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Supporting Information

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Regiosymmetric Poly(dialkylphenylenedioxythiophenes) (Poly[PheDOT(R_2)]): Electron Rich Stackable π-Conjugated Nanoribbons

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FULL REFERENCE:

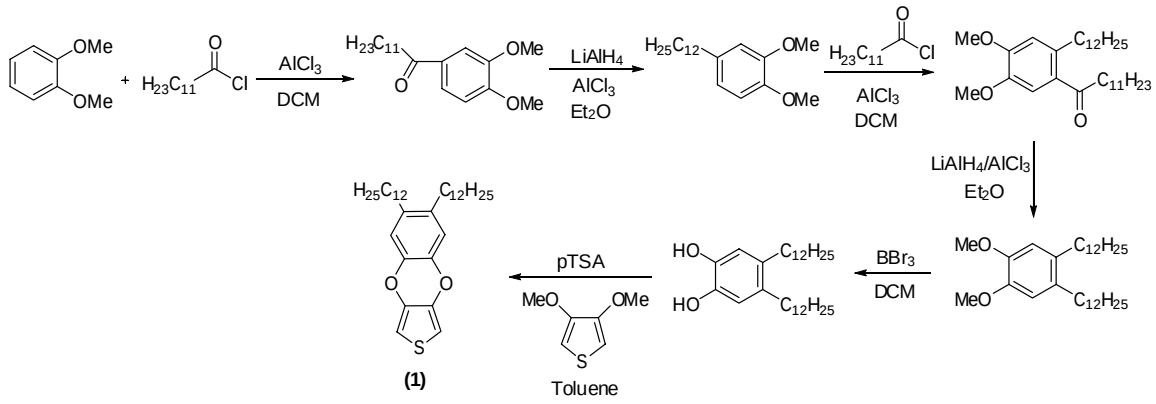
[1f] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw *Nature* **1999**, *401*, 685-688.
[18d] P. Leclere, M. Surin, P. Jonkheijm, O. Henze, A. P. H. J. Schenning, F. Biscarini, A. C. Grimsdale, W. J. Feast, E. W. Meijer, K. Mullen, J. L. Bredas, R. Lazzaroni *Eur. Polym. J.* **2004**, *40*, 885-892.

EXPERIMENTAL:

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer using thin films drop-cast from a toluene solution on KBr pellets. NMR spectra were recorded on a Gemini 300 FT-NMR or a VXR 300 FTNMR. High-resolution mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. Electrochemical studies were carried out using an EG&G PAR model 273A potentiostat/galvanostat in a three electrode cell configuration consisting of a Ag° wire

pseudo reference electrode calibrated with Fc/Fc^+ couple, a platinum button ($S=0.02\ cm^2$) as the working electrode, and a Pt flag as the counter electrode in a 0.1 M tetrabutylammonium perchlorate acetonitrile solution. For the spectroelectrochemistry, acetonitrile was replaced by propylene carbonate to avoid solvent evaporation as well as to prevent delamination of the oxidized film, often observed with films cast on ITO. Absorption spectra (thermochromism and spectroelectrochemistry) were carried out on a Varian Cary 500 scan UV-vis-NIR spectrophotometer. Thermochromism was performed using a SPV 1*1 Varian Cary dual cell Peltier accessory. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA7 thermogravimetric analyzer. DSC analysis was carried out on a TA Instrument DSC Q1000 calorimeter. GPC analysis was performed on a PL220 high temperature GPC (Polymer Laboratories, Inc., Amherst MA). The sample was injected at 5 mg/mL concentration using 1,2,4-trichlorobenzene at 135 °C, 1 mL/min as mobile phase. Separation was achieved using a set of 4 Polymer Labs Mixed A columns (7.5 x 300 mm). The polymer was detected by differential refractive index. Molecular weights were obtained relative to polystyrene standards. Films for AFM were obtained by spin-coating from a 0.2 mg/mL solution in o-dichlorobenzene at a rate of 2000 rpm. AFM imaging was carried out in tapping mode with a Nanoscope III AFM (Digital Instruments, Inc., Santa Barbara, CA) using silicon probes (Nanosensor dimensions: T = 3.8-4.5μm, W = 26-27 μm, L = 128 μm). The images were processed with a second-order flattening routine. The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens detector. A double graphite monochromator for the Cu-Kα radiation (λ=0.154 nm) was used.

Synthesis and characterization of compounds 1, 2, and P3 and intermediates.



Scheme S1 : Synthesis of electropolymerizable PheDOT(C_{12})$_2$.

1-(3,4-dimethoxyphenyl)dodecan-1-one: In a 2L 3-neck flask equipped with an argon inlet and a pressure-equalizing addition funnel was dissolved aluminum trichloride (26g, 200 mmol, 1.1 eq.) in dry dichloromethane (700ml, distilled from CaH_2). The reaction was cooled at 0°C, and a solution of veratrole (25g, 180 mmol, 1 eq.) in dry dichloromethane (150ml) was added dropwise followed by addition of a lauroyl chloride solution (40g, 180 mmol, 1eq.) in dry dichloromethane (150ml). The mixture is refluxed for 24 hours, then cooled at 0°C. The excess aluminum chloride was quenched by slow addition of 6M HCl (100 ml). The aqueous phase is further extracted with dichloromethane (2×200ml). The combined organic layers are washed with water (3×400ml), and dried with magnesium sulfate. The solvent is removed under vacuum to yield a white solid, purified by recrystallization from toluene. The product is obtained as a white solid (52g, 90% yield); ^{1}H NMR (300MHz, $CDCl_3$) 0.83-0.93 (t, 3H), 1.18-1.43 (m, 16H), 1.64-1.8 (m, 2H), 2.88-2.95 (m, 2H), 3.94 (s, 3H), 3.95 (s, 3H), 6.88 (d, 1H, J_1=8.3Hz), 7.54 (d, 1H, J_2=1.9Hz), 7.59 (dd, 1H, J_1= 8.3Hz and J_2=1.9Hz) ; ^{13}C NMR

(75 MHz, $CDCl_3$) 14.32, 22.90, 25.03, 29.55, 29.72, 29.84, 32.12, 38.38, 56.18, 110.16, 110.42, 122.84, 130.57, 149.2, 153.28, 199.44.

4-dodecyl-1,2-dimethoxybenzene: In a 3L 3-neck flask equipped with an argon inlet was dissolved LAH (12.6g, 331.4 mmol, 4.5eq) in dry diethyl ether (500 ml, distilled from Na/benzophenone). A solution of $AlCl_3$ (14.8g, 110.5 mmol, 1.5eq.) in dry diethylether (500 ml) was added via cannula to the LAH solution, cooled at 0°C. After 15 min, a solution of 1-(3,4-dimethoxyphenyl)dodecan-1-one (23.6g, 73.64 mmol, 1eq.) in diethylether (500ml) was added dropwise to the reaction (maintained at 0°C). Upon completion of the addition, the mixture was allowed to warm up to room temperature. After four hours, the reaction was cooled back to 0°C and quenched slowly by addition of 200 ml of 6M HCl. The organic layer was washed with water (3×400ml) and dried with magnesium sulfate. The organic solvent was removed under vacuum, to yield a white solid purified by column chromatography on silica gel using 50/50 dichloromethane/hexanes as eluent. This yields the product as a white solid (14g, 62% yield). ^{1}H NMR (300MHz, $CDCl_3$) 0.83-0.92 (t, 3H), 1.2-1.38 (m, 18H), 1.52-1.65 (m, 2H), 2.5-2.58 (m, 2H), 3.86 (s, 3H), 3.88 (s, 3H), 6.68-6.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.34, 22.92, 29.58, 29.77, 29.90, 31.95, 32.16, 35.82, 56.02, 56.16, 111.41, 112.01, 120.32, 135.87, 147.21.

1-(2-dodecyl-4,5-dimethoxyphenyl)dodecan-1-one: In a 1L 3-neck flask equipped with an argon inlet and a pressure-equalizing addition funnel was dissolved aluminum chloride (7.2g, 55 mmol, 1.1 eq.) in dry dichloromethane (300ml, distilled from CaH_2). To the

reaction cooled at 0°C, a solution of 4-dodecyl-1,2-dimethoxybenzene (15.2g, 50 mmol, 1 eq.) in dry dichloromethane (100ml) was added dropwise followed by the addition of a solution of lauroyl chloride (10.82g, 50 mmol, 1eq.). The mixture is refluxed for 24 hours, then cooled at 0°C. The excess aluminum chloride was quenched by slow addition of 6M HCl (150 ml). The aqueous phase is further extracted with dichloromethane (2×200ml). The combined organic layers are washed with water (3×200ml), and dried with magnesium sulfate. The solvent is removed under vacuum to yield a yellow-white solid, purified by column chromatography on silica gel (50/50 hexanes/dichloromethane as eluent). The product is obtained as a white solid (16.2g, 67% yield); ^{1}H NMR (300MHz, $CDCl_3$) 0.82-0.96 (t, 6H), 1.18-1.42 (m, 34H), 1.45-1.60 (m, 2H), 1.62-77 (m, 2H), 2.74-2.9 (m, 4H), 3.88 (s, 3H), 3.92 (s, 3H), 6.72 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.33, 22.92, 24.98, 29.59, 29.76, 29.88, 30.03, 32.15, 32.4, 34.23, 41.99, 56.11, 56.41, 112.36, 113.88, 137.70, 146.45, 151.28, 203.53; HRMS [M^+] calcd for $C_{34}H_{52}O_2SBr_2$ 488.4229 amu Found 488.4219 amu.

1,2-didodecyl-4,5-dimethoxybenzene: In a 2L 2-neck flask equipped with an argon inlet was dissolved LAH (8.76g, 230 mmol, 6eq) in dry diethyl ether (250 ml, distilled from Na/benzophenone). A solution of $AlCl_3$ (7.56g, 60 mmol, 2eq.) in dry diethylether (250 ml) was added via cannula to the LAH solution, cooled at 0°C. After 15 min, a solution of 1-(2-dodecyl-4,5-dimethoxyphenyl)dodecan-1-one (16.2g, 33mmol, 1eq.) in diethylether (200ml) was added dropwise to the reaction (maintained at 0°C). Upon completion of the addition, the mixture was allowed to warm up to room temperature. After four hours, the reaction was cooled to 0°C and quenched slowly by addition of 100

ml of 6M HCl. The reaction mixture was poured in 500ml water. The aqueous phase was further extracted with diethylether (2×200ml) and the combined organic layers were washed with water (3×300ml). After drying with magnesium sulfate, the organic solvent was removed under vacuum, to yield a white solid purified by column chromatography on silica gel using 50/50 dichloromethane/hexanes as eluent. This yields the product as a white solid (13g, 80% yield). ^{1}H NMR (300MHz, $CDCl_3$) 0.84-0.93 (t, 6H), 1.18-1.42 (m, 36H), 1.44-1.6 (m, 4H), 2.47-2.57 (m, 4H), 3.84 (s, 6H), 6.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.36, 22.94, 29.91, 31.95, 32.17, 32.71, 56.17, 112.87, 132.86, 146.99.

4,5-didodecylbenzene-1,2-diol: In a 2L three-neck flask equipped with an argon inlet was added 1,2-didodecyl-4,5-dimethoxybenzene (13g, 27.4mmol, 1eq.) in dry dichloromethane (600 ml, distilled from CaH_2). Boron tribromide (10.5 ml, 110mmol, 4eq.) was added dropwise using a pressure-equalizing addition funnel. After 12 hours, the mixture was poured in a 2L Erlenmeyer filled with 1L of ice. The aqueous phase was further extracted with dichloromethane (2×200ml) and the combined organic layers were washed with water (3×300ml). The organic phase is dried with magnesium sulfate and the solvent was evaporated under vacuum to yield the product as an off-white solid (11g, 90% yield). ^{1}H NMR (300MHz, $CDCl_3$) 0.84-0.93 (t, 6H), 1.27-1.4 (m, 36H), 1.42-1.58 (m, 4H), 2.42-2.5 (m, 4H), 6.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.35, 22.93, 29.60, 29.93, 31.68, 32.17, 32.29, 116.36, 133.66, 141.27; HRMS [M^+] calcd for $C_{34}H_{52}O_2SBr_2$ 446.4124 amu Found 446.4118 amu.

PheDOT-(C_{12})$_2$ (1): In a 100ml round bottom flask, 4,5-didodecylbenzene-1,2-diol (5g, 11.2 mmol,1eq) was dissolved in 60 ml of dry toluene (distilled from Na/benzophenone). To this solution was added 3,4-dimethoxythiophene (1.6g, 11.2 mmol, 1eq.) and p-toluenesulfonic acid (213 mg, 1.12mmol, 0.1eq). The flask was equipped with a soxhlet apparatus containing a thimble filled with $CaCl_2$. The mixture was refluxed for three days. Triethylamine (1ml) and water (200ml) were added and the product was extracted with diethylether (3×100ml). After drying with sodium sulfate and removal of the solvent under reduced pressure, the resulting brown solid was purified by column chromatography on silica gel using pentane as eluent. The product was obtained as a white solid (1.15g, 20% yield). ^{1}H NMR (300MHz, $CDCl_3$) 0.84-0.95 (t, 6H), 1.2-1.42 (m, 36H), 1.45-1.6 (m, 4H), 2.44-2.56 (m, 4H), 6.4 (s, 2H), 6.7 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.35, 22.92, 29.59, 29.76, 29.79, 29.82, 29.88, 29.90, 29.92, 31.28, 32.16, 32.17, 100.74, 117.01, 136.36, 138.53, 139.66; HRMS [M^+] calcd for $C_{34}H_{52}O_2SBr_2$ 526.3845 amu Found 526.3863 amu.

PheDOT-(C_{12})$_2$-Br_2 (2): PheDOT-(C_{12})$_2$ (0.5g, 0.95 mmol) was dissolved in 100 mL of DMF. After the solution was bubbled with argon for one hour, N-bromosuccinimide (0.42g, 2.37 mmol, 2.5 eq.) was added in one portion. The solution was stirred overnight after which 200 mL of water was added. The product was extracted with ether, washed with water and the organic layer dried with magnesium sulfate. The solvent was evaporated under vacuum and the resulting yellowish white solid was purified by column chromatography on silica using pentane as eluent. The product was obtained as a white solid (0.48g, 74% yield). ^{1}H-NMR (300MHz, $CDCl_3$) δ 0.87 (t, 6H), 0.97-1.4 (bs, 36H),

1.4-1.6 (bs, 4H), 2.5 (t, 4H), 6.81 (s, 2H); ^{13}C-NMR (75MHz, CDCl3) 14.35, 22.92, 29.59, 29.76, 29.79, 29.81, 29.90, 31.14, 32.16, 32.18, 86.73, 117.13, 137.21, 137.53, 137.94; HRMS [M^+] calcd for $C_{34}H_{52}O_2SBr_2$ 682.2055 amu Found 682.2038 amu; Elemental analysis Calcd. For $C_{34}H_{52}O_2SBr_2$ %C 59.65, %H 7.66 Found %C 59.53, %H 7.43. MP 77-79°C.

Poly[PheDOT-(C_{12})$_2$]: To a solution of PheDOT-(C_{12})$_2$-Br_2 (415 mg, 0.606 mmol) in 30 mL of freshly distilled THF (from Na/benzophenone), was added CH_3MgBr via syringe (solution freshly titrated, C=0.94M) (0.67 mL, 0.606 mmol). The solution was refluxed for 2 hours. Then Ni(dppp)Cl_2 (6.6mg, 0.012 mmol) was added in one portion. The solution was refluxed for 24hrs. The polymer was then precipitated in 100 mL MeOH and filtered through a soxhlet thimble. The polymer was purified via soxhlet extraction with MeOH, hexanes and then extracted with toluene. The product was obtained as a dark purple solid (220mg, 69% yield). The product after toluene soxhlet extraction was a dark black-purple solid. ^{1}H NMR (300MHz, $C_2D_2Cl_4$, 120°C) δ 0.9-1.1 (bs, 6H), 1.25-1.6 (bs, 36H), 1.6-1.8 (bs, 4H), 2.6-2.8 (bs, 4H), 6.9-7.1 (bs, 2H); GPC (135ºC, trichlorobenzene) Mn= 14,800 g mol-1, Mw= 28,900 g mol-1, PDI= 1.95. Elemental analysis Calcd. For $C_{34}H_{52}O_2S$ (repeat unit) %C 77.51 %H 10.33 Found %C 74.82; %H 10.6.

IR data of PheDOT(C_{12})$_2$, PheDOT(C_{12})$_2$$Br_2$, PPheDOT($C_{12}$)$_2$

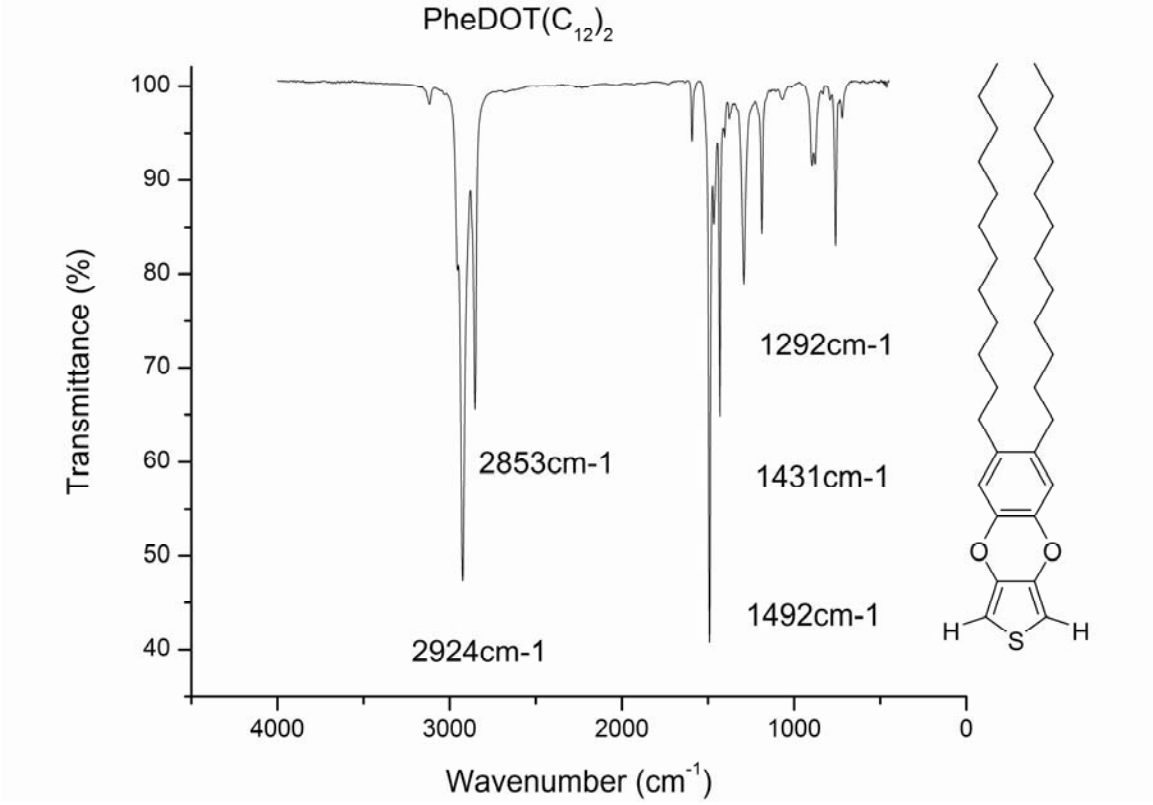


Figure S1: IR spectrum of a drop-cast film of PheDOT(C_{12})$_2$.

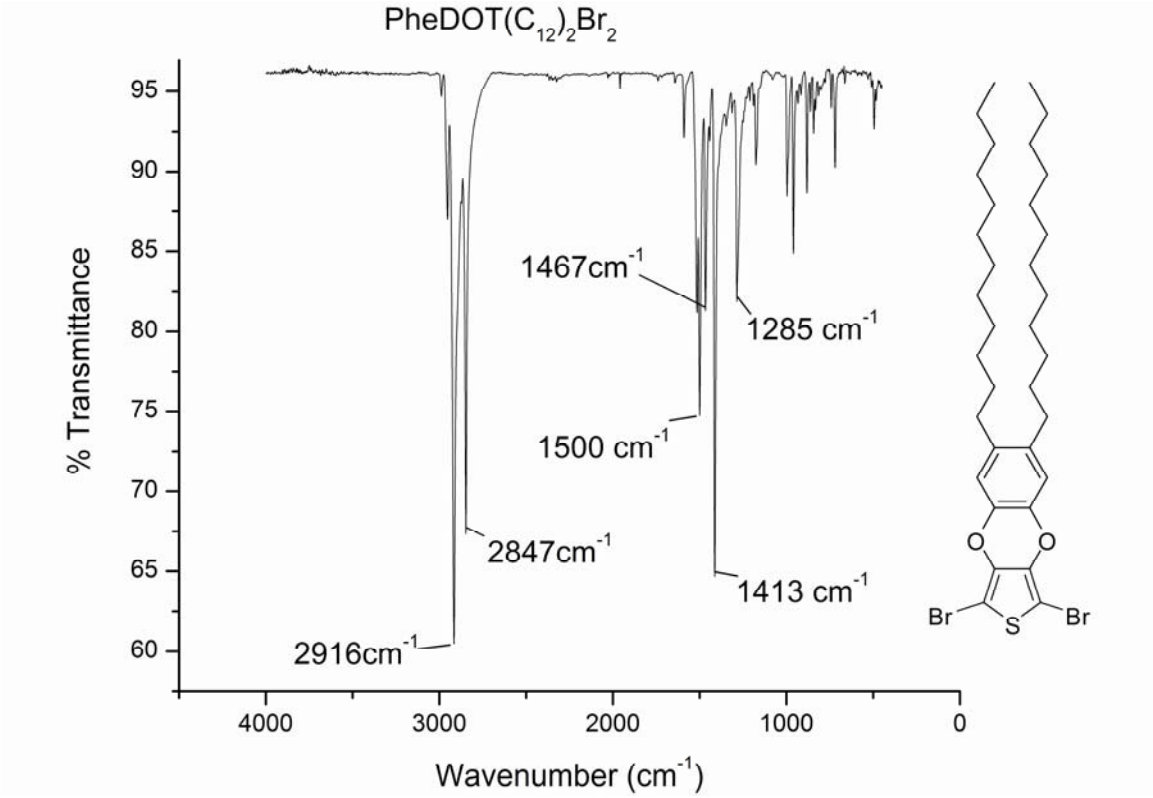


Figure S2: IR spectrum of a drop-cast film of PheDOT(C_{12})$_2$$Br_2$

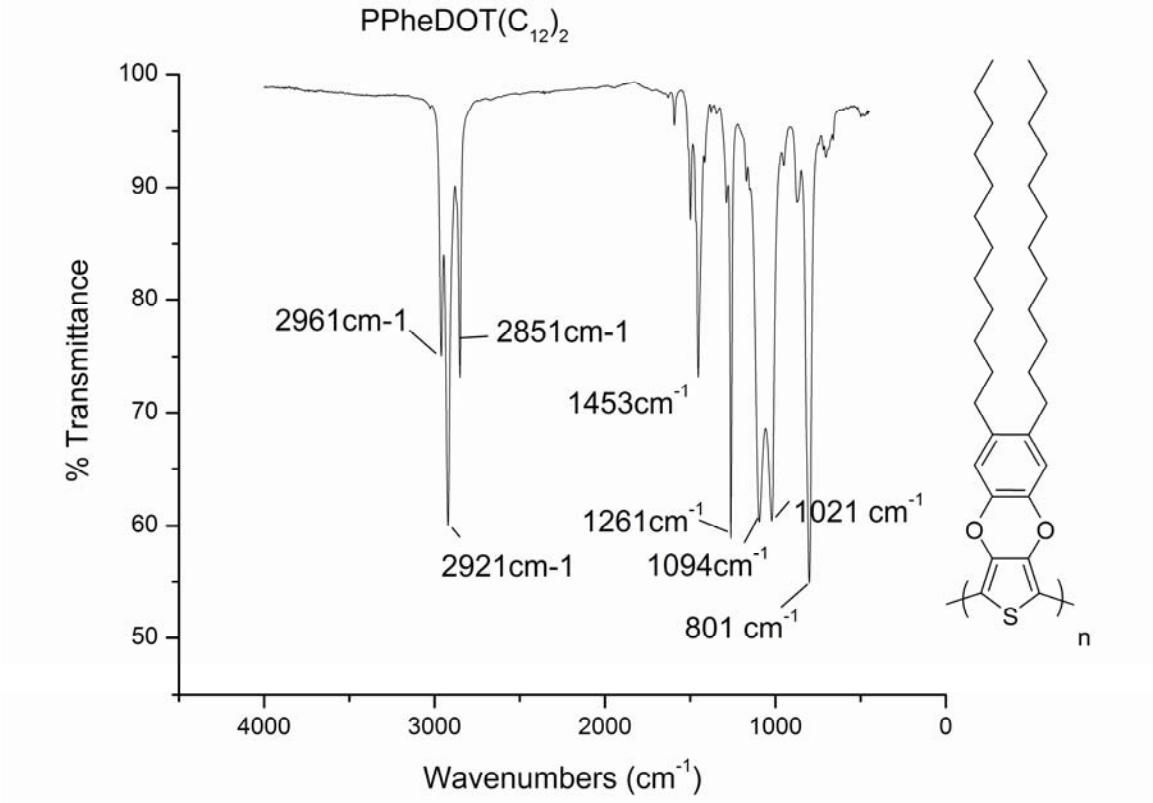


Figure S3: Infrared spectrum of a drop cast film of PPheDOT(C_{12})$_2$

NMR spectra of PheDOT(C_{12})$_2$, PheDOT(C_{12})$_2$Br$_2$, PPheDOT(C_{12})$_2$.

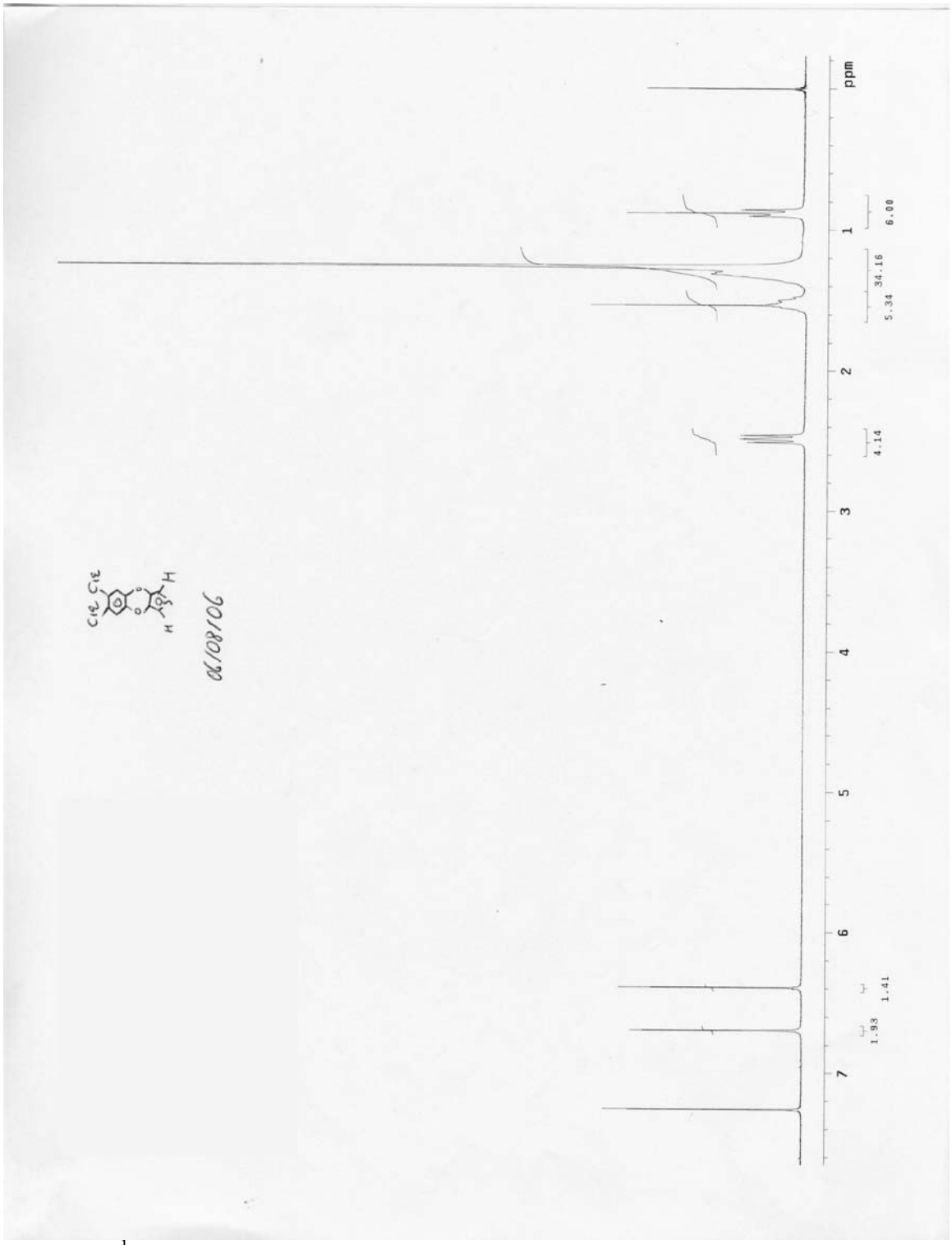


Figure S4: ^{1}H NMR of PheDOT(C_{12})$_2$ in $CDCl_3$, 300MHz

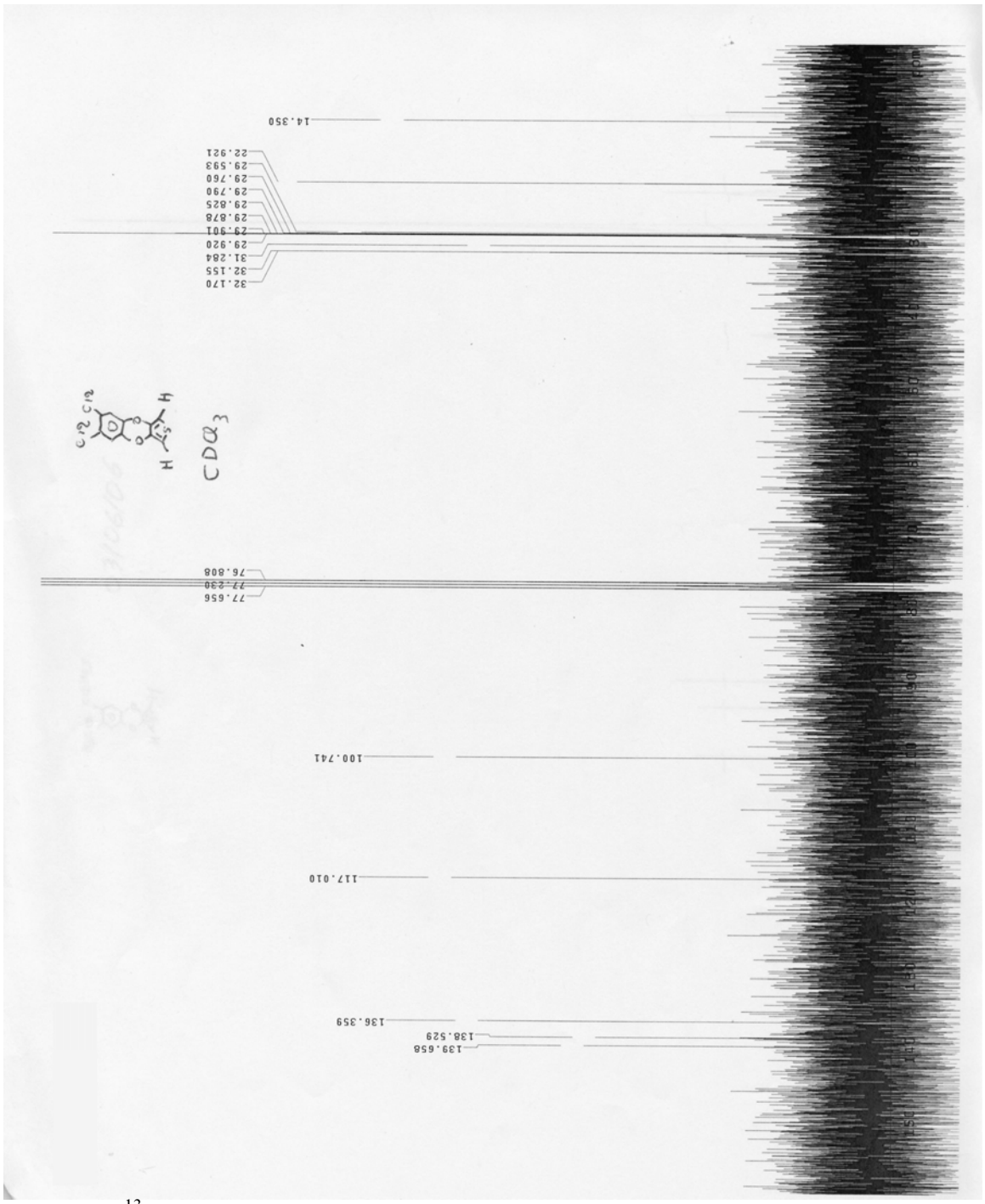


Figure S5: ^{13}C NMR of PheDOT(C_{12})$_2$ in $CDCl_3$, 300MHz

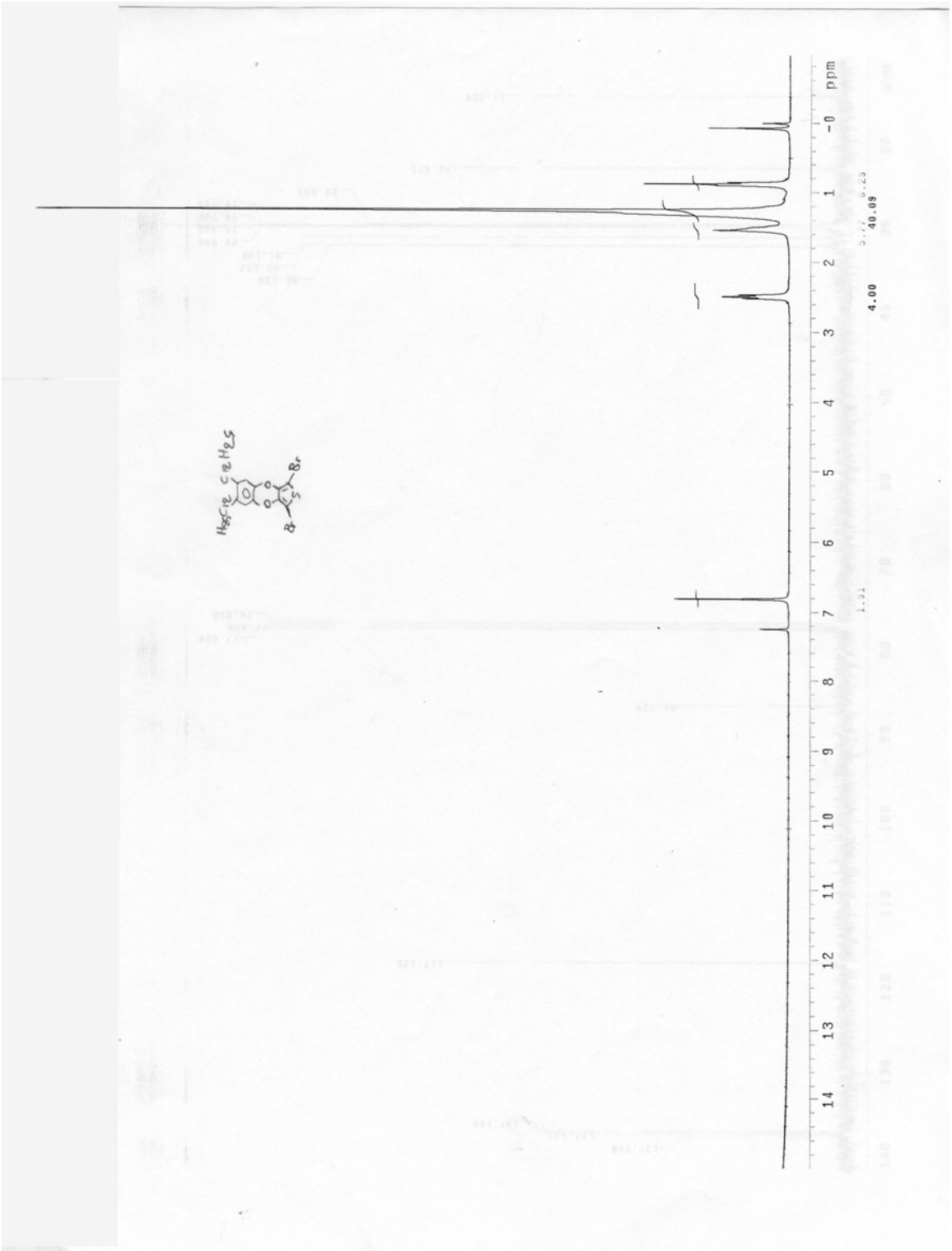


Figure S6: ^{1}H NMR of PheDOT$(C_{12})_2Br_2$ in $CDCl_3$, 300MHz

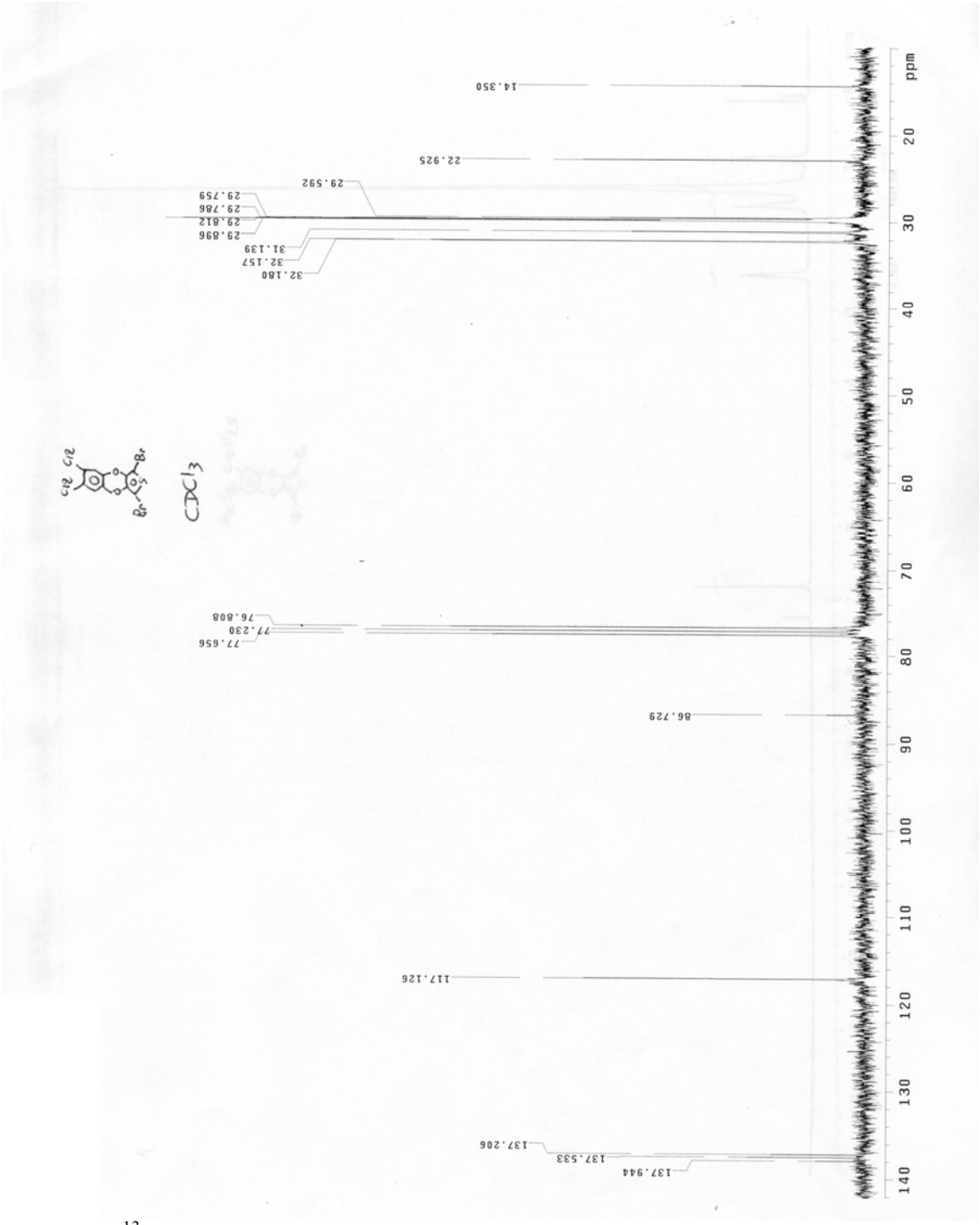


Figure S7: ^{13}C NMR of PheDOT$(C_{12})_2Br_2$ in $CDCl_3$, 300MHz

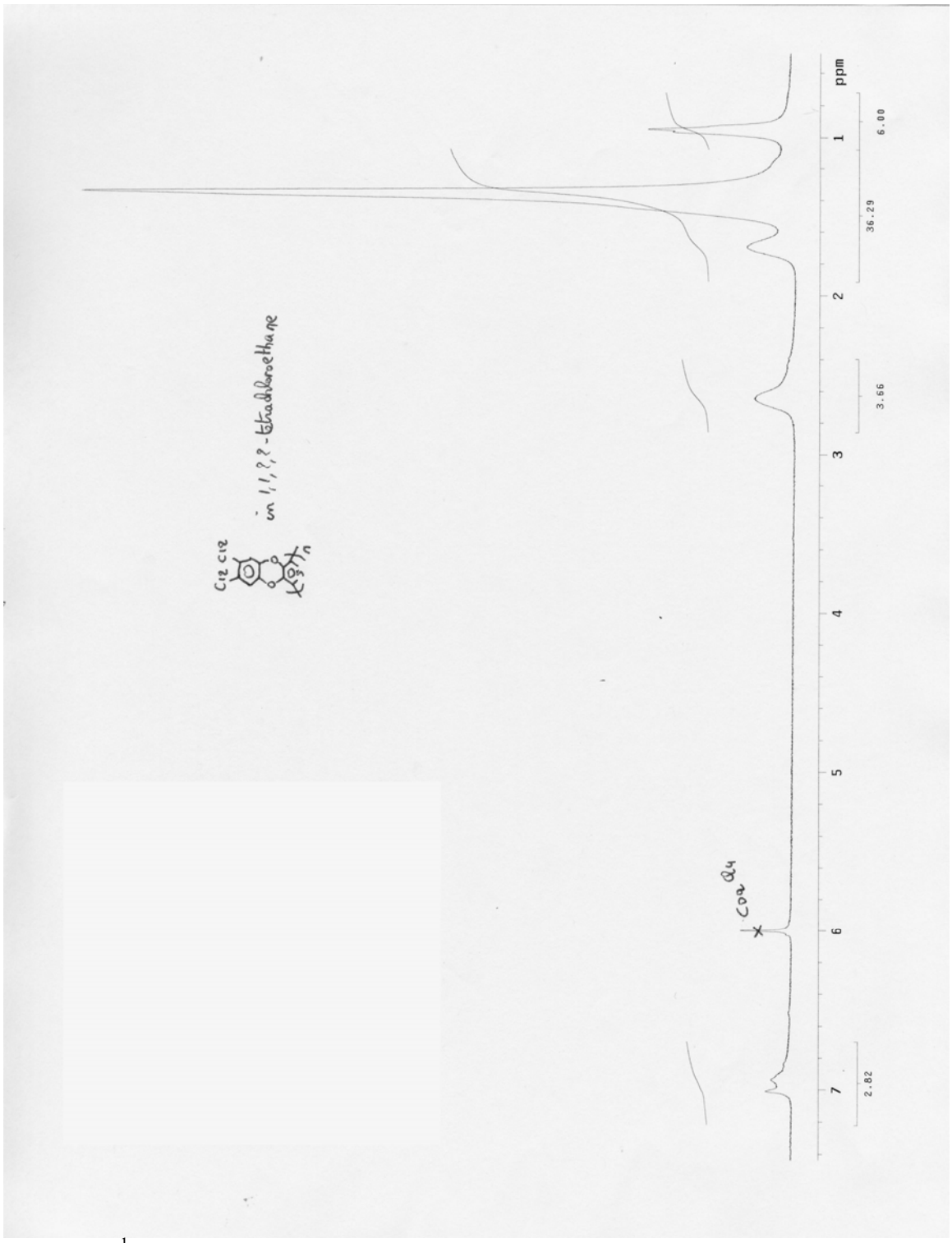


Figure S8: ^{1}H NMR of PPheDOT(C_{12})$_2$ in $C_2D_2Cl_4$, 300MHz. 120°C.

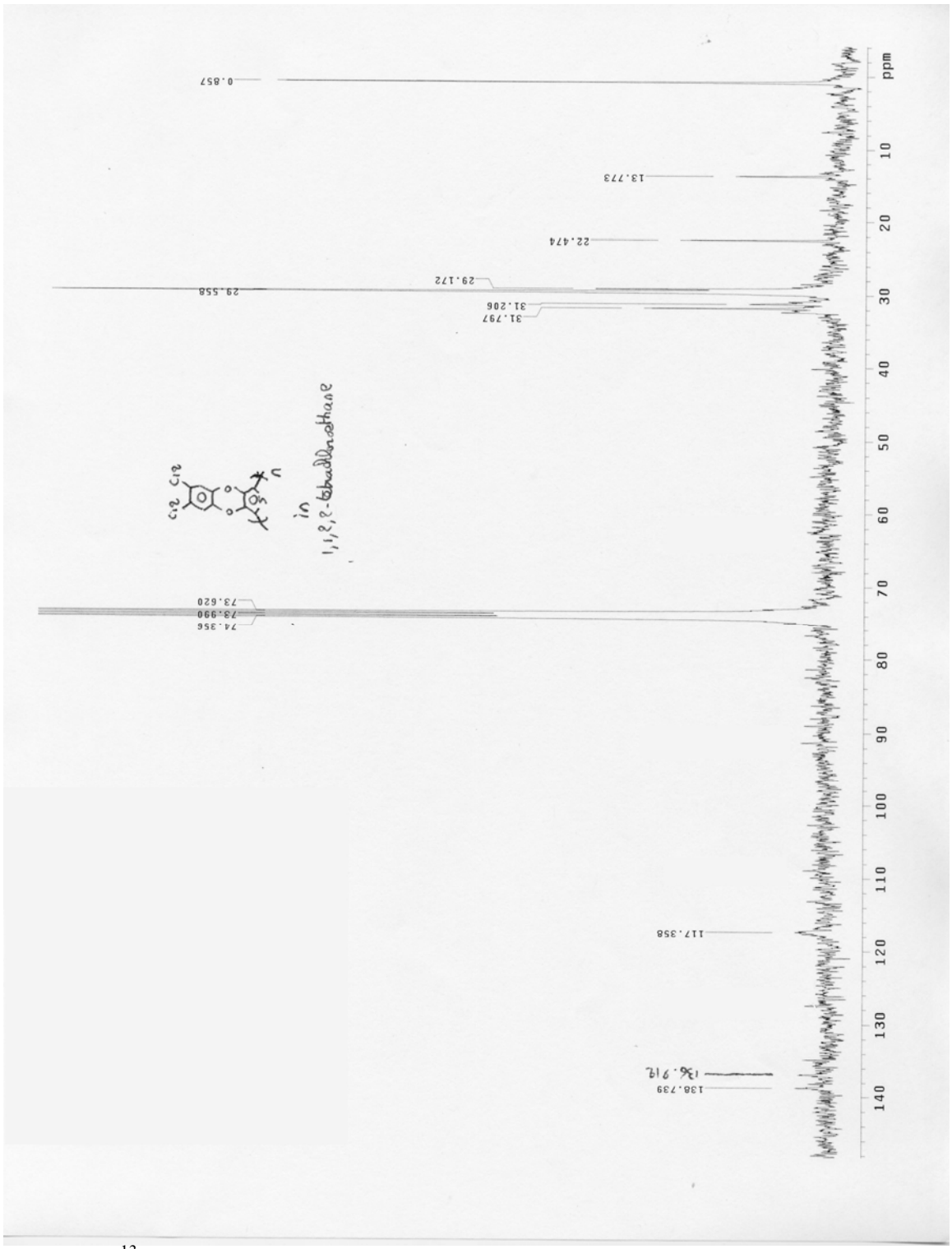


Figure S9: ^{13}C NMR of PPheDOT(C_{12})$_2$ in $C_2D_2Cl_4$, 300MHz, 120°C.

Electrochemistry data on a drop-cast film of PPheDOT(C_{12})$_2$:

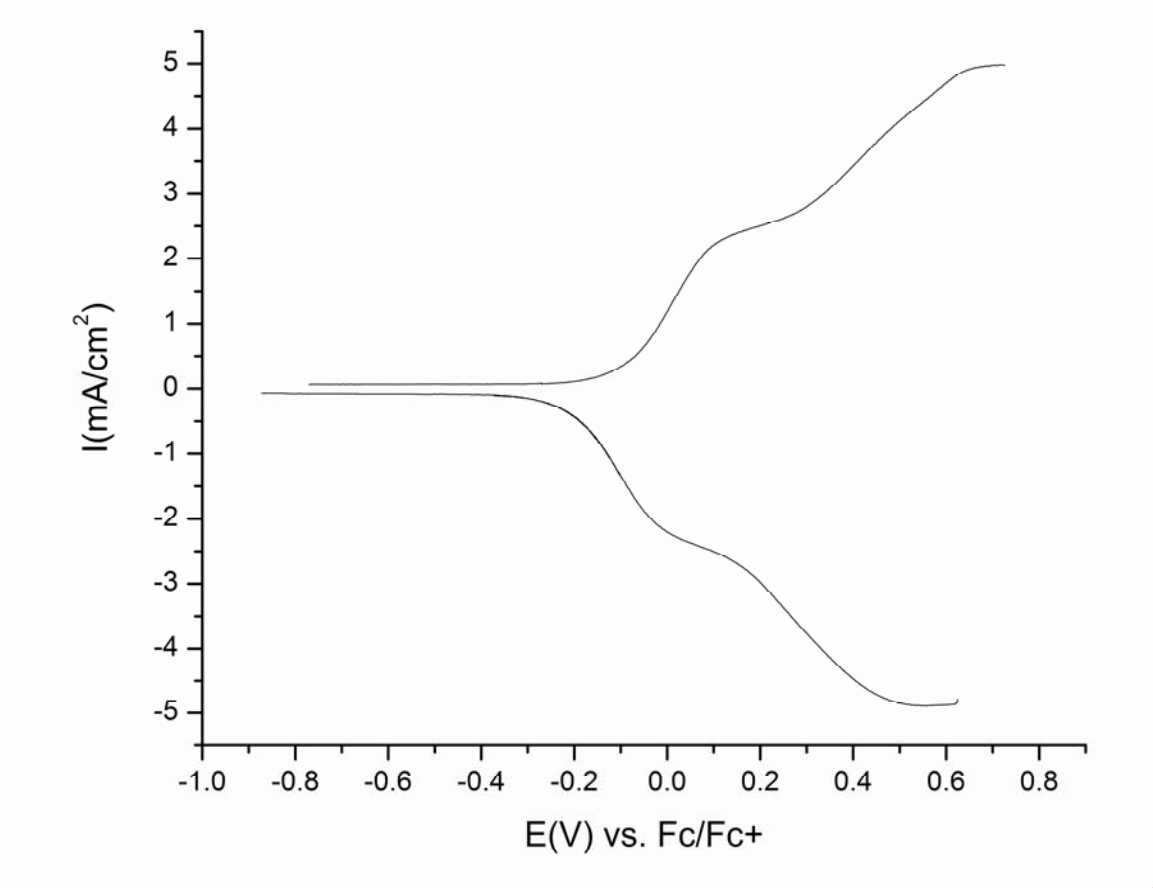


Figure S10: Differential Pulse Voltammetry Experiment on a PPheDOT(C_{12})$_2$ thin film drop-cast on Pt Button.

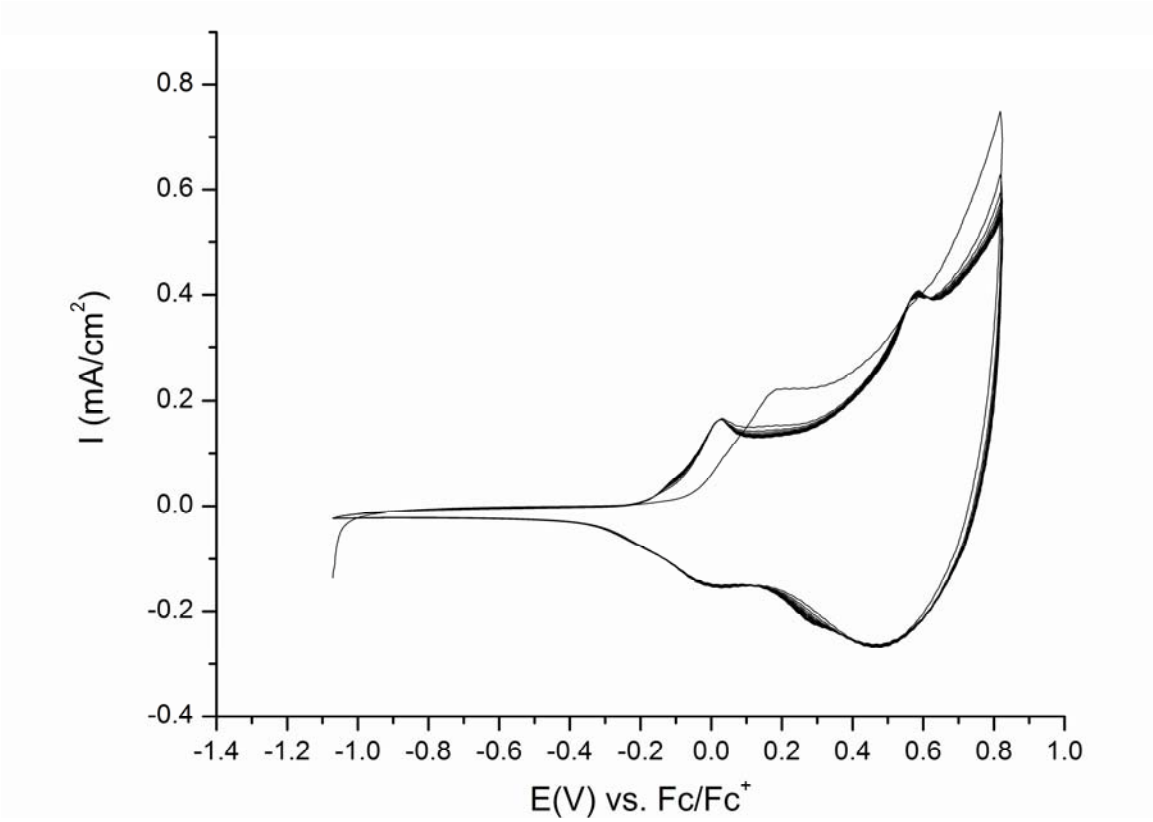


Figure S11: Cyclic voltammetry of a PPheDOT(C_{12})$_2$ thin film drop-cast on Pt Button.

Thermal Analysis of PPheDOT(C_{12})$_2$

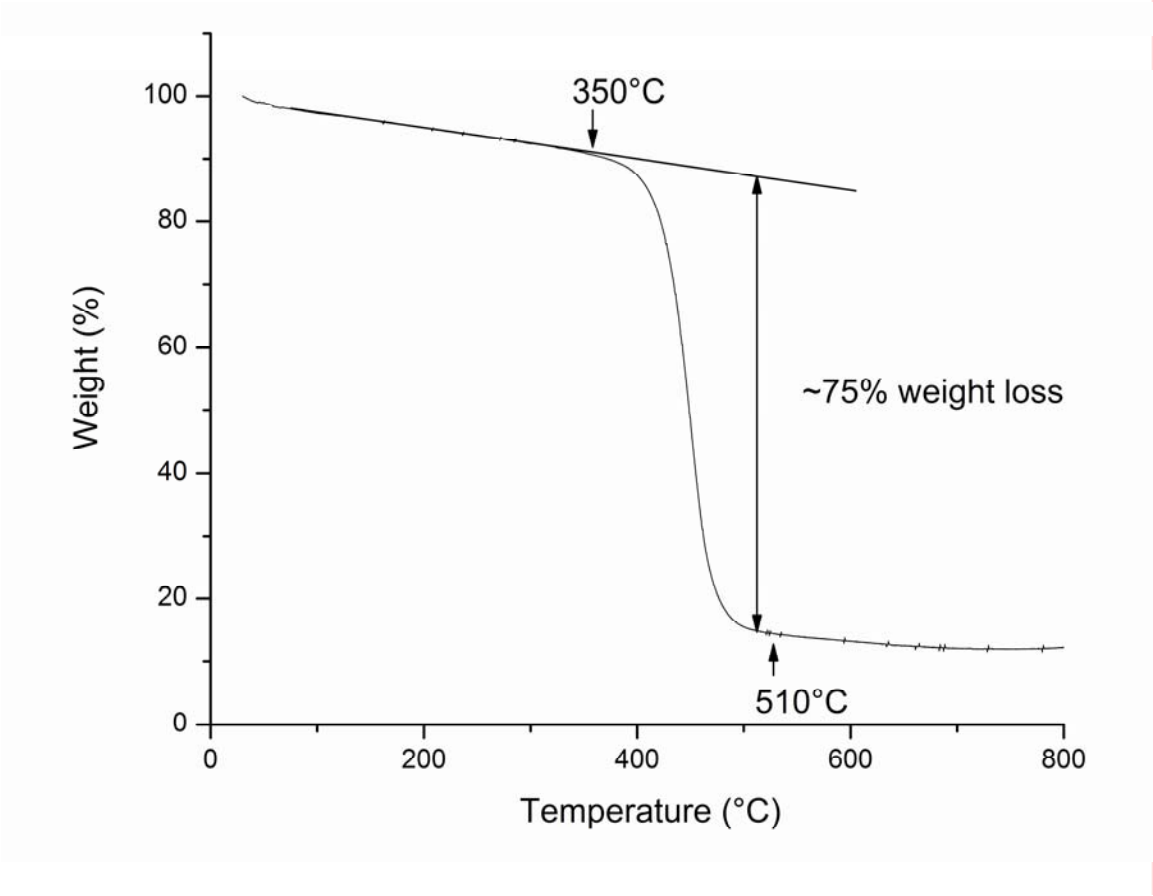


Figure S12: Thermogravimetric analysis of PPheDOT(C_{12})$_2$

AFM study of PPheDOT spin-coated from a cold (25°C) ODCB solution.

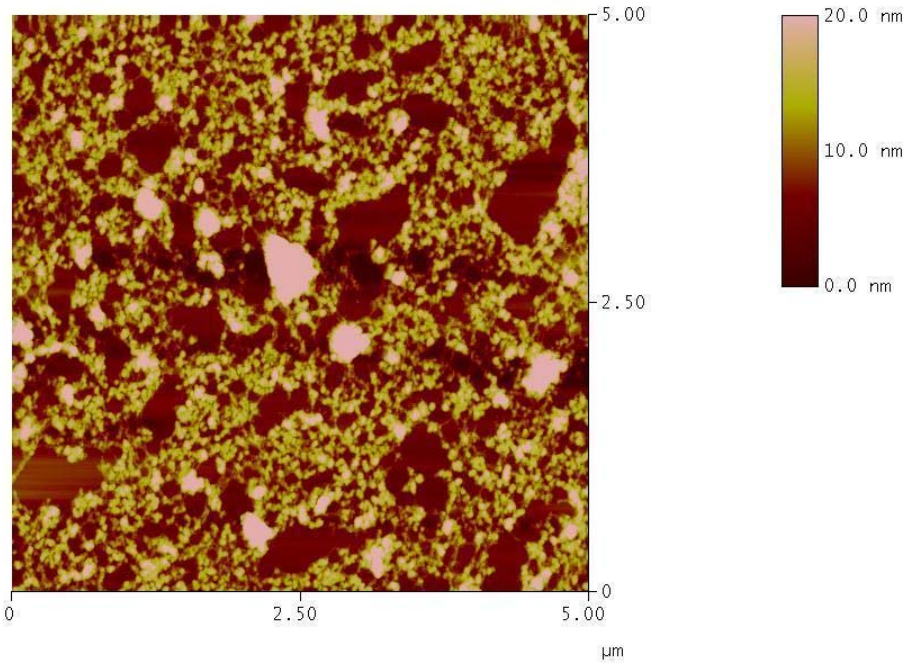


Figure S13: AFM picture of PPheDOT(C_{12})$_2$ spin-coated from cold ODCB

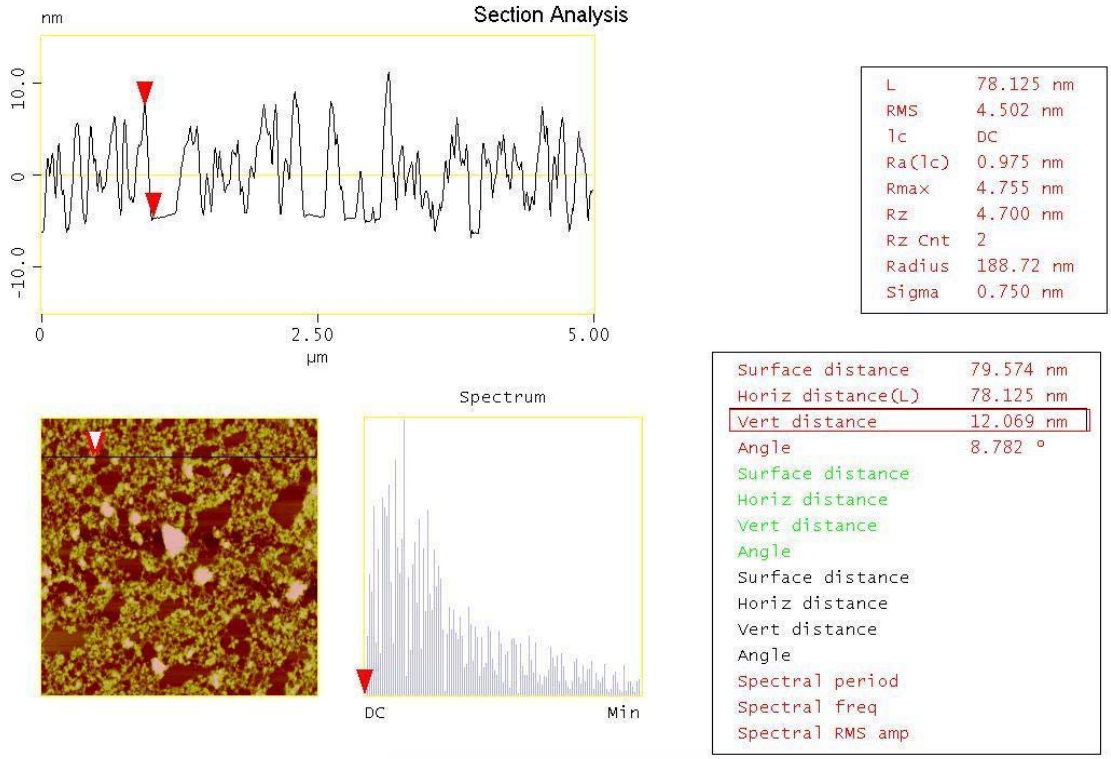


Figure S14: Cross-section analysis of Figure S13

2D-WAXS data of an extruded fiber of PPheDOT(C_{12})$_2$

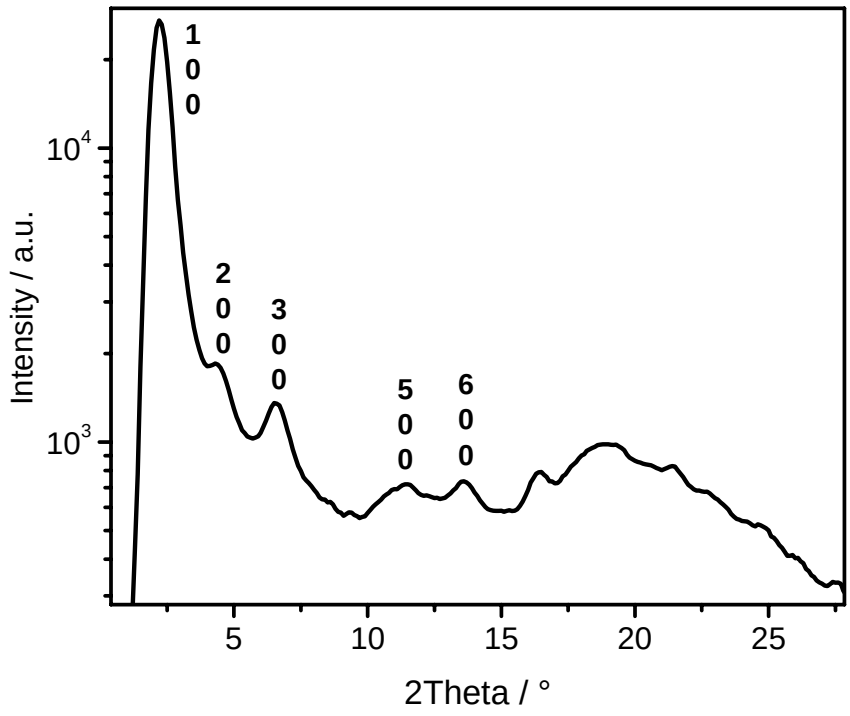


Figure S15: Equatorial reflection intensity distribution recorded at 30 °C as a function of the scattering angle. Reflections are indexed by the Miller's indexes

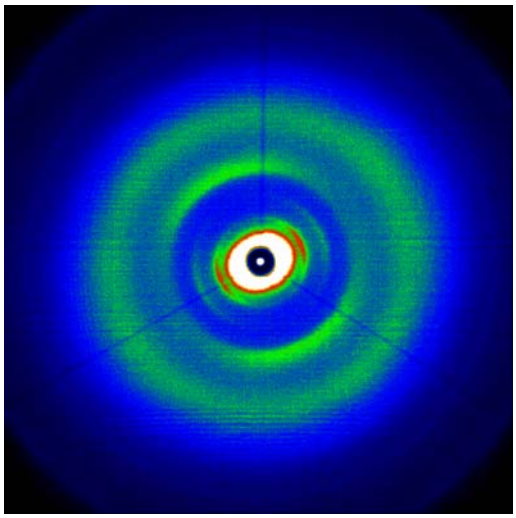


Figure S16: 2D-WAXS pattern of PPheDOT-(C_{12})$_2$ at 150 °C.