

Electronic Supplementary Information

Impact of the dopant location in the semi-crystalline structure of alternated donor-acceptor copolymers on the polarity switching p → n mechanism

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1. Materials and methods

All the starting materials, reagents and catalysts were purchased from commercial suppliers and used without any further purification unless otherwise stated. Purification of organic compounds were carried out through silica gel using 230-400 mesh size.

NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with trace of chloroform in CDCl₃ as the internal reference.

High temperature size exclusion chromatography (HT-SEC) analyses were performed using a Viscotek system, from Malvern Instruments. 1,2,4-trichlorobenzene (TCB) was used as the sample solvent and the eluent phase at 150 °C. The separation was performed on a combination of three columns (PLgel Olexis from Agilent Technologies, 300 mm × 7.5 mm, 13µm).

UV-Vis spectra were recorded on a Jasco V-670 spectrometer (400-1500 nm) for thin film measurements (drop cast from *o*-dichlorobenzene solution).

Cyclic voltammetry (CV) was performed on a Biologic Applied Research MPG2 multi-channel potentiostat, and CV experiments were performed at room temperature with a conventional three-electrode setup consisting of a platinum disk working electrode, silver wire and platinum wire respectively as reference and counter electrodes. The potential of the reference electrode was calibrated using Fc/Fc⁺ couple as an internal standard. All the measurements were conducted in anhydrous acetonitrile media under a nitrogen atmosphere using Bu₄NClO₄ (0.1M) as a supporting electrolyte at a scan rate of 50 mV/s. The HOMO energy levels of polymers, were calculated from the equation of $E_{\text{HOMO}} = -[5.1 + E_{\text{ox}}]\text{eV}$.¹

The preparation of oriented thin films of PAQM2T-TVT and PDPP2T-TVT followed the approach described in references.^{2,3} All PSC films were prepared by doctor blading a polymer solution in ortho-dichlorobenzene (10-15 mg/ml) on a sacrificial film of sodium poly(styrene sulfonate) (NaPSS). The NaPSS film was prepared by spin-coating (1 g/l, 3000 RPM, 60s). The polymer films were rubbed using a homemade setup as described in the literature. The rotating speed of the cylinder covered with a microfiber cloth was 640 RPM and the applied pressure was in the range 2-3 bar. The film thickness was extracted from the film absorbance using a calibration curve. The film thickness was measured by AFM for non-oriented thin films floated on silicon substrates. The thickness-absorbance curves yield slopes of 193 nm/abs for PAQM2T-TVT and 225 nm/abs for PDPP2T-TVT (for PAQM2T-TVT films, the absorbance was measured at 734 nm whereas for PDPP2T-TVT films it was measured at 710 nm). For oriented polymer films, the thickness was determined from the average of the absorbances measured in the directions parallel ($A_{//}$) and perpendicular (A_{\perp}) to the rubbing i.e. using $(A_{//}+A_{\perp})/2$. Table S1 collects the thicknesses as well as the dichroic ratio of all the films used in this study. Conductivities and Seebeck coefficients were performed on the same rubbed samples used for UV-vis-NIR spectroscopy and TEM by selecting 3 different nearby zones.

Table S1. Orientation level (dichroic ratio) and film thickness as determined from the UV-vis-NIR absorbance $(A_{//}+A_{\perp})/2$ for rubbed films of PAQM2T-TVT and PDPP2T-TVT used for conductivity/Seebeck, TEM and polarized UV-vis-NIR investigations.

Polymer /dopant	FeCl ₃			MB		
	$(A_{//}+A_{\perp})/2$	Film thickness (nm)	Dichroic Ratio	$(A_{//}+A_{\perp})/2$	Film thickness (nm)	Dichroic Ratio
PAQM2T-TVT	0.77	140±5	8.6	0.42	81±5	7.7
PDPP2T-TVT	0.38	84±5	6.5	0.24	54±3	8.6

For TEM analysis, the thin films were coated with a thin amorphous carbon film, floated on distilled water and recovered on copper grids. The doping of the films was made by immersion in solutions of dopants for 40s -1 min. No rinsing step was used to avoid dedoping. For TEM, a FEI CM12 microscope with a MVIII camera were used. Calibration of the reticular distances in electron diffraction was performed using an oriented poly(tetrafluoroethylene) thin films prepared by friction transfer.

Polarized UV-vis-NIR spectroscopy was performed on a Carry 5000 spectrometer (1 nm resolution). AFM was performed on a Multimode Brucker 8 and a Nanoscope V controller (Scan Asyst-Air tips with a force of 0.4 N/m).

Measurements of charge conductivity and Seebeck coefficients were performed in a Campus Jacomex glovebox (N₂ atmosphere, PO₂≤2 ppm and PH₂O≤ 2 ppm). A Semiprobe lab assist prober with tungsten tips and a Keithley 2634B sourcemeter were used for transport measurements. The details of the 4-point probe electrode geometry and preparation are given in reference.⁴ Seebeck coefficients were measured by a differential temperature method, ramping the temperature gradient between 0 and 12 K around ambient. For a given doping condition, four devices were measured.

2. Synthesis

The synthesis of intermediates **3**, **4**, **5**, **6** and **PAQM2T-TVT** polymer has been already reported in reference 1.

The Synthesis of intermediates **8**, **9** and **PDPP2T-TVT** polymer was synthesized by reference 5 and 6.

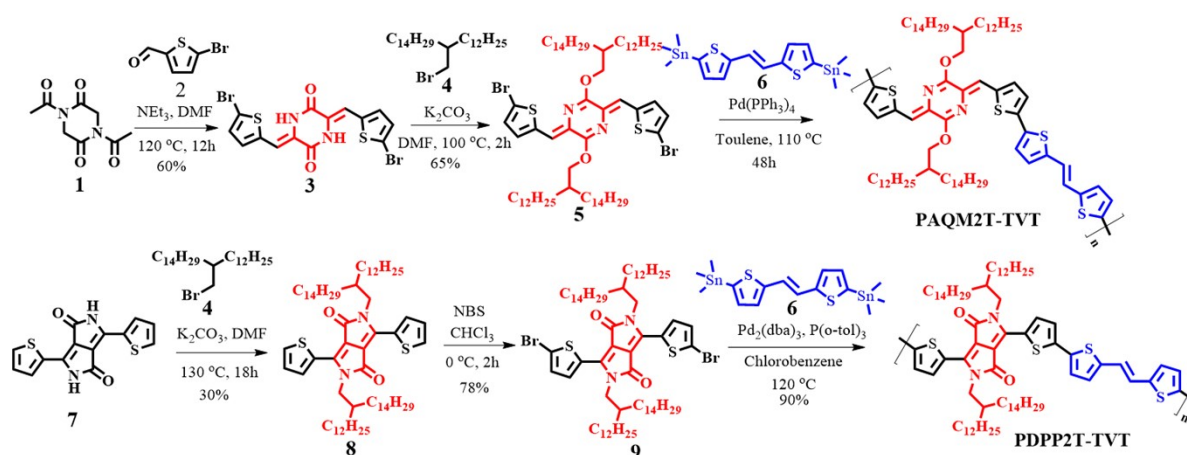


Figure S1: Synthetic route for PAQM2T-TVT and PDPP2T-TVT polymers.

Synthesis of 2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**):

A mixture of 3,6-dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c] pyrrole-1,4-dione (2.00g, 6.66 mmol) and anhydrous K_2CO_3 (3.55g, 26.6 mmol) were dissolved in dry DMF (40 mL). The reaction mixture was heated at 130 °C under N_2 for 1 h. Then, 2-dodecyl 1-bromohexadecane (14.21 g, 30 mmol) was added dropwise. The reaction mixture was further stirred and heated at 140 °C overnight. The reaction mixture was cooled to room temperature and poured into 200 ml of ice. The product was extracted with CH_2Cl_2 , washed with water and brine. The combined organic layer was dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (Eluent: Petroleum ether and dichloromethane, 7:3) to afford the dark red solid **8** (2.1g, 30%). 1H NMR (300 MHz, $CDCl_3$) δ 8.88 (dd, $J = 3.9, 1.1$ Hz, 2H), 7.62 (dd, $J = 5.0, 1.1$ Hz, 2H), 7.29 – 7.24 (m, 2H), 4.01 (d, $J = 7.7$ Hz, 4H), 1.89 (dd, $J = 13.2, 5.7$ Hz, 2H), 1.22 (d, $J = 12.7$ Hz, 115H), 0.87 (t, $J = 6.7$ Hz, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.71, 140.39, 135.18, 130.40, 129.83, 128.35, 107.92, 46.19, 37.71, 31.89, 31.85, 31.16, 29.98, 29.62, 29.60, 29.53, 29.47, 29.33, 29.27, 26.18, 22.66, 22.64, 14.09.

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-dodecylhexadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**9**):

In a 250 mL single-neck round-bottom flask, **8** (2 g, 1.8 mmol) was dissolved in chloroform (80 mL) under ambient conditions. After the reaction mixture was stirred in an ice bath at 0 °C for 20 min, NBS (0.72 g, 4.0 mmol) was added in small portions over 30 min and the reaction was stirred at this temperature for 1h. The reaction mixture was then warmed up to room temperature and water was added. The reaction mixture was extracted with CH_2Cl_2 , washed

with water and brine. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Eluent: Petroleum ether and toluene, 7:3) to afford the purple solid **9** (1.8 g, 78%). ^1H NMR (300 MHz, CDCl_3) δ 8.63 (d, $J = 4.2$ Hz, 1H), 7.22 (d, $J = 4.2$ Hz, 1H), 3.92 (d, $J = 7.7$ Hz, 2H), 1.92 – 1.83 (m, 1H), 1.35 – 1.16 (m, 58H), 0.88 (t, $J = 6.7$ Hz, 7H).

Synthesis of PDPP2T-TVT: **6** (0.124 g, 0.24 mmol), **9** (0.3 g, 0.24 mmol), $\text{Pd}_2(\text{dba})_3$ (7.2 mg), and $\text{P}(\text{o-tol})_3$ (18.3 mg) were added to a 50 mL round bottom flask. The tube was purged with argon for three times. Dry chlorobenzene (10 mL) was added to the solids and the mixture was stirred for 48 h at 120°C under argon atmosphere and protected with alumina foil. After cooling down to room temperature, the black solution was precipitated in 200 mL of methanol. The crude polymer was collected by filtration and washed with methanol. The dark solid was further purified by Soxhlet extraction with methanol, acetone, and finally cyclohexane. The cyclohexane fraction was concentrated to 10 mL and the polymer was precipitated in 200 mL of methanol. The polymer was collected by filtration and dried under vacuum (0.27 g, 90%).

3) Figures & Tables

3.1) UV-visible absorption spectra, Cyclic voltammograms and energy level diagram of PAQM2T-TVT and PDPP2T-TVT

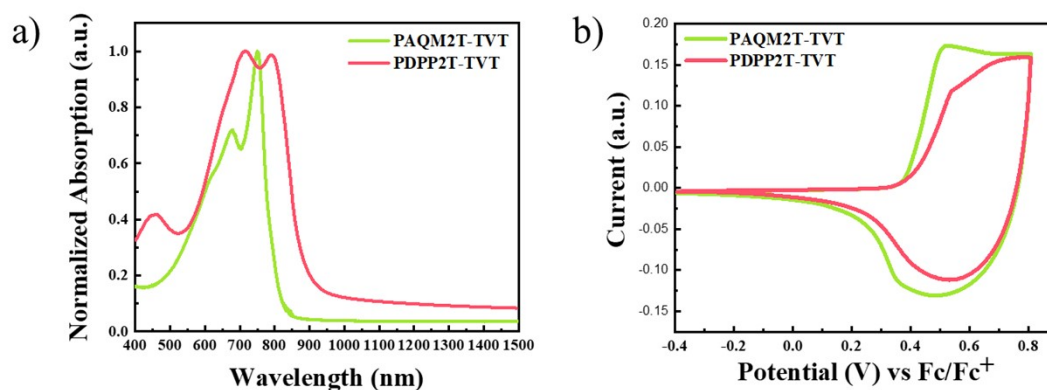


Figure S2: a) Normalized UV-vis-NIR absorption spectra of PAQM2T-TVT and PDPP2T-TVT polymers b) Cyclic voltammograms of PAQM2T-TVT and PDPP2T-TVT.

Table S2: Measured and calculated parameters of PDPP2T-TVT polymer.

<i>Polymer</i>	M_n (kDa)	M_w (kDa)	<i>PDI</i>	λ_{max} (nm) ^a	λ_{onset} (nm)	E_g^{opt} (eV) ^b	E_{HOMO} (eV) ^c	E_{LUMO} (eV) ^d
PDPP2T-TVT	10.0	30.6	3.0	715, 790	903	1.37	-5.50	-4.13

^a)UV-vis-NIR absorption spectra measured in thin film state ^b)Optical bandgap estimated from the onset wavelength of the optical absorption by the equation: band gap =1240/ λ_{onset} ^c)Calculated by using cyclic voltammetry (thin film state). ^d)Calculated from the difference between the HOMO level and optical band gap.

3.2) Size exclusion chromatography

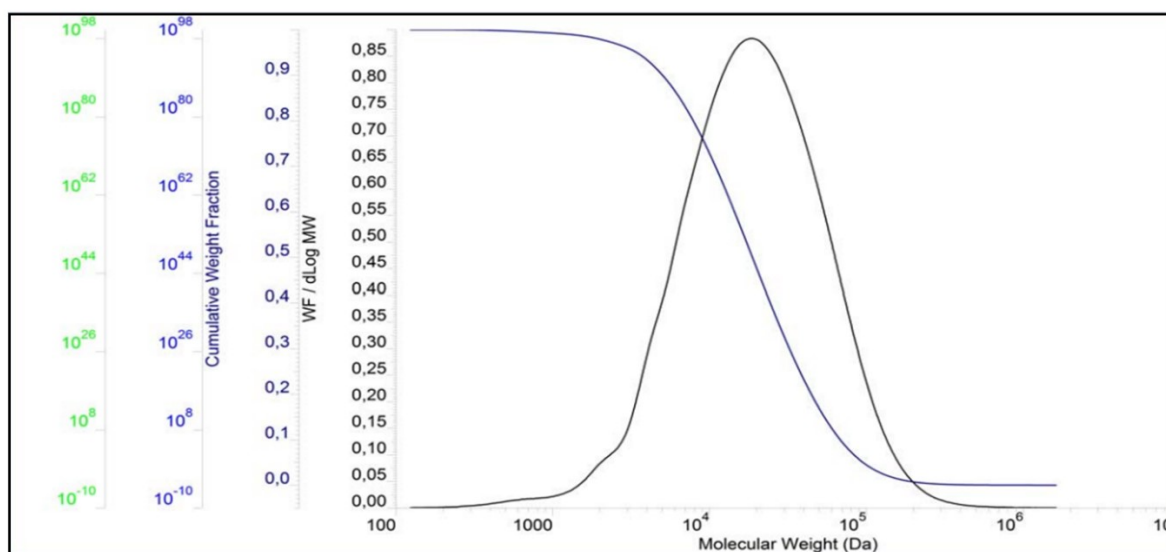


Figure S3: Size Exclusion Chromatography (SEC) data of PDPP2T-TVT polymer

3.3) High temperature rubbing of PAQM2T-TVT and PDPP2T-TVT

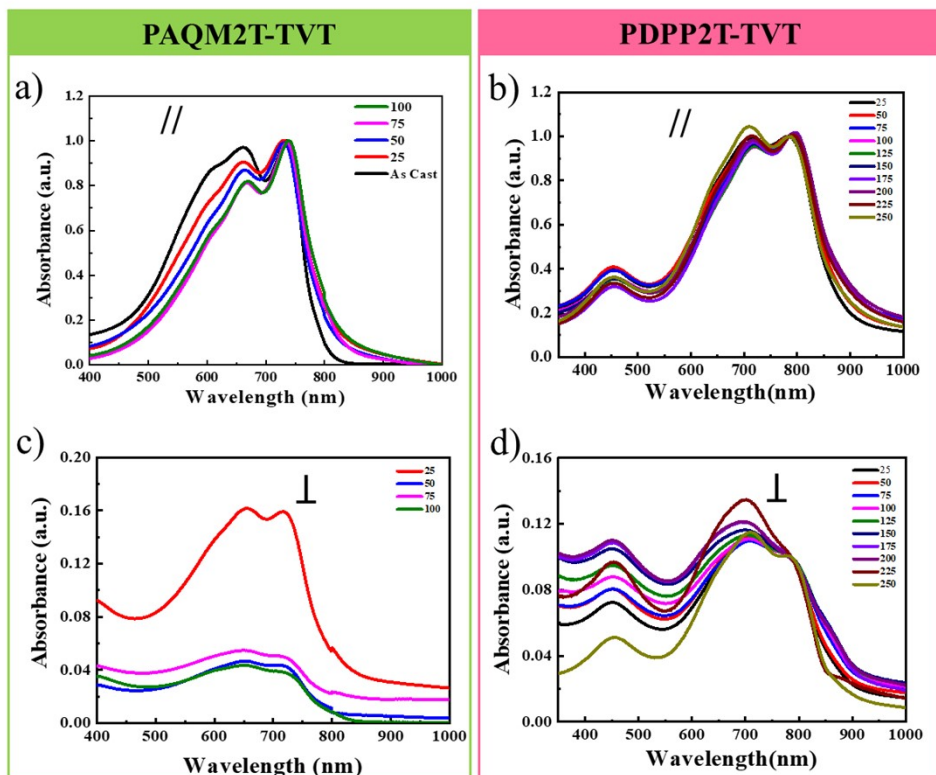


Figure S4: High temperature rubbing of PAQM2T-TVT and PDPP2T-TVT a,c) along the rubbing direction (//) and b,d,) perpendicular to it.

3.4) Evolution of the P1 and P2 band absorbance versus doping level.

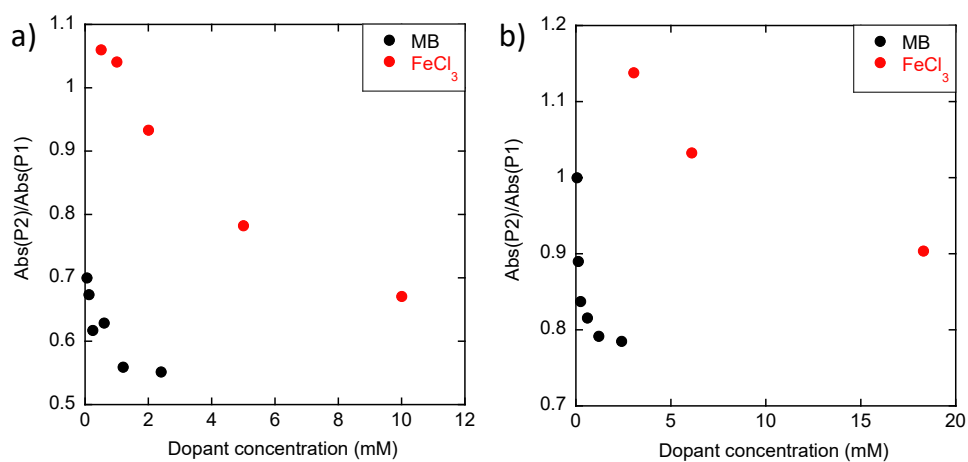


Figure S5. Evolution of the ratio between the absorbances of the P2 and P1 bands as a function of increasing dopant concentration (FeCl_3 and Magic Blue) in oriented films of a) **PAQM2T-TVT** and b) **PDPP2T-TVT** thin films. For **PAQM2T-TVT**, the P2 band absorbance is measured at 1208 nm (1258nm) for MB (FeCl_3) and the P1 band at 2500nm. For **PDPP2T-TVT**, the P2 band absorbance is measured at 1333 nm (1340nm) for MB (FeCl_3) and the P1 band at 2500nm.

3.5) Electron diffraction patterns of PAQM2T-TVT and PDPP2T-TVT

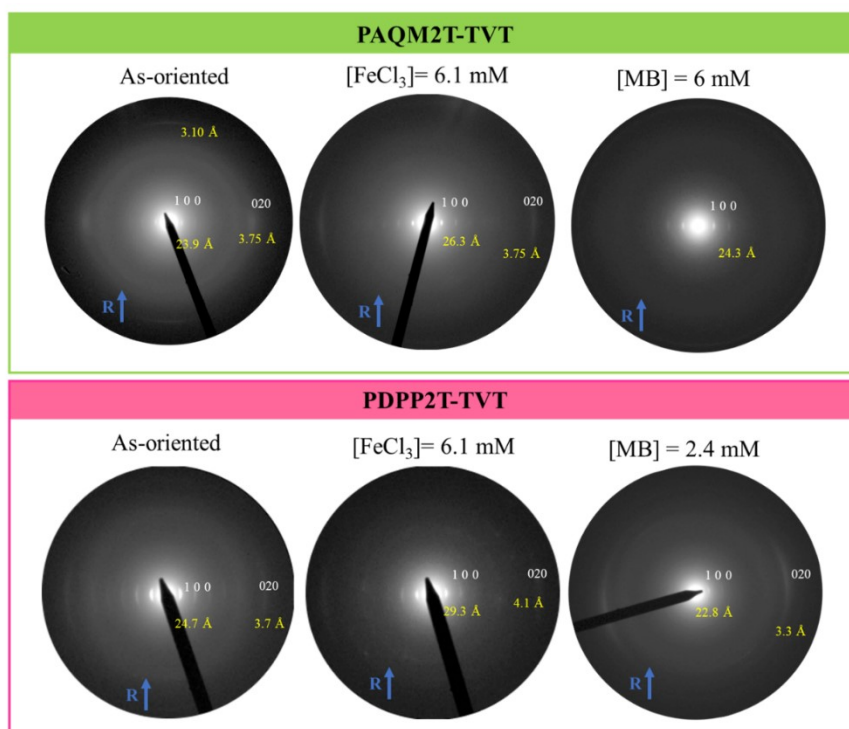


Figure S6: Representative electron diffraction patterns of oriented films of PAQM2T-TVT and PDPP2T-TVT aligned by high temperature rubbing (as oriented) and subsequently doped with FeCl_3 in nitromethane or MB in acetonitrile. The blue arrow indicates the rubbing direction R.

3.6) Power factors of PAQM2T-TVT and PDPP2T-TVT

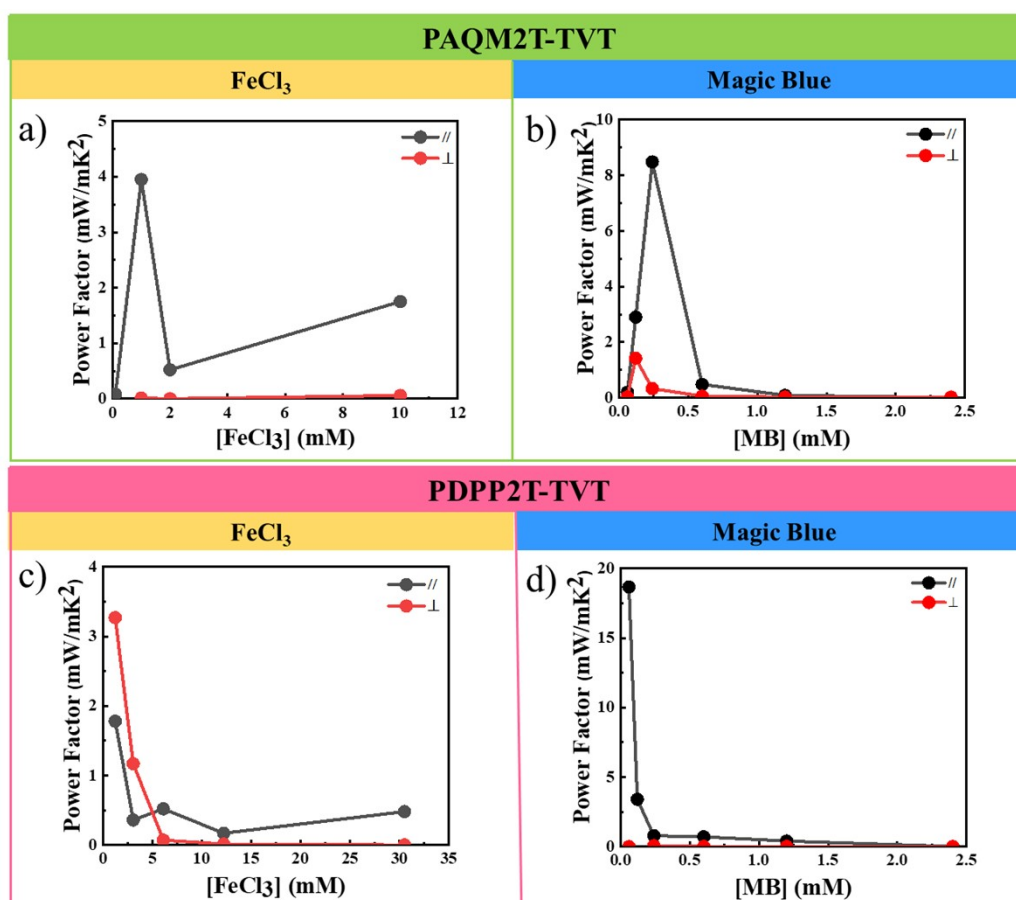


Figure S7: Evolution of the anisotropic power factor (PF) of oriented PAQM2T-TVT and PDPP2T-TVT polymers with a,c) FeCl_3 doped and b,d) MB doped polymer films.

4. NMR

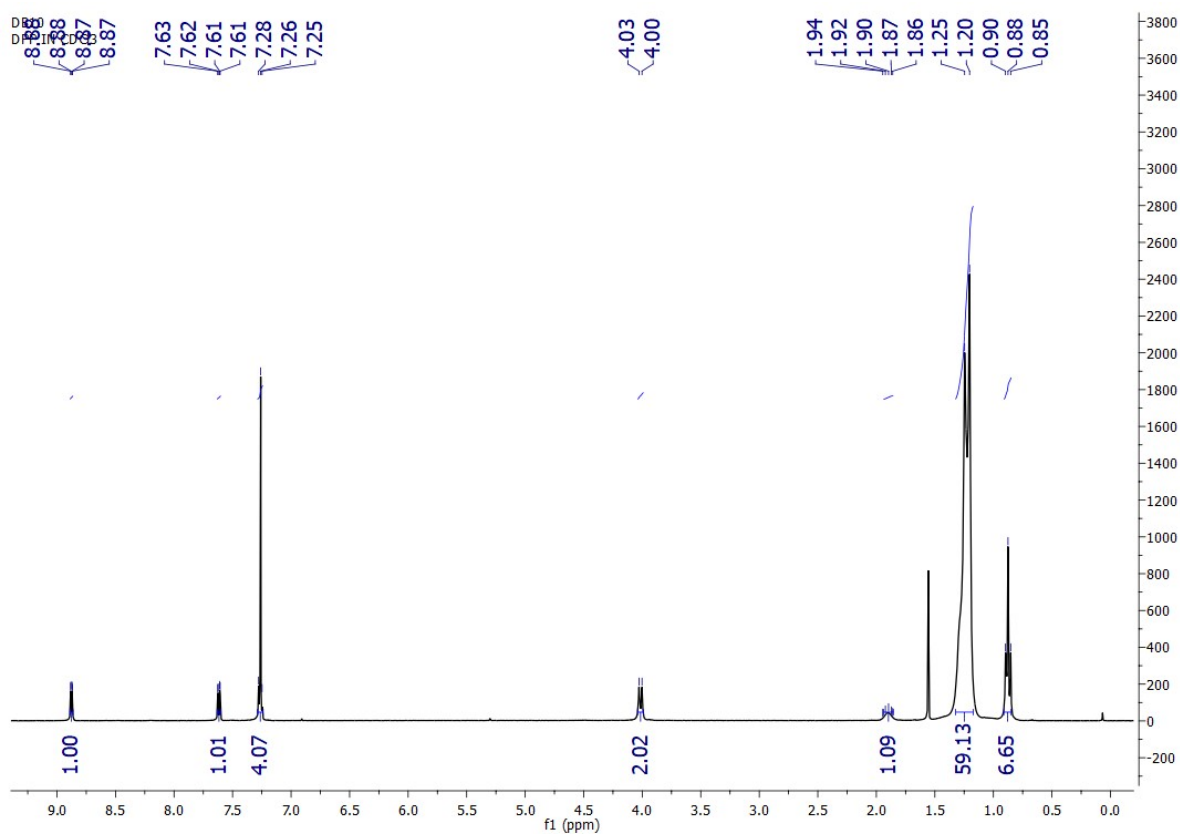


Figure S8: ^1H NMR spectrum of 2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**).

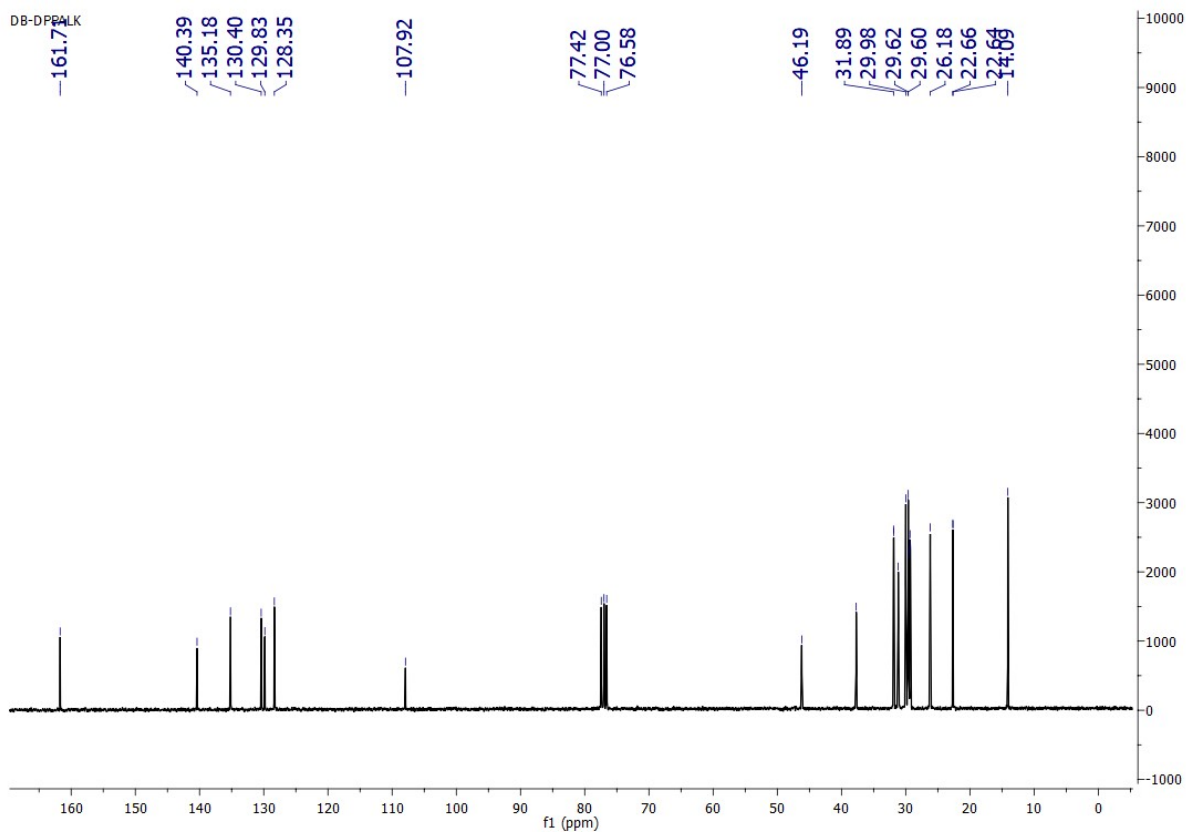


Figure S9: ^{13}C NMR spectrum of 2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**).

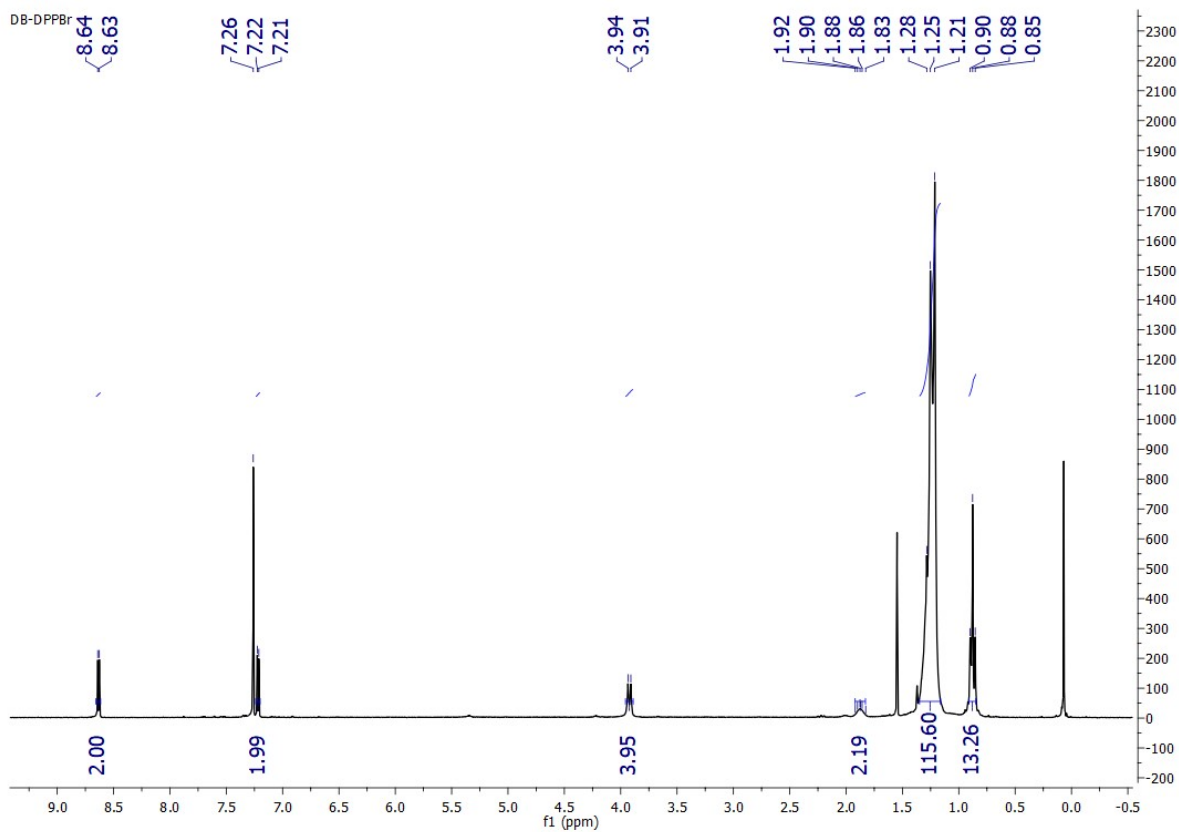


Figure S10: ^1H NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-dodecylhexadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**9**).

5. References:

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