Electronic Supplementary Information (ESI)

Facile synthesis of ultralow-band-gap alkoxythiophene-flanked Diketopyrrolopyrrole homopolymers via $FeCl_3$-mediated oxidative polymerization

*Samala Venkateswarlu,[a] Ravinder Singh,[a] Songbo Cui,[a] Andrew Stella,[a] Jimmy Papazotos,[a] Naixin Zhao,[a] Yi Yuan,[a] Haitao Liu,[b] Xu Li,[b] Jinliang Wang,[b] and Yuning Li[a,]**

[a] *Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN), University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

E-mail: yuning.li@uwaterloo.ca

[b] *Institute of Chemistry, Henan Academy of Sciences, 56 Hongzhuan Road, Jinshui District, Zhengzhou, Henan, China, 450002*

1. General Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX 300-MHz spectrometer, with chemical shifts referenced to tetramethylsilane (TMS, 0 ppm). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Autoflex Speed in reflection positive ionization mode using dithranol as matrix. TGA measurements were conducted on a TGA Q500 (TA Instruments) at a heating rate of 10 °C min^{-1} under nitrogen. High-temperature gel permeation chromatography (HT-GPC) measurements were conducted on an Agilent PL-GPC220 system utilizing 1,2,4-trichlorobenzene as an eluent at 150 °C with a sample concentration of 10 mg mL^{-1}. UV–vis–NIR absorption spectra of homopolymer in solution and films on glass substrates were recorded using a Cary 7000 Universal Measurement Spectrophotometer (UMS). Cyclic Voltammetry (CV) measurements were performed using a CHI600E electrochemical analyzer with an Ag/AgCl reference electrode and two Pt disk electrodes as the working and counter electrodes, respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate solution in dry acetonitrile at a scan rate of 50 mV s^{-1}. Ferrocene was used as a reference with a HOMO energy level of −4.8 eV. Atomic force microscopy (AFM) images were obtained using a Bruker FastScan/Icon® system. X-ray diffraction (XRD) measurements were conducted on Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) using polymer films spin-coated from chloroform solutions onto SiO_2 substrates. Density functional theory (DFT) calculations were carried out using the Gaussian 9.0 package at the B3LYP/6-31G(d,p) level, with molecular structures visualized using GaussView 9.0.

2. Fabrication and characterization of OTFT devices

Bottom-gate bottom-contact (BGBC) organic thin-film transistor (OTFT) devices were fabricated on heavily doped silicon wafers with a 300 nm thermally grown SiO_2 gate dielectric with areal capacitance 11.5 nF/cm^{-2}. Gold source and drain electrodes were patterned on the SiO_2 surface by conventional photolithography with channel length of 30 μm and channel width of 1000 μm. The substrates were sequentially cleaned with deionized (DI) water, acetone, and isopropanol (IPA), followed by drying under a nitrogen stream. The cleaned substrates were then immersed for 1 min in an aqueous solution containing DI water (20 mL) and a mixture of HNO_3:HCl:H_2O (1:10:10, ~0.05 mL). After thorough rinsing with DI water and IPA, the substrates were dried under nitrogen and further heated on a hot plate at 120 °C for 10 min. To modify the SiO_2 surface, the substrates were immersed in a dodecyltrichlorosilane (DDTS) solution in toluene (10 mg mL^{-1}) for 15 min, followed by rinsing with toluene and drying under nitrogen. Polymer solutions of PDPPC_{12}OT-C_{12} and PDPPC_{20}OT-C_8 (10 mg mL^{-1} in chloroform) were then spin-coated onto the substrates at 2000 rpm for 80 seconds, yielding films with thickness of ~50-60 nm, which were optionally annealed at 100, 150, 200, or 250 °C for 20 min inside the glove box to complete the device fabrication.

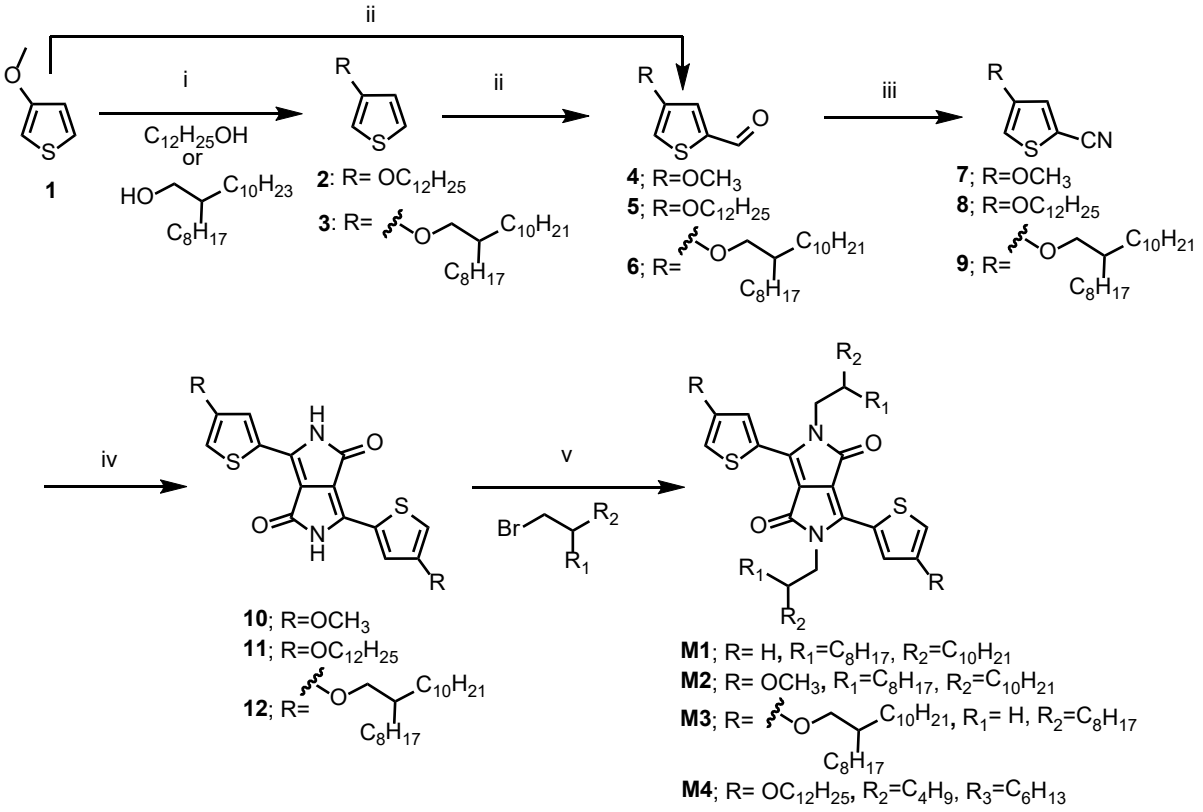
Electrical characterization was performed inside a nitrogen-filled glovebox or under imbuement conditions (22 °C, 55% relative humidity) in dark using an Agilent 2902B semiconductor parameter analyzer. Carrier mobility (μ) was calculated from the data in the saturated regime (gate voltage, V_G < source-drain voltage, V_{SD}) using **Equation 1**:

$$I_{SD} = C_i \mu (W/2L) (V_G - V_T)^2 \qquad \textbf{(Eqation 1)}$$

where I_{SD} is the drain current at the saturated regime, W and L are the channel width and length, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage, respectively. The threshold voltage was determined from the linear extrapolation of the square root of I_{SD} in the saturated regime to $I_{SD} = 0$.

3. Synthesis of monomers M1 – M4

The synthetic routes for monomers **M1**–**M4** are outlined in Scheme S1. Monomer **M1** was synthesized following previously reported procedures.[1]



Scheme S1. Synthetic routes to monomers **M1**-**M4**: (i) p-TSA, toluene, 110°C, 24 h; (ii) n-BuLi, THF, -78°C-r.t., 12 h; (iii) $NH_2OH.HCl$, DMSO, 90°C, 5 h; (iv) Na metal, $FeCl_3$, diethyl succinate, *tert*-amyl alcohol, 100°C, 24 h; (v) K_2CO_3, DMF, 110°C, 24 h.

3.1. General method of transesterification for the preparation of compounds 2 and 3[2]

To a 100mL round-bottom flask, 3-methoxythiophene (1) (10.0 mmol) and alkyl alcohol (10.0 mmol) and p-toluenesulfonic acid (1.0 mmol) were added. HPLC grade toluene (17 mL) was added to the flask, and the solution was heated under reflux for 48 h. The reaction mixture was allowed to cool to room temperature and deionized water (50 mL) was added to quench the reaction. The solution was extracted with toluene, dried with Na_2SO_4 and the crude compound was obtained after removal of toluene by rotary evaporator before purifying by column chromatography (hexane) to afford desired compounds.

*Preparation of 3-(dodecyloxy)thiophene (**2**)***:** Compound **2** was prepared as a white solid from Compound **1** (1.14 g, 10.0 mmol) with lauryl alcohol (1.86 g, 10.0 mmol) through general method of transesterification. Yield: 1.58 g, 59%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (dd, *J* = 5.4, 3.3 Hz, 1H), 6.76 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.23 (dd, *J* = 3.0, 1.5 Hz, 1H), 3.94 (t, *J* = 6.3 Hz, 2H), 1.82-1.72 (m, 2H), 1.47-1.39 (m, 2H), 1.31-1.27 (br, 16H), 0.89 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.07, 124.52, 119.56, 96.92, 70.27, 31.96, 29.70, 29.68, 29.64, 29.61, 29.44, 29.39, 29.30, 26.09, 22.73, 14.16.

*Preparation of 3-((2-octyldodecyl)oxy)thiophene (**3**)***:** Compound 3 was prepared as a light-yellow oil from Compound **1** (1.14 g, 10.0 mmol) with 2-octyldodecan-1-ol (2.99 g, 10.0 mmol) via above mentioned transesterification method. Yield: 2.21 g, 58%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.77 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.23 (dd, *J* = 3.0, 2.1 Hz, 1H), 3.83 (d, *J* = 5.7 Hz, 2H), 1.81-1.72 (m, 1H), 1.31-1.27 (br, 32H), 0.89 (t, *J* = 3.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.34, 124.40, 119.66, 96.76, 73.17, 38.02, 31.95, 31.36, 30.04, 29.67, 29.63, 29.38, 26.87, 22.72, 14.15.

3.2. General method for the preparation of Compounds 4-6:[3]

3-Alkoxy thiophenene (Compounds **1**, **2**, or **3**) (10.0 mmol) was added into a 250 mL oven-dried two-neck round-bottom flask equipped with stir bar, dissolved with tetrahydrofuran (50 mL), then n-BuLi in hexanes (2.5 M) (4.43 mL, 11 mmol) was added dropwise at -78°C under nitrogen atmosphere. The reaction mixture was stirred for 1 hour under the same conditions, then dimethylformamide (DMF) (0.94 mL, 12 mmol) was added before allowing the reaction mixtures to room temperature, and stirred overnight. After completion of the reaction, which were monitored by thin layer chromatography, reaction mixtures were poured into water (100 mL) then extracted with dichloromethane (3×50 mL) and dried with Na_2SO_4. The crude product was obtained after removal of the solvent and purified further by column chromatography on silica using a mixture of ethyl acetate and hexane in 5:95 ratios to afford pure Compounds **4**, **5**, or **6**.

*Preparation of 4-methoxythiophene-2-carbaldehyde (**4**)***:**[3] Compound **4** was prepared as a light-yellow solid from compound **1** (1.14 g, 10 mmol) by following the above-mentioned general method. Yield: 0.48 g, 34%.

*Preparation of 4-(dodecyloxy)thiophene-2-carbaldehyde (**5**)***:** Compound **5** was prepared as a light-yellow solid from Compound **2** (2.68 g, 10.0 mmol) by following the above-mentioned general method. Yield: 1.07 g, 36%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.82 (d, *J* = 0.9 Hz, 1H),

7.40 (d, *J* = 1.5 Hz, 1H), 6.73 (d, *J* = 1.2 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.82 (p, 2H), 1.46-1.42 (m, 2H), 1.30-1.26 (br, 16H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 182.78, 158.22, 141.17, 126.68, 108.24, 70.72, 31.92, 29.66, 29.64, 29.59, 29.56, 29.36, 29.12, 25.95, 22.70, 14.14.

*Preparation of 4-((2-octyldodecyl)oxy)thiophene-2-carbaldehyde (**6**)***:** Compound **6** was prepared as a yellow oil from Compound **3** (3.81 g, 10.0 mmol) with n-BuLi (4.43 mL, 11 mmol) and DMF (0.94 mL, 12.0 mmol) by following the above-mentioned general method. Yield: 1.31 g, 32%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.82 (d, *J* = 0.9 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 6.72 (t, *J* = 1.5 Hz, 1H), 3.85 (d, *J* = 5.7 Hz, 2H), 1.80-1.72 (m, 1H), 1.26 (br, 32H), 0.86 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 182.74, 158.47, 141.13, 126.76, 108.12, 73.60, 37.93, 31.92, 31.90, 31.24, 29.98, 29.66, 29.65, 29.62, 29.58, 29.36, 29.33, 26.82, 22.69, 14.12.

3.3. General cynation method for the preparation of Compounds 7-9

In a 100 mL round-bottom flask, Compounds **4**, **5**, or **6** (5.0 mmol) and $NH_2OH{\cdot}HCl$ (0.42 g, 6.0 mmol) in DMSO (20 mL) was stirred at 90 °C for 5 h. Upon completion, which was monitored via thin layer chromatography (TLC) utilizing a solvent system of 5% ethyl acetate in hexane, the reaction mixture was allowed to cool to room temperature and then diluted with H_2O. The resulting mixture was subsequently extracted with diethyl ether (Et_2O) and dried over Na_2SO_4 prior to the evaporation of the organic solvent, yielding the crude product. Purification was achieved through flash chromatography on silica using 5% ethyl acetate in hexane, leading to the isolation of pure Compound **7**, **8**, or **9**.

*Preparation of 4-methoxythiophene-2-carbonitrile (**7**)***:** Compound **7** was prepared according to the literature procedure[4,5] as a yellow solid from Compound **4** (0.71 g, 5.0 mmol) and $NH_2OH{\cdot}HCl$ (0.42 g, 6.0 mmol) by following the general cyanation method. Yield: 0.30 g, 42%.

*Preparation of 4-(dodecyloxy)thiophene-2-carbonitrile (**8**)***:** Compound **8** was prepared as a yellow solid from Compound **5** (1.48 g, 5.0 mmol) and $NH_2OH{\cdot}HCl$ (0.42 g, 6.0 mmol) by following the general cyanation method. Yield: 0.98 g, 67%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.23 (d, *J* = 1.8 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.80 (p, 2H), 1.44-1.39 (m, 2H), 1.26 (br, 16H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.14, 128.61, 114.32, 105.00, 70.94, 31.92, 29.65, 29.64, 29.58, 29.53, 29.36, 29.31, 29.03, 25.91, 22.70, 14.14.

*Preparation of 4-((2-octyldodecyl)oxy)thiophene-2-carbonitrile (**9**)*: Compound **9** was prepared as yellow oil from Compound **6** (2.04 g, 5.0 mmol) and $NH_2OH{\cdot}HCl$ (0.42 g, 6.0 mmol) by following the general cyanation method. Yield: 1.02 g, 50%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.24 (d, *J* = 1.8 Hz, 1H), 6.50 (d, *J* = 1.5 Hz, 1H), 3.83 (d, *J* = 5.7 Hz, 2H), 1.76-1.70 (m, 1H), 1.26 (br, 32H), 0.88 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.38, 128.67, 114.31, 108.38, 104.87, 73.80, 37.89, 31.92, 31.90, 31.19, 29.95, 29.65, 29.64, 29.61, 29.57, 29.35, 29.32, 26.80, 22.69, 14.12.

3.4. Common procedure for the preparation of Compounds 10-12:[1]

To a 100 mL oven-dried, three-neck round-bottomed flask fitted with a 10 mL dropping funnel and a stir bar, sodium (0.21 g, 9.0 mmol) and *tert*-amyl alcohol (10 mL) were added at room temperature under N_2 atmosphere. The reaction mixture was stirred overnight at 95-100 °C, until the sodium metal was dissolved completely. The resultant mixture was allowed to reach 85 °C and carbonitriles **7**, **8**, or **9** (7.5 mmol) were added, then diethyl succinate (0.52 g, 3.0 mmol) in 2 mL of *tert*-amyl alcohol was added dropwise using dropping funnel. The reaction mixture was further stirred overnight at 105 °C, then after completion cooled to 50 °C, slowly neutralized with ~3 mL of glacial acetic acid, and then diluted with 20 mL of methanol and refluxed briefly. The reaction mixtures were filtered using Buckner-funnel and the solid was washed several times with water and hot methanol. The resulting solids were then dried in vacuum at 50 °C to afford dark red solids of Compounds **10**, **11**, or **12**. The obtained solids were used directly for the next step without any further purification.

*Preparation of 3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**10**)*: Following the above-mentioned common procedure, Compound **10** was prepared according the literature procedure[5] as a dark-purple solid from Compound **7** (1.05 g, 7.5 mmol) and diethyl succinate (0.52 g, 3.0 mmol). Yield: 0.76 g, 70%.

*Preparation of 3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**11**)*: Using the above-mentioned common procedure, Compound **11** was prepared as dark purple solid from Compound **8** (2.2 g, 7.5 mmol) and diethyl succinate (0.52 g, 3.0 mmol). Yield: 1.21 g, 60%. Due to poor solubility and strong aggregation in organic solvents, ^{1}H and ^{13}C were not recorded. MALDI-MS calcd for $C_{38}H_{56}N_2O_4S_2$ [M^+] 669.00; found 669.26.

*Preparation of 3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**)*: Following the above-mentioned common procedure, Compound **12** was prepared as a dark-purple solid from Compound **9** (3.04 g, 7.5 mmol) and diethyl succinate

(0.52 g, 3.0 mmol). Yield: 1.08 g, 40%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.1-7.9 (br, 2H), 6.57-6.40 (br, 2H), 3.86 (br, 4H), 1.74 (br, 2H), 1.24 (br, 64H), 0.87 (br, 12H). ^{13}C NMR was not recorded due to aggregation in organic solvents. MALDI-MS calcd for $C_{54}H_{88}N_2O_4S_2$ [M^+] 893.43; found 893.40.

3.5. General procedure for the preparation of Monomers M2-M4

In an oven dry two-neck 100 mL round bottom flask, Compound **10**, **11**, or **12** (1.0 mmol) and anhydrous K_2CO_3 (0.42 g, 3.0 mmol) were dissolved in anhydrous DMF (15 ml) under N_2 atmosphere. The reaction mixtures were heated to 100 °C for 1 h and then alkyl bromides (3.0 mmol) were added. The reaction mixtures were further stirred at 105 °C overnight and cooled down to room temperature before being poured into water which was then further stirred for 30 min. These residues were extracted with chloroform, dried with $MgSO_4$ and the organic solvents were removed by rotary evaporator to get crude compounds. The crude products were then purified using column chromatography on silica gel using a mixture of hexane and dichloromethane (1:1) as eluent. After removal of the solvent, the resulting solid was further recrystallized from isopropyl alcohol to afford **M2**, **M3**, or **M4** as a purple solid.

*Preparation of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**)*:[1] **M2** was prepared as a dark-purple solid from Compound **10** (0.36 g, 1.0 mmol) and 2-octyl-1-dodecylbromide (1.1 g, 3.0 mmol) by following the above-mentioned general method. Yield: 0.23 g, 25%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.52 (d, J = 1.5 Hz, 2H), 6.61 (d, J = 1.5 Hz, 2H), 3.98 (d, J = 7.8 Hz, 4H), 3.89 (s, 6H), 1.91 (br, 2H), 1.26-1.21 (br, 64H), 0.89 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 161.57, 159.00, 140.02, 128.25, 125.09, 108.06, 103.78, 57.75, 46.16, 37.71, 31.94, 31.90, 31.18, 30.04, 29.66, 29.59, 29.53, 29.38, 29.32, 26.23, 22.71, 22.69, 14.14. MALDI-MS calcd for $C_{56}H_{92}N_2O_4S_2$ [M^+] 921.48; found 921.66.

*Preparation of 2,5-dioctyl-3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M3**)*: **M3** was prepared as a dark-purple solid from Compound **12** (0.90 g, 1.0 mmol) and 1-bromooctane (0.58 g, 3.0 mmol) by following the above-mentioned general method. Yield: 0.34 g, 30%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.59 (d, J = 1.5 Hz, 2H), 6.59 (d, J = 1.8 Hz, 2H), 4.06 (t, J = 7.8 Hz, 4H), 3.91 (d, J = 5.4 Hz, 4H), 1.75-1.68 (br, 6H), 1.26 (br, 84H), 0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 161.25, 158.83, 139.69, 127.88, 125.83, 107.73, 103.92, 73.32, 42.22, 38.11, 31.93, 31.92, 31.78, 31.21,

30.01, 29.69, 29.66, 29.62, 29.37, 29.36, 29.23, 29.21, 26.91, 22.70, 22.63, 14.12, 14.09. MALDI-MS calcd for $C_{70}H_{120}N_2O_4S_2$ [M^+] 1117.86; found 1117.99.

*Preparation of 2,5-bis(2-butyloctyl)-3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M4**)*: **M4** was prepared as a dark-purple solid from compound 11 (0.67 g, 1.0 mmol) and 5-(bromomethyl)undecane (0.75 g, 3.0 mmol) by following the above-mentioned general method. Yield: 0.22 g, 21%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.51 (d, *J* = 1.5 Hz, 2H), 6.58 (d, *J* = 1.5 Hz, 2H), 4.04-3.96 (m, 8H), 1.92 (br, 2H), 1.82 (p, 4H), 1.46 (br, 4H), 1.27-1.21 (br, 64H), 0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 161.64, 158.36, 140.08, 128.01, 125.50, 108.01, 104.03, 70.64, 46.14, 37.68, 31.94, 31.79, 31.17, 30.90, 29.69, 29.65, 29.63, 29.59, 29.43, 29.38, 29.29, 28.46, 26.20, 26.04, 23.08, 22.71, 22.64, 14.14. MALDI-MS calcd for $C_{62}H_{104}N_2O_4S_2$ [M^+] 1005.64; found 1005.54.

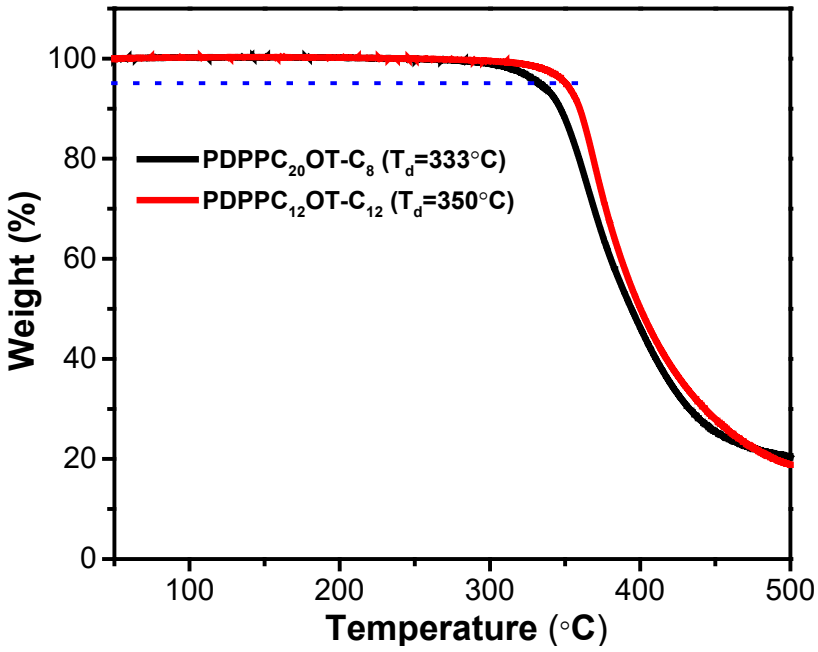


Figure S1. Thermogravimetric analysis (TGA) curves of $PDPPC_{20}OT\text{-}C_8$ and $PDPPC_{12}OT\text{-}C_{12}$ at a heating rate of 10°C min^{-1} under nitrogen atmosphere.

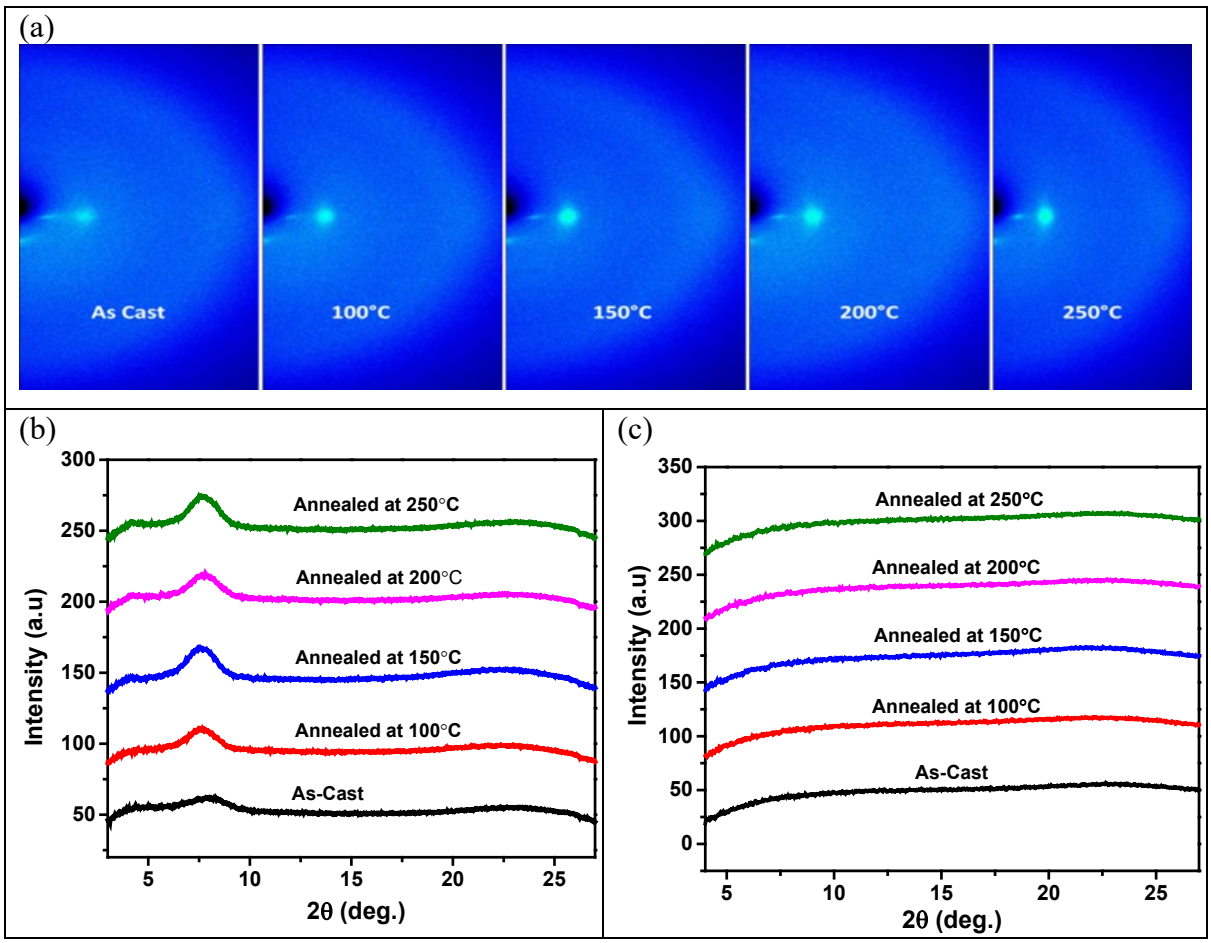


Figure S2. GIXRD data of $PDPPC_{12}OT\text{-}C_{12}$ (a) 2D-GIXRD images, (b) out-of-plane (OOP) pattern and (c) in-plane (IP) pattern.

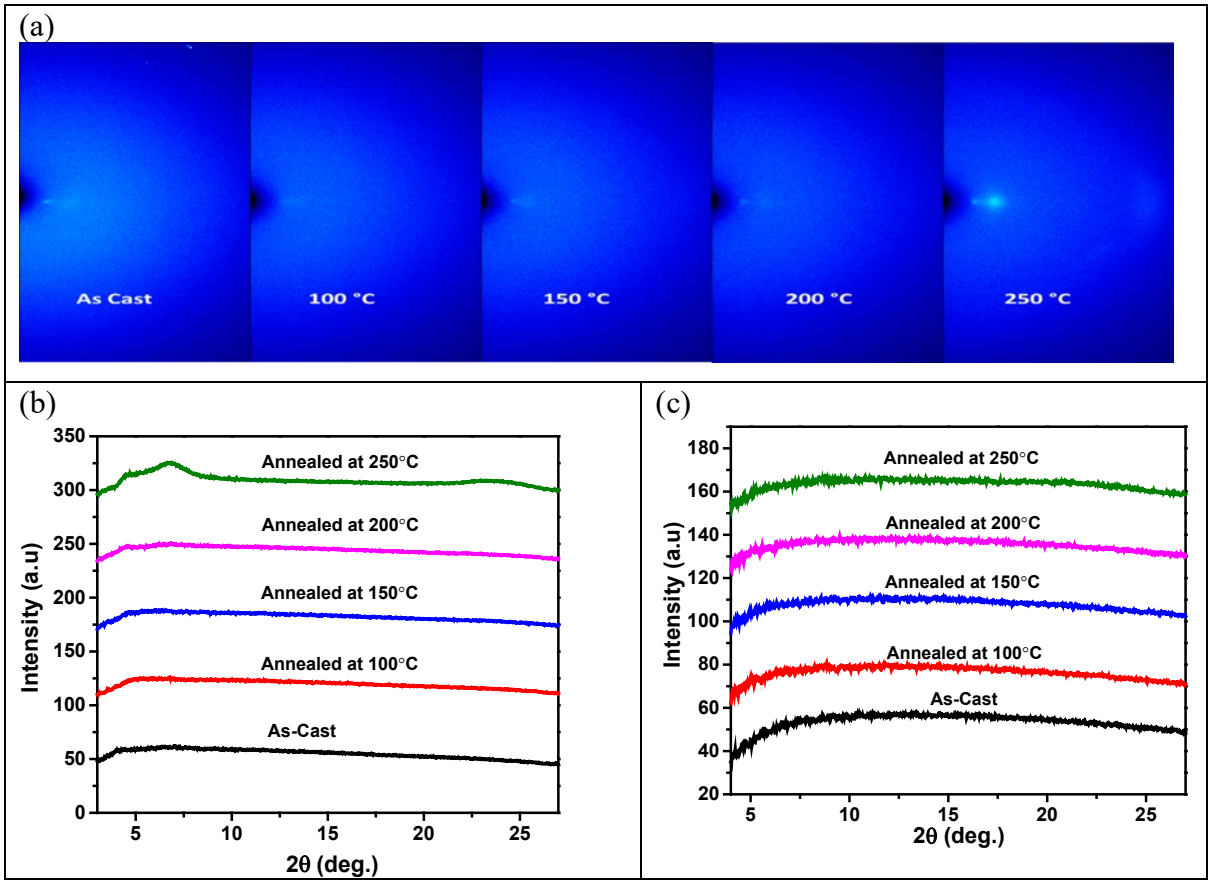


Figure S3. GIXRD data of PDPPC$_{20}$OT-C$_8$ (a) 2D-GIXRD images, (b) out-of-plane (OOP) pattern and (c) in-plane (IP) pattern.

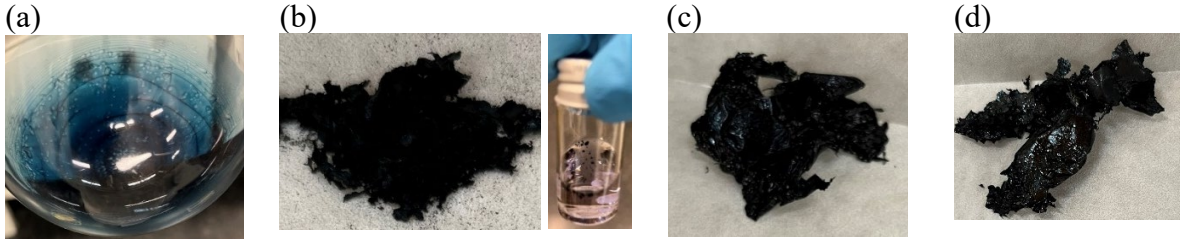


Figure S4. Photographs of (a) PDPPT-C$_{20}$ obtained from the hexane fraction of Soxhlet extraction; (b) PDPPC$_1$OT-C$_{20}$ shown as a solid and dispersion in chloroform; (c) PDPPC$_{12}$OT-C$_{12}$ obtained from the chloroform fraction of Soxhlet extraction; and (d) PDPPC$_{20}$OT-C$_8$ obtained from the chloroform fraction of Soxhlet extraction.

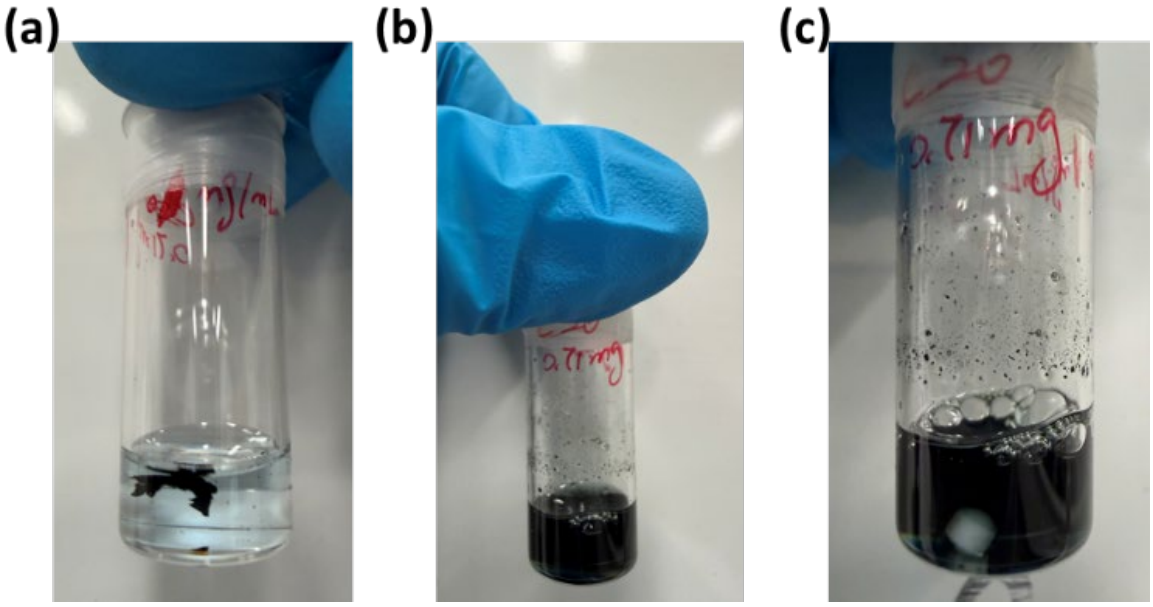


Figure S5. Photographs of PDPPC$_1$OT-C$_{20}$ after stirring in 1,2,4-trichlorobenzene (1 mg/mL) for 8 h at (a) room temperature, (b) 150°C, and (c) 200°C.

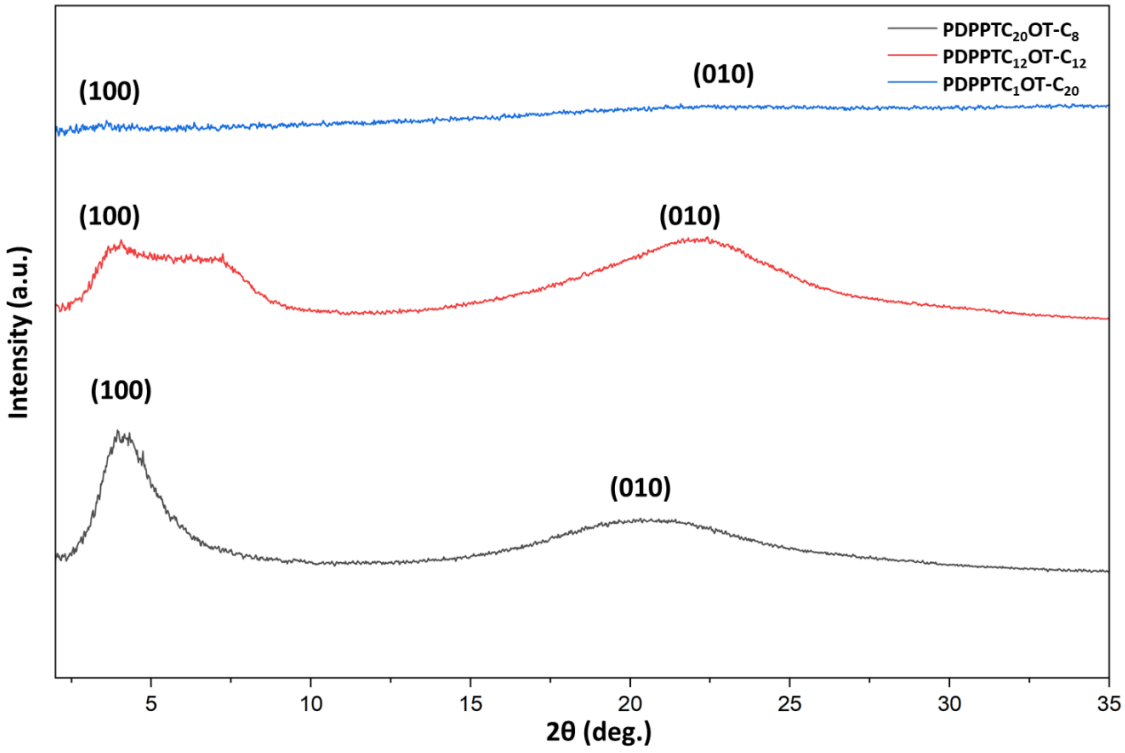


Figure S6. Powder XRD patterns of PDPPC$_{20}$OT-C$_8$, PDPPC$_{12}$OT-C$_{12}$ and PDPPC$_1$OT-C$_{20}$.

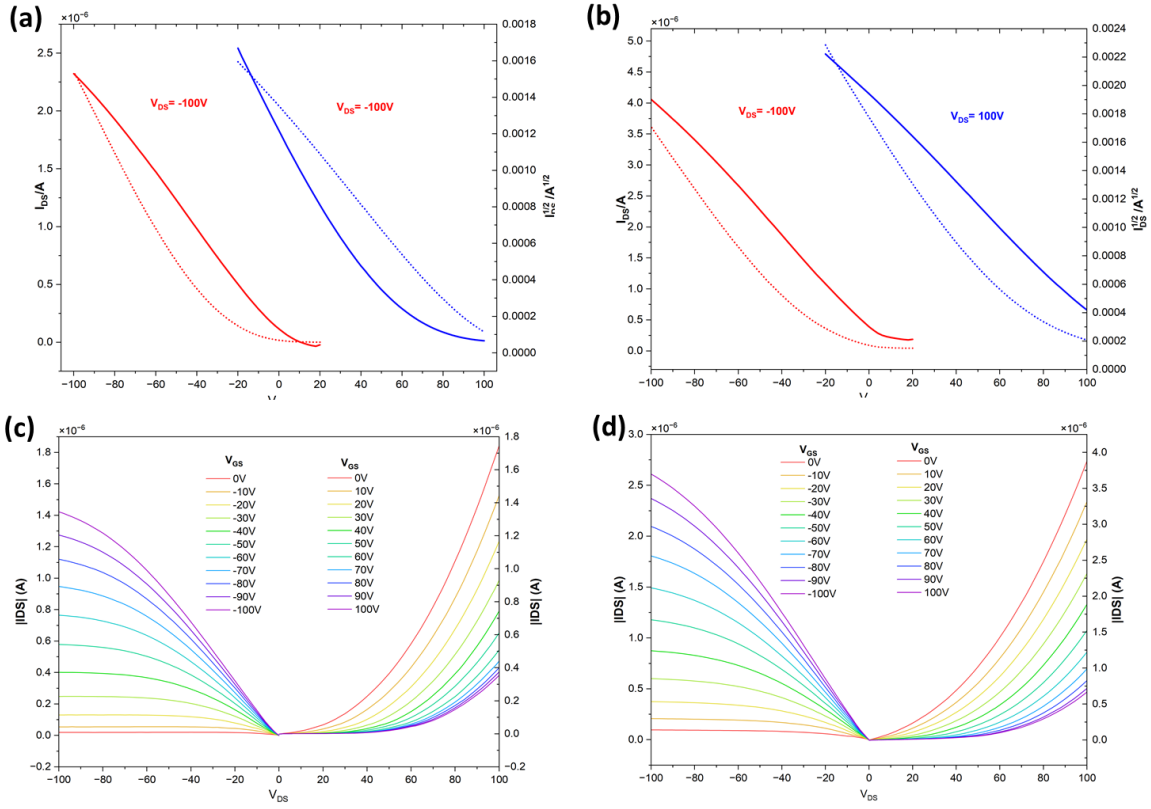


Figure S7. Representative transfer and output characteristics of OTFT devices fabricated based on (a, c) PDPPC$_{20}$OT-C$_8$ after annealing at 200 °C for 20 min and (b, d) PDPPC$_{12}$OT-C$_{12}$ after annealing at 250 °C for 20 min in a glove box filled with nitrogen, measured under ambient conditions (22 °C, 55% relative humidity).

Table S1. OTFT performance of PDPPC$_{20}$OT-C$_8$ and PDPPC$_{12}$OT-C$_{12}$ annealed at 200°C and 250°C, respectively, for 20 min inside a glove box filled with nitrogen, measured under ambient conditions (22 °C, 55% relative humidity).

Homo polymer	Annealing Temperature [°C]	Max. μ_h [$cm^2V^{-1}s^{-1}$][a)]	Avg. $\mu_h \pm$ Std [$cm^2V^{-1}s^{-1}$][b)]	Max. μ_e [$cm^2V^{-1}s^{-1}$][a)]	Avg. $\mu_e \pm$ Std [$cm^2V^{-1}s^{-1}$][b)]	I_{on}/I_{off}[c)] hole/ electron	V_{th} [V][d)] hole/ electron
PDPPC$_{20}$OT-C$_8$	200	1.27×10^{-3}	$1.04\times10^{-3}\pm 9.2\times10^{-5}$	–	–	10^2/–	–3.1/–
PDPPC$_{12}$OT-C$_{12}$	250	1.58×10^{-3}	$1.18\times10^{-3}\pm 7.74\times10^{-5}$	–	–	10^2/–	15/–

[a)] Maximum hole/electron mobility in the saturated region (Max. μ_h/ μ_e); [b)] Average hole mobility in the saturated region and standard deviation (std) from five devices; [c)] On-current (I_{on}) to off-current (I_{off}) ratio; [d)] Average threshold voltage (V_{th}).

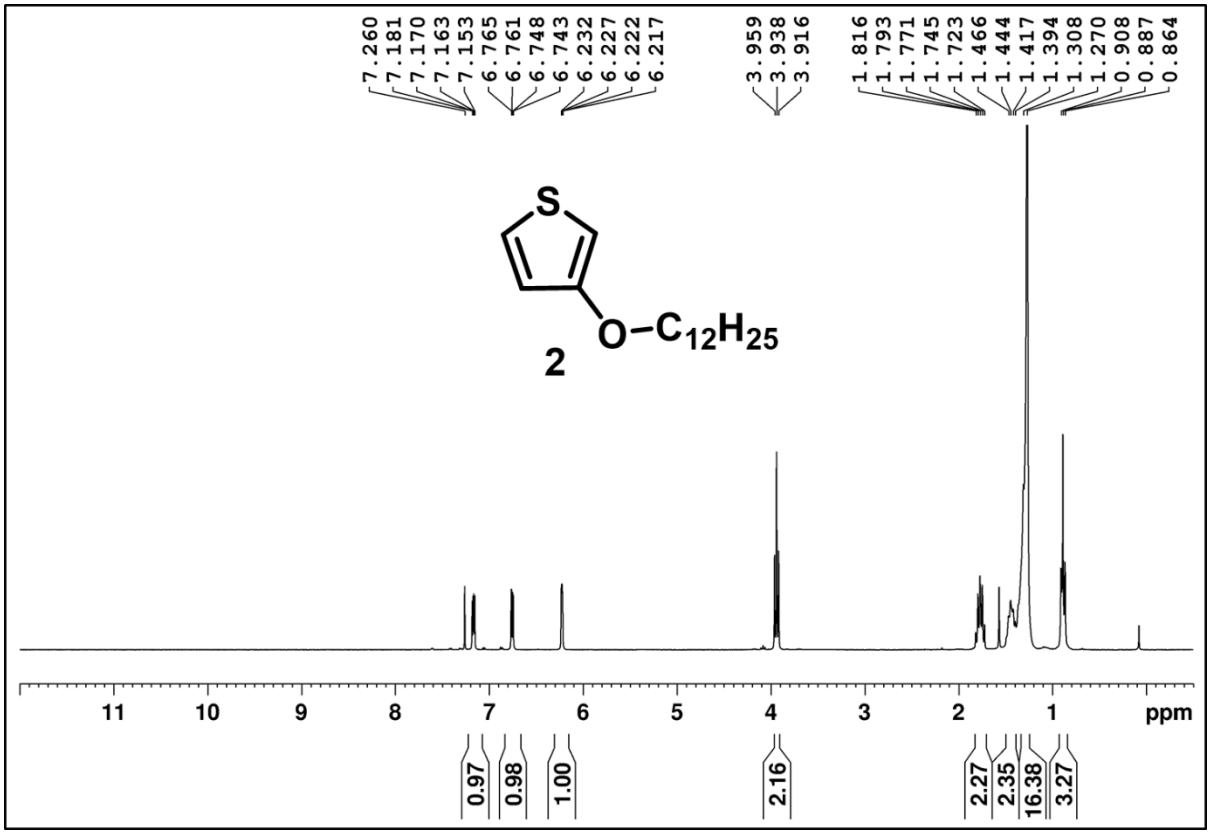


Figure S8. ^{1}H-NMR of 3-(dodecyloxy)thiophene (**2**) in $CDCl_3$.

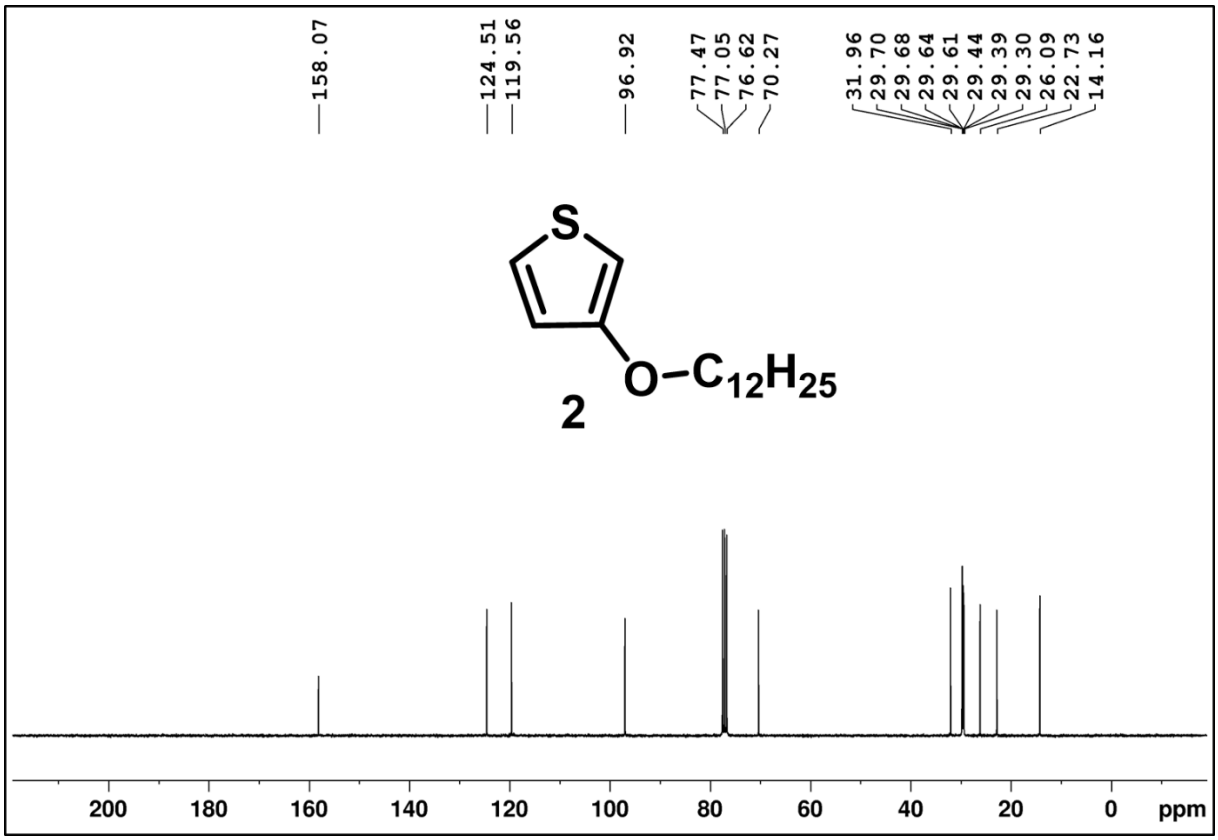


Figure S9. ^{13}C-NMR of 3-(dodecyloxy)thiophene (**2**) in $CDCl_3$.

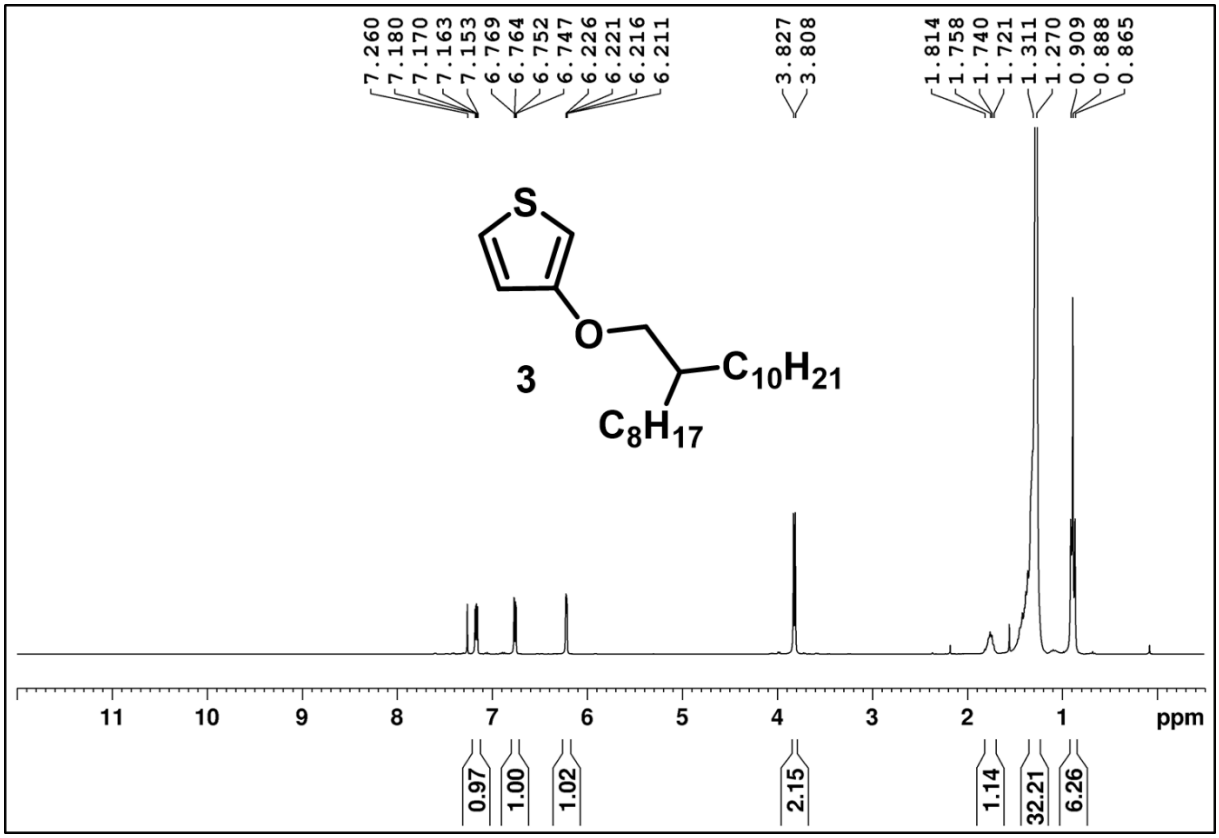


Figure S10. ^{1}H-NMR of 3-((2-octyldodecyl)oxy)thiophene (**3**) in $CDCl_3$.

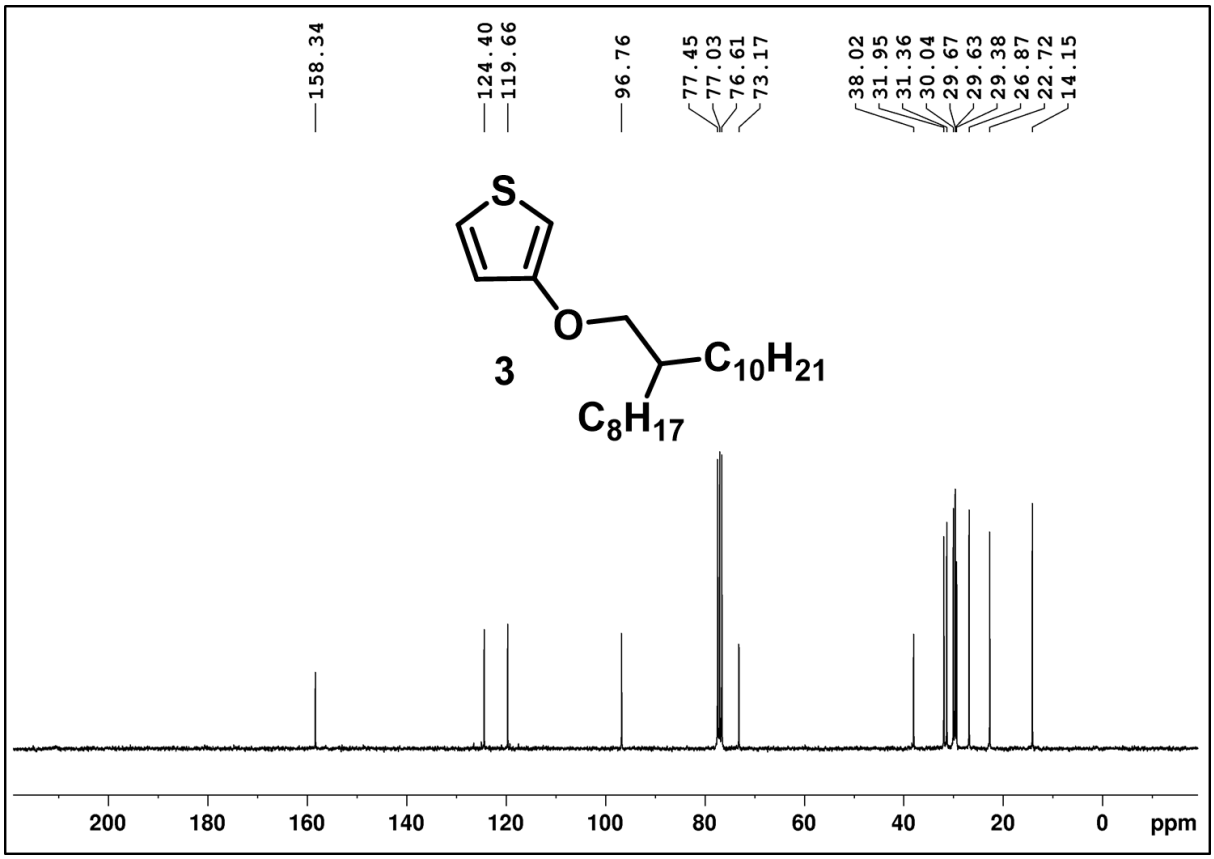


Figure S11. ^{13}C-NMR of 3-((2-octyldodecyl)oxy)thiophene (**3**) in $CDCl_3$.

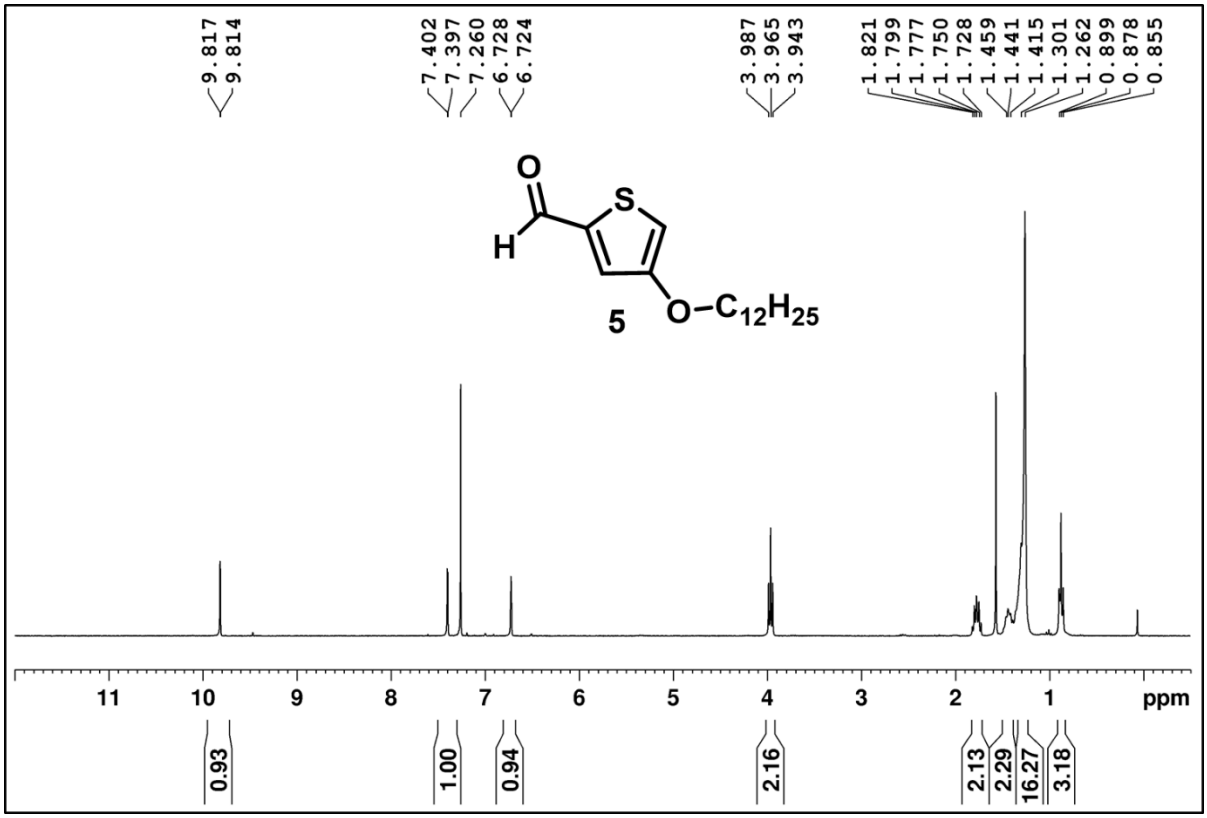


Figure S12. ^{1}H-NMR of 4-(dodecyloxy)thiophene-2-carbaldehyde (**5**) in $CDCl_3$.

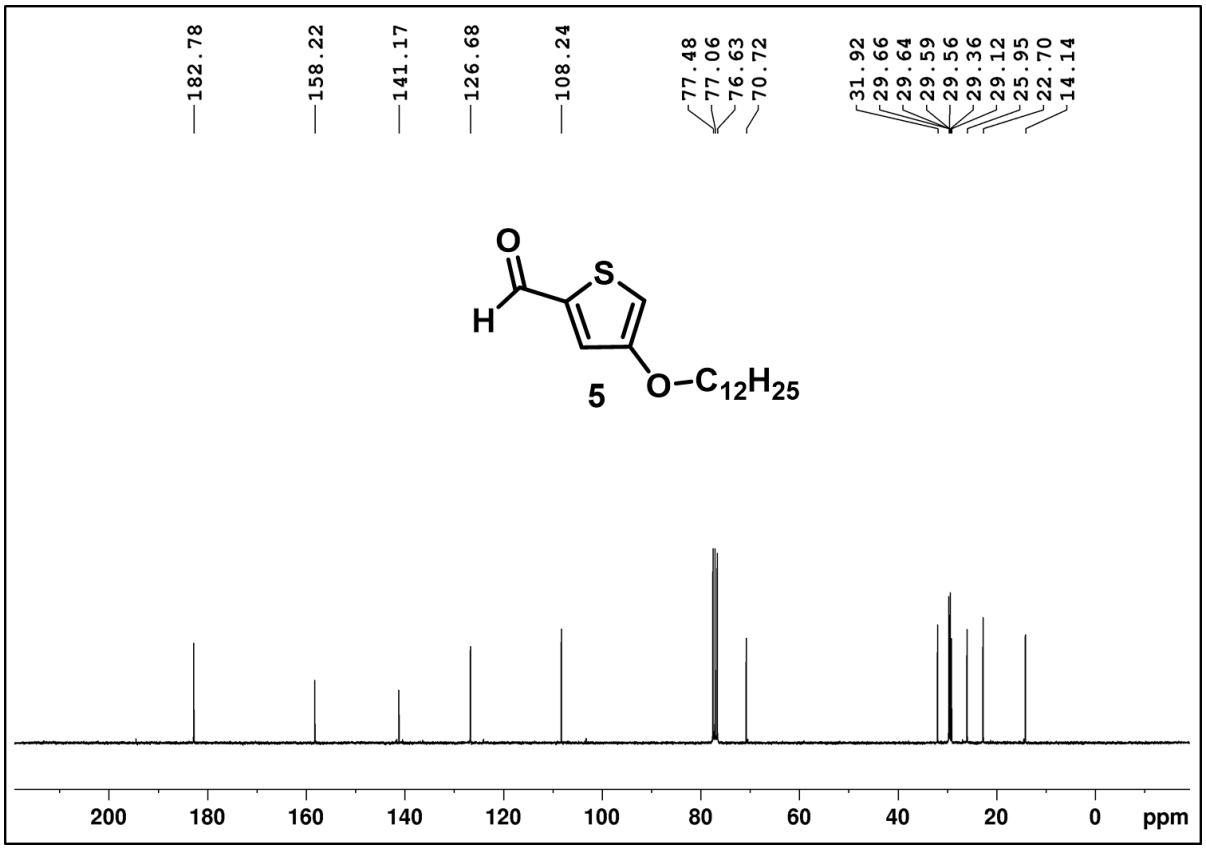


Figure S13. ^{13}C-NMR of 4-(dodecyloxy)thiophene-2-carbaldehyde (**5**) in $CDCl_3$.

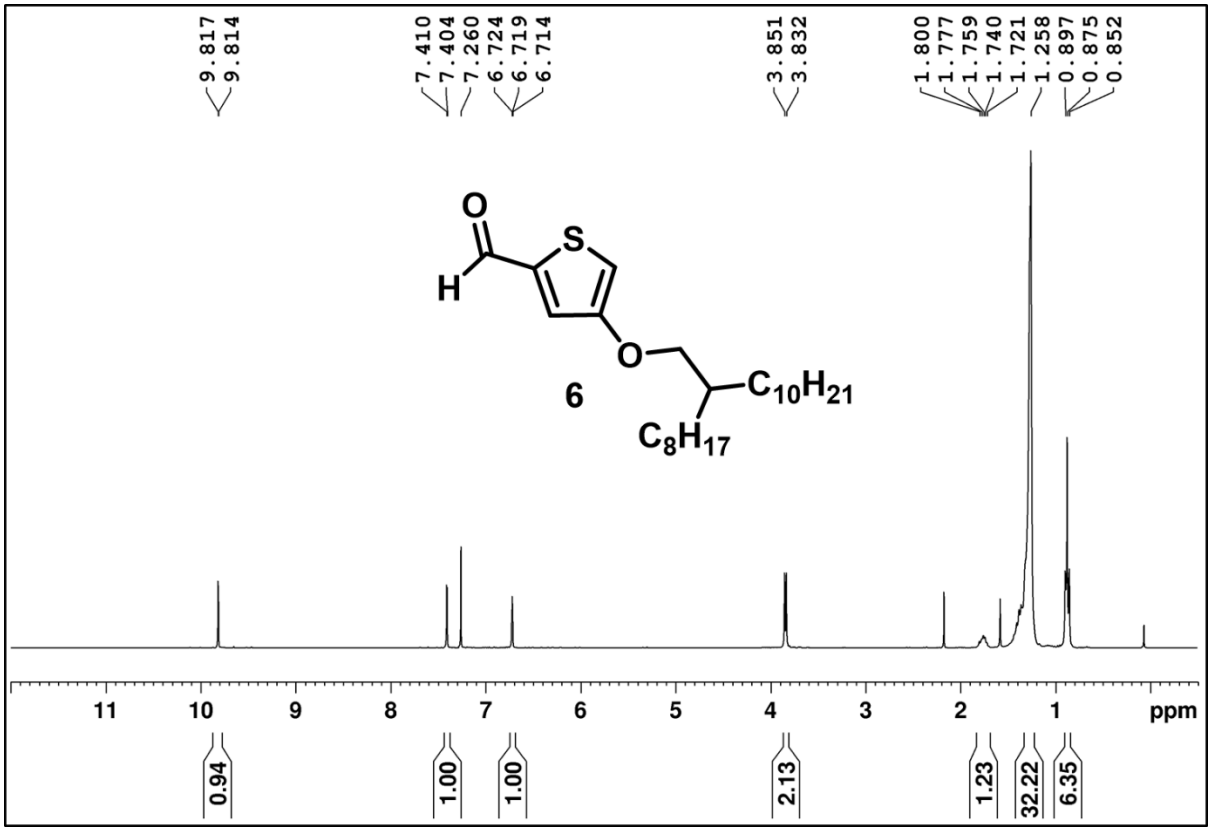


Figure S14. ^{1}H-NMR of 4-((2-octyldodecyl)oxy)thiophene-2-carbaldehyde (**6**) in $CDCl_3$.

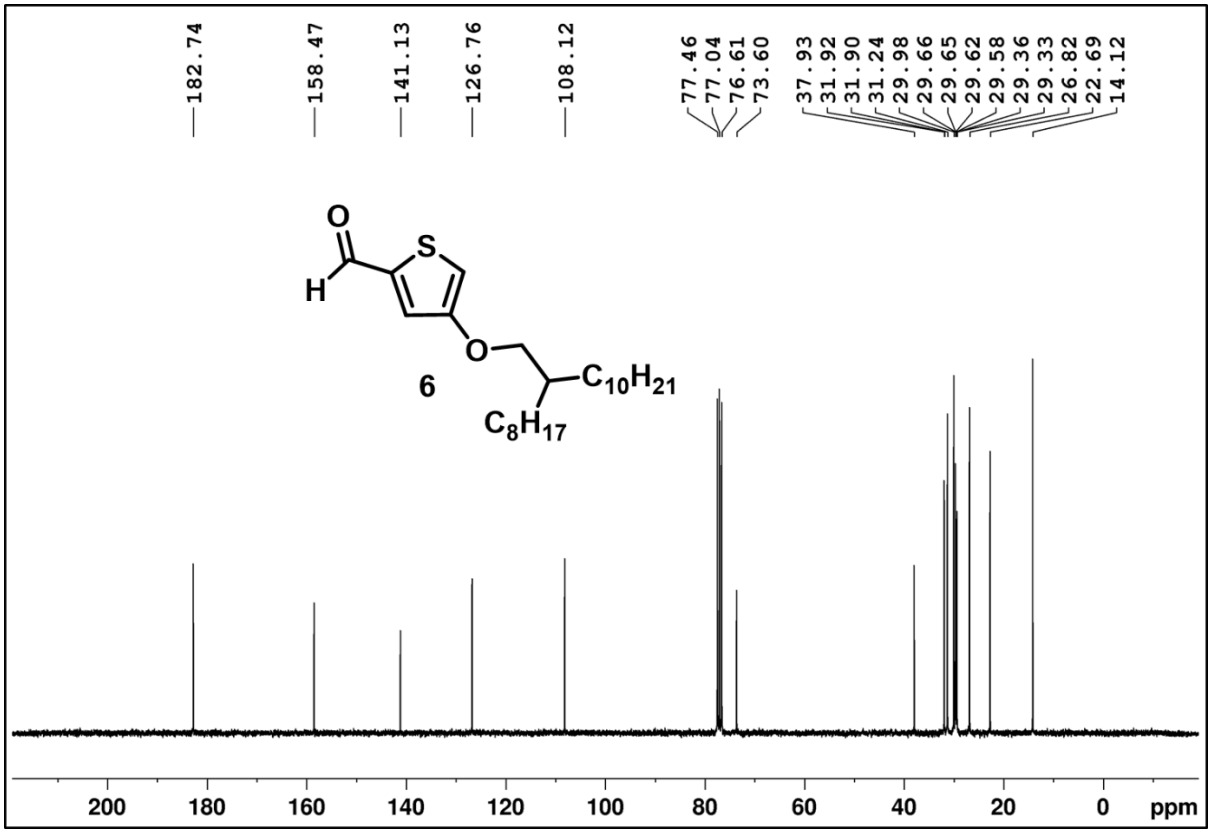


Figure S15. ^{13}C-NMR of 4-((2-octyldodecyl)oxy)thiophene-2-carbaldehyde (**6**) in $CDCl_3$.

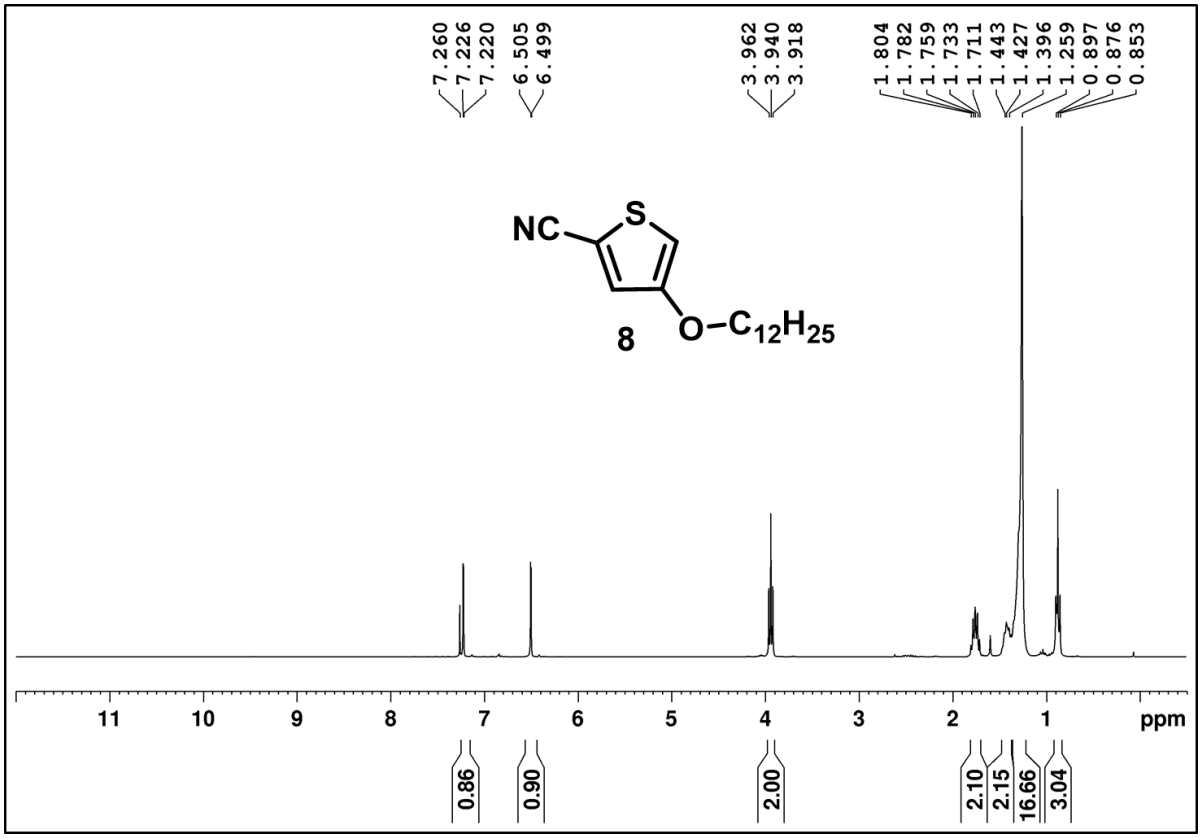


Figure S16. ^{1}H-NMR of 4-(dodecyloxy)thiophene-2-carbonitrile (**8**) in $CDCl_3$.

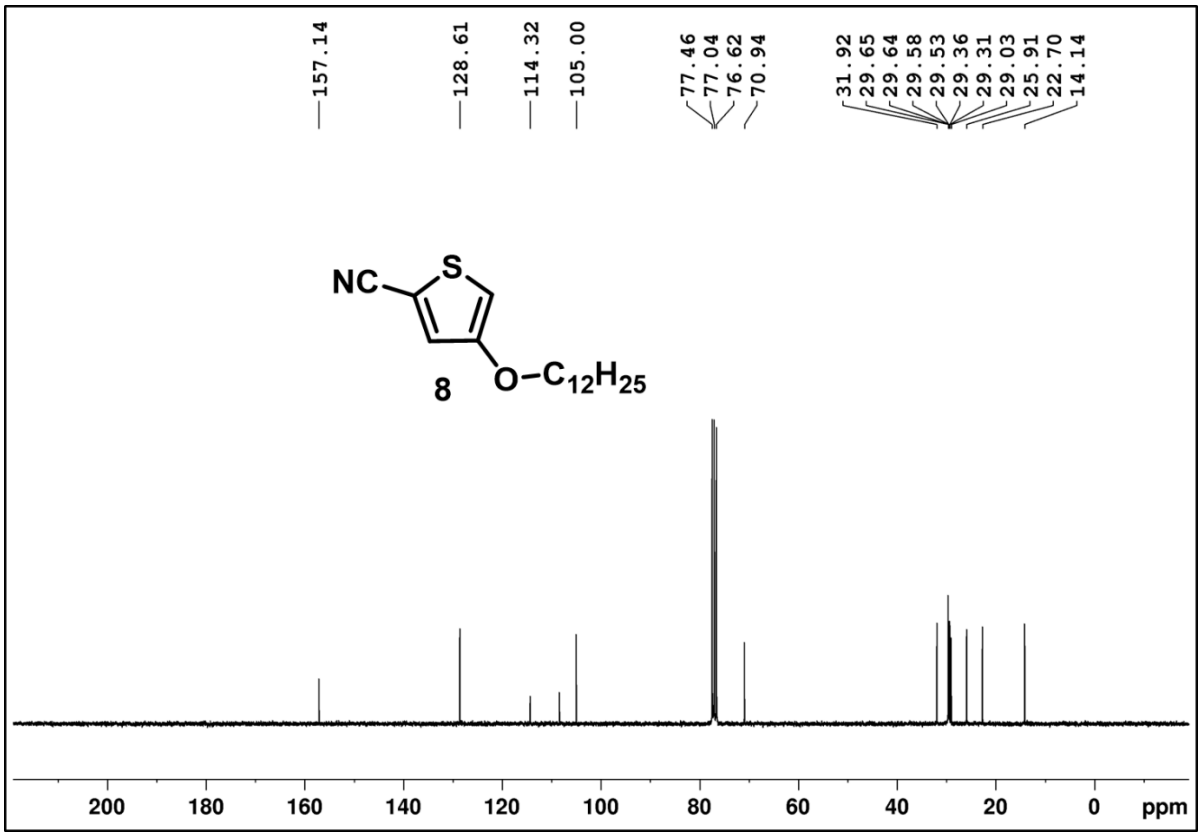


Figure S17. ^{13}C-NMR of 4-(dodecyloxy)thiophene-2-carbonitrile (**8**) in $CDCl_3$.

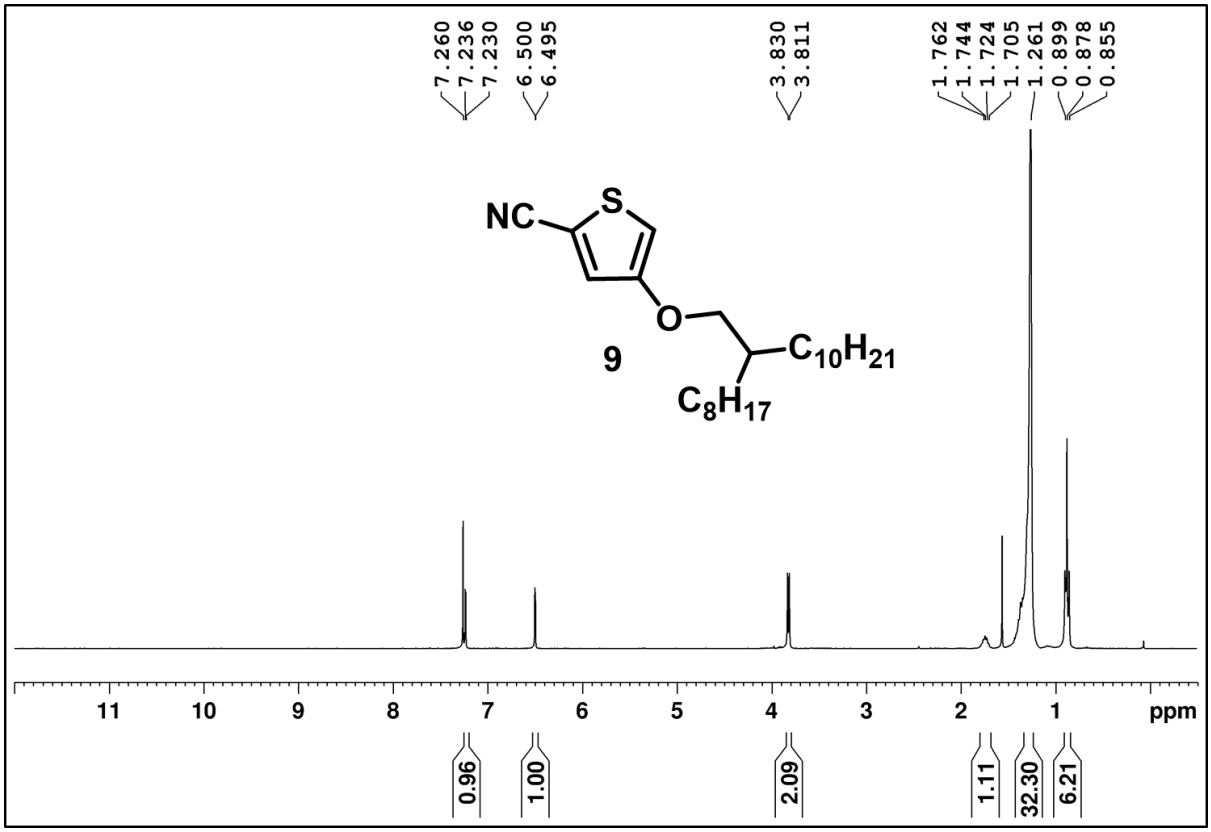


Figure S18. ^{1}H-NMR of 4-((2-octyldodecyl)oxy)thiophene-2-carbonitrile (**9**) in $CDCl_3$.

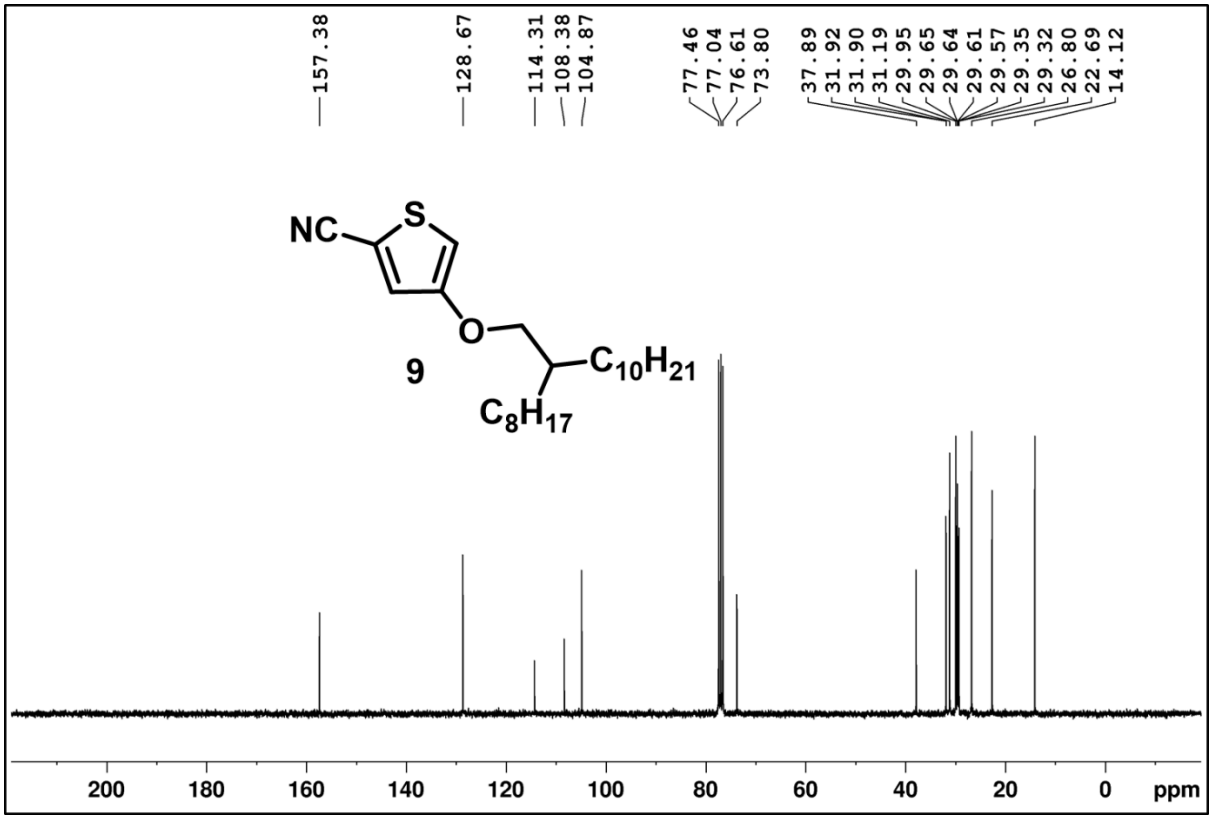


Figure S19. ^{13}C-NMR of 4-((2-octyldodecyl)oxy)thiophene-2-carbonitrile (**9**) in $CDCl_3$.

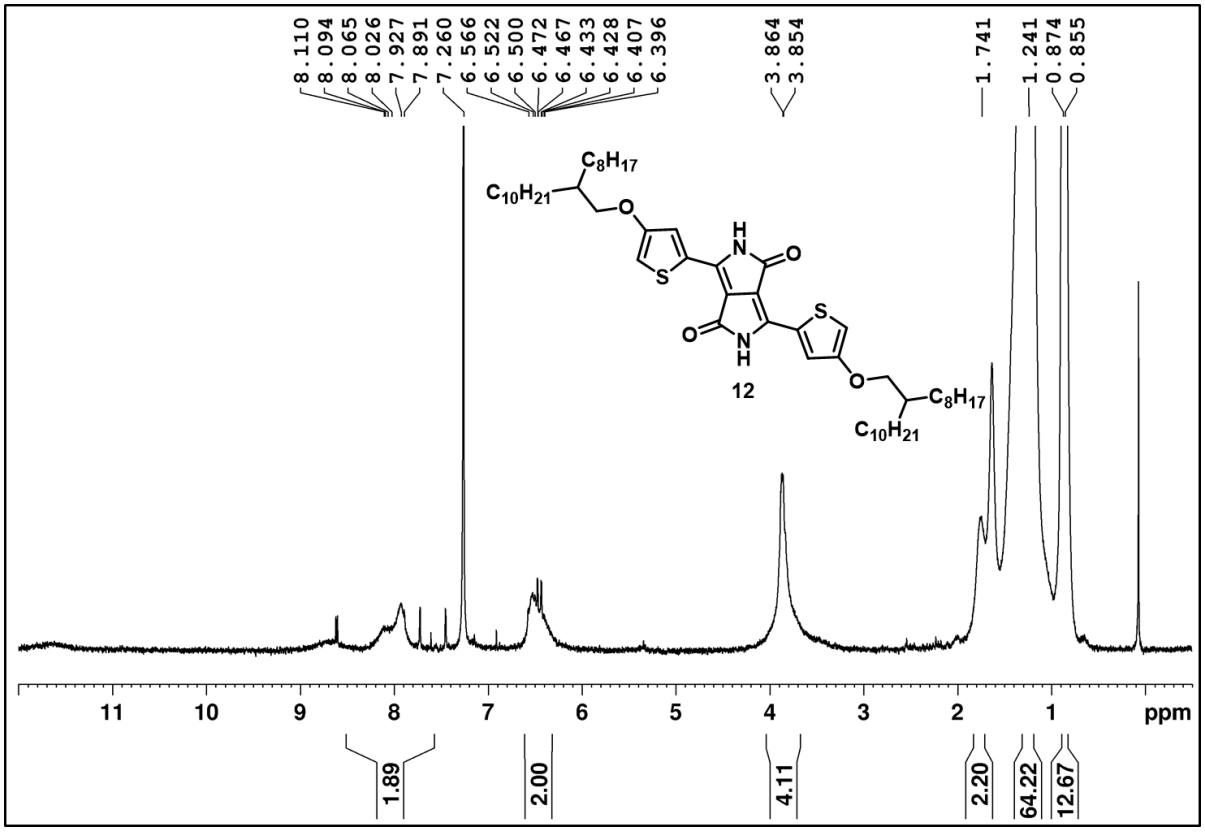


Figure S20. ^{1}H-NMR of 3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**) in $CDCl_3$.

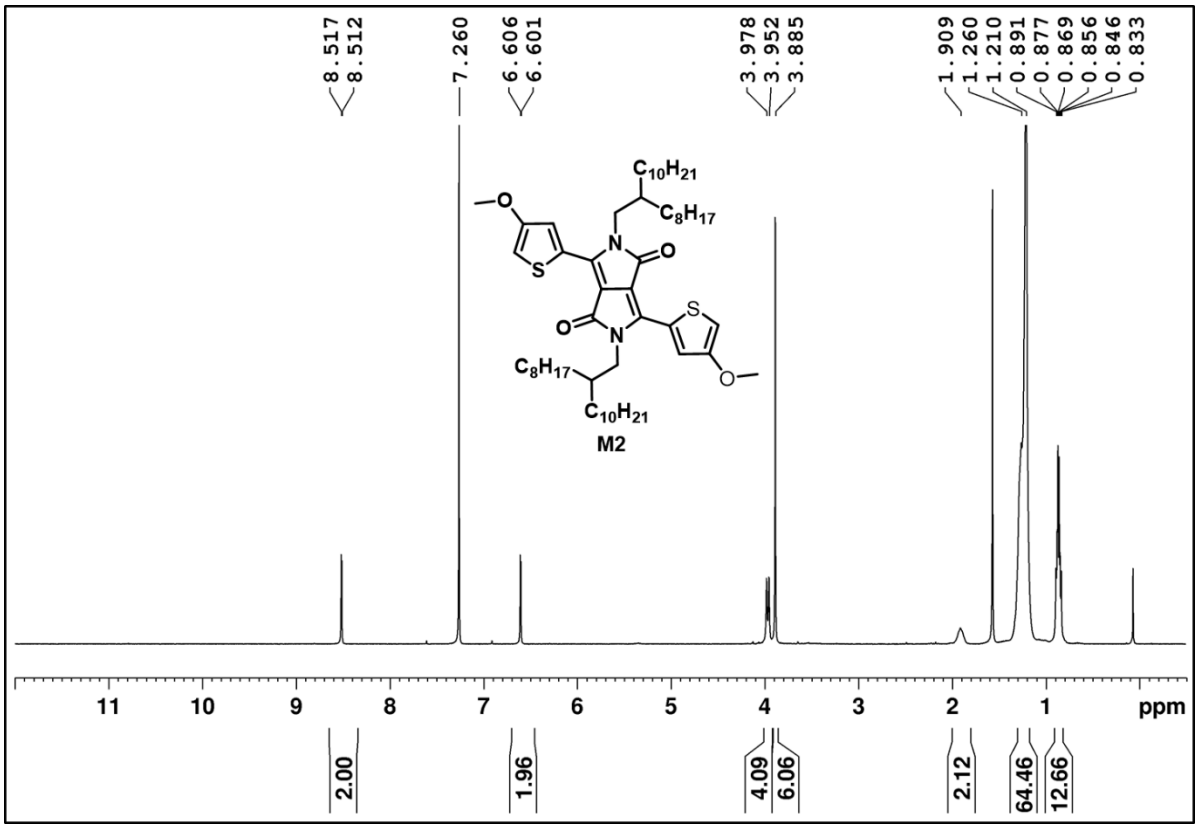


Figure S21. ^{1}H-NMR of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**) in $CDCl_3$.

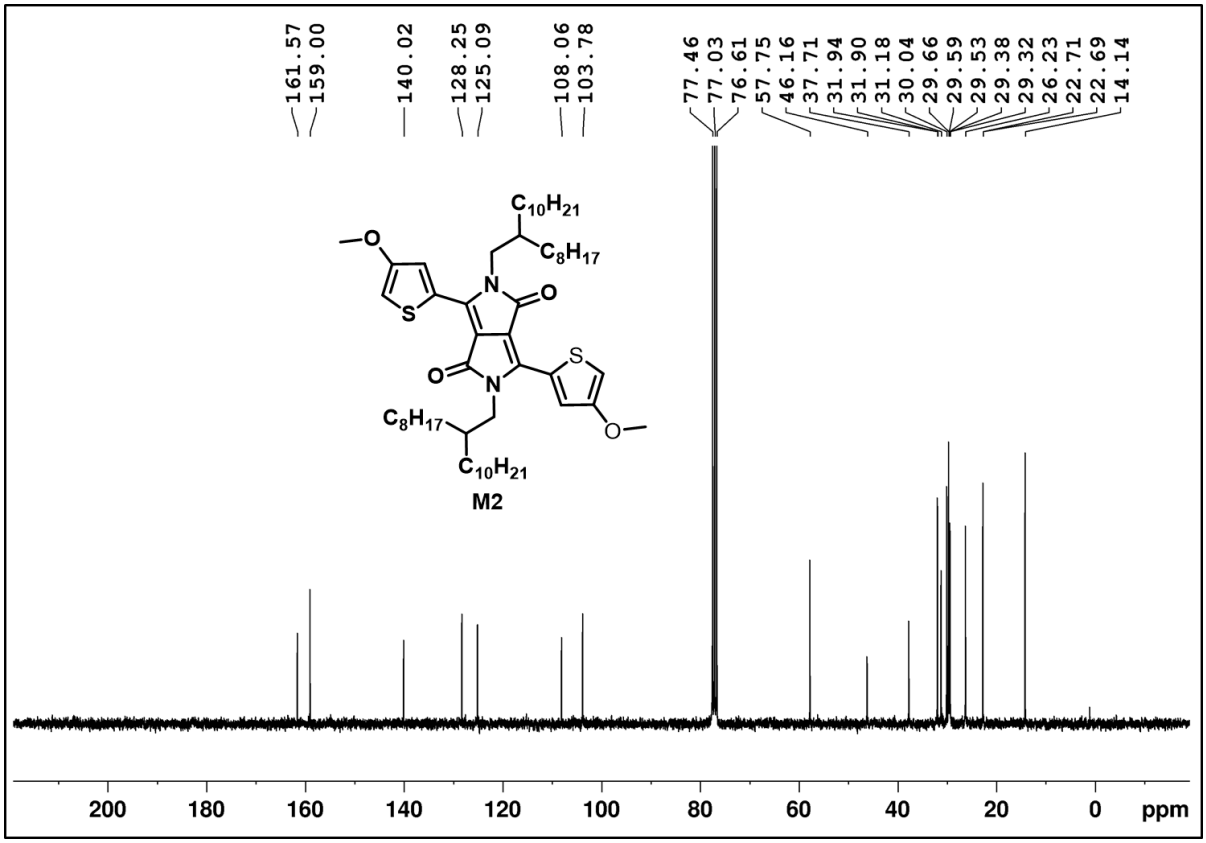


Figure S22. ^{13}C-NMR of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**) in $CDCl_3$.

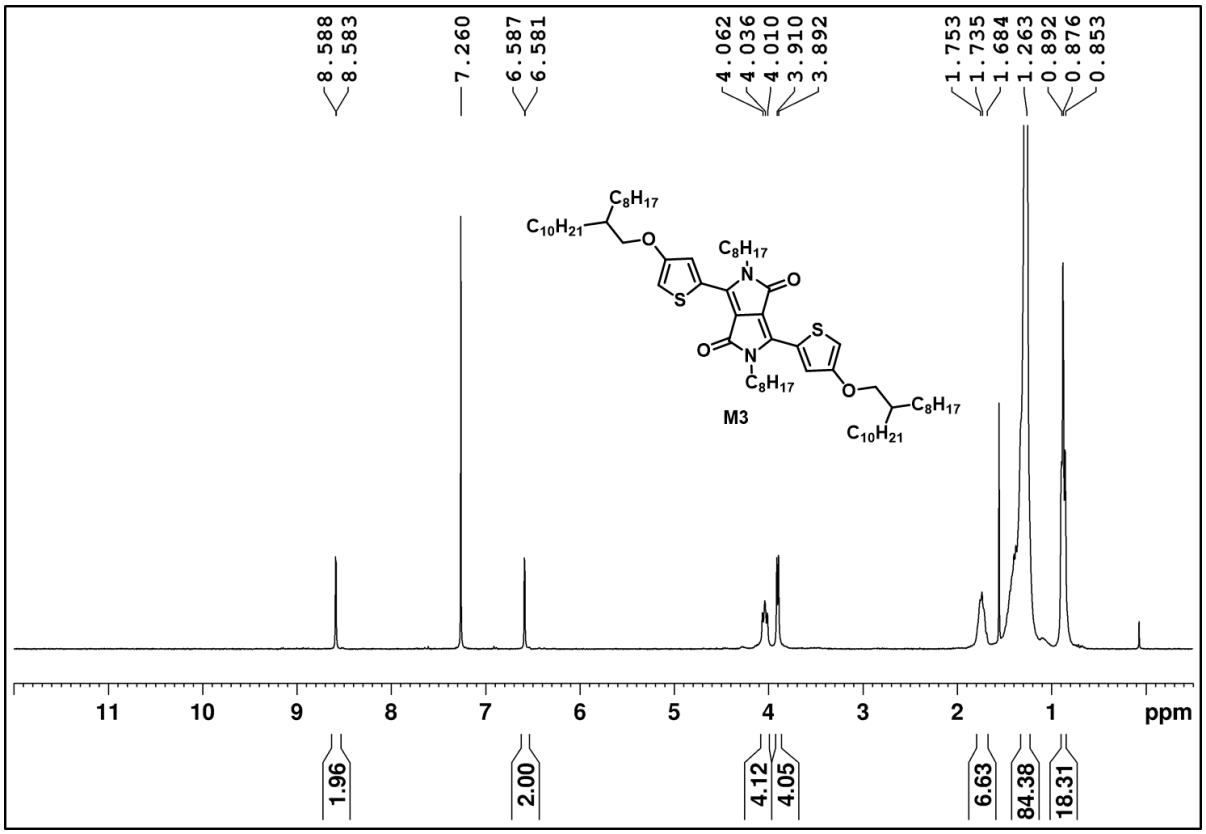


Figure S23. ^{1}H-NMR of 2,5-dioctyl-3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M3**) in $CDCl_3$.

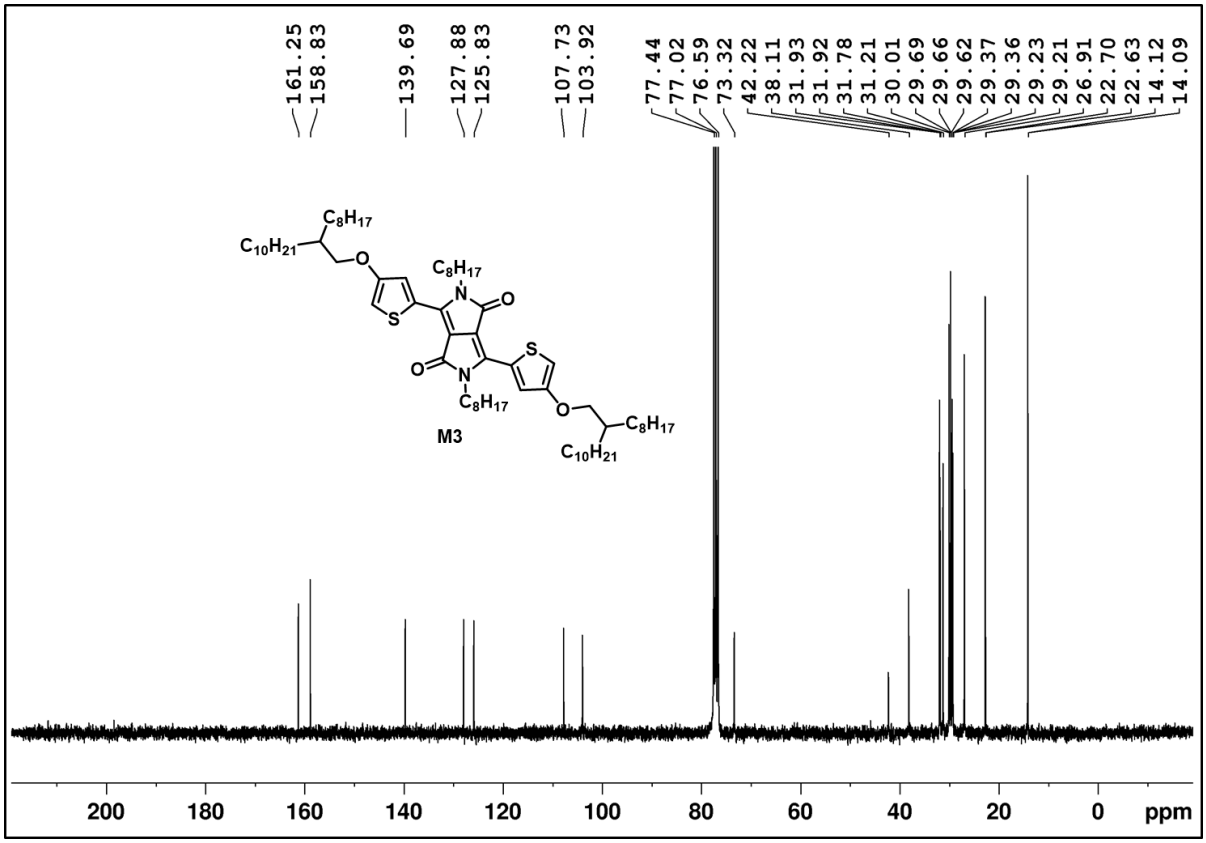


Figure S24. ^{13}C-NMR of 2,5-dioctyl-3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M3**) in $CDCl_3$.

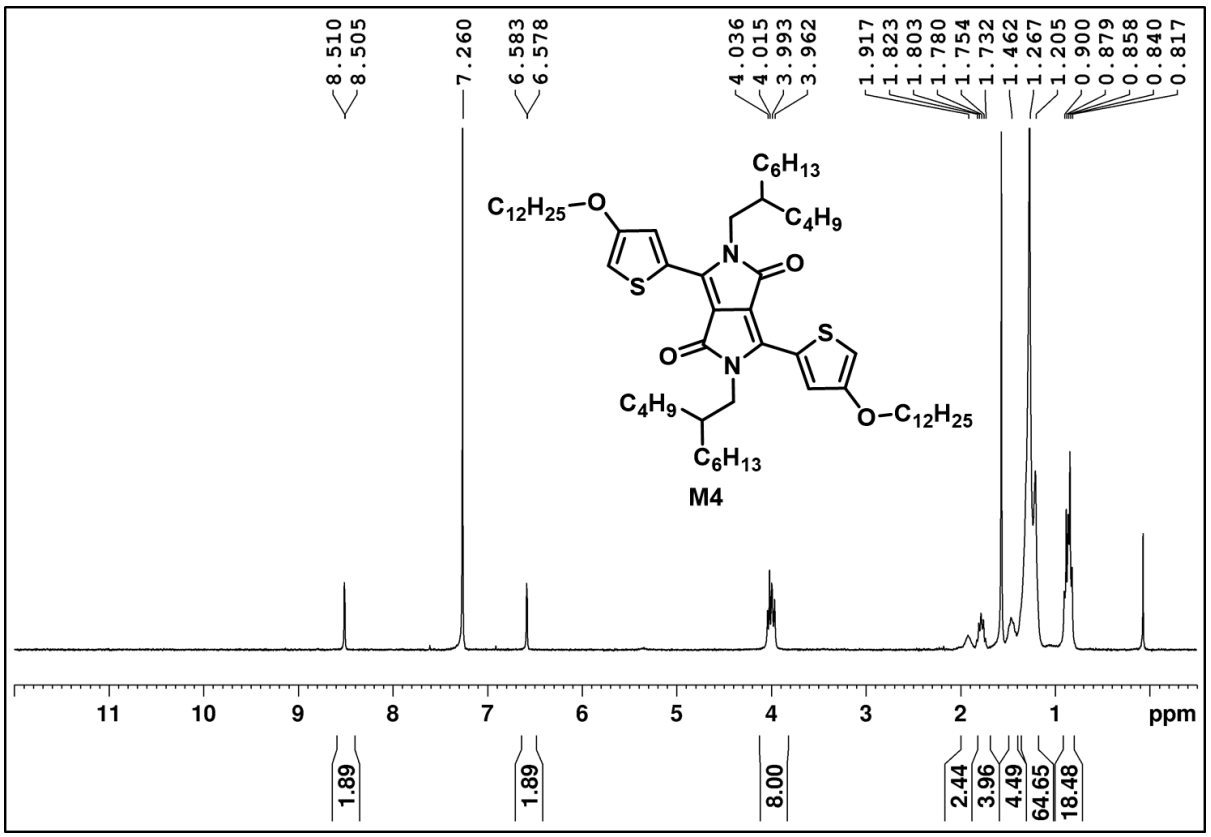


Figure S25. ^{1}H-NMR of 2,5-bis(2-butyloctyl)-3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M4**) in $CDCl_3$.

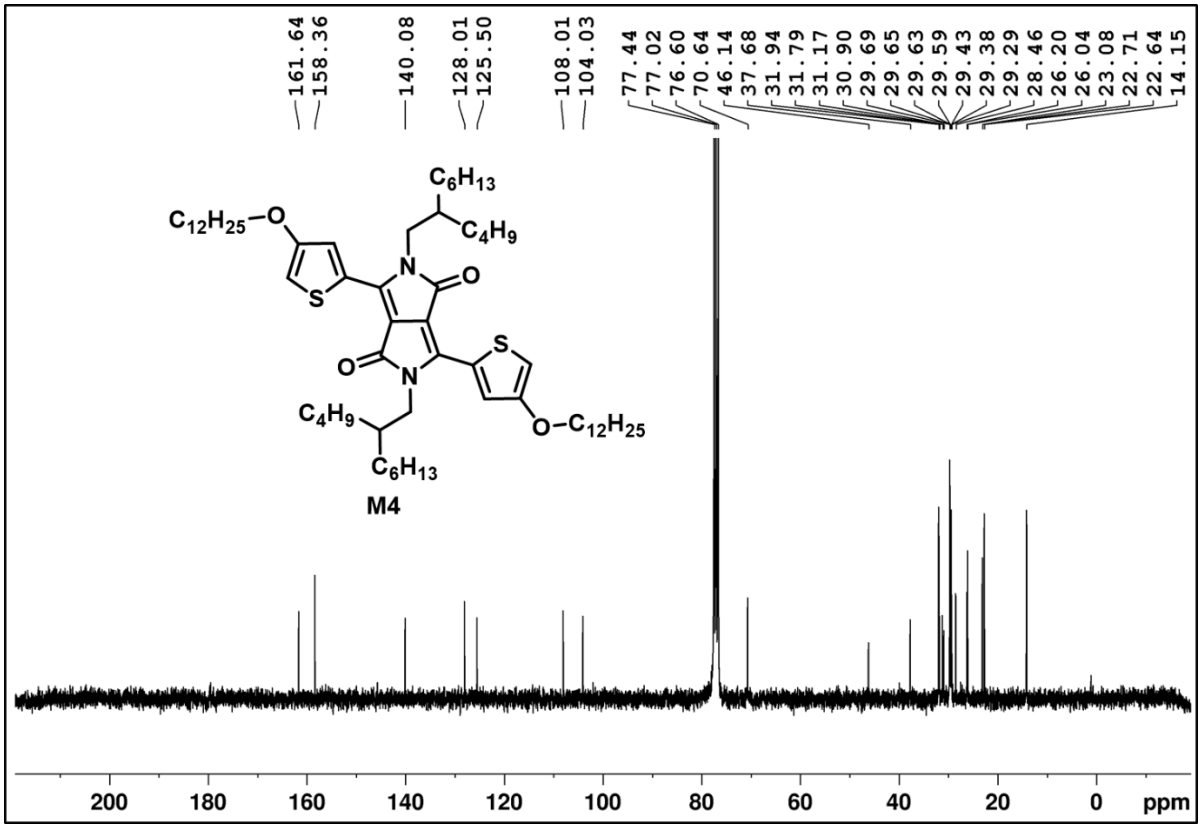


Figure S26. ^{13}C-NMR of 2,5-bis(2-butyloctyl)-3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M4**) in $CDCl_3$.

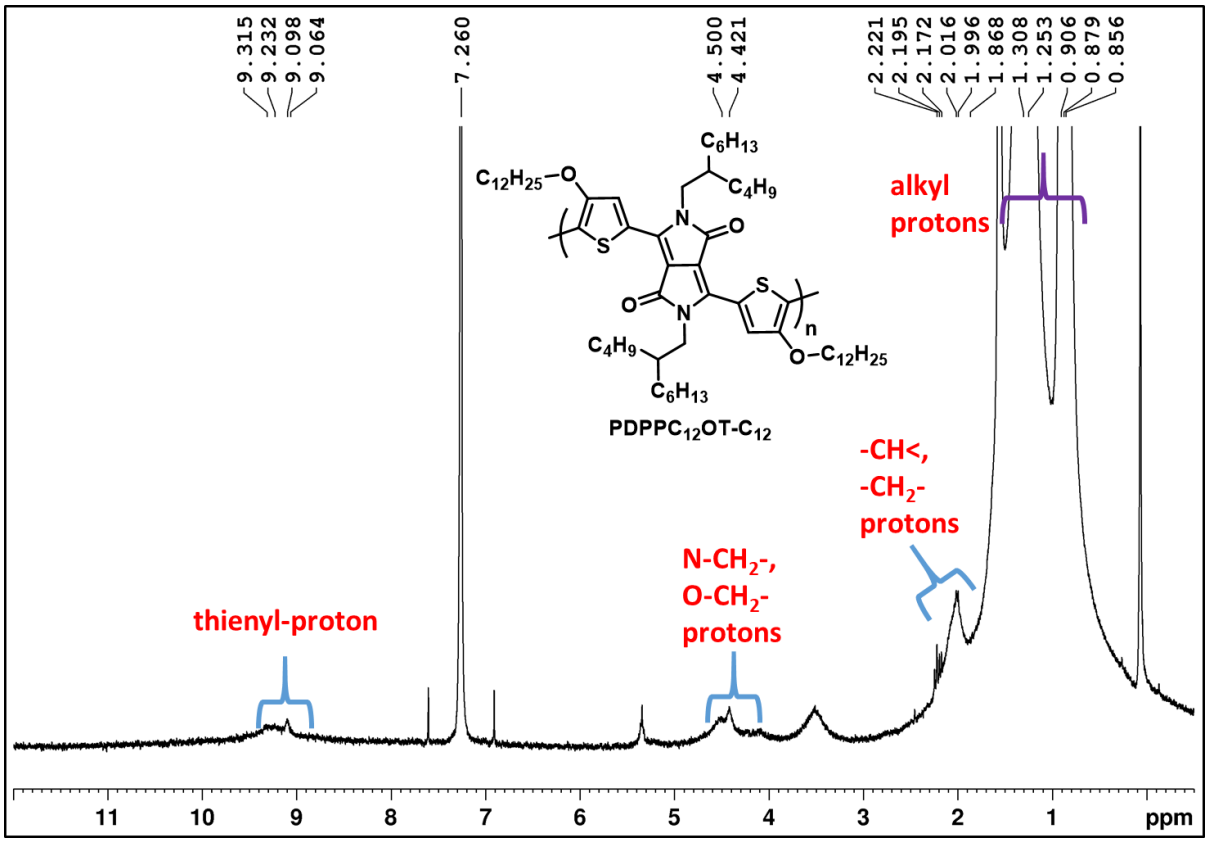


Figure S27. ^{1}H-NMR of poly(2,5-bis(2-butyloctyl)-3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**PDPPC$_{12}$OT-C$_{12}$**) in $CDCl_3$.

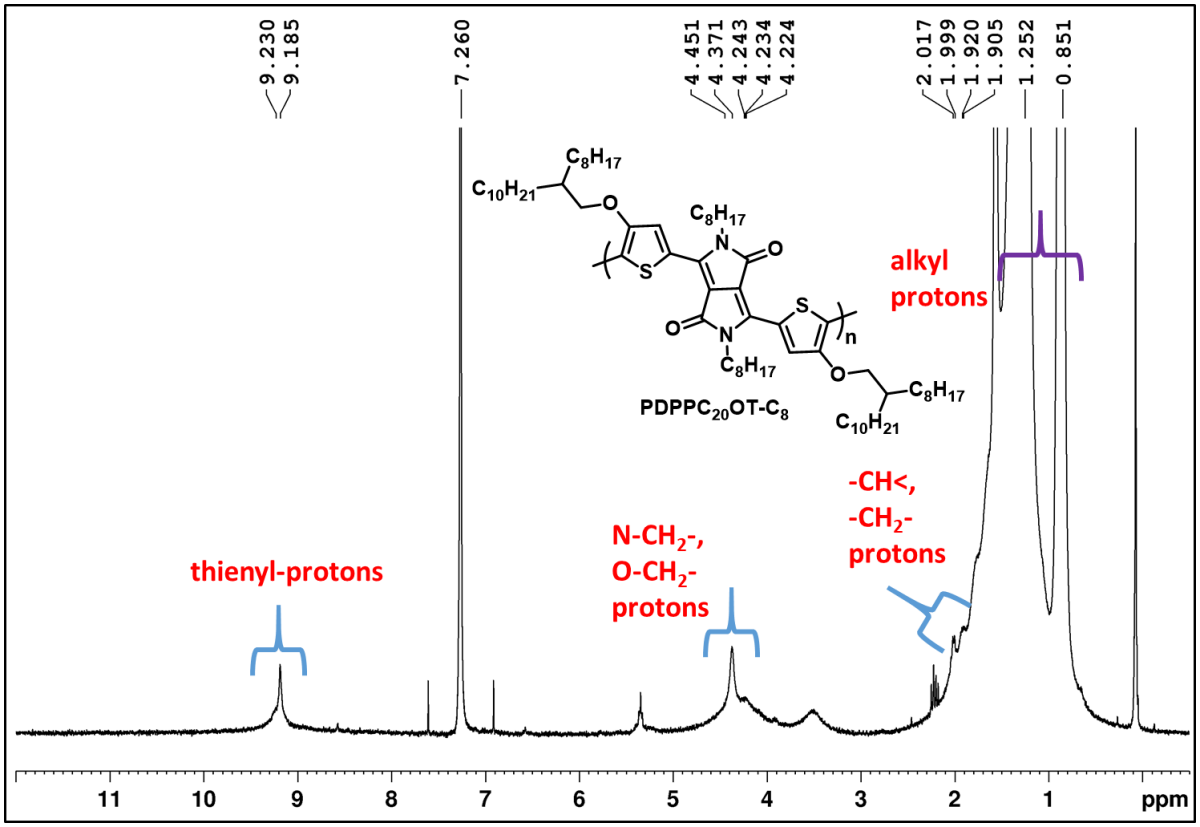


Figure S28. ^{1}H-NMR of poly(2,5-dioctyl-3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**PDPPC$_{20}$OT-C$_8$**) in $CDCl_3$.

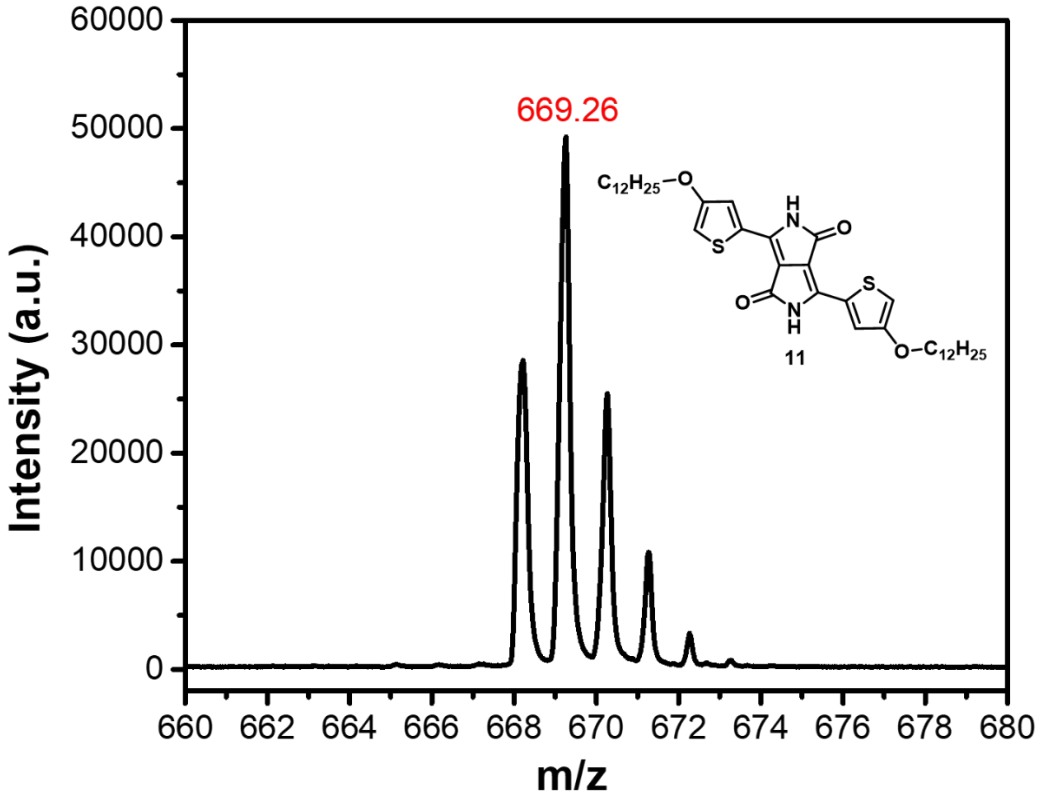


Figure S29. MALDI-MS of 3,6-bis(4-(dodecyloxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**11**).

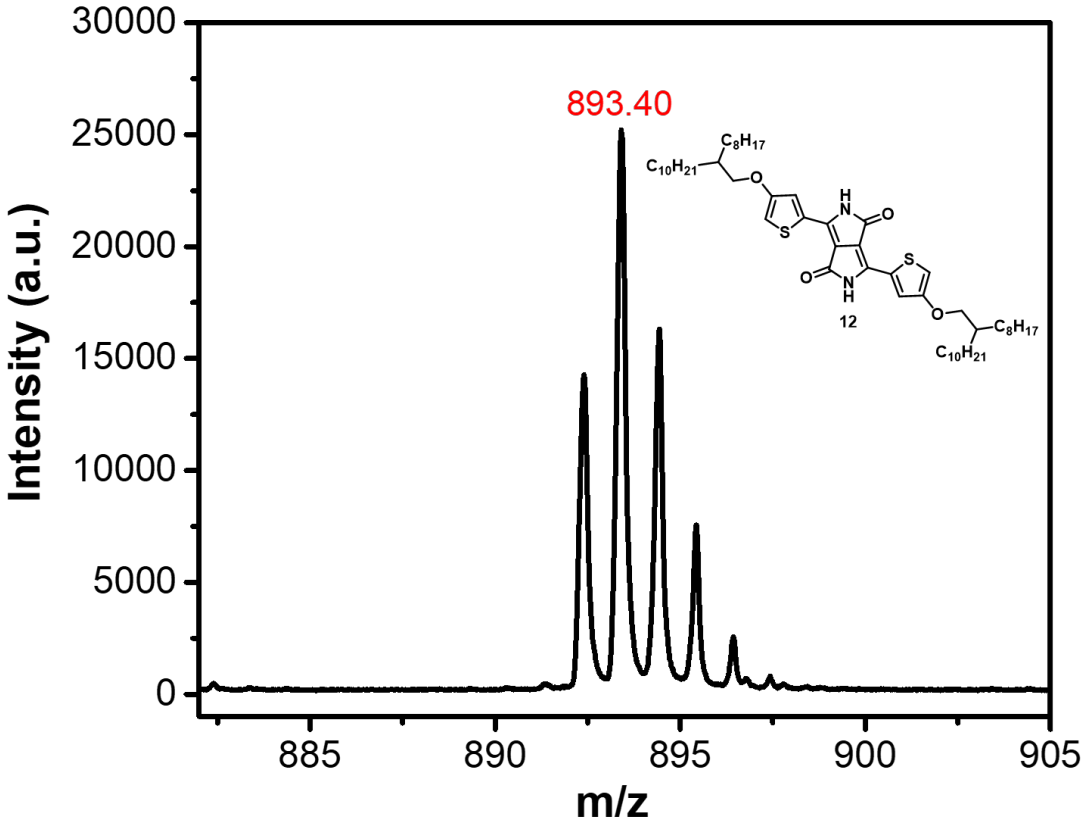


Figure S30. MALDI-MS of 3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**).

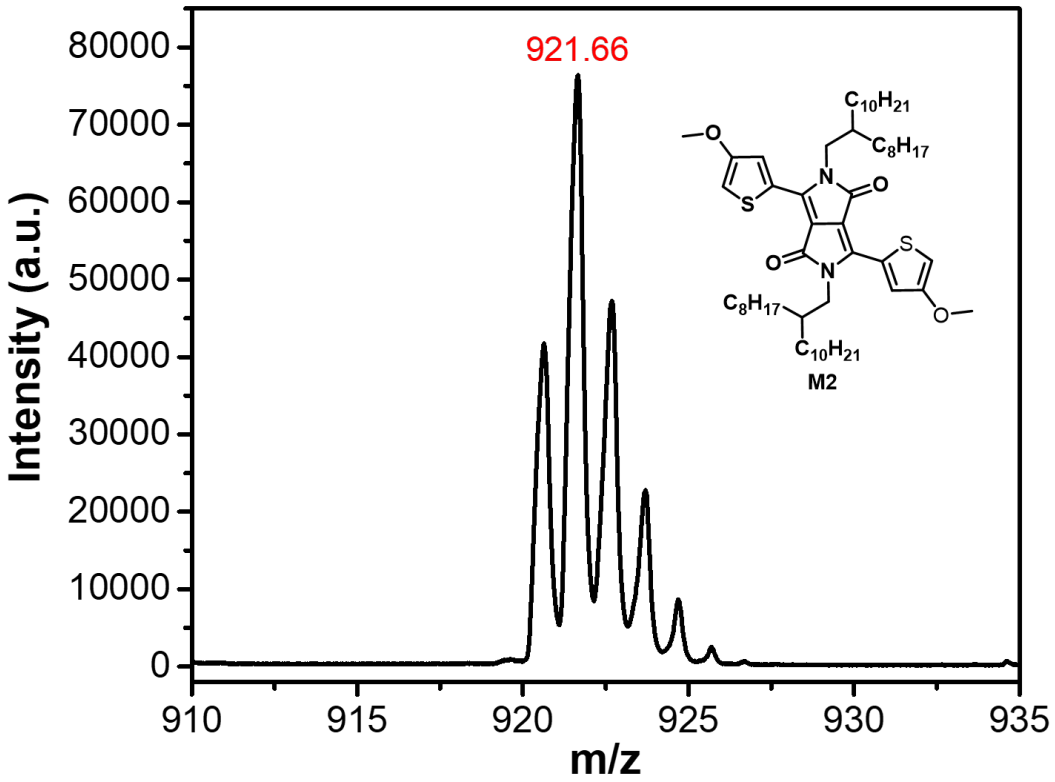


Figure S31. MALDI-MS of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**).

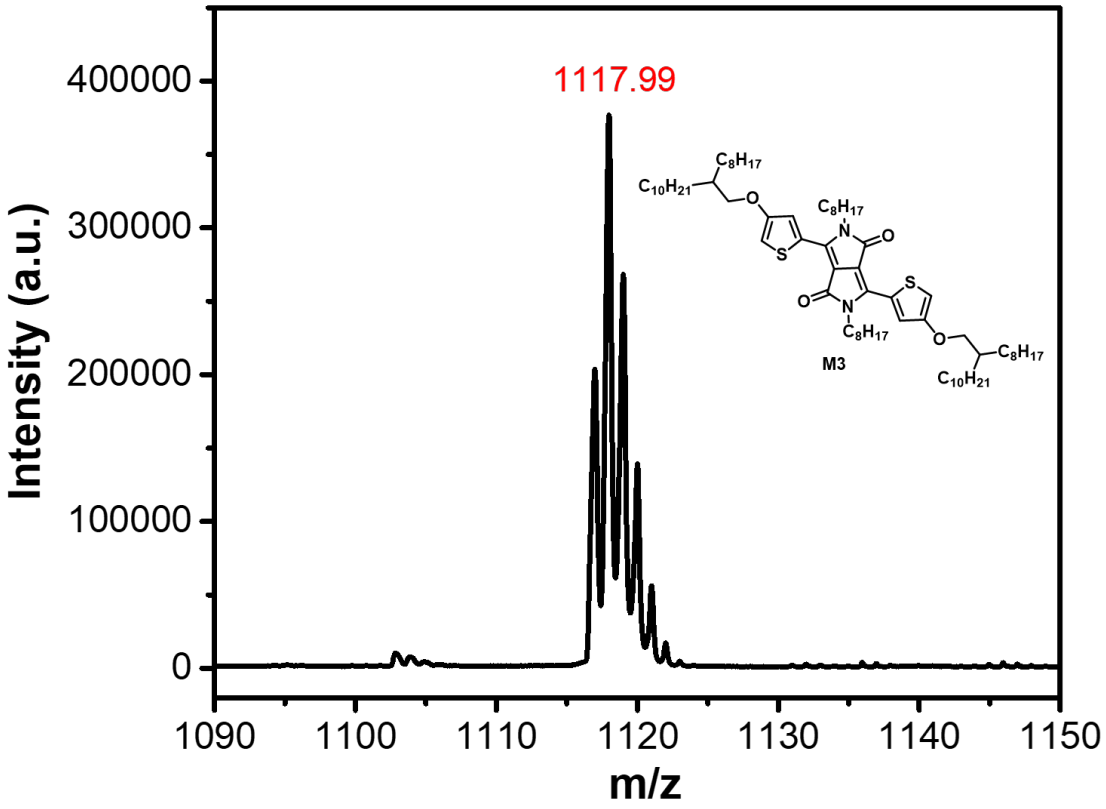


Figure S32. MALDI-MS of Preparation of 2,5-dioctyl-3,6-bis(4-((2-octyldodecyl)oxy)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M3**).

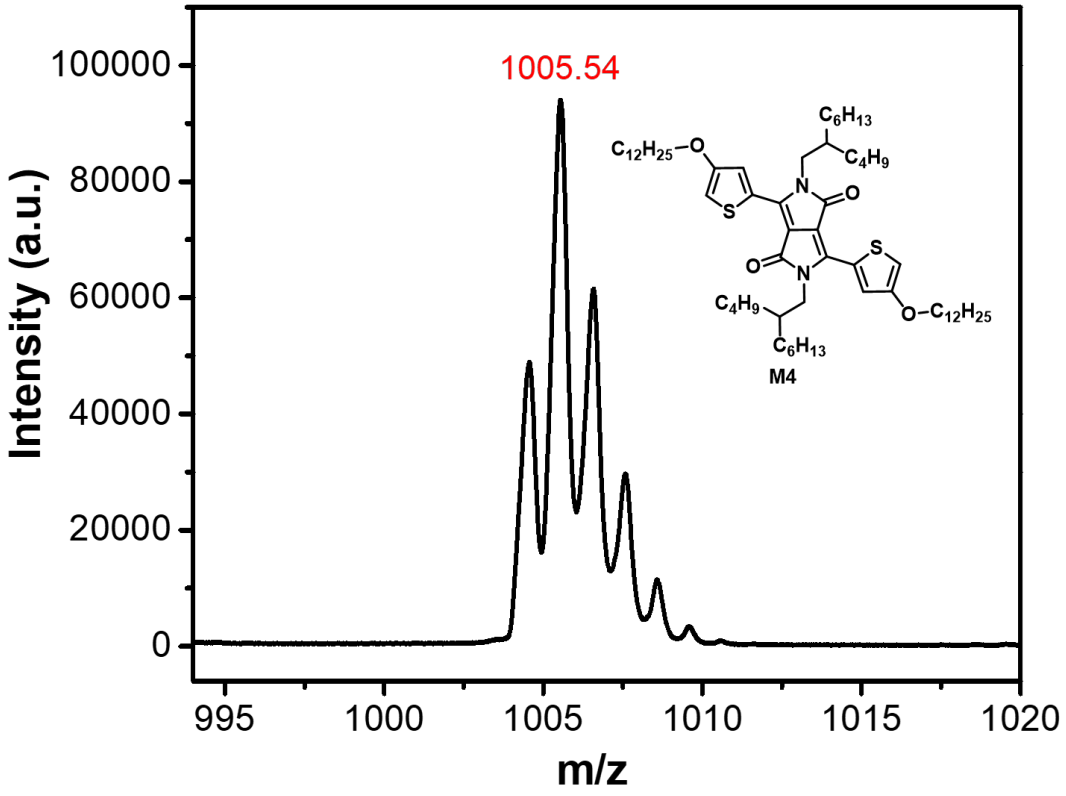


Figure S33. MALDI-MS of Preparation of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M4**).

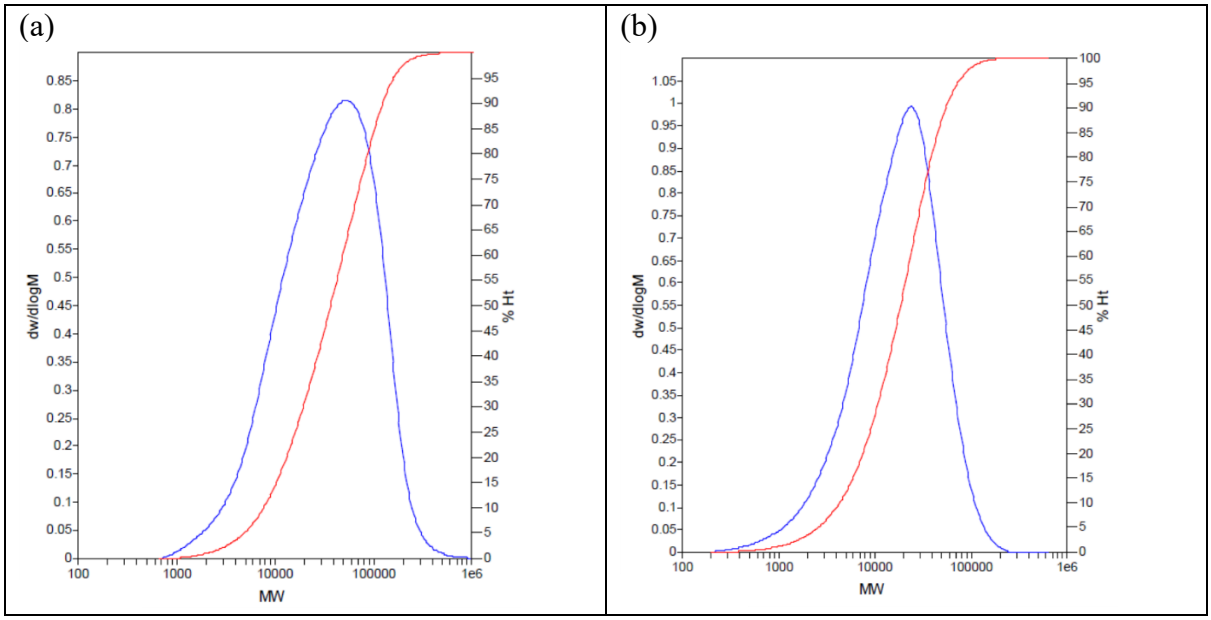


Figure S34. HT-GPC chromatograms of (a) **PDPPC$_{20}$OT-C$_8$** and (b) **PDPPC$_{12}$OT-C$_{12}$** at 150 °C using 1,2,4-trichlorobenzene.

References

1 Y. Li, S. P. Singh and P. Sonar, *Advanced Materials*, 2010, **22**, 4862–4866.
2 J. H. L. Ngai, Z. Li, J. Wang, J. He, J. Ding and Y. Li, *Small Methods*, 2024, **8**, 2301521.
3 R. Saruengkhanphasit, L. Ngiwsara, K. Lirdprapamongkol, J. Chatwichien, W. Niwetmarin, C. Eurtivong, P. Kittakoop, J. Svasti and S. Ruchirawat, *RSC Med. Chem.*, 2024, **15**, 2483–2495.
4 A. Domokos, S. D. Aronow, T. Tang, N. E. Shevchenko, D. J. Tantillo and A. S. Dudnik, *ACS Omega*, 2019, **4**, 9427–9433.
5 D. Giri, S. K. Saha, I. Anderson, A. Chakraborty, J. Kala, J. S. Müller, J. Nelson, R. K. Canjeevaram Balasubramanyam and S. Patil, *Adv Funct Materials*, 2025, **35**, 2410815.