Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electron Deficient Diketopyrrolopyrrole Dyes for Organic Electronics: Synthesis by Direct Arylation, Optoelectronic Characterization, and Charge Carrier Mobility

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SUPPORTING INFORMATION

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S1. Materials and Methods

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O_2-free N_2via Schlenk line techniques and/or an Innovative Technology inc.N_2 atmosphere glove box. For the final purification of compounds 1-4, multiple purification using silica-gel chromatrogrpahy may be needed to achieve analytical (pristine) samples.

Materials:4-bromo-phthalic anhydride**,** 4-bromo-naphthalic anhydride, N,N'-dimethylacetamide (DMA), 2-cyanofuran, and pivalic acid (PivOH) were purchased from TCI America and used without further purification. N-octylamine, 2-cyanothiophene, dimethyl succinate, 2-ethylhexylbromide and 1-bromooctane were purchased from Sigma-Aldrich and were used without further purification. Anhydrous potassium carbonate (K_2CO_3) was purchased from ACP Chemicals, and after initial usage, was stored in a Gallenkamph Hotbox oven at 100°C.Glacial acetic acid (CH_3COOH) was purchased from Fisherbrand and used without further purification. Palladium acetate [$Pd(OAc)_2$] was purchased from Strem Chemicals and was used without further purification. Sodium metal was purchased from Fischer Scientific and was 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): ^{1}H and $^{13}C\{^{1}H\}$ (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 $SiMe_4$. All experiments were performed in deuterated chloroform ($CDCl_3$).

UV-Visible Spectroscopy (UV-vis): UV-vis spectra were recorded using a Agilent Cary 60 spectrophotometer at room temperature. All solution UV-vis experiments were run in $CHCl_3$ in telfon capped 1mm quartz cuvettes under . Films were prepared by spin-coating solutions from $CHCl_3$ onto glass substrates cut from corning Micro slides at 1000 rpm for 10 seconds. Annealed films were annealed at 100°C for 10 min by direct mounting on a hotplate.

Flouresence Spectroscopy: The emission profiles were recored on a Cary Eclispe spectrophotometer. Soltuion spectra were recorded in $CHCl_3$. Neat hhin-flms of 1-5 were cast from 1% wt/v $CHCl_3$ solutions at 1000 rpm onto glass.

Cyclic Voltammetry (CV): All were carried out using a BASi Cell Stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with Ag/AgCl electrode, Pt wire and Glassy carbon electrode (dia. 3 mm), as the pseudo reference, counter electrode and working electrode respectively, as well as a N_2 bubbler. Glassy carbon electrodes were polished with alumina. The CV experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All solutions were scanned at 100mV/s, both with and without a Fc/Fc^+ standard, after being purged with N_2 for one minute to agitate the solution and remove water. Under these conditions, a Fc/Fc^+ standard was calibrated to be ~0.48 V. Solution CV measurements were carried out with a small molecule concentration of ~1mg/mL in CH_2Cl_2. The HOMO and LUMO levels were obtained

by correlating the onsets ($E_{ox}^{Fc/Fc+}$, $E_{rd}^{Fc/Fc+}$) to the normal hydrogen electrode (NHE), assuming HOMO of Fc/Fc^{+} to be 4.80 eV.[1]

Mass Spectrometry: Mass spectrometry measurements were performed courtesy of Dr. 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.

Differential Scanning Calorimetry (DSC): All experiments were carried out on a TA instruments Q-1000 DSC instrument with compressed air as the purging gas.

Thermogravimetric Analysis (TGA): All experiments were carried out 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 N_2 atmosphere.

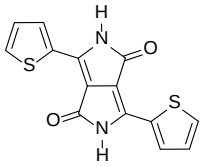
Ultraviolet Photoelectron Spectroscopy (UPS):0.2% and 0.4% w/v solutions of each compound were spin coated from chloroform at 5000 rpm, to produce films of two different thicknesses on top of polished float glass coated with 80nm of ITO (Delta Technologies). All films were prepared in air and immediately transferred to the UPS chamber, where they were held under high vacuum for several hours prior to measuring. The UPS analysis chamber was equipped with a hemispherical energy analyzer (Phoibos 150) and was maintained at a base pressure of 10^{-10} mbar. The UPS measurements were carried out using a He I ($h\nu$ = 21.22 eV) source. A sample bias of -3V was used to measure the onset of photoemission. Reproducibility of UPS spectra between the two film thicknesses was confirmed for each compound.

Theoretical Analysis: See section 7 for complete details.

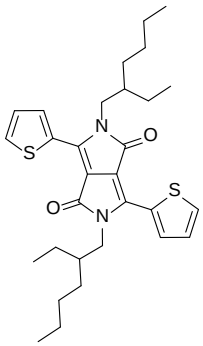
FET devices: n-channel bottom-gate top-contact transistors were formed on heavily doped Si wafers (n-type; arsenic; <0.035 Ω cm) with 300 nm thermal SiO_2. Si coupons were sonicated in isopropyl alcohol, blown dry with compressed air, followed by UV-ozone treatment for 20 minutes. Cytop dielectric was prepared by spin coating 3 parts Cytop CTL-809 M dissolved in 14 parts CTSolv-180 at 5000 rpm for 60 s on top of the 300 nm SiO_2. Capacitors were fabricated by depositing metal electrodes through a stencil mask to measure the specific capacitance, which was found to be 10.7 nF/cm^2. Following dielectric preparation, the samples were transferred to a vacuum deposition system (base pressure 1 x 10^{-6} Torr). 30 nm of each compound was deposited through a stencil mask at 0.02-0.05 nm/s onto the coupons held at 100 °C. The samples were allowed to cool to <40 °C before vacuum was broken, and a source-drain stencil mask was aligned with the active semiconductor. Aluminum source-drain contacts were deposited at a rate of 0.05 nm/s to a thickness of 50 nm. Each coupon contained an array of 24 transistors with channel lengths ranging from 25 μm to 250 μ m and widths between 0.5 mm and 1.5 mm. After metal deposition, the samples were briefly exposed to air again for a few minutes before transferring to an Ar glove box for testing. Two Kiethley 236 source-measure units were used to measure the current-voltage characteristics of the devices.

S2. Synthetic Details

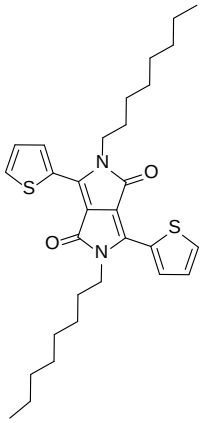
Synthesis of Diketopyrrolopyrrole building blocks



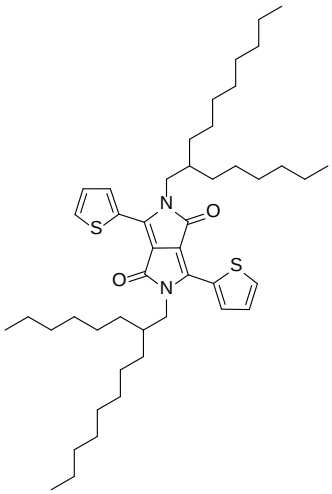
Synthesis of 3,6-(bis-thiophen-2-yl)2,5-Diketopyrrolo[3,4-c]pyrrole(A1): On the bench top, 1 g (42.8 mmol) of sodium metal was weighed out and chopped into fine pieces. Petroleum ether was then used to rinse away excess mineral oil which coated the sodium. A three neck round bottom flask was charged with a stir-bar and 75mL of *tert*-amyl alcohol. The sodium pieces were added to the neck flask using a side arm over a period of 10 minutes. The reaction mixture was refluxed at 110°C for 6h while under a flow of nitrogen gas. After the complete reaction of the sodium with the alcohol, thiophene-2-carbonitrile (4g, 42.8mmol) was added to the solution in one portion using a side arm. Immediately following the addition of the thiophene-2-carbonitrile, dimethyl succinate (2.10g , 14.3mmol) was added drop wise over a period of one hour. Addition of the dimethyl succinate causes the reaction mixture to turn blood red in color. The reaction was then allowed to reflux at 110 °C for 48 hours. The reaction was then cooled to 80°C and 50mL of methanol was added to help stirring. Acetic acid (2mL) was added drop wise to neutralize the product. The addition of acetic acid caused the reaction mixture to develop a brown color. After complete addition of acetic acid the reaction mixture was refluxed at 80°C for24 hours to ensure complete neutralization of the product. The reaction mixture was cooled to room temperature and filtration using a Buchner funnel with an aspirator gave a dark red/ brown solid filter cake. The dark red/brown filter cake was added to an Erlenmeyer flask containing H_20:MeOH (50:50, 500mL) and stirred before a second filtration using a Buchner funnel and aspirator. This step helped to remove any remaining by-products of the reaction and left over starting materials. The dark red/brown solid was then stored in a vial and put in the vac-oven overnight at room temperature to yield pure product. Spectroscopic data matched those previously reported.[2]Yield: 3.80g (89%).



Synthesis of 3,6-(bis-thiophene-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dion(A2): The reaction was carried out in a 10-20mL Biotage microwave vial with a stir bar. On the benchtop, 3,6-(bis-thiophen-2-yl)2,5-diketopyrrolo[3,4-c]pyrrole(229mg 0.762mmol) , K_2CO_3 (430mg 3.1mmol) and 2-ethylhexylbromide (0.7mL 6.6mmol) were added to the vial and the vial was crimped under a blanket of N_2. The reaction vial was placed in an oil bath and heated to 110°C with stirring for 17h. The reaction may also be carried out using microwave heating to produce alkyl DPPs in a reduced timeframe. (60 minutes, 150°C, reported yields are from conventional heating) The reaction progress was monitored using TLC (50:50 CH_2Cl_2:petroleumether). Upon completion, the reaction contents were poured into 600mL stirring H_2O and stirred for 24h before filtering. After stirring for a day the product had formed a red-sticky mass coating the stir bar. The filtered red solid, along with the red-sticky mass on the stir bar were dissolved in 100mL dichloromethane and subsequently brought to dryness using a rotary evaporator. The crude solid product was recrystallized from boiling ethanol:water (90:10), left to cool in the refrigerator for 14 hours and filtered. The red solid was washed with water, and dried in the vacuum oven at room temperature overnight to yield pure product. Spectroscopic data matched those previously reported.[2] Yield (172mg, 51%).

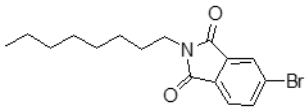


Synthesis of 3,6-(bis-thiophene-2-yl)-2,5-bis-(n-octyl)-6-(thiophene-2-yl) -2,5-dihydro-pyrrole-1,4-dion(A3): This compound was synthesized in a similar fashion to compound **A2**, substituting 1-bromo-octane for 2-ethylhexylbromide during the alkylation step. Spectroscopic data matched those previously reported.[2] Yield: 522mg (45%).

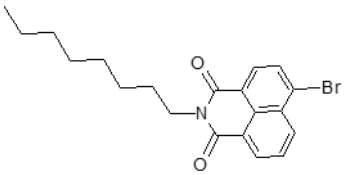


Synthesis of 3,6-(bis-thiophene-2-yl)-2,5-bis-(2-hexadecyl) -2,5-dihydro-pyrrole-1,4-dion(A5):This compound was synthesized in a similar fashion to compound **A2**, substituting 2-hexyl-decyl for 2-ethylhexylbromide during the alkylation step. Spectroscopic data matched those previously reported.[4] Yield: 522mg (19%).

Synthesis of Phthalimide and Naphthalimide building blocks



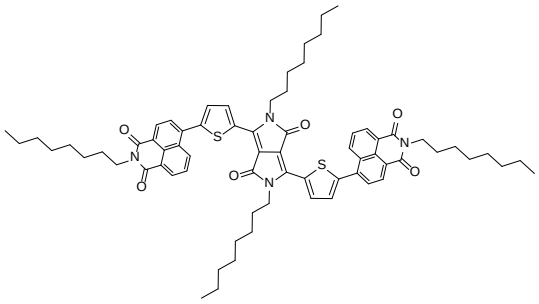
Synthesis of 5-bromo-N-octyl phthalimide(A6): On the benchtop, bromo-phthalic anhydride (2g, 8.85mmol) was added to a 100mL round-bottom flask containing a stir bar. Acetic acid (15mL) was added to the flask as a solvent and octylamine (1.75mL,10.6 mmol) was added in one portion prior to refluxing the solution at 130°C for 5h. Upon completion of reaction, solvent was removed using a rotary evaporator resulting in a colorless oil which solidified to a white solid on standing (~ 1 hour, cool to r.t. from rotary evaporator bath temperature). The crude solid was dissolved in a minimal amount of boiling isopropanol and recrystallized from solution yielding colorless crystalline product which was collected by filtration in a Buchner funnel. Spectroscopic data matched those previously reported.[5] Yield: 1.71g (60%)



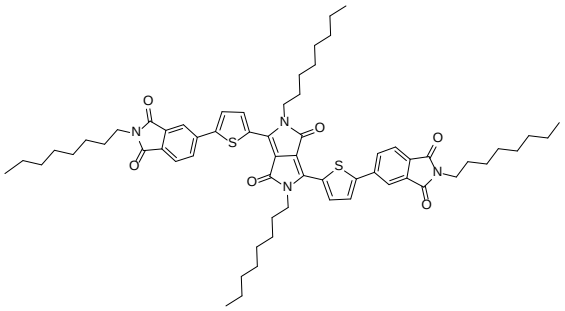
Synthesis of 5-bromo-N-octyl naphthalimide(A7): On the benchtop,bromo-naphthalic anhydride (1g,3.61mmol) was added to a 100mL round-bottom flask containing a stir bar. Acetic acid (15mL) was added to the flask as a solvent and octylamine (1.138g, 7.22mmol) was added in one portion prior to refluxing the solution at 130°C for 5h. Upon completion, the reaction was cooled

to room temperature. A white crystalline solid formed upon cooling which was filtered using a Buchner funnel and washed with 50mL of cold isopropanol to give pure crystalline product. An additional portion of product was obtained by removing the isopropanol solvent from the filtrate, and the obtained crude solid was dissolved in a minimal amount of boiling isopropanol and recrystallized from solution yielding colorless crystalline product which was recovered using a Buchner funnel. Both portions were identical via ^{1}H NMR analysis. Spectroscopic data matched those previously reported.[5] Yield: 1.31g (93%)

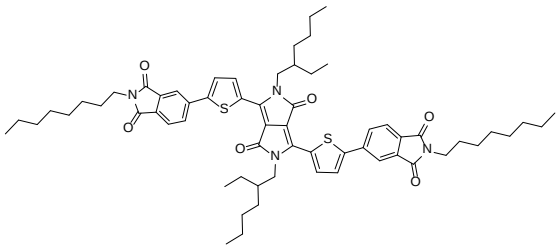
Synthesis of final small molecules



Synthesis of3,6-(bis-(N-octyl naphthalimide))-2,5-bis-(n-octyl)-2,5-dihydro-pyrrole-1,4-dion(1): On the benchtop,3,6-(bis-thiophene-2-yl)-2,5-bis-(n-octyl)-2,5-dihydro-pyrrole-1,4-dion(100mg, 0.191 mmol), K_2CO_3 (66 mg, 0.476 mmol) and 5-bromo-N-octyl naphthalimide (135mg, 0.4 mmol) were added together in a 2-5mL microwave vial equipped with a stir bar. $Pd(OAc)_2$ (11mg, 12 mol%) and pivalic acid (10mg, 25mol%) were added to the vial under an inert atmosphere and N,N'-dimethylacetamide (2mL) was used as a solvent. The reaction vial was crimped under an atmosphere of N_2. Microwave Conditions:180°C, 17m, 20s pre stir, 600rpm. The reaction may also be carried out using conventional heating to 110°C with stirring for 18h.Upon reacting, a color change from red to blue was observed. The reaction vial was cooled to room temperature and brought to atmospheric pressure before de-crimping. The vial contents were poured into stirring methanol (500mL) and stirring was continued for 1 hour. The reaction was filtered, resulting in a dark red-orange filtrate and a dark blue-black solid. The blue-black solid was washed with methanol (2x30mL) and collected. The product was purified using column chromatography using pentanes to first flush the column and a gradient from 100% ethyl acetate to 100% $CHCl_3$ was used to elute the product fraction. Removal of volatiles using a rotary evaporator gave a metallic blue-black film which was collected by slurrying in methanol and filtering. Yield: 30.9%. **^{1}H NMR:** ($CDCl_3$, TMS/ppm) δ 9.04 (d, ^3J=0.4.1Hz, 2H), 8.69-8.60 (m, 8H), 7.89 (d, ^3J=7.6 Hz, 2H), 7.81 (d of d, ^3J=8.6Hz,7.3Hz 2H), 7.53 (d, ^3J=4.1Hz, 2H), 4.21 (m,8H), 1.87-1.74 (m, 8H), 1.44-1.24 (m, 40H), 0.89-0.80 (m, 12H). **^{13}C NMR:** δ163.92, 163.66, 161.27, 145.25, 139.49, 137.17, 135.96, 131.62, 131.57, 131.36, 130.45, 130.29, 129.72, 128.85, 128.77, 127.68, 123.21, 122.93, 108.59, 42.43, 42.41, 40.65, 31.81, 31.75, 31.72, 30.08, 30.05, 29.68, 29.33, 29.21, 29.20, 29.16, 28.11, 27.11, 26.89, 22.63, 22.59, 14.07, 14.04, 14.00. **LRMS (EI):** *m/z*, calcd for$C_{70}H_{82}N_4O_6S_2$, (M^+): 1139.56; found: 1139.6.

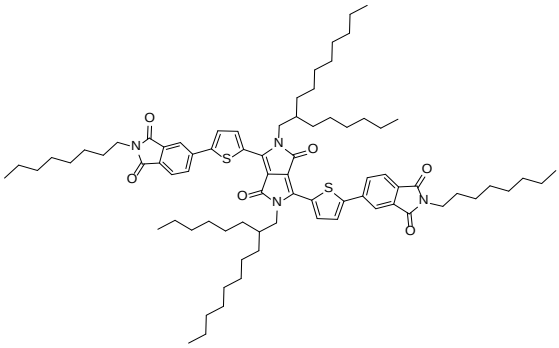


Synthesis of 3,6-(bis-(2-octyl-5-(thiophen-2-yl)isoindoline-1,3-dione))-2,5-bis-(n-octyl)-2,5-dihydro-pyrrole-1,4-dion,(2): On the benchtop,3,6-(bis-thiophene-2-yl)-2,5-bis-(n-octyl)-2,5-dihydro-pyrrole-1,4-dion (200mg,0.381 mmol), K_2CO_3 (132 mg,0.953mmol) and 5-bromo-N-octyl phthalimide (270mg,0.8mmol) were added together in a 2-5mL microwave vial equipped with a stir bar. $Pd(OAc)_2$ (14mg, 0.00572mmol) and pivalic acid (16mg,0.157mmol) were added to the vial under an inert atmosphere and N,N'- dimethylacetamide (2mL) was used as a solvent. The reaction vial was crimped under an atmosphere of N2. Microwave Conditions:180°C, 17m, 20s pre stir, 600rpm. The reaction may also be carried out using conventional heating to 110°C with stirring for 18h.Upon reacting, a color change from red to blue was observed. The reaction vial was cooled to room temperature and brought to atmospheric pressure before de-crimping. The vial contents are poured into stirring methanol (500mL) and stirring was continued for 1 hour. The reaction was filtered, resulting in a dark red-orange filtrate and a dark blue- black solid. The blue-black solid was washed with methanol (2x30mL) and collected. The product was purified using column chromatography using pentanes to first flush the column and a gradient from 100% ethyl acetate to 100% $CHCl_3$ was used to elute the product fraction. Removal of volatiles using a rotary evaporator gave a metallic blue- black film which was collected by slurrying in methanol and filtering. Microwave Yield: 62% (245mg). **^{1}H NMR:** ($CDCl_3$, ppm)δ 9.03 (d, ^3J=4.2 Hz, 2H), 8.14 (m, 2H), 8.03-7.89 (m, 4H), 7.66 (d, ^3J=4.2 Hz, 2H), 4.15 (t,4H ^3J=7.3 Hz), 3.72 (t,4H ^3J=7.3Hz), 1.87-1.66 (m, 8H), 1.51-1.20 (m, 40H), 0.92-0.86 (m, 12H). **^{13}C NMR:** δ167.69, 138.68, 136.67, 133.42, 131.26, 130.81, 130.73, 126.62, 123.98, 120.25, 120.23, 108.90, 42.36, 38.32, 31.76, 30.07, 29.22, 29.1428.57, 26.92, 26.87, 22.61, 14.05. **LRMS (EI):** *m/z*, calcd for$C_{62}H_{78}N_4O_6S_2$, (M^+): 1039.54 ; found: 1039.



Synthesis of ,3,6-(bis(2-octyl-5-(thiophen-2-yl)isoindoline-1,3-dione))-2,5-bis-(2-ethylhexyl) – 2,5-dihydro-pyrrole-1,4-dion(3):On the benchtop,3,6-(bis-thiophene-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dion (150mg,0.286mmol), K_2CO_3 (100 mg,0.715mmol)

and 5-bromo-N-octyl phthalimide (193mg,0.572mmol) were added together In a 2-5mL microwave vial equipped with a stir bar. $Pd(OAc)_2$ (14mg, 0.00572mmol) and pivalic acid (16mg,0.157mmol) were added to the vial under an inert atmosphere and N,N'-dimethylacetamide (2mL) was used as a solvent. The reaction vial was crimped under an atmosphere of N_2. Microwave Conditions:180°C, 17m, 20s pre stir, 600rpm. The reaction may also be carried out using conventional heating to 110°C with stirring for 18h. Upon reacting, a color change from red to blue was observed. The reaction vial was cooled to room temperature and brought to atmospheric pressure before de-crimping. The vial contents were poured into stirring methanol (50mL) and stirring was continued for 1 hour. The reaction was filtered, resulting in a dark red-orange filtrate and a dark blue-black solid. The blue-black solid was washed with methanol (2x30mL) and collected. The product was purified using column chromatography using pentanes to first flush the column and a gradient from 100% ethyl acetate to 100% $CHCl_3$ was used to elute the product fraction. Removal of volatiles using a rotary evaporator gave a metallic blue-black film which was collected by slurrying in methanol and filtering. Microwave Yield: 62% (245mg) **^{1}H NMR:** ($CDCl_3$, TMS/ppm) δ 8.97 (d, ^3J=4.2 Hz, 2H), 8.13 (m, 2H), 8.01-7.89 (m, 4H), 7.65 (d, ^3J=4.2 Hz, 2H), 4.12-4.09 (m,2H), 3.72 (t,4H ^3J=7.3 Hz), 1.96-1.91 (m, 2H), 1.74-1.68 (m, 4H), 1.45-1.26 (m, 36H) 0.996-0.870 (m, 18H). **^{13}C NMR:** δ167.79, 167.73, 161.54, 146.77, 139.75, 138.76, 136.73, 133.45, 131.25,, 130.83, 130.76, 126.49, 124.06, 124.02, 120.23, 109.07, 39.29, 38.31, 31.80 ,31.75, 30.88, , 29.20, 29.13, 28.56, 28.49, 26.86, 23.71, 23.68, 23.62, 23.08, 23.06, 22.60, 18.41, 14.04,14.0113.96, 10.56. **LRMS (EI):** *m/z*, calcd for$C_{62}H_{78}N_4O_6S_2$,(M^+): 1039.54; found: 1039.6.



Synthesis of 3,6-(bis-(2-octyl-5-(thiophen-2-yl)isoindoline-1,3-dione))-2,5-bis-(2-hexyldecyl)-2,5-dihydro-pyrrole-1,4-dion(4): On the benchtop,3,6-(bis-thiophene-2-yl)-2,5-bis-(2-hexyldecyl) -2,5-dihydro-pyrrole-1,4-dion (40mg, 0.0534mmol), K_2CO_3 (21 mg, 0.152mmol) and 5-bromo-N-octyl phthalimide(50.1mg, 0.149mmol) were added together in a 0.5-2mL microwave vial equipped with a stir bar. $Pd(OAc)_2$ (2mg 0.092mols) and pivalic acid (6.05mg, 0.059mmol) were added to the vial under an inert atmosphere using N,N'- Dimethylacetamide (2mL) as a solvent. The reaction vial was crimped under an atmosphere of N_2. The reaction was carried out using microwave heating to 180°C, 17m, 20s pre stir, 600rpm. Upon reacting, a color change from red to blue was observed. The reaction vial was cooled to room temperature and brought to atmospheric pressure before de-crimping. The vial contents were poured into stirring H_2O:MeOH (1:1, ~200mL) and stirring was continued for 30 minutes. The reaction was filtered, resulting in a dark filtrate and a dark blue-black solid. The blue-black solid was washed with methanol (2x30mL) and collected. The product was purified using column chromatography using pentanes to first flush the column and a gradient from 100% Ethyl Acetate to 100% $CHCl_3$ was used to elute the product fraction. Removal of volatiles using a rotary evaporator gave a blue-black film which could be collected by slurrying in methanol and filtering.Yield: 59% (57mg). **^{1}H NMR:** ($CDCl_3$, ppm) δ 8.91(d, ^3J=4.2 Hz, 2H), 8.109(m, 2H), 7.98-7.85 (m, 4H), 7.62(d, ^3J=4.2 Hz, 2H), 4.06(d,4H ^3J=7.4Hz), 3.72 (t,4H ^3J=7.3 Hz), 1.72-1.68(m, 7H), 1.39-1.12 (m, 70H)0.91-0.76 (m, 24H).**^{13}C NMR:** δ167.81, 161.55, 146.73, 139.77, 138.77, 136.68, 133.43, 131.22, 130.82, 130.76, 126.47, 124.05, 124.03, 120.23, 109.18, 46.40, 38.32, 37.92, 31.86, 31.78, 31.27, 30.02, 29.68, 29.54, 29.30, 28.58,26.88, 26.34, 26.31, 22.65.

S3. NMR Spectroscopy of compounds 1-4

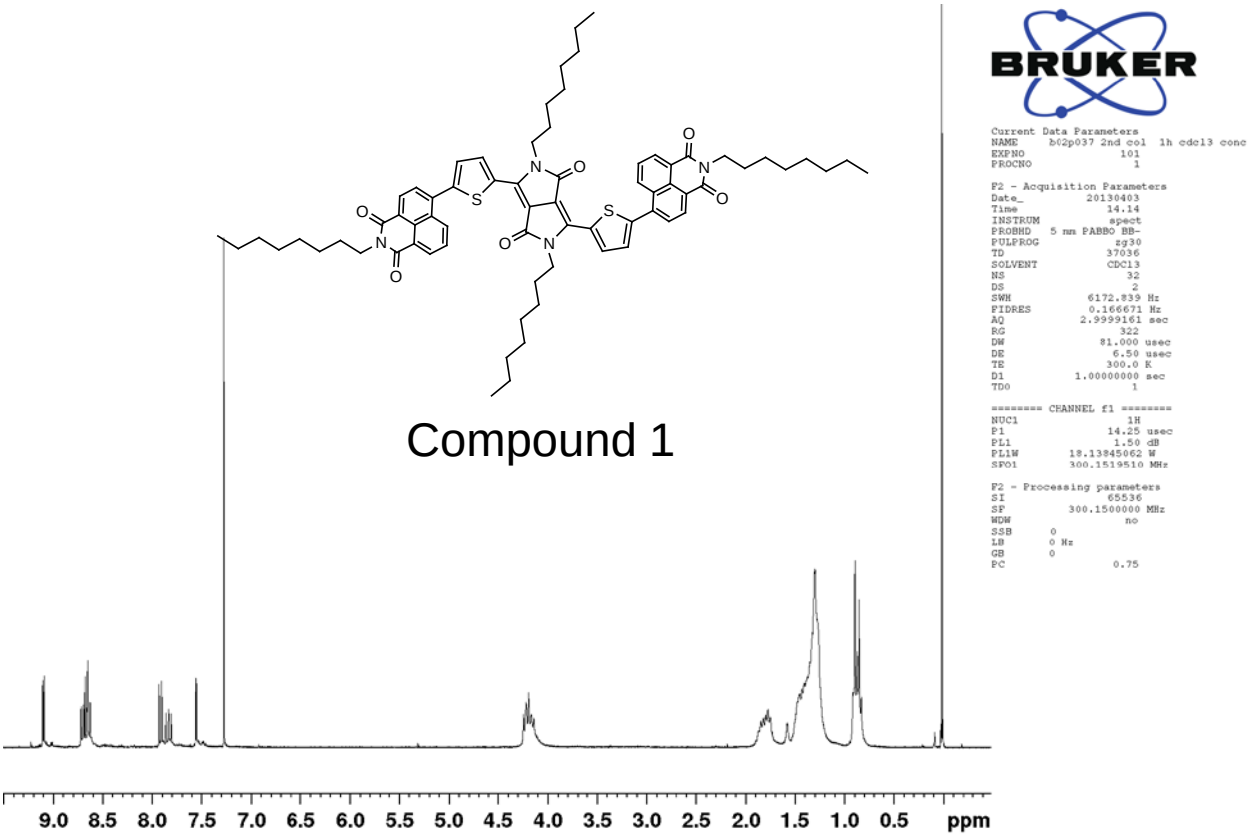


Figure S1: ^{1}H NMR spectrum for compound **1** at 295K in $CDCl_3$ (δ 7.26 ppm).

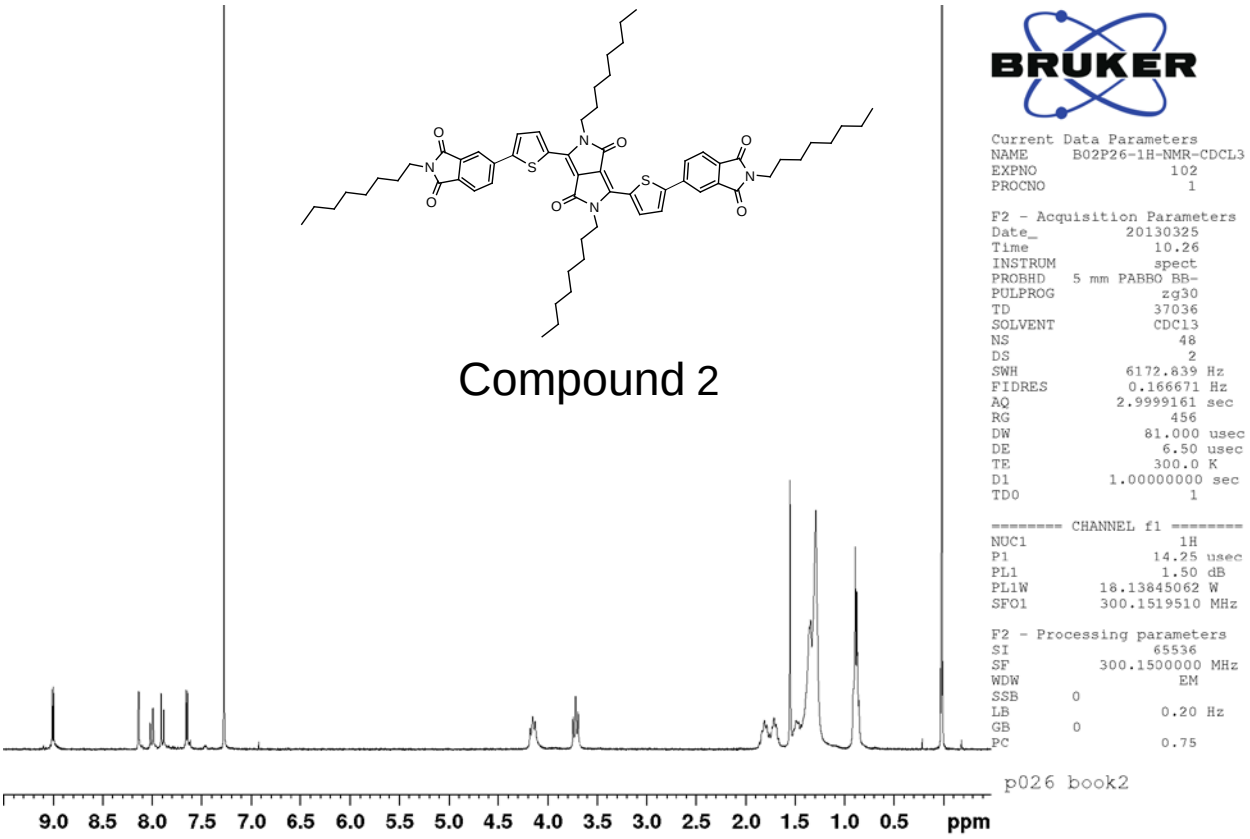


Figure S2: ^{1}H NMR spectrum for compound **2** at 295K in $CDCl_3$ (δ 7.26 ppm).

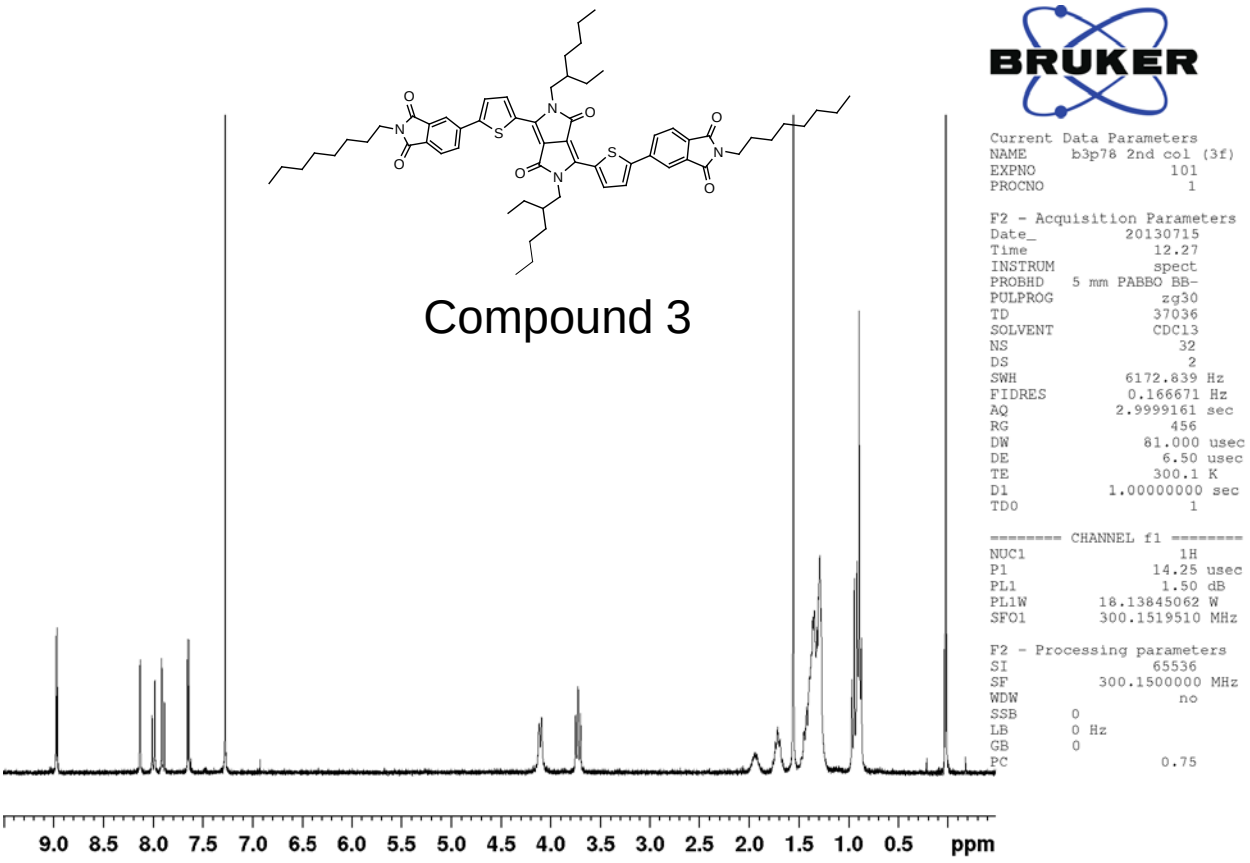


Figure S3: ^{1}H NMR spectrum for compound **3** at 295K in $CDCl_3$ (δ 7.26 ppm).

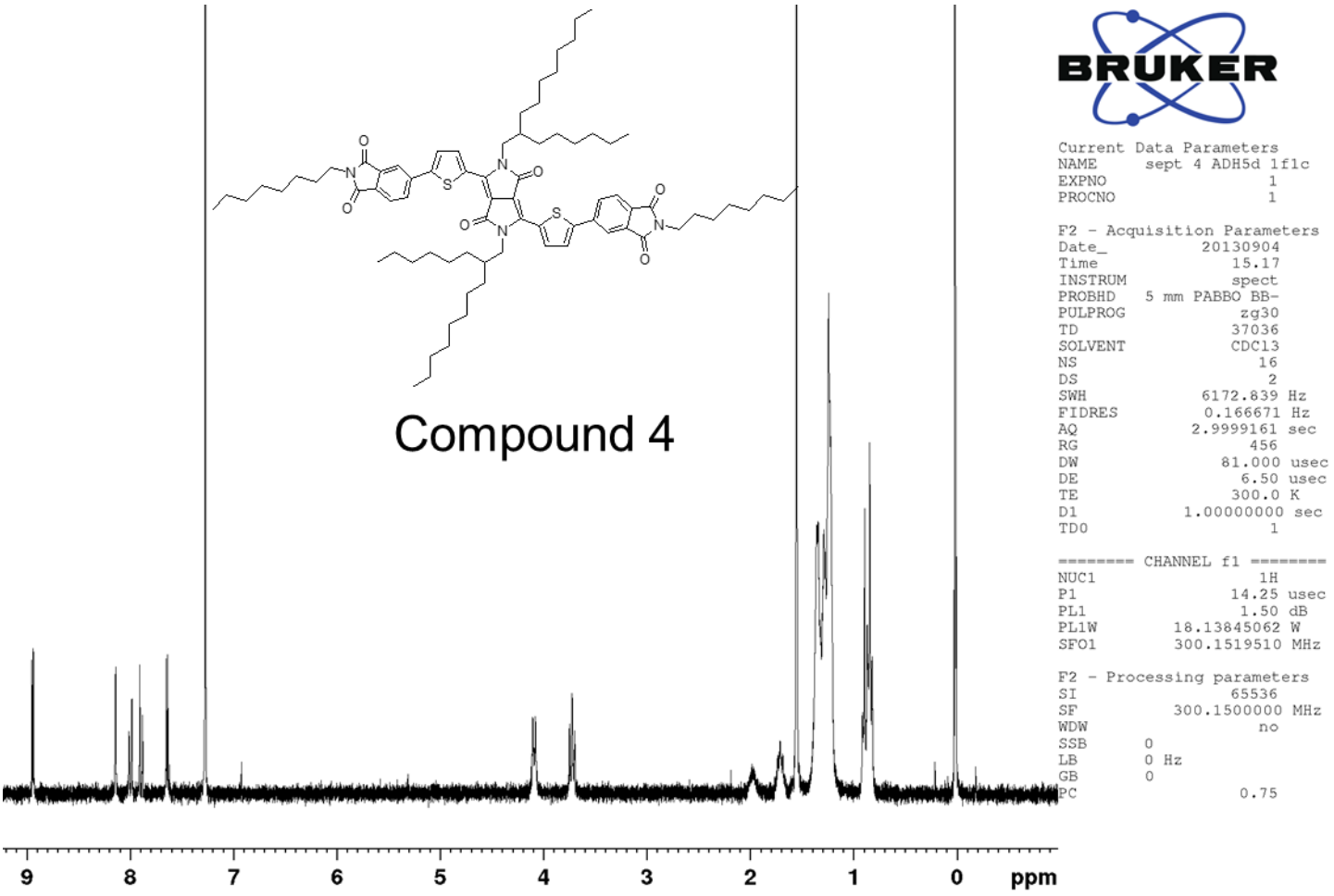


Figure S4: ^{1}H NMR spectrum for compound **4** at 295K in $CDCl_3$ (δ 7.26 ppm).

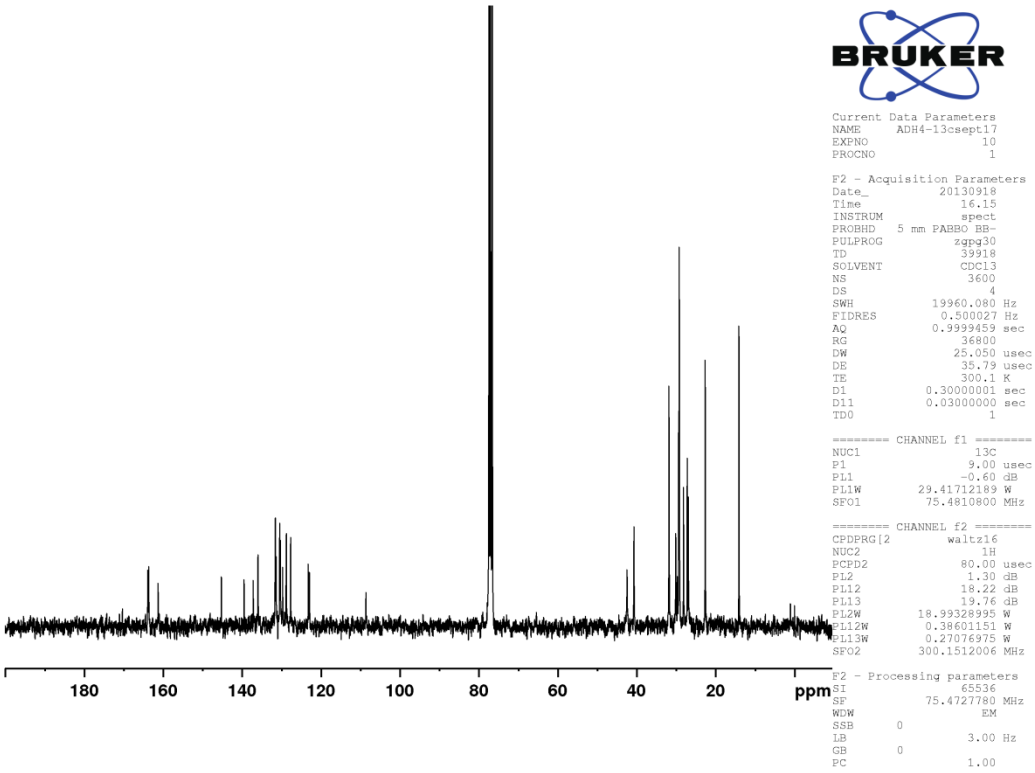


Figure S5: ^{13}C NMR spectrum for compound **1** at 295K in $CDCl_3$

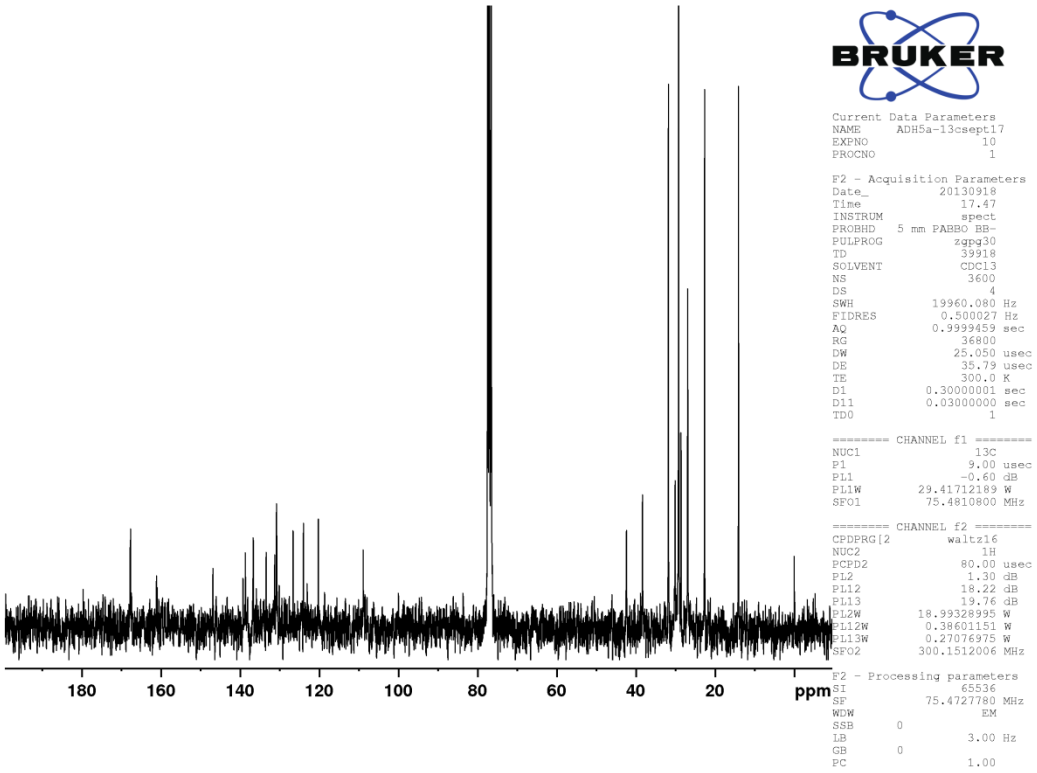


Figure S6: ^{13}C NMR spectrum for compound **2** at 295K in $CDCl_3$

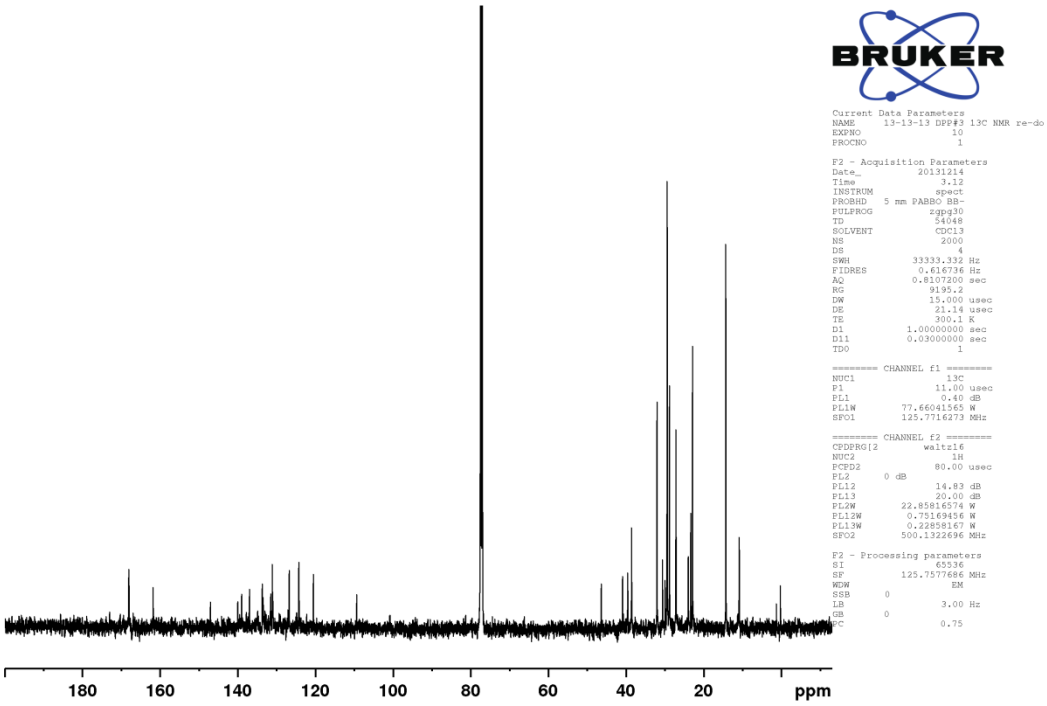


Figure S7: ^{13}C NMR spectrum for compound **3** at 295K in $CDCl_3$

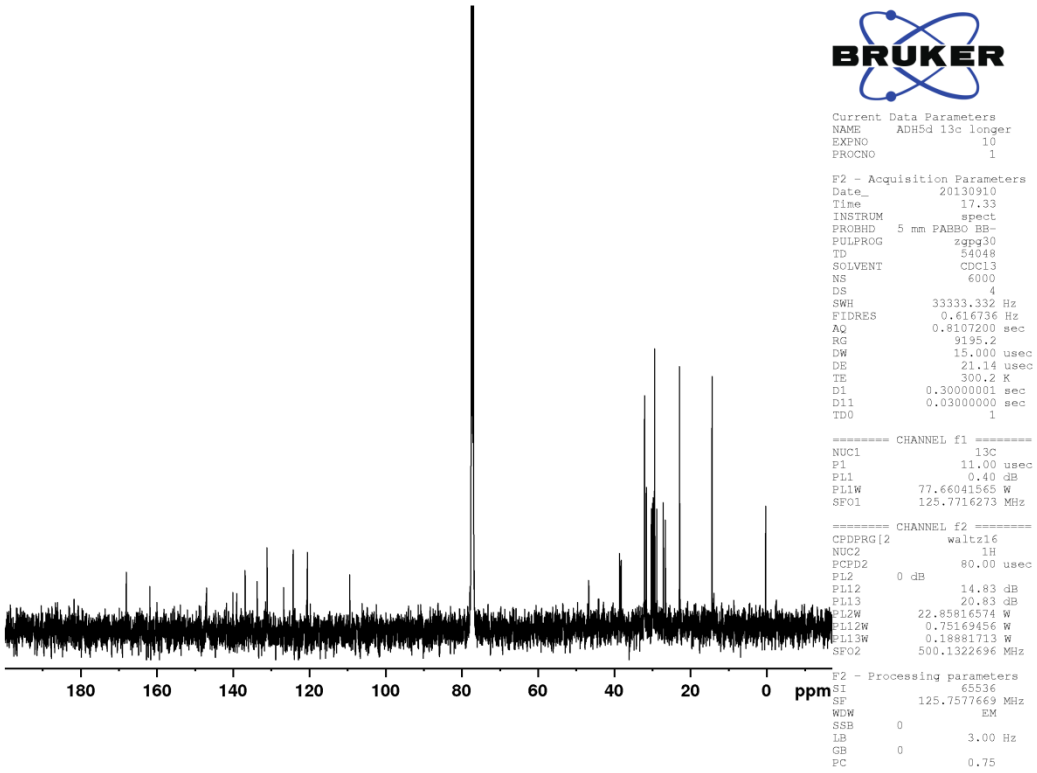


Figure S8: ^{13}C NMR spectrum for compound **4** at 295K in $CDCl_3$

S4. Cyclic Voltammetry

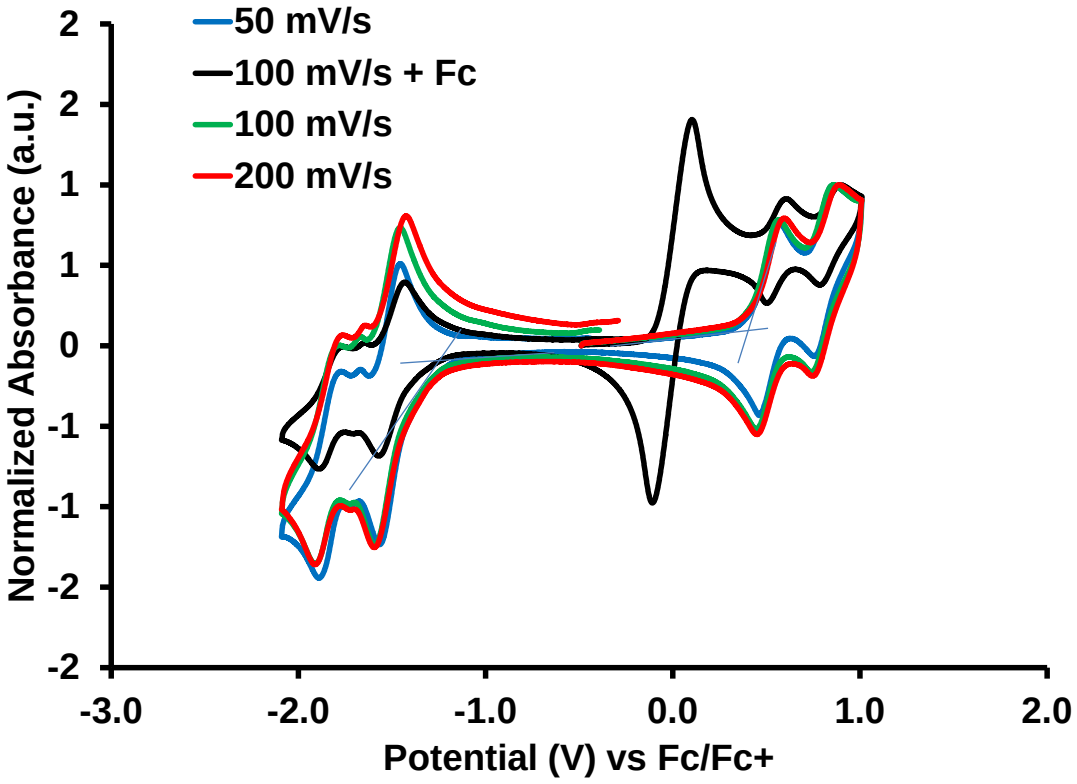


Figure S9: Cyclic voltammetry for compound **1** at varying sweep rates.

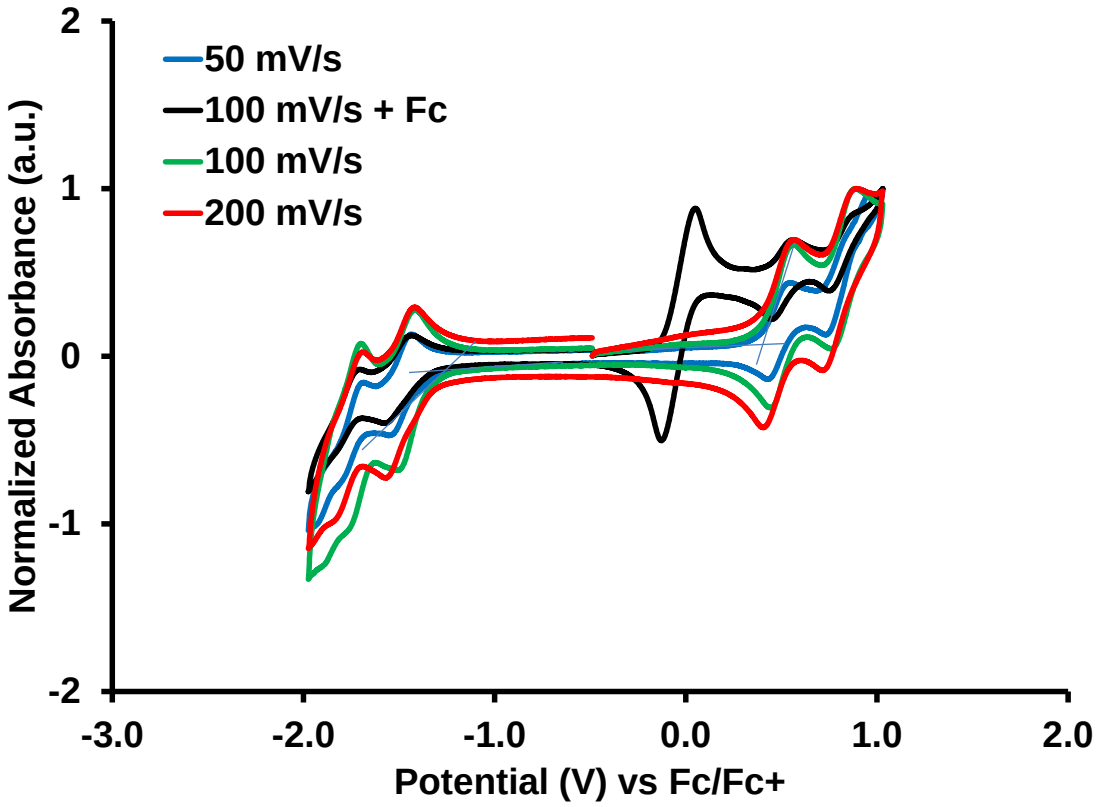


Figure S10: Cyclic voltammetry for compound **2** at varying sweep rates.

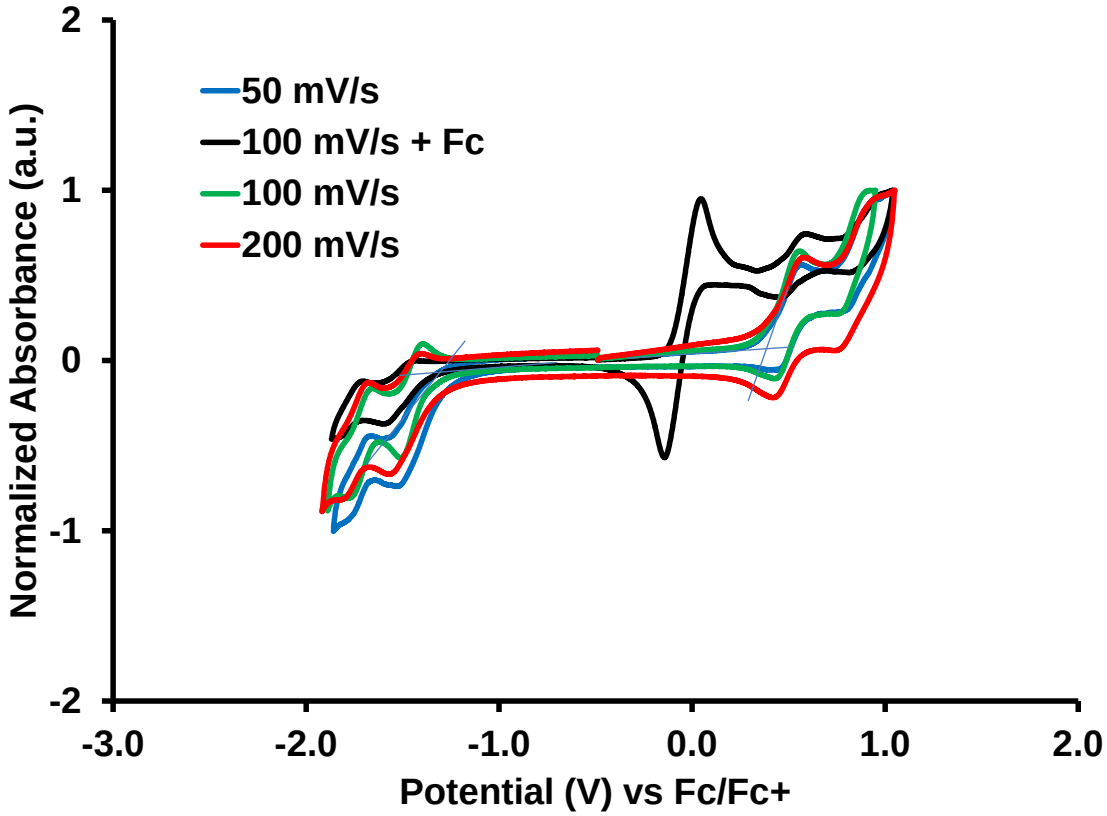


Figure S11: Cyclic voltammetry for compound **3** at varying sweep rates.

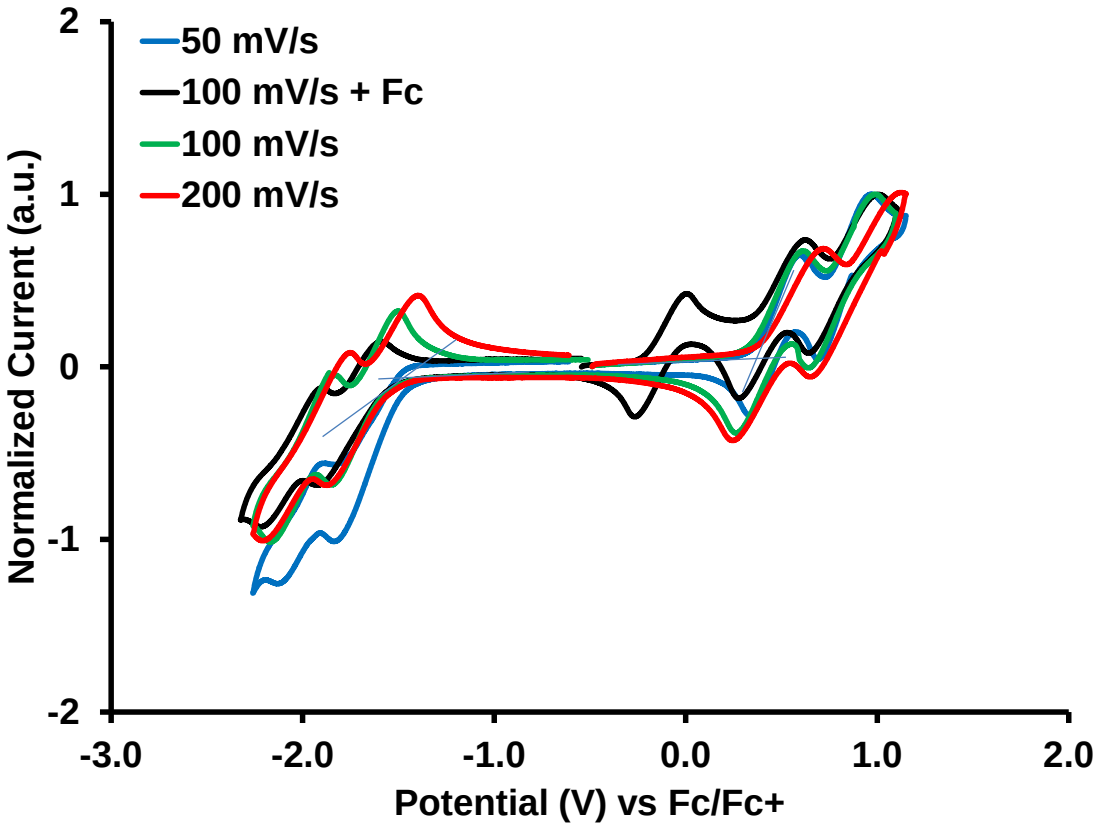


Figure S12: Cyclic voltammetry for compound **4** at varying sweep rates.

S5. UV-Visible Spectroscopy

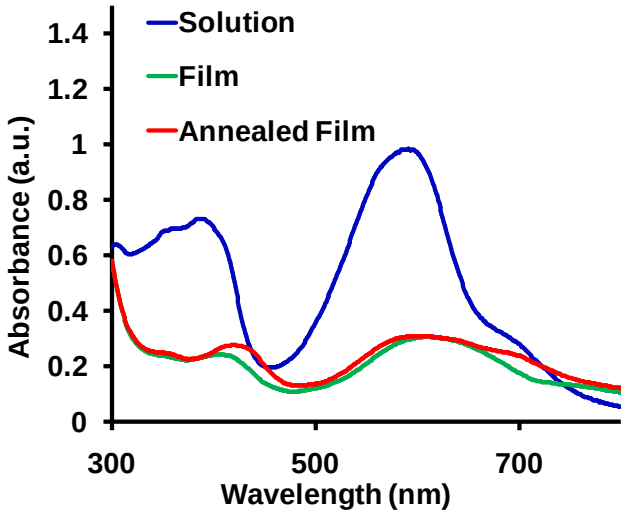


Figure S13: Solution and thin-film UV-visible spectroscopy for compound **1**.Raw absorbance profiles shown. Blue = chloroform solution, Green = thin-film on glass spin cast from 1% wt/v chloroform solutions at 1000 rpm, Red = thin-film annealed at 100°C for 10 minutes in air.

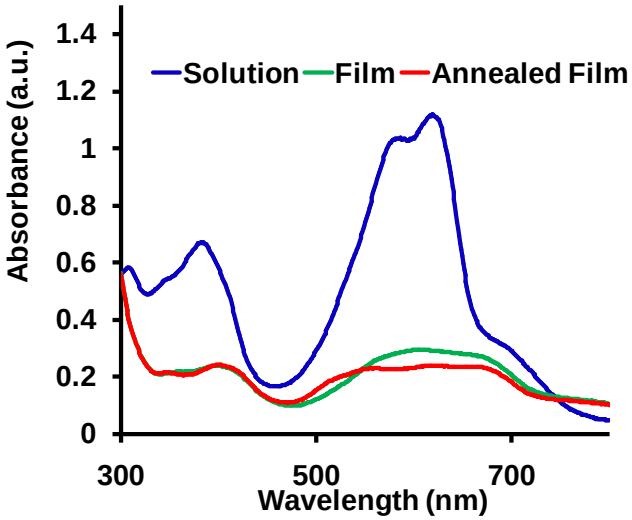


Figure S14*:* Normalized solution and thin-film UV-visible spectroscopy for compound **2**. Blue = chloroform solution, Green = thin-film on glass spin cast from 1% wt/v chloroform solutions at 1000 rpm, Red = thin-film annealed at 100°C for 10 minutes in air.

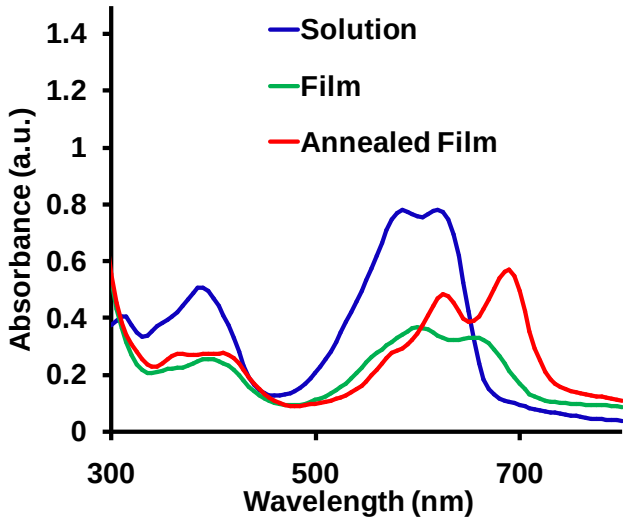


Figure S15: Normalized solution and thin-film UV-visible spectroscopy for compound **3**. Blue = chloroform solution, Green = thin-film on glass spin cast from 1% wt/v chloroform solutions at 1000 rpm, Red = thin-film annealed at 100°C for 10 minutes in air.

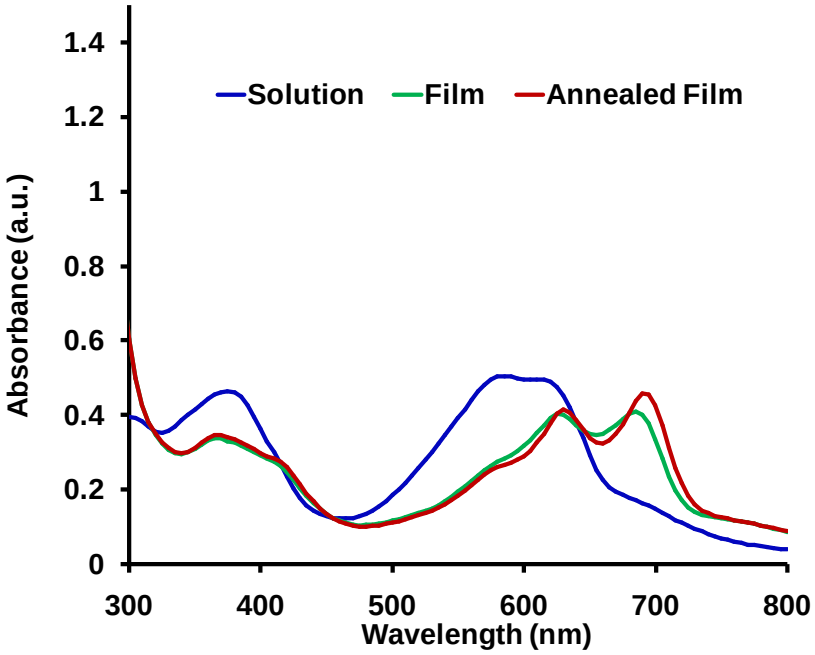


Figure S16: Normalized solution and thin-film UV-visible spectroscopy for compound **4**. Blue = chloroform solution, Green = thin-film on glass spin cast from 1% wt/v chloroform solutions at 1000 rpm, Red = thin-film annealed at 100°C for 10 minutes in air.

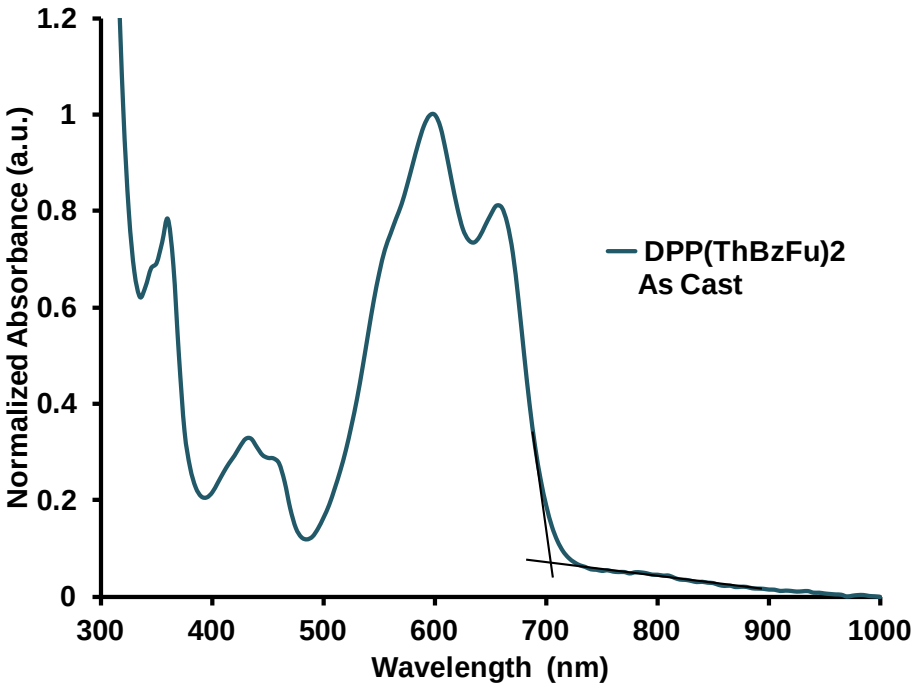


Figure S17: Normalized thin-film UV-visible spectroscopy for DPP $(ThBzFu)_2$.

As-cast thin-film on glass spin cast from 1% wt/v chloroform solutions at 1000 rpm

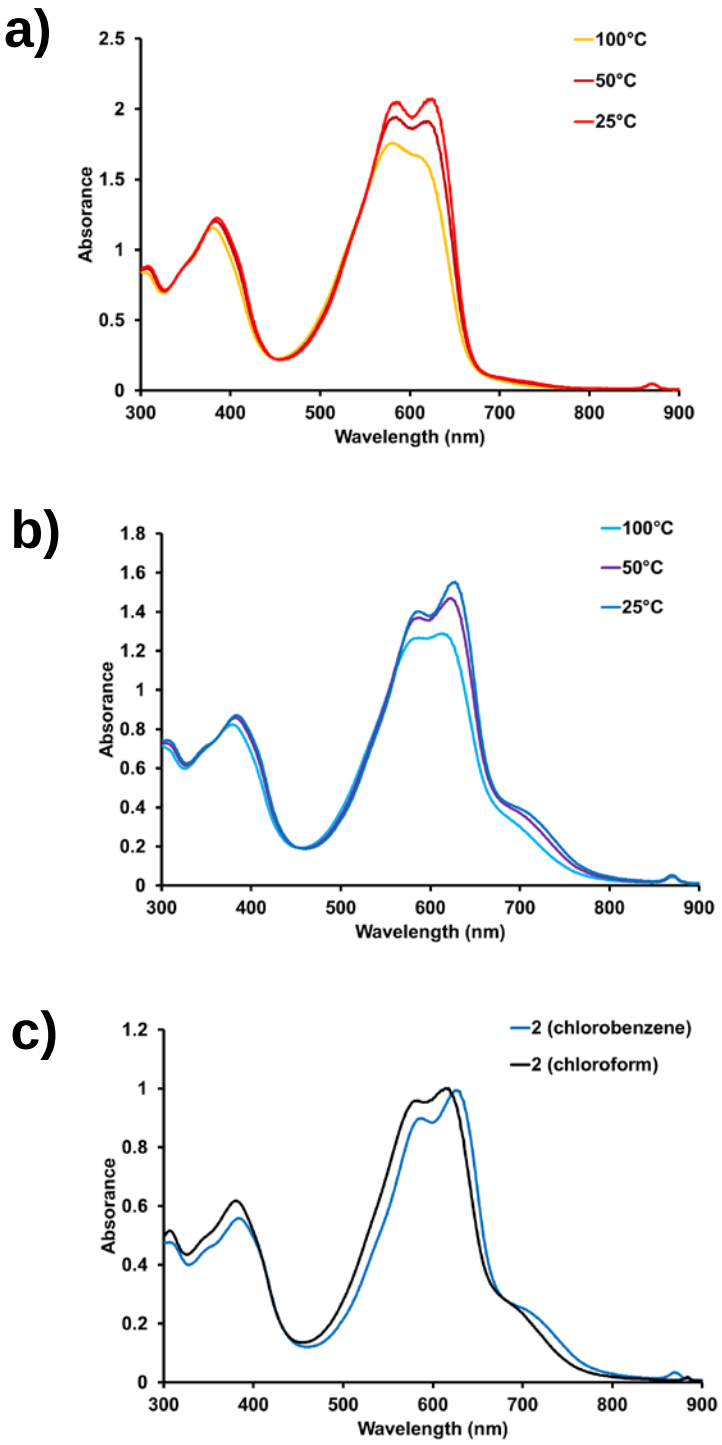
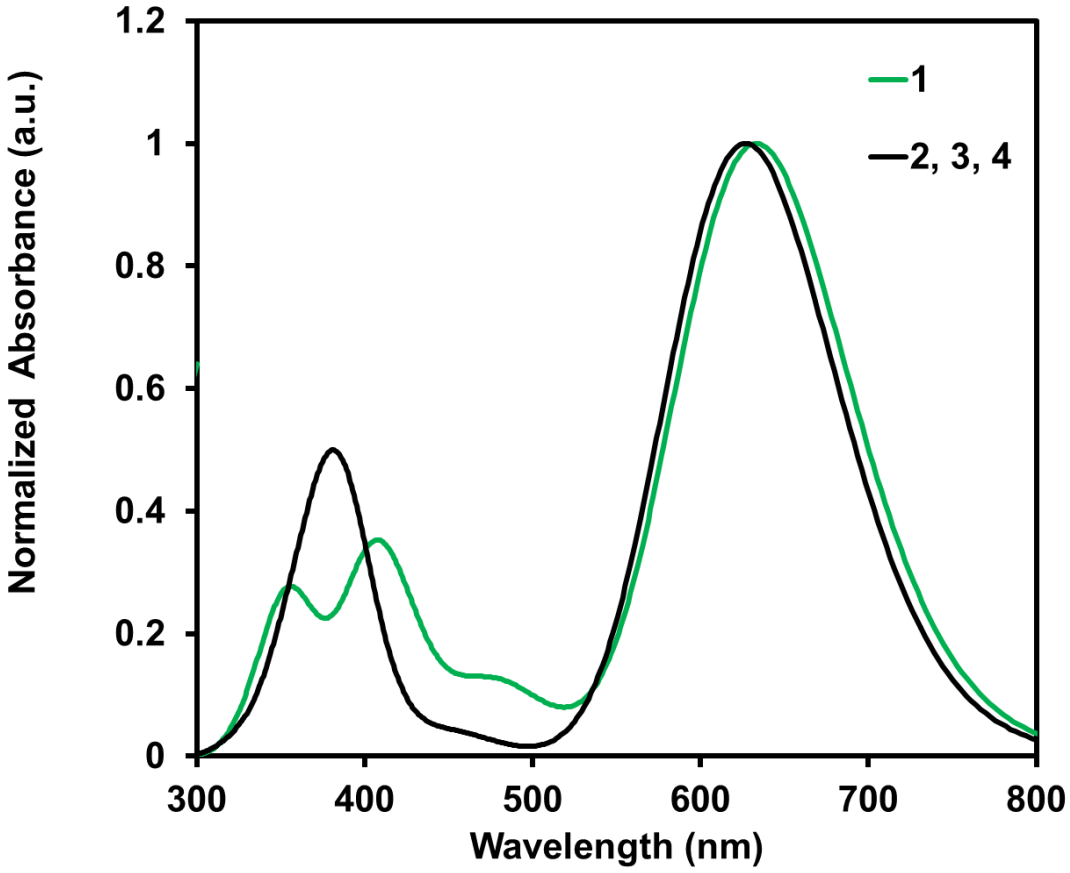


Figure S19: Variable temperature UV-visible absorption spectra of a) compound **4**in chlorobenzene and b) compound **2** in chlorobenzene. c) UV-visible spectra of compound **2** at 25 °C in chlorobenzene (CB) and chloroform (CF) solution. Spectra obtained for comparison since all spectra in parent manuscript were obtained in CF, while temperature dependent spectra were obtained in CB, due to limited temperature range of CF.

S6. Computational Data

To delve further into the nature of the geometric and electronic properties of **1-4**, gas-phase B3LYP/6-31G(d,p) ground-state equilibrium geometry optimizations were considered within Gaussian 09.[6] In order to reduce the computational cost while still accounting for the electron-donating ability of the substituent, the solubilizing chains along the conjugated backbone of **1-4** were truncated in all our calculations and represented as methyl groups. This modeling choice resulted in structures **2**, **3**, and **4** being represented by one computational structure (denoted as **2,3,4** in the text). The dihedral angles that control the relative orientation of the π-systems were systematically altered for these three structures to help ensure that lower energy minima were not missed, where each resulting structure was characterized through frequency calculations at the same level of theory.

The low-lying singlet excited states of were also calculated using time-dependent density functional theory (TD-DFT) with B3LYP/6-31G(d,p) on the ground-state global minimum geometries. The absorption spectra were simulated through convolution of the vertical transition energies and oscillator strengths with Gaussian functions characterized by a full-width at half-maximum of 3000 cm^{-1}.



Structure	State	E_{opt} (eV)	λ (nm)	f	Composition
1	S_1	1.96	633	1.220	H → L (98%)
	S_3	2.59	478	0.147	H → L+2 (94%)
	S_5	3.04	408	0.420	H – 2 → L (93%)
	S_9	3.47	357	0.251	H – 1 → L + 1 (74%)
2,3,4	S_1	1.98	627	1.262	H → L (100%)
	S_6	3.22	385	0.563	H – 2 → L (85%)

Figure S20: Calculated optical absorption data for napthalimide (**1**) and phthalimide (**2,3,4**), based DPP compounds at the B3LYP-6-31G(d,p) level of theory.

S7. OFET Plots

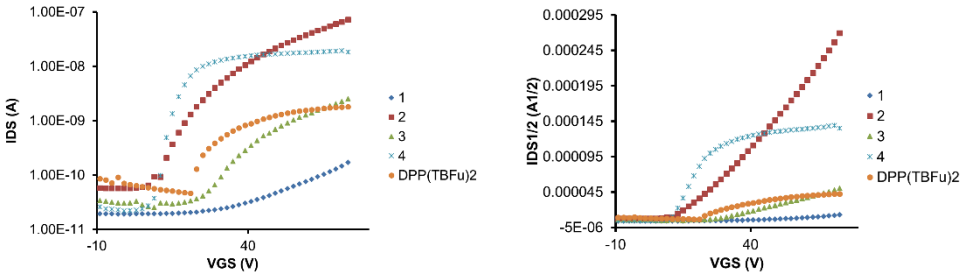


Figure S21: Transistor transfer curves for compounds **1-4** and for DPP(TBFu)$_2$, a related compound studied in the literature. V_{DS} is 75 V for each plot.

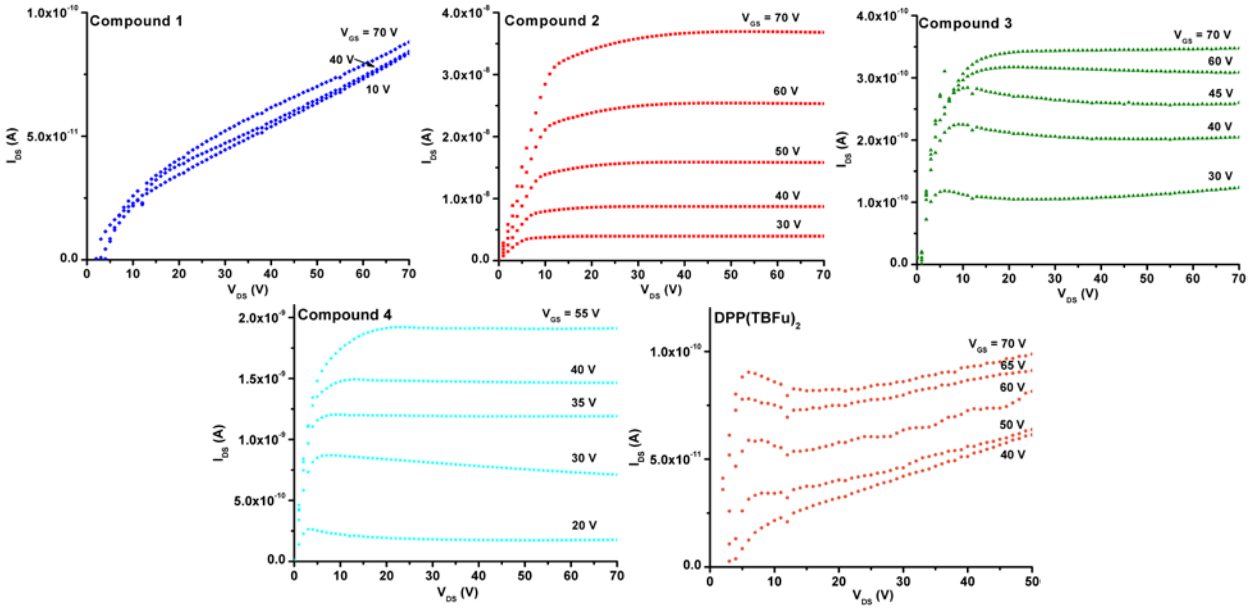


Figure S22. Transistor output curves for compounds **1-4** and for DPP(TBFu)$_2$. The relatively small increase in current for output curves with increasing V_{GS} in **1** is due to the electron mobility being orders of magnitude lower than the other compounds.

S9. References

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