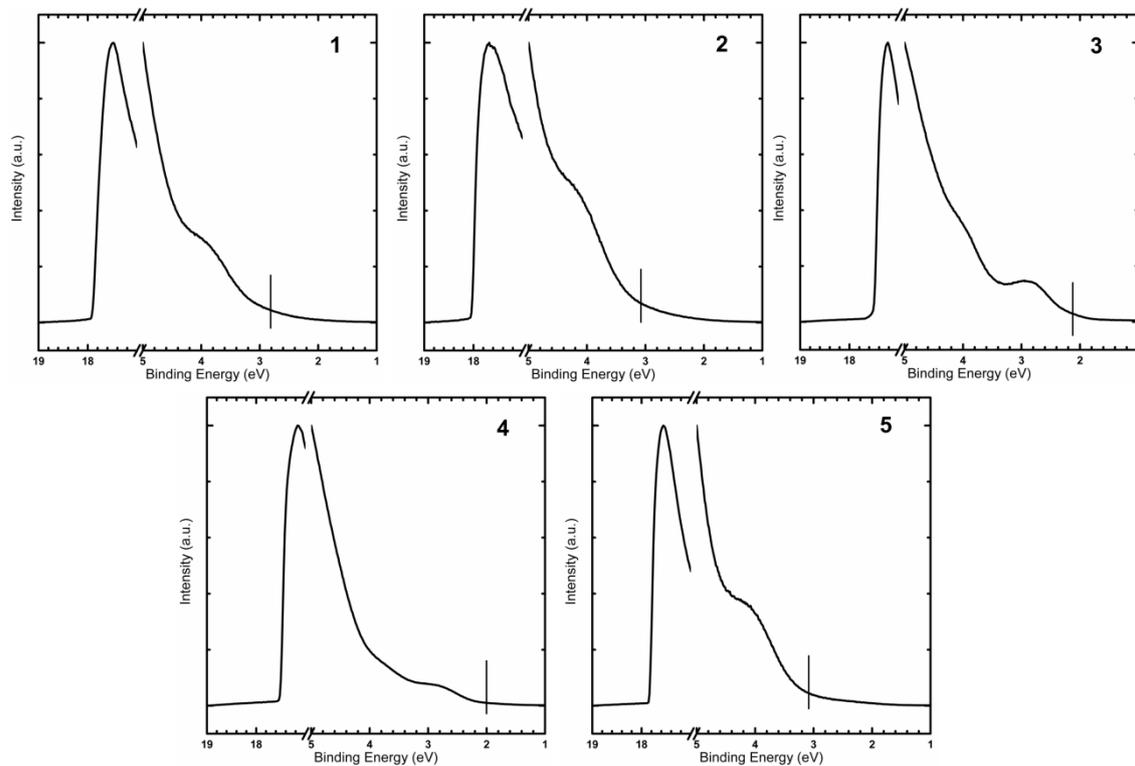


Figure S10. UPS HeI spectra of compounds **1-5**.

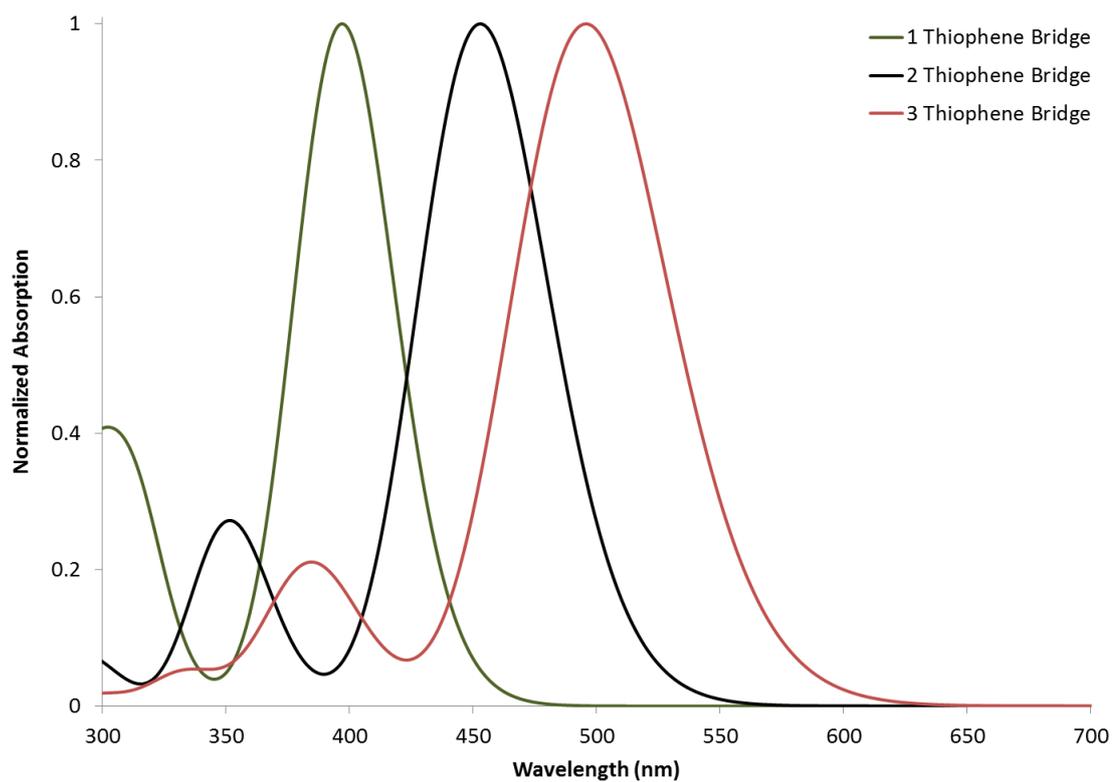


Figure S11. Calculated absorption spectra from TD-B3LYP/6-31G(d,p) calculations comparing structures with 1, 2 and 3 thiophenes in the core of the molecule.

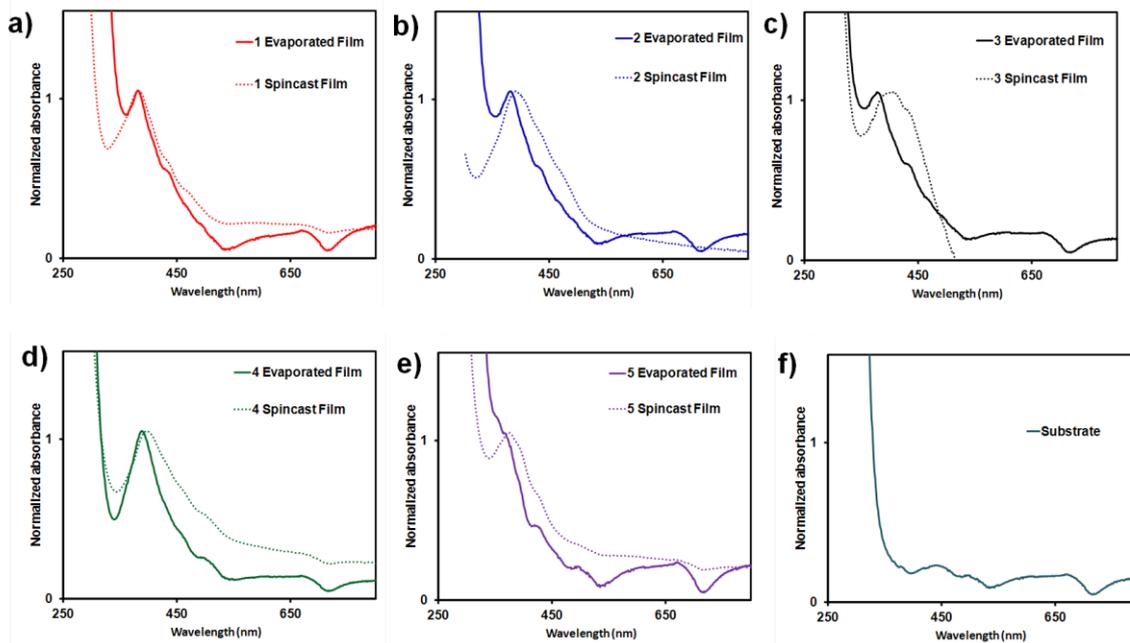


Figure S12. a-e) UV-vis spectra of evaporated (solid lines) and spin cast (dotted lines) thin films of compounds 1-5, and f) Cytod dielectric.

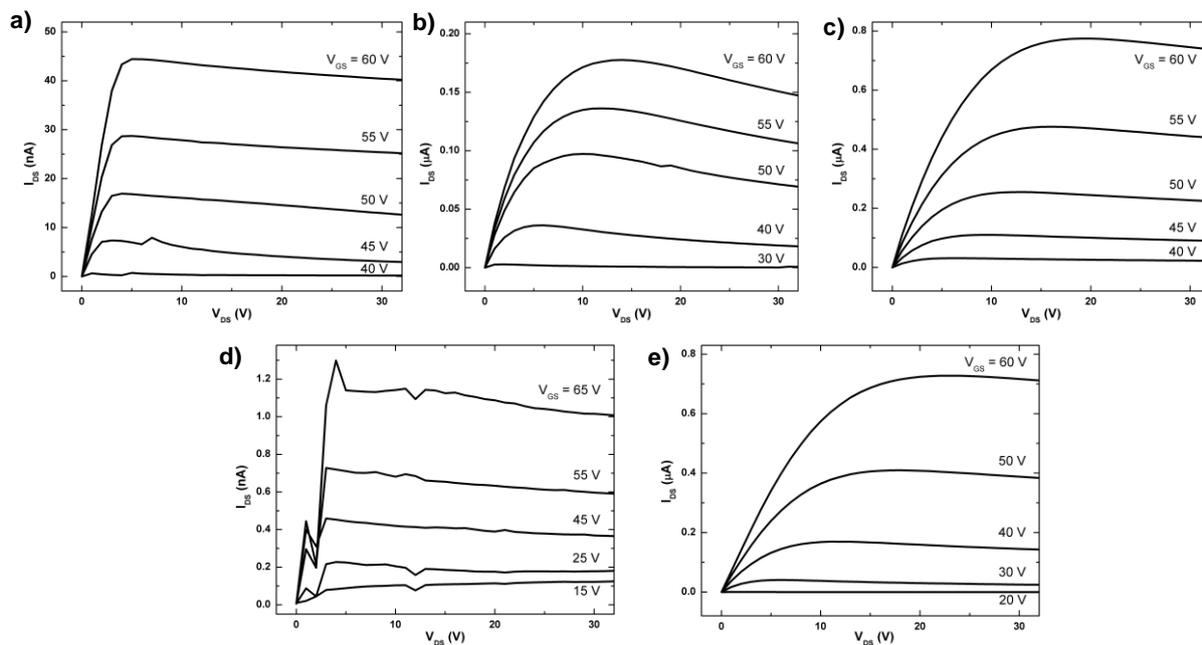


Figure S13. a-e) Output curves of OFET devices made from compounds **1-5**. The downward slope at higher drain voltages for **1**, **2** and **4** indicate threshold voltage instability during operation. The operating current of **4** is orders of magnitude lower than the other compounds and results in a noisier signal.

[1] A. D. Hendsbee, C. M. Macaulay, G. C. Welch, *Dyes Pigments*. DOI: 10.1016/j.dyepig.2013.10.046