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## Electronic Supplementary Information

# The effect of alkyl side chain length on the formation of two semi-crystalline phases in low band gap conjugated polymers

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## Experimental Procedures

### 1. Materials

All synthetic procedures were performed under an argon atmosphere. Commercial (dry) solvents and reactants were used without further purification, unless stated otherwise. Diethyl ether was dried over a column containing 4 Å molecular sieves. *N*-bromosuccinimide (NBS) was recrystallized from deionized water prior to use. 5,5′-Bis(trimethylstannyl)-2,2′-bithiophene and triphenylphosphine ($PPh_3$) were recrystallized from methanol prior to polymerization. Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) was purchased from Strem Chemicals Inc. [70]PCBM was purchased from Solenne BV. 3,6-Bis(4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**1**) was synthesized as described previously.[1] All other chemicals and solvents were obtained from Sigma-Aldrich Co.

### NMR spectroscopy

$^1$H-NMR and $^{13}$C-NMR spectra were measured on a Bruker Avance III ($^1$H 400 MHz, $^{13}$C 100 MHz) spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS) as internal standard.

### Mass spectrometry

Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry was performed on a Bruker Autoflex Speed spectrometer.

### Gel permeation chromatography

Polymer molecular-weight distributions were estimated by GPC at 140 °C on a PL-GPC 120 system using a PL-GEL 10 mm MIXED-C column with *o*-DCB as the eluent and calibrated by polystyrene internal standards. Samples were first dissolved in *o*-DCB at 140 °C in a concentration of 0.1 mg $mL^{-1}$.

### Optical spectroscopy

A PerkinElmer Lambda 1050 spectrophotometer was used to measure UV-vis-NIR absorption for solutions and thin films. Photoluminescence spectra were recorded using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a near-IR sensitive photomultiplier (Hamamatsu) cooled by liquid nitrogen.

### Square-wave voltammetry

Square-wave voltammetry (SWV) measurements were performed on polymer thin films, coated on a platinum wire working electrode, using an Autolab PGSTAT30 (Ecochemie, The Netherlands) potentiostat in a three-electrode configuration under a nitrogen atmosphere. A 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dry acetonitrile was used as electrolyte and a silver wire and a silver/silver chloride (Ag/AgCl) electrode served as counter electrode and quasi-reference electrode, respectively. Details of the measurement and extraction of data have been described previously.[2]

## Kinetics of polymorph formation

A halogen lamp was utilized as light source, and a fiber optic cable that was connected with a spectrometer (Avantes Avaspec-2048×14) was used to collect the signal transmitted through the wet/dry film.

## Thermal properties

Differential scanning calorimetry (DSC) was conducted via a TA Instruments Q2000 DSC in Tzero hermetic pans using a scan rate of 10 °C $\text{min}^{-1}$. *In situ* absorption measurements during annealing were performed by fixing a Linkam heating stage into the PerkinElmer Lambda 1050 spectrophotometer with a home-made holder. During the heating/cooling procedures, the samples were protected under nitrogen atmosphere.

## 2D GIWAXS

All samples were spin-coated on $Si/SiO_2$ substrates and annealed at 100 °C for 30 min to remove residual solvent. Films were characterized on a GANESHA 300XL+ system from JJ X-ray in the X-ray lab at DSM Materials Sciences Center (DMSC). The instrument is equipped with a Pilatus 300K detector, with pixel size of 172 μm × 172 μm. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic "3D version" optimized for SAXS) (30 W). The wavelength used was $\lambda$ = 1.5408 Å. The minimized background scattering plus high-performance detector allows for a detectable $q$-range varying from $3 \times 10^{-3}$ to 3 $\text{Å}^{-1}$ (0.2 to 210 nm). The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. The primary slit has a size of 0.3 mm × 0.5 mm, and the guard slit has a size of 0.1 mm × 0.3 mm. The accumulation time was 6 h for each measurement. Data plot and data reduction was conducted using GIXSGUI[3] and SAXSGUI program. In the case of samples with TCB, the attempt on the deconvolution of (010) peak through two matched Gaussians failed, which can be attributed to the impact of X-ray incident angle and film roughness on the reflection intensity. Note that the coexistence of $\beta_1$ and $\beta_2$ in broad (010) peaks is still possible.

## TEM measurement

TEM images were recorded using a Tecnai G2 Sphera transmission electron microscope (FEI) operated at 200 kV.

## Thin film transistor fabrication and characterization

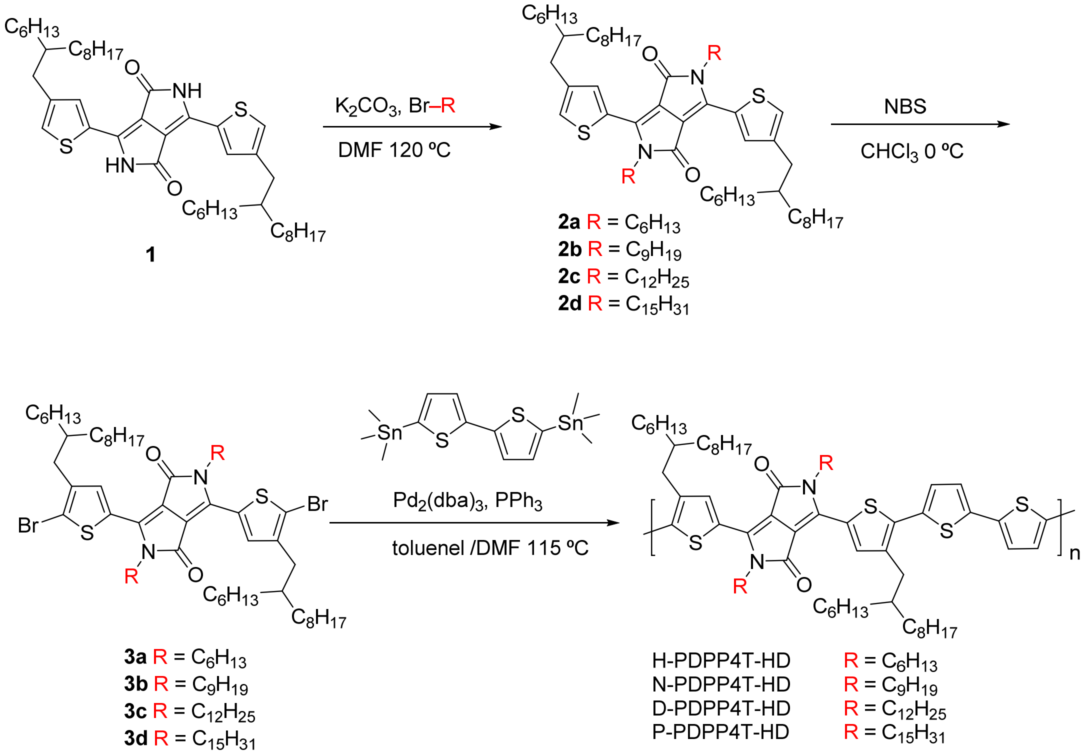
A bottom-contact top-gate architecture was used for OFETs. As substrates, the $Si/SiO_2$ wafers were cleaned by 10 min ultrasonication in acetone and subsequent 10 min ultrasonication in isopropanol, and then dried by the nitrogen flow. The source and drain electrodes with 50 nm in thickness were deposited by Au evaporation with the deposition rate of 0.5 Å/s, preceded by a 2 nm Cr adhesion layer, with a channel length of 50 μm and channel length to width ratio of 1:20. Polymers were spin coated from 3 mg $\text{mL}^{-1}$ solutions. A CYTOP insulator was spin coated on top of polymer thin films as dielectric layer (900 nm), followed by annealing at 100 °C for 1 h. The capacitance of the CYTOP was 2.0 nF $\text{cm}^{-2}$. Finally, 50-nm Ag was evaporated with the deposition rate of 0.5 Å/s as gate electrode. A Keithley 4200-SCS was used for all standard OFET measurements which were recorded in Janis probe station (ST-500-2-6TX) under vacuum. The saturated field-effect mobilities were extracted from the transfer characteristics shown in Fig. S11, following a recommended protocol for data analysis.[4]

**Solar cell fabrication and characterization**

Pre-patterned indium tin oxide (ITO) substrates (15 Ω per square, Naranjo Substrates) were used for photovoltaic devices with a conventional configuration (ITO/PEDOT:PSS/polymer:[70]PCBM/LiF/Al). All photoactive layers were spin-coated from different solvents with the active area of 0.09 or 0.16 $cm^2$. The white light (~100 mW $cm^{-2}$) from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter was used for illumination. $J-V$ characteristics were measured in a $N_2$-filled glove box at ambient temperature using a Keithley 2400 source meter from +2 to −2 V in 0.01 V step size at a rate of 30 ms per data point. Short-circuit currents under AM1.5G conditions were estimated from the EQE and integration with the AM1.5G (100 mW $cm^{-2}$) solar spectrum. The EQE was recorded by a lock-in amplifier (Stanford Research Systems SR 830) under simulated 1 sun operation conditions with bias light from a 530 nm high-power LEDs (Thorlabs). As probe light, the light from a 50 W tungsten halogen lamp (Osram64610) was modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) for wavelength selection using a 2 mm diameter aperture to illuminate the active area. A calibrated Si cell was used as reference. Polymer solar cells were kept behind a quartz window in a nitrogen filled container.

## Synthesis

Scheme S1 shows the synthesis route to the four DPP polymers. In the subsequent sections the synthetic procedures and molecular characterization are provided.



**Scheme S1.** Synthesis of the PDPP4T-HD polymers

### 2,5-Dihexyl-3,6-bis(4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2a)

Compound **1** (0.519 g, 6.93 × $10^{-4}$ mol), finely crushed potassium carbonate ($K_2CO_3$) powder (0.287 g, 2.08 × $10^{-3}$ mol), and DMF (2 mL) were heated to 120 °C for 1 hour in a 2-neck round bottom flask. Subsequently, 1-bromohexane (0.343 g, 2.08 × $10^{-3}$ mol) was dropwise added and the mixture stirred overnight at 120 °C. After cooling to room temperature the reaction was quenched with water and extracted with DCM. The combined organic phase was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The remaining purple solid was added to a mixture of 1,4-dioxane (120 mL), HCl (2 mL) and water (2 mL) and refluxed for 1 hour. After evaporation of the solvent the crude product was further purified by column chromatography (silica gel, eluent gradient 100:0 > 70:30 heptane:DCM). A final recrystallization step in ethanol resulted in pure compound **2a** (441 mg, yield: 70%), obtained as solid purple flakes. $^{1}$H-NMR (400 MHz, $CDCl_3$, $\delta$): 8.70 (s, 2H); 7.20 (d, 2H); 4.05 (m, 4H); 2.64 (d, $J = 6.7$ Hz, 4H); 1.82-1.67 (m, 6H); 1.46-1.20 (m, 64H); 0.97-0.82 (m, 18H). $^{13}$C-NMR (100 MHz, $CDCl_3$, $\delta$): 161.31; 143.77; 139.82; 136.71; 129.28;

126.61; 107.42; 42.19; 38.80; 34.82; 33.25; 33.23; 31.91; 31.87; 31.43; 30.02; 29.90; 29.69; 29.60; 29.33; 26.54; 26.50; 26.48; 22.67; 22.58; 14.10; 13.98. (Note: several peaks in the $^{13}$C-NMR spectrum overlap). MALDI-TOF-MS: [M$^+$] calc: 916.69 found: 916.69.

**2,5-Dinonyl-3,6-bis(4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2b)**

The same procedure as for **2a** was followed, using 350 mg ($4.67 \times 10^{-4}$ mol) of compound **1**, 194 mg (1.40 mmol) finely crushed potassium carbonate ($K_2CO_3$) powder, 290 mg 1-bromononane (1.40 mmol) and 5 mL DMF. 216 mg (yield: 46%) of a red fluffy solid was obtained after recrystallization in ethanol. $^1$H-NMR (400 MHz, $CDCl_3$, $\delta$): 8.70 (s, 2H); 7.20 (s, 2H); 4.04 (m, 4H); 2.64 (d, $J$ = 6.8 Hz, 4H); 1.84-1.62 (m, 6H); 1.51-1.05 (m, 72H); 0.97-0.75 (m, 18H). $^{13}$C-NMR (100 MHz, $CDCl_3$, $\delta$): 161.34; 143.80; 139.85; 136.74; 129.32; 126.64; 107.46; 42.20; 38.82; 34.85; 33.28; 33.25; 31.94; 31.90; 31.86; 30.05; 29.97; 29.73; 29.63; 29.53; 29.36; 29.30; 29.24; 26.90; 26.53; 26.51; 22.69; 22.67; 14.13; 14.11. (Note: several peaks in the $^{13}$C-NMR spectrum overlap). MALDI-TOF-MS: [M$^+$] calc: 1000.79 found: 1000.81.

**2,5-Didodecyl-3,6-bis(4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2c)**

Compound 2c was synthesized as described previously.[1]

**2,5-Dipentadecyl-3,6-bis(4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2d)**

The same procedure as for **2a** was followed, using 350 mg ($4.67 \times 10^{-4}$ mol) of compound **1**, 194 mg (1.40 mmol) finely crushed potassium carbonate ($K_2CO_3$) powder, 408 mg 1-bromopentadecane (1.40 mmol) and 5 mL DMF. 283 mg (yield: 52%) of a purple solid was obtained after recrystallization in ethanol. $^1$H-NMR (400 MHz, $CDCl_3$, $\delta$): 8.70 (s, 2H); 7.20 (s, 2H); 4.04 (m, 4H); 2.64 (d, $J$ = 6.8 Hz, 4H); 1.86-1.61 (m, 6H); 1.47-1.06 (m, 96H); 0.99-0.76 (m, 18H). $^{13}$C-NMR (100 MHz, $CDCl_3$, $\delta$): 161.34; 143.80; 139.85; 136.74; 129.32; 126.64; 107.45; 42.21; 38.82; 34.85; 33.28; 33.25; 31.94; 31.91; 30.06; 29.98; 29.70; 29.67; 29.64; 29.60; 29.37; 29.31; 26.92; 26.53; 26.51; 22.70; 14.13. (Note: several peaks in the $^{13}$C-NMR spectrum overlap). MALDI-TOF-MS: [M$^+$] calc: 1168.97 found: 1169.00.

**3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-2,5-dihexyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3a)**

240 mg ($2.62 \times 10^{-4}$ mol) of compound **2a** was dissolved in 5 mL chloroform in a dried Schlenk tube. The solution was kept in the dark and cooled to 0 °C. 98 mg ($5.49 \times 10^{-4}$ mol)

recrystallized NBS was added and the reaction mixture allowed to warm to room temperature. After 1 hour the reaction was quenched with water and the organic phase washed with water and dried over magnesium sulfate. Subsequently the solvent was evaporated *in vacuo.* The crude solid was purified further by recrystallization in ethanol with a small amount of toluene and dried overnight inside the vacuum oven. Monomer **3a** was obtained as a purple powder (261 mg, yield: 93%). $^1$H-NMR (400 MHz, $CDCl_3$, δ): 8.55 (s, 2H); 3.97 (m, 4H); 2.59 (d, J = 7.2 Hz, 4H); 1.82-1.64 (m, 6H); 1.45-1.20 (m, 64H); 0.92-0.83 (m, 18H). $^{13}$C-NMR (100 MHz, $CDCl_3$, δ): 160.99; 143.33; 138.87; 136.02; 129.00; 116.80; 107.63; 38.37; 34.13; 33.33; 33.29; 31.91; 31.87; 31.39; 29.99; 29.94; 29.67; 29.59; 29.33; 26.50; 26.44; 26.42; 22.67; 22.54; 14.10; 13.98. (Note: several peaks in the $^{13}$C-NMR spectrum overlap). MALDI-TOF-MS: [M+] calc: 1072.51 found: 1072.51. The $^1$H-NMR spectrum is shown in Fig. S13.

### 3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-2,5-dinonyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3b)

The same procedure as for compound **3a** was used. Now 194 mg ($1.94 \times 10^{-4}$ mol) of compound **2b** was dissolved in 3.6 mL chloroform and 72 mg ($4.07 \times 10^{-4}$ mol) recrystallized NBS was added under dark conditions at 0 °C. Monomer **3b** was obtained as a dark purple fluffy solid (177 mg, yield: 79%). $^1$H-NMR (400 MHz, $CDCl_3$, $\delta$): 8.55 (s, 2H); 3.97 (m, 4H); 2.59 (d, $J$ = 7.1 Hz, 4H); 1.85-1.60 (m, 6H); 1.50-1.06 (m, 72H); 0.96-0.76 (m, 18H). MALDI-TOF-MS: [$M^+$] calc: 1156.61 found: 1156.64. The $^1$H-NMR spectrum is shown in Fig. S13.

### 3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-2,5-didodecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3c)

Compound 3c was synthesized as described previously.[1]

### 3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-2,5-dipentadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3d)

The same procedure as for compound **3a** was used. Now 241 mg ($2.06 \times 10^{-4}$ mol) of compound **2d** was dissolved in 3.8 mL chloroform and 77 mg ($4.33 \times 10^{-4}$ mol) recrystallized NBS was added under dark conditions at 0 °C. Monomer **3d** was obtained as a light purple solid (219 mg, yield: 80%). $^1$H-NMR (400 MHz, $CDCl_3$, $\delta$): 8.55 (s, 2H); 3.96 (m, 4H); 2.59 (d, $J$ = 7.2 Hz, 4H); 1.90-1.63 (m, 6H); 1.51-1.15 (m, 96H); 1.05-0.76 (m, 18H). $^{13}$C-NMR (100 MHz, $CDCl_3$, $\delta$): 161.02; 143.35; 138.90; 136.05; 129.04; 116.83; 107.65; 42.24; 38.40; 34.15; 33.35; 33.32; 31.94; 31.90; 30.02; 30.00; 29.71; 29.69; 29.62; 29.61; 29.56; 29.37; 29.26; 26.86; 26.46; 26.45; 22.70; 14.13. (Note: several peaks in the $^{13}$C-NMR spectrum overlap). MALDI-TOF-MS: [$M^+$] calc: 1324.79 found: 1324.81. The $^1$H-NMR spectrum is shown in Fig. S13.

**H-PDPP4T-HD**

54.9 mg (112 µmol) freshly recrystallized 5,5’-bis(trimethylstannyl)-2,2′-bithiophene, 120 mg (112 µmol) of compound **3a**, 1.76 mg (6.70 µmol) recrystallized triphenylphosphine and 1.53 mg (1.67 µmol) $Pd_2(dba)_3$ were placed in a dried Schlenk tube and placed under argon. 1.8 mL toluene and 0.2 mL DMF were added and the mixture degassed with argon for 10 min at 40 °C. The mixture was then reacted at 115 °C overnight. The viscous polymer solution was dissolved in warm 1,1,2,2-tetrachloroethane (TCE) and precipitated in methanol. The polymer was dissolved in chloroform with ethylenediaminetetraacetic acid (EDTA) and refluxed for one hour. Water was added, refluxed for one hour and subsequently the organic layer was washed with water. The organic layer was concentrated under reduced pressure and the polymer precipitated in methanol. The polymer was then subjected to Soxhlet extraction with acetone, hexane, dichloromethane and chloroform. Swollen polymer remaining inside the Soxhlet thimble was dissolved in hot TCE and the solution was filtrated over a heated cellulose filter. Finally, the TCE solution was concentrated *in vacuo* and the purified polymer was precipitated in acetone. TCE-fraction: 90 mg, yield: 75%. GPC (*o*-DCB, 140 °C): $M_n$= 20.0 kDa, $M_w$ = 49.7 kDa, $Đ$ = 2.48. (Note: the polymer was not completely dissolved upon filtration).

**N-PDPP4T-HD**

The same procedure as for the polymerization of H-PDPP4T-HD was used, with 42.4 mg (86.2 µmol) 5,5’-bis(trimethylstannyl)-2,2′-bithiophene, 100 mg (86.2 µmol) **3b**, 1.36 mg (5.17 µmol) recrystallized $PPh_3$ and 1.19 mg (1.29 µmol) $Pd_2(dba)_3$. $CHCl_3$ fraction: 88 mg, yield: 88%. GPC (*o*-DCB, 140 °C): $M_n$ = 56.5 kDa, $M_w$ = 118 kDa, $Đ$ = 2.08.

**D-PDPP4T-HD**

D-PDPP4T-HD was synthesized as described previously.[1]

**P-PDPP4T-HD**

The same procedure as for the polymerization of H-PDPP4T-HD was used, with 37.0 mg (75.3 µmol) 5,5’-bis(trimethylstannyl)-2,2′-bithiophene, 100 mg (75.3 µmol) **3d**, 1.19 mg (4.52 µmol) recrystallized $PPh_3$ and 1.03 mg (1.13 µmol) $Pd_2(dba)_3$. $CHCl_3$ fraction: 81 mg, yield: 81%. GPC (*o*-DCB, 140 °C): $M_n$ = 33.6 kDa, $M_w$ = 79.7 kDa, $Đ$ = 2.37.

## Supplementary Figures

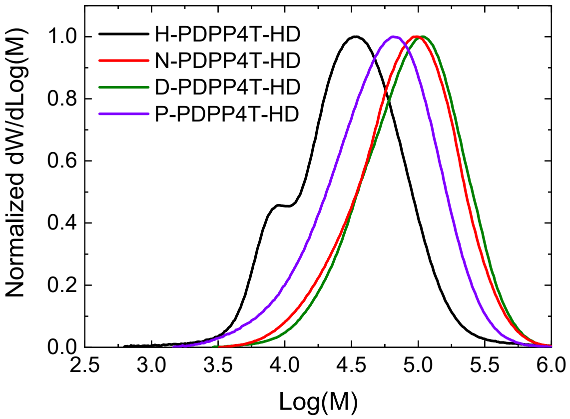


**Fig. S1**. GPC of PDPP4T-HD polymers recorded in *o*-DCB at 140 °C

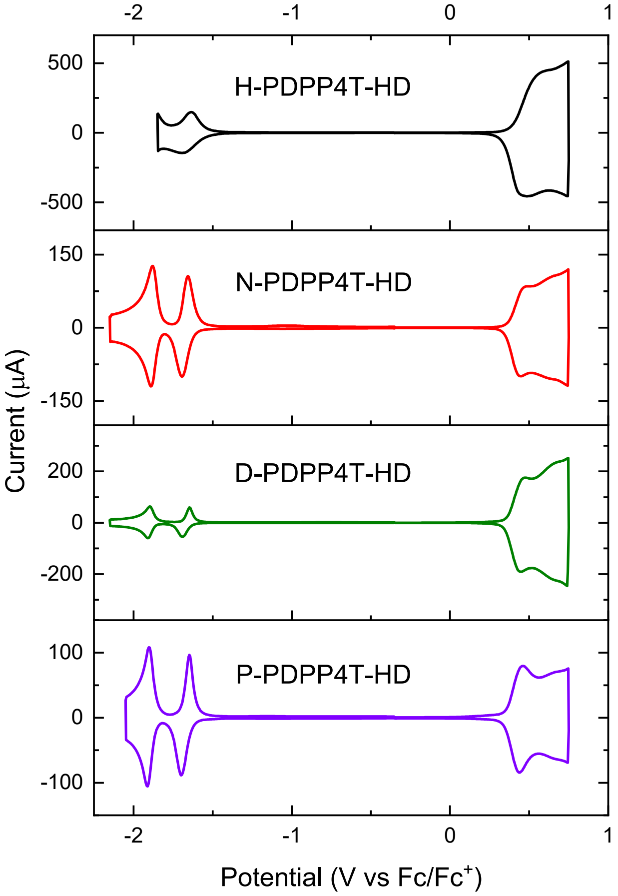


**Fig. S2.** Square-wave voltammograms of PDPP4T-HD polymers.

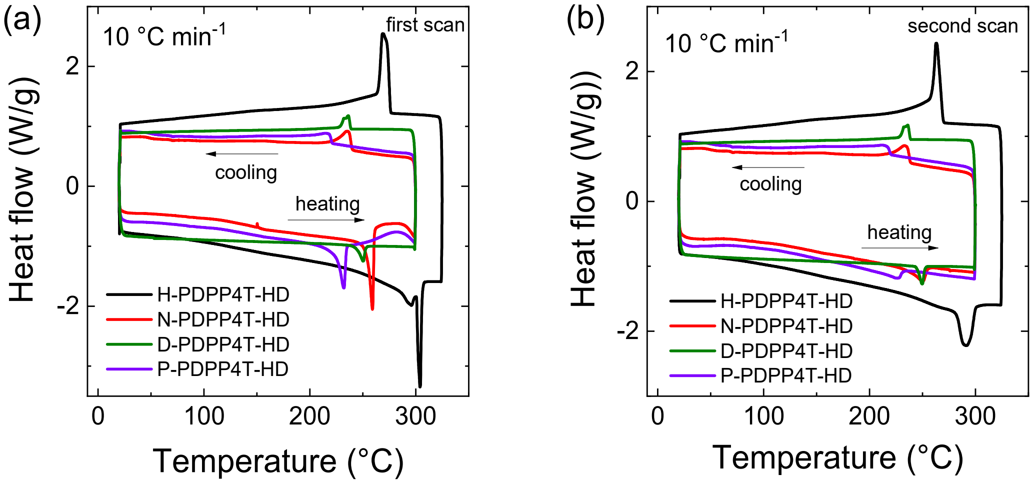


**Fig. S3.** DSC thermograms of PDPP4T-HD polymers. (a) First scan. (b) Second scan. The scan rate is 10 °C min$^{-1}$.

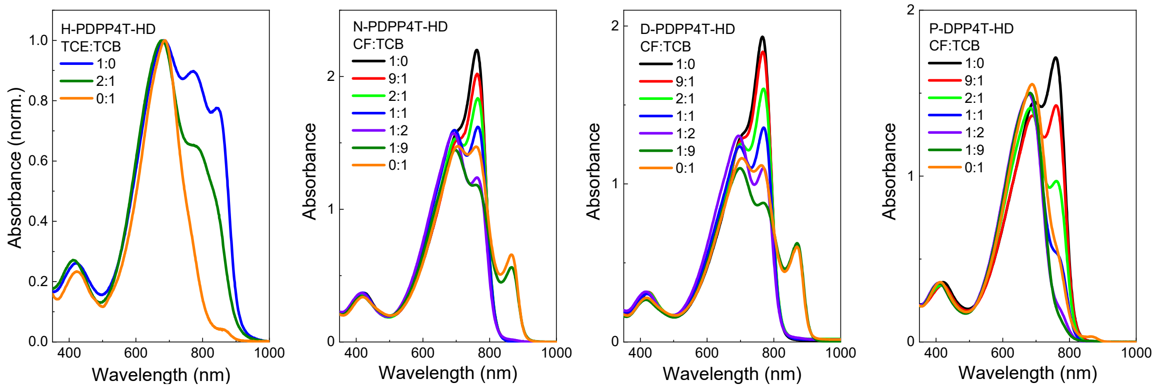


**Fig. S4.** UV-vis-NIR absorption of polymer solutions in different solvent mixtures. For H-PDPP4T-HD, mixtures of TCE and TCB were used. For N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD, mixtures of CF and TCB were used.

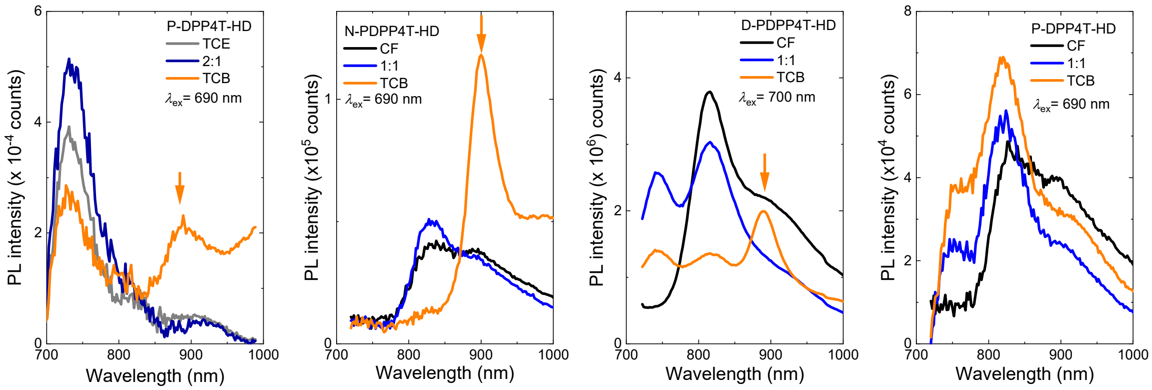


**Fig. S5.** Photoluminescence spectra of polymer solutions in different solvent mixtures. For H-PDPP4T-HD, mixtures of TCE and TCB were used. For N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD, mixtures of CF and TCB were used. Excitation wavelength is given in the legend.

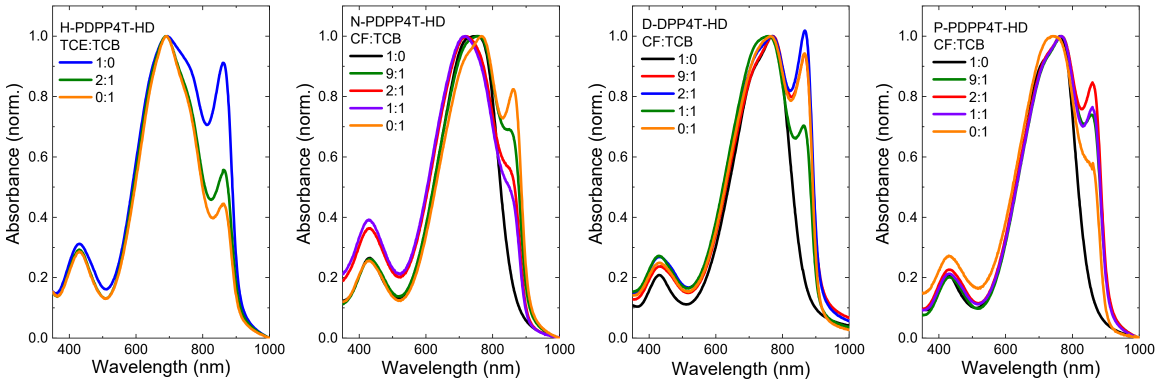


**Fig. S6.** Normalized UV-vis-NIR absorption spectra of polymer thin films processed from different solvent mixtures. All films were spin-coated on glass substrates from 3 mg mL$^{-1}$ solutions. For H-PDPP4T-HD, mixtures of TCE and TCB were used. For N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD, mixtures of CF and TCB were used.

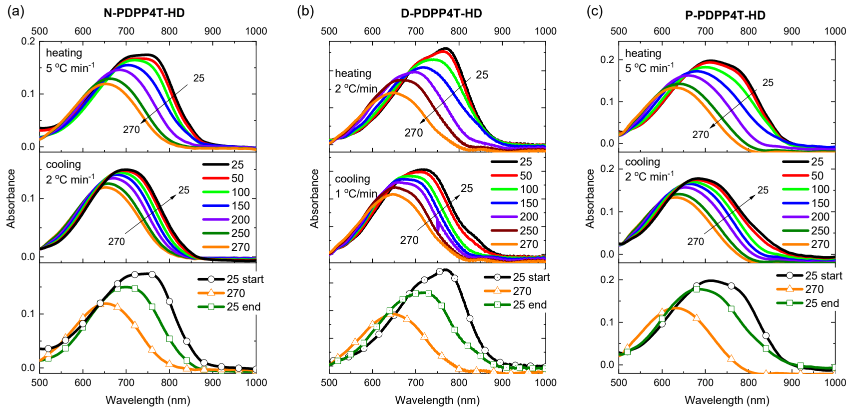


**Fig. S7.** UV-vis-NIR optical absorption of PDPP4T-HD polymer films under $N_2$ atmosphere recorded at different temperatures during heating (5 °C min$^{-1}$, top panels) and cooling (2 °C min$^{-1}$, middle panels). The bottom panels compare the optical absorption before and after thermal annealing. (a) N-PDPP4T-HD. (b) D-PDPP4T-HD. (c) P-PDPP4T-HD. Thin films were processed from CF to generate the semi-crystalline $\beta_1$ phase. Upon heating the $\beta_1$ phase transforms into the amorphous $\alpha$ phase. Subsequent cooling only partly restores the $\beta_1$ phase.

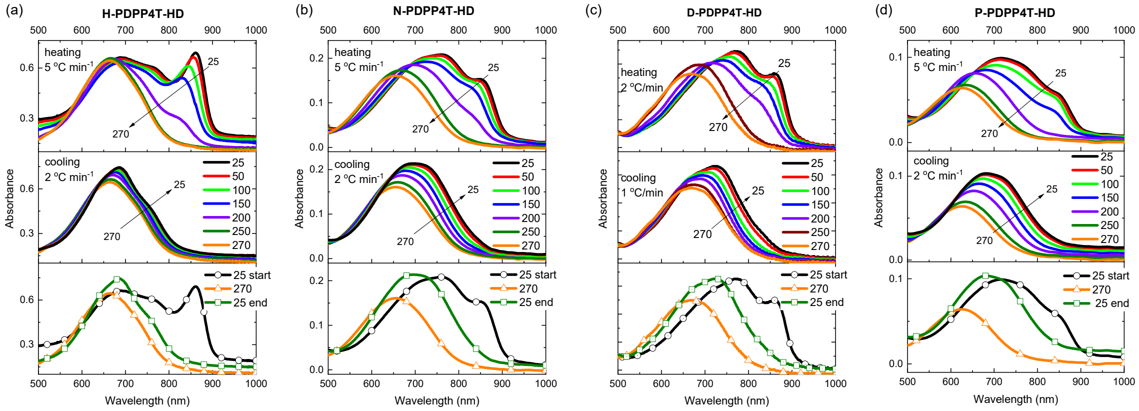


**Fig. S8.** UV-vis-NIR optical absorption of PDPP4T-HD polymer films under $N_2$ atmosphere recorded at different temperatures during heating (5 °C min$^{-1}$, top panels) and cooling (2 °C min$^{-1}$, middle panels). The bottom panels compare the optical absorption before and after thermal annealing. (a) H-PDPP4T-HD. (b) N-PDPP4T-HD. (c) D-PDPP4T-HD. (d) P-PDPP4T-HD. Thin films were processed from CF/TCB (9:1) or pure TCE for H-PDPP4T-HD to generate the semi-crystalline $\beta_2$ phase. Upon heating the $\beta_2$ phase transforms into the amorphous $\alpha$ phase. Subsequent cooling does not restore the $\beta_2$ phase, but gives a red shift.

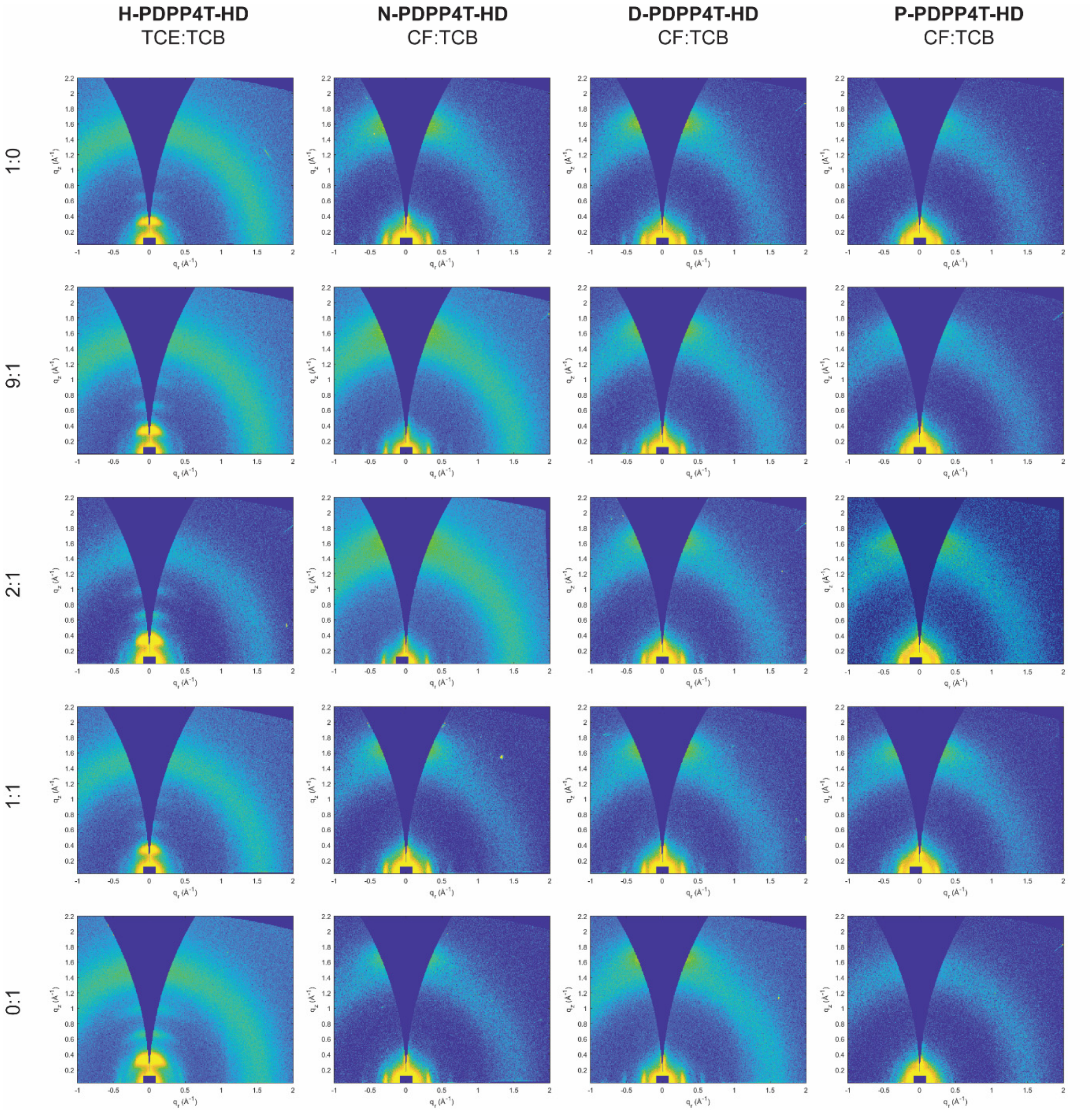


**Fig. S9.** 2D GIWAXS patterns of the PDPP4T-HD polymers spin-coated from various solvent mixtures.

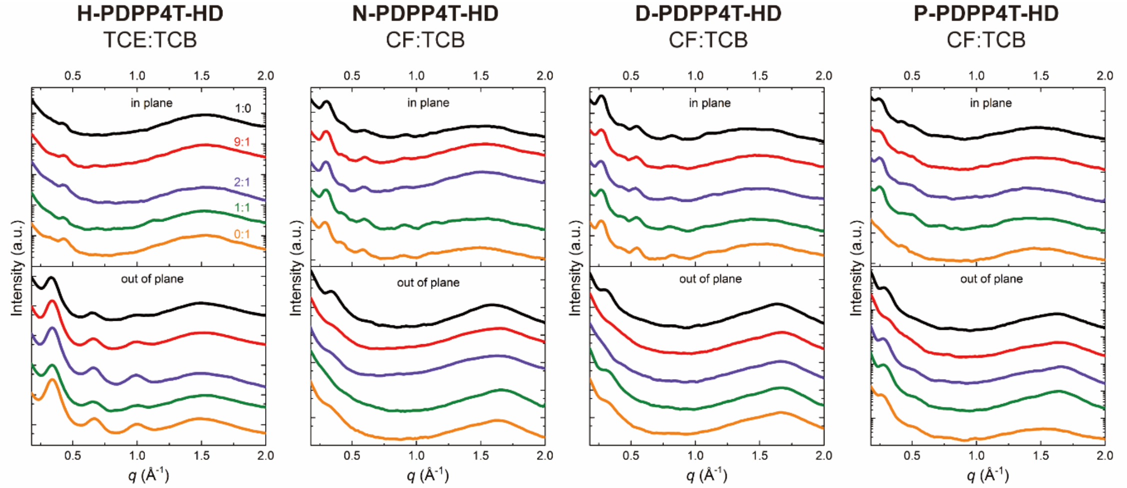


**Fig. S10.** In-plane and out-of-plane GIWAXS profiles of PDPP4T-HD polymers spin-coated from different solvent mixtures.

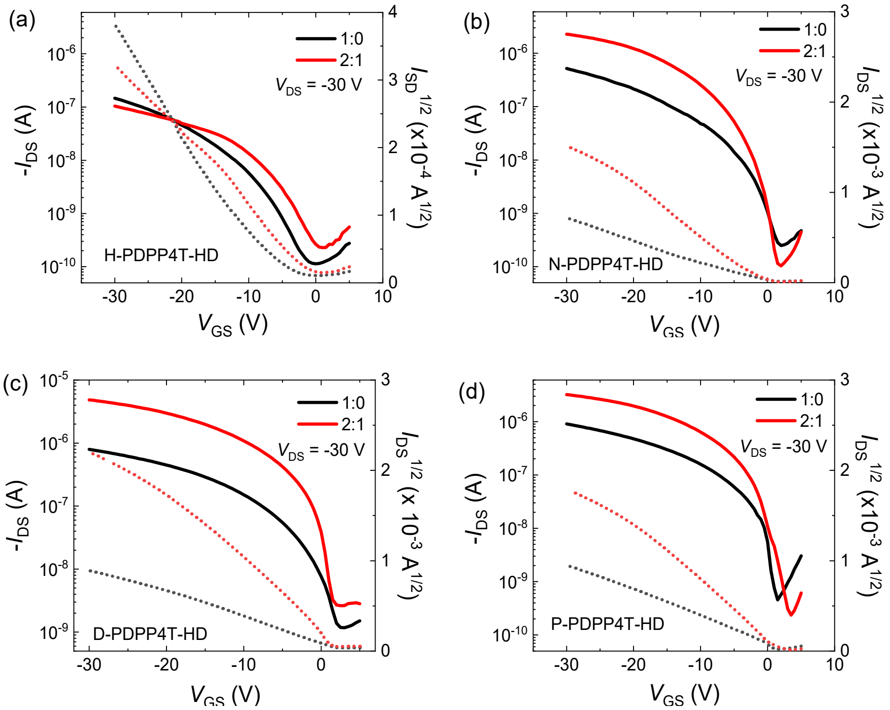


**Fig. S11**. Transfer characteristics of polymer field-effect transistors where a drain voltage ($V_{DS}$) of −30 V was applied and the gate potential ($V_{GS}$) was varied between +5 and −30 V. Solid lines represent $I_{SD}$ (left axis); dotted lines $I_{SD}^{1/2}$ (right axis). (a) H-PDPP4T-HD. (b) N-PDPP4T-HD. (c) D-PDPP4T-HD. (d) P-PDPP4T-HD. Thin films of H-PDPP4T-HD were processed from TCE/TCB in ratios of 1:0 and 2:1. Thin films of N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD were processed from CF/TCB in ratios of 1:0 and 2:1.

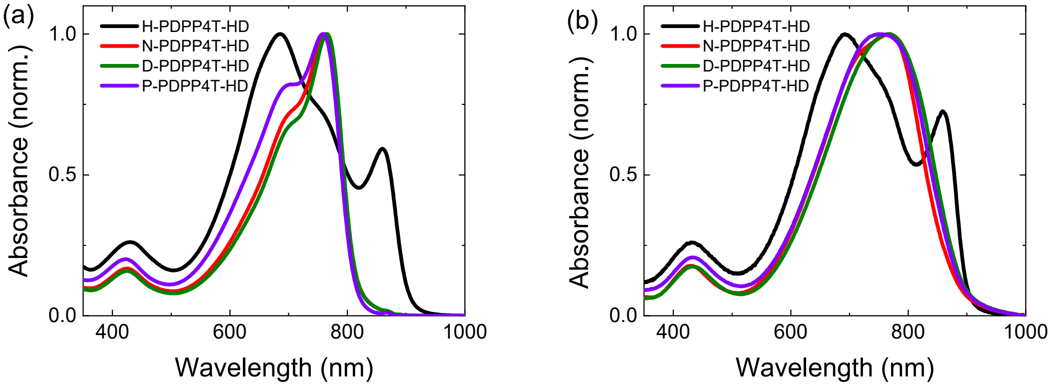
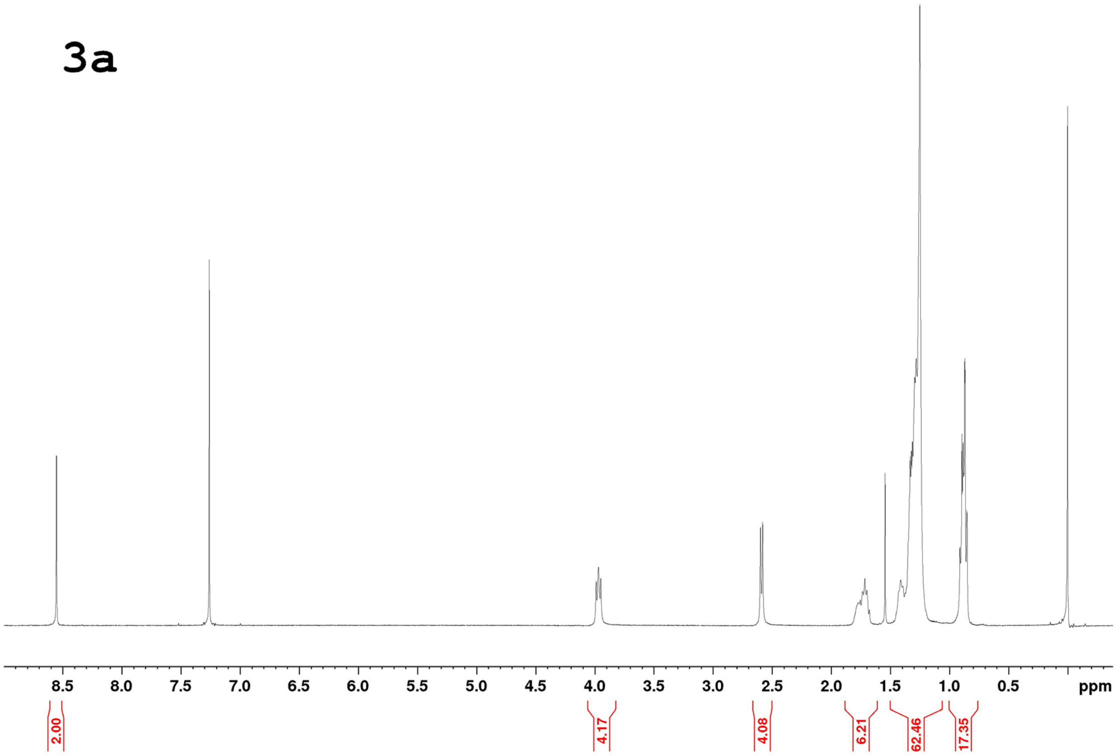
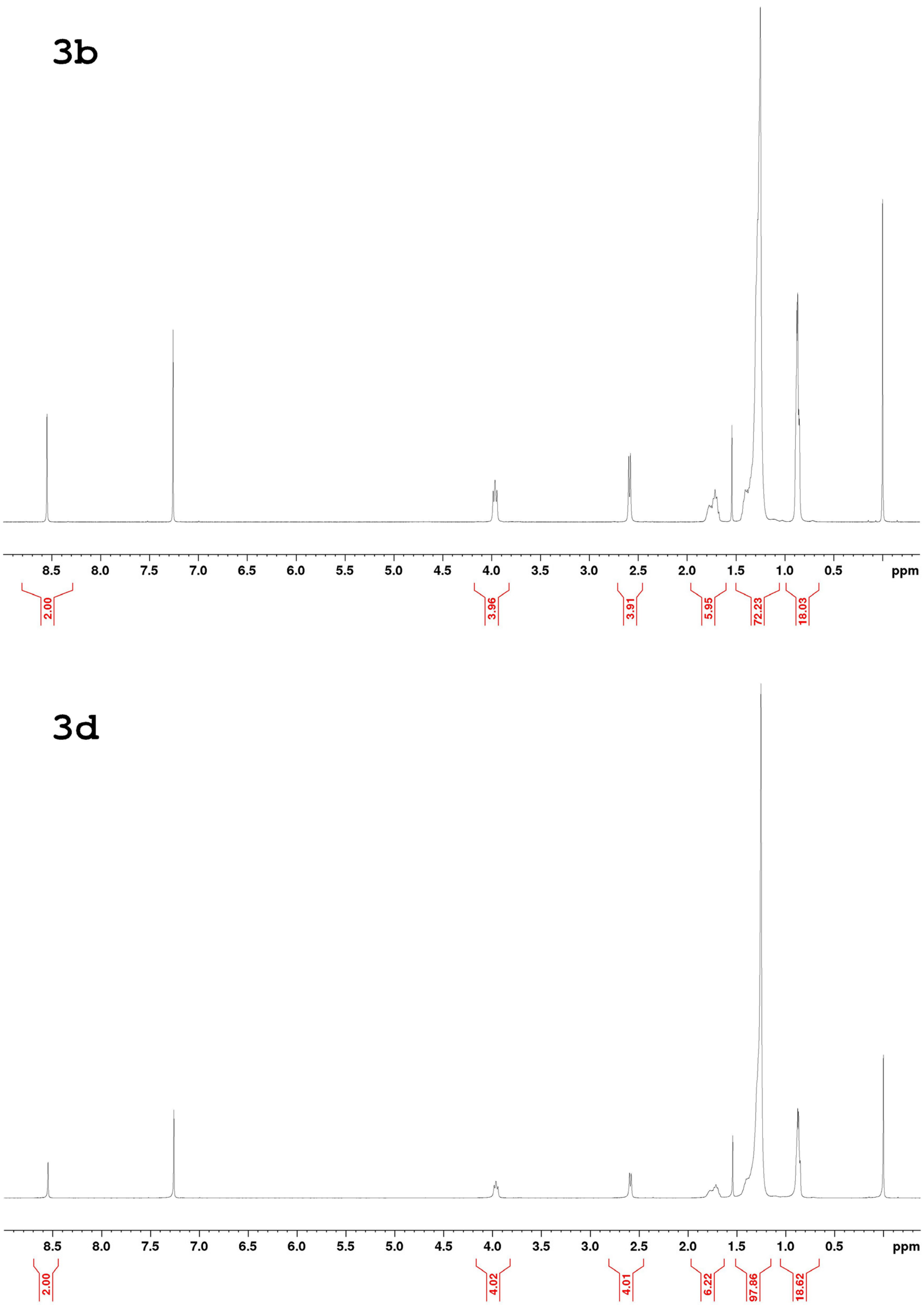


**Fig. S12.** UV-vis-NIR absorption spectra of (a) solutions and (b) thin films with 10% DPE. For H-PDPP4T-HD, the main solvent is TCE, while it is CF for N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD. Films of N-PDPP4T-HD, D-PDPP4T-HD, and P-PDPP4T-HD show no clear signal of the $\beta_2$ phase although the falling edge at the long wavelength is slightly red shifted compared to spectra of the polymers cast from pure CF (Fig. S6). The film of H-PDPP4T-HD was cast from a solution of TCE/DPE at 140 °C onto a room temperature substrate. The other films were cast from CF/DPE solutions on a room temperature substrate.





**F Fig. S13**. $^1$H-NMR spectra of **3a**, **3b** and **3d**.

## References

1 G. H. L. Heintges, P. J. Leenaers and R. A. J. Janssen, *J. Mater. Chem. A*, 2017, **5**, 13748−13756.

2 R. E. M Willems, C. H. L. Weijtens, X. de Vries, R. Coehoorn and R. A. J Janssen, *Adv. Energy Mater.*, 2019, **9**, 1803677

3 Z. Jiang, *J. Appl. Cryst.*, 2015, **48**, 917−926.

4 D. Choi, P.-H. Chu, M. McBride and E. Reichmanis, *Chem. Mater.*, 2015, **27**, 4167−4168.