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Supporting Information

Fluorination in Thieno[3,4-*c*]pyrrole-4,6-idone Copolymers leading to Electron Transport, high Crystallinity and End-on Alignment

*Tina Weller,[a] Marion Breunig,[a] Christian J. Müller,[a] Elliot Gann[c], Christopher R. McNeill[b] and Mukundan Thelakkat[a]**

[a.] Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany. *E-Mail: mukundan.thelakkat@uni-bayreuth.de

[b.] Department of Materials Engineering, Monash University, Wellington Road, Clayton VIC, 3800, Australia.

[c.] Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Dr, Gaithersburg, MD 20899, USA.

* Corresponding author: mukundan.thelakkat@uni-bayreuth.de

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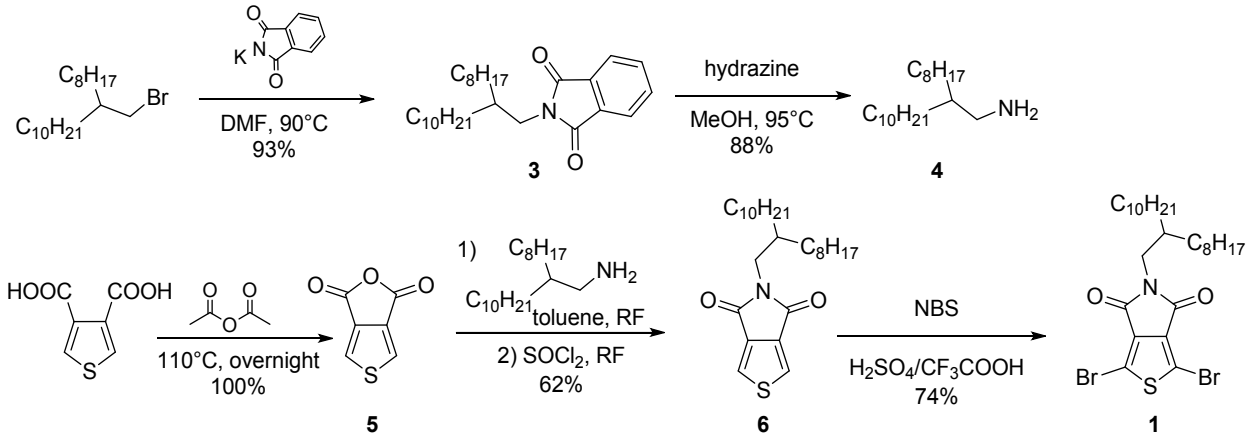
1 Monomer Syntheses

1.1 Materials and Methods

Water and air sensitive reactions were conducted in Schlenk apparatuses under argon, which were previously baked out in high vacuum. Commercially available solvents were purchased from Sigma Aldrich and Acros Organics in sealed bottles with mole sieve. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer with deuterated solvents purchased from Deutero. On this spectrometer, also ^{19}F-NMR was recorded using hexafluorobenzene as external standard. Chemical shifts are reported in ppm relative to the known value of residual solvent signal. Molecular weights were assessed by the electron ionization mass spectrometry performed on a Finnigan MAT 8500 spectrometer (70 eV) at the Department of Chemistry of University Bayreuth. 9-(Bromomethyl)nonadecane was synthesized as reported in the literature.[1]

1.2 Synthesis of the TPD monomer

The overall synthesis of the TPD monomer is shown in scheme S1 and the synthetic procedures are adapted from literature.[2,3]



Scheme S1. Synthesis of the TPD monomer.

***N*-(2-Octyldodecyl)-phthalimide 3**

To a solution of 9-(bromomethyl)nonadecane (20.0 g, 55.3 mmol, 1 eq) in 60 mL anhydrous dimethylformamide potassium phthalimide (11.3 g, 60.9 mmol, 1.1 eq) was added. After stirring for 18 h at 90 °C, the mixture was cooled to room temperature followed by the addition of 100 mL water. The aqueous phase was extracted with dichloromethane (3 x 50 mL) and the combined organic phases were washed with aqueous solution of KOH (0.2 M) followed by water and saturated aqueous solution of NH_4Cl (each 200 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The crude oil was purified by flash column chromatography (silica; Hex:DCM 1:1) yielding *N*-(2-octyldodecyl)-phthalimide **3** (21.9 g, 51.2 mmol, 93%) as a colorless liquid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.79-7.91 (m, 2H), 7.63-7.78 (m, 2H), 3.56 (d, *J* = 7.3 Hz, 2H), 1.78-1.96 (m, 1H), 1.14-1.39 (m, 32 H), 0.79-0.94 ppm (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.92, 134.00, 132.28, 123.34, 42.49, 37.18, 32.10, 32.08, 31.62, 30.15, 29.82, 29.79, 29.74, 29.53, 29.48, 26.46, 22.86, 14.32 ppm. EI-MS (70 eV): *m/z* 427 (M^+).

2-Octyl-1-dodecylamine 4

To a solution of *N*-(2-octyldodecyl)-phthalimide 3 (21.9 g, 51.2 mmol, 1 eq) in 200 mL methanol were added hydrazine (4.80 mL, 154 mmol, 3 eq). The reaction mixture was stirred for 5 h at 95 °C until fully conversion was detected by TLC. After cooling to room temperature the solvent was reduced using rotary evaporation. Addition of 250 mL aqueous solution of KOH (10 wt%) was followed by extraction with DCM (3 x 200 mL). The combined organic layers were washed with saturated, aqueous solution of NaCl (300 mL) and dried over $MgSO_4$. After filtration

the solvent was removed under reduced pressure and dried in high vacuum yielding 2-octyl-1-dodecylamine 4 (13.4 g, 45.0 mmol, 88%) as a colorless liquid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.64 (d, *J* = 5.5 Hz, 2H), 2.38 (br, 2H), 1.13-1.46 (m, 33 H), 0.78-0.94 ppm (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 32.11, 30.25, 30.17, 30.03, 29.88, 29.84, 29.80, 29.57, 29.54, 26.79, 22.88, 14.32 ppm. EI-MS (70 eV): *m/z* 297 (M^+).

Thieno[3,4-c]furan-1,3-dione 5

Thiophene-3,4-dicarboxylic acid (25.0 g, 145 mmol) was dissolved in 250 mL acetic anhydride and stirred at 110 °C overnight. After cooling to room temperature the solvent was removed under reduced pressure yielding thieno[3,4-c]furan-1,3-dione **3** (22.4 g, 145 mmol, 100%) as a light brown solid.

^{1}H-NMR (300 MHz, $CHCl_3$): δ = 8.09 ppm (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.50, 135.69, 129.48, 129.44 ppm. EI-MS (70 eV): *m/z* 155 $(M+H)^+$.

5-(2-Octyl-1-dodecyl)-4*H*-thieno[3,4-c]pyrrol-4,6(5*H*)-dione 6

A solution of octyl-1-dodecylamine **4** (13.4 g, 45.0 mmol, 1.5 eq) and thieno[3,4-c]furan-1,3-dione **3** (4.60 g, 30.0 mmol, 1.0 eq) in 200 mL toluene was stirred for 24 h under reflux. After cooling to room temperature the solvent was removed under reduced pressure followed by the addition of 200 mL thionylchloride. The solution was stirred for 3 h at 75 °C and the thionylchloride was subsequent removed in high vacuum. Purification was carried out with column chromatography (silica; Hex:DCM 2:1) yielding 5-(2-octyl-1-dodecyl)-4*H*-thieno[3,4-c]pyrrol-4,6(5*H*)-dione **6** (9.60 g, 22.2 mmol, 74%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.80 (s, 2H), 3.50 (d, *J* = 7.3 Hz, 2H), 1.75- 1.91 (m, 1H), 1.15-1.43 (m, 32H), 0.80-0.93 ppm (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.11, 136.77,

125.62, 128.58, 42.92, 37.04, 32.10, 32.08, 31.58, 30.16, 29.82, 29.79, 29.74, 29.53, 29.49, 26.42, 22.88, 22.86, 14.32 ppm. EI-MS (70 eV): *m/z* 591 (M^+).

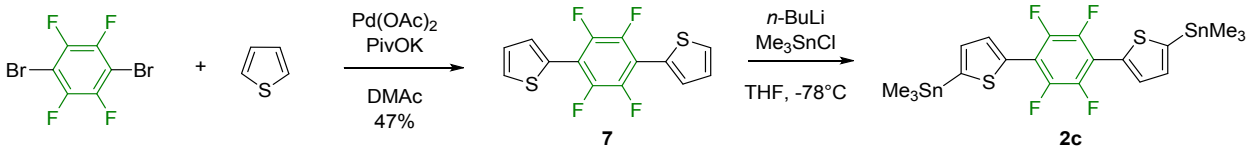
1,3-Dibromo-5-(2-octyl-1-dodecly)-4*H*-thieno[3,4-c]pyrrol-4,6(5*H*)-dione 1

In a mixture of 25 mL sulfuric acid and 75 mL trifluoroacetic acid 5-(2-octyl-1-dodecyl)-4*H*-thieno[3,4-c]pyrrol-4,6(5*H*)-dione **6** (6.00 g, 13.8 mmol, 1 eq) was dissolved and cooled to 0 °C. After addition of *N*-bromosuccinimide (7.40 g, 41.5 mmol, 3 eq) in portions the cooling bath was removed and the solution was stirred overnight at room temperature. The solution was added dropwise to ice water resulting in a yellow suspension, which was extracted with DCM (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification was carried out with column chromatography (silica; gradient: Hex:DCM 4:1 - 2:1) yielding 1,3-dibromo-5-(2-octyl-1-dodecly-4*H*-thieno[3,4-c]pyrrol-4,6(5*H*)-dione 1 (5.1 g, 8.59 mmol, 62%) as a light yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.47 (d, *J* = 7.3 Hz, 2H), 1.74-1.87 (m, 1 H), 1.25 (s, 29 H), 0.82-0.93 ppm (m, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 160.84, 134.88, 113.10, 43.27, 37.02, 32.11, 32.08, 31.61, 30.10, 29.83, 29.79, 29.75, 29.54, 29.49, 26.46, 22.88, 22.87, 14.33 ppm. EI-MS (70 eV): *m/z* 647 (M^+).

1.3 Synthesis of the TPF_4T monomer

Synthetic procedure are adapted from literature.[4,5]



Scheme S2. Synthesis of the TPF_4T monomer.

2,2'-(Perfluoro-1,4-phenylene)dithiophene 7

A solution of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (2.00 g, 6.50 mmol, 1.0 eq), thiophene (7.70 mL, 97.0 mmol, 15 eq) and potassium pivalate (2.28 g, 16.2 mmol, 2.5 eq) in 34 mL anhydrous dimethylacetamide was degassed for 10 min followed by addition of palladium(II)acetate (73.0 mg, 0.325 mmol, 0.05 eq). After stirring for 3 days at 80 °C, the solution was cooled to room temperature. The solvent was removed under reduced pressure. Purification was carried out by column chromatography (silica; Hex) yielding 2,2'-(perfluoro-1,4-phenylene)dithiophene **7** (1.0 g, 3.2 mmol, 49%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 4.0 Hz, 2H), 7.57 (dd, *J* = 5.3, 1.1 Hz, 2H), 7.21 ppm (dd, *J*=4.7, 4.1 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.12 (d, $J_{C\text{-}F}$ = 249 Hz), 130.38, 128.50, 128.00, 127.50, 112.61 ppm. EI-MS (70 eV): *m/z* 314 (M^+).

(5,5'-(Perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) 2c

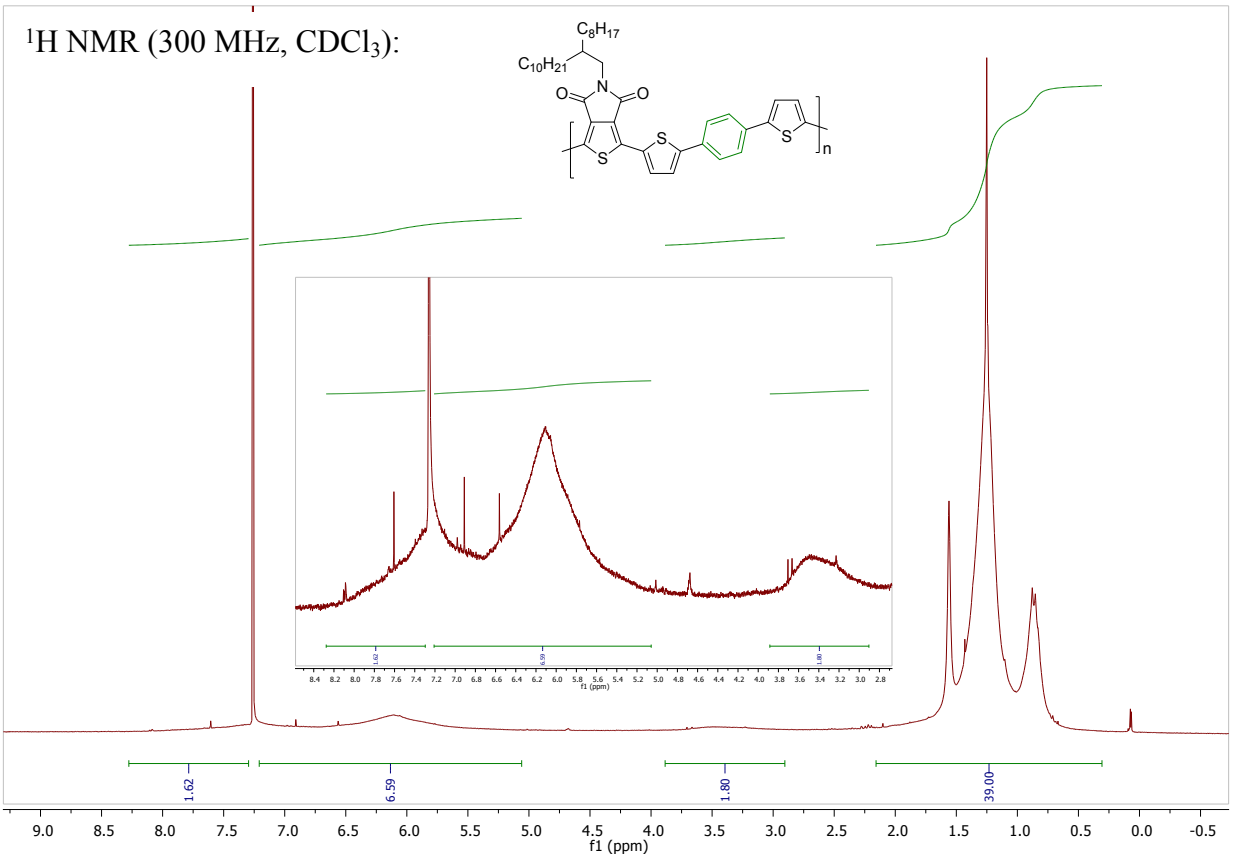
A solution of 2,2'-(perfluoro-1,4-phenylene)dithiophene **7** (0.60 g, 1.9 mmol, 1 eq) in 60 mL anhydrous THF was cooled to -78 °C followed by the addition of a 2.5 M solution of *n*-butyl lithium in hexane (1.6 mL, 4.0 mmol, 2.1 eq). The reaction mixture was stirred for 1 h at -78 °C and trimethyltinchloride (0.80 g, 4.0 mmol, 2.1 eq) was added. After stirring for 1 h at -78 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. Water (50 mL) was added and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic

layers were washed with water and saturated, aqueous solution of NaCl (each 150 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol yielding (5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) **2c** (0.50 mg, 0.78 mmol, 41%) as a colorless solid.

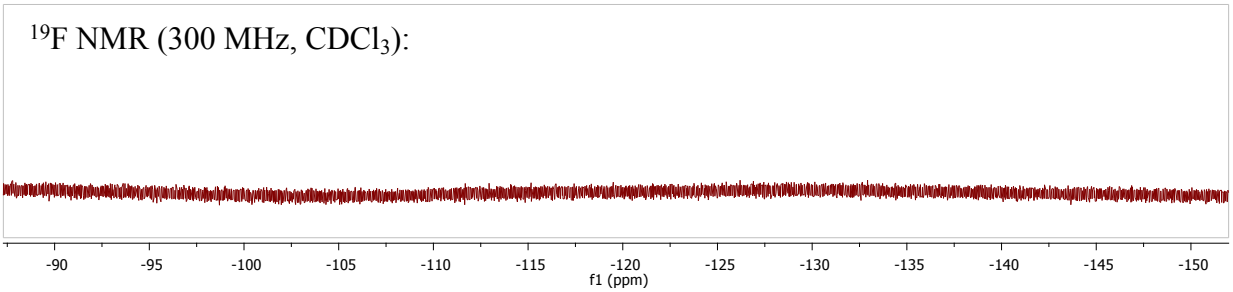
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 3.6 Hz, 2H), 7.28 (d, *J* = 3.6 Hz, 3H), 0.43 ppm (s, 16H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.91 (d, J_{C-F} = 254 Hz), 135.43, 135.38, 133.53, 131.10, 131.07, -7.92, -7.99 ppm. EI-MS (70 eV): *m/z* 640 (M^+).

2 Polymer NMR spectra

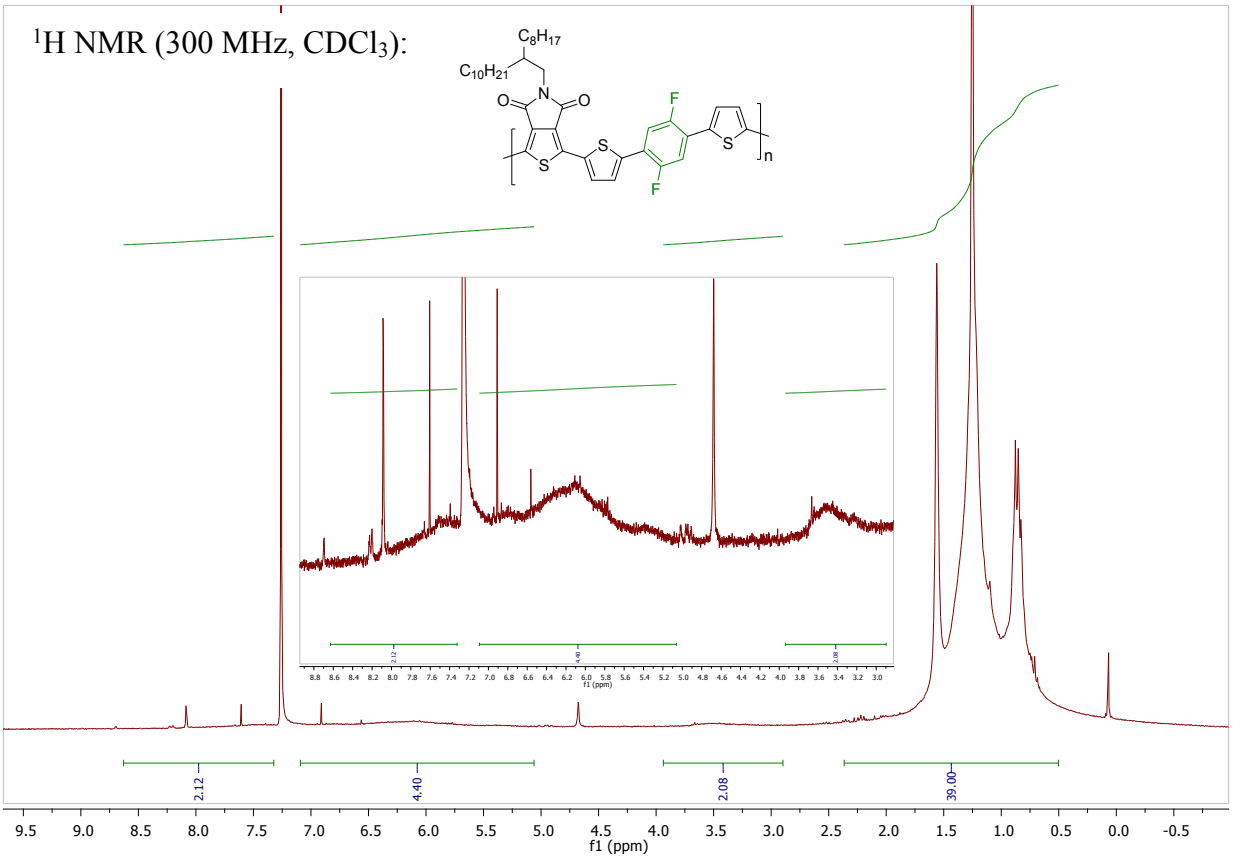
^{1}H NMR (300 MHz, $CDCl_3$):



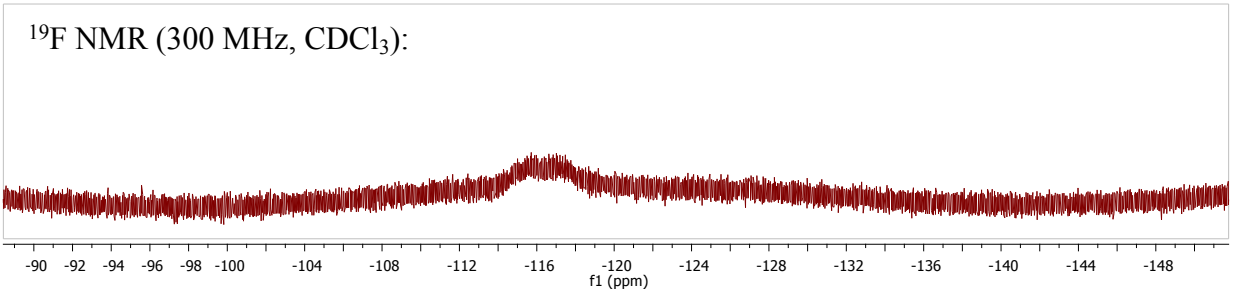
^{19}F NMR (300 MHz, $CDCl_3$):



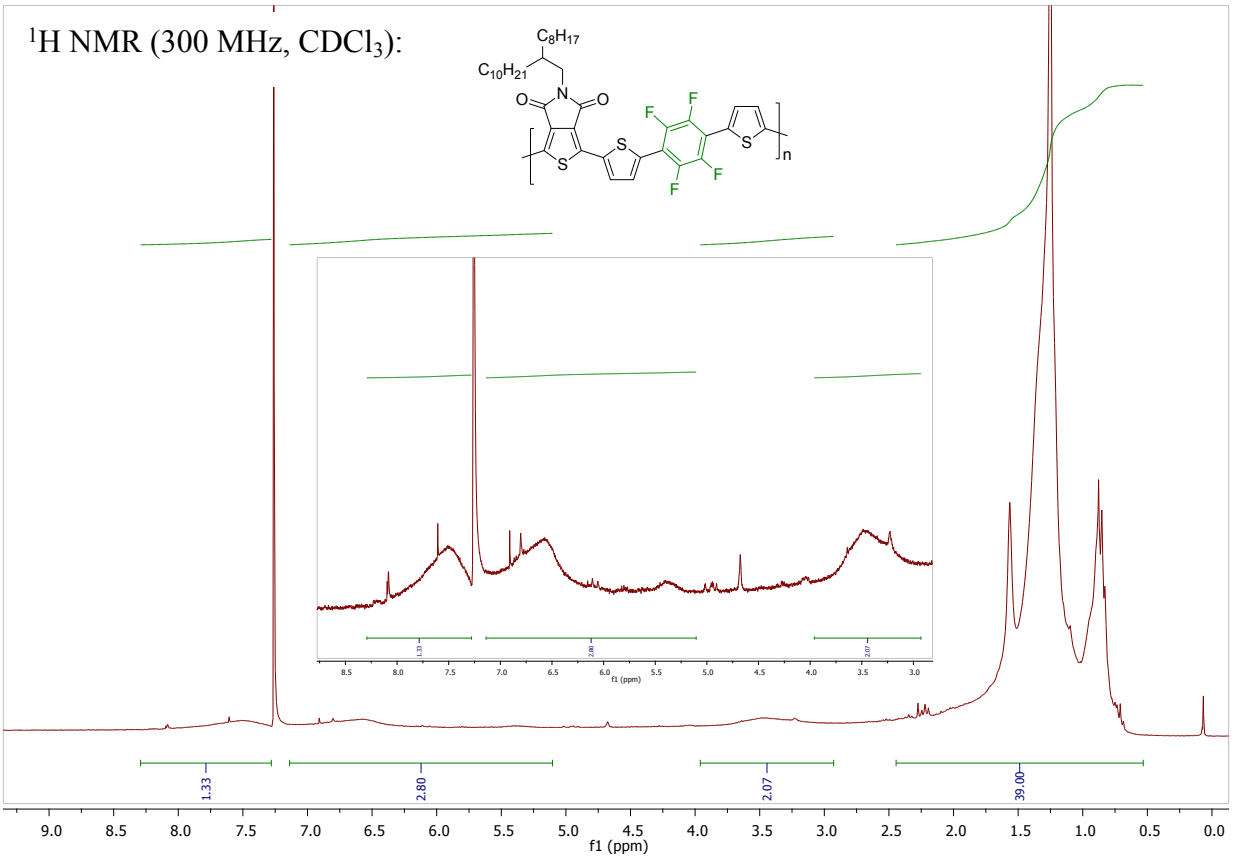
^{1}H NMR (300 MHz, $CDCl_3$):



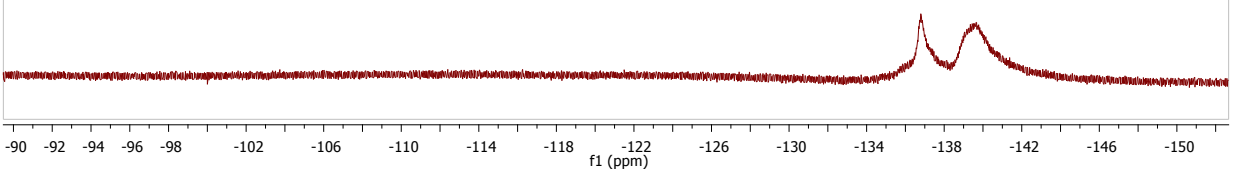
^{19}F NMR (300 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



^{19}F NMR (300 MHz, $CDCl_3$):



3 Thermal Properties

3.1 Thermogravimetric Analysis (TGA)

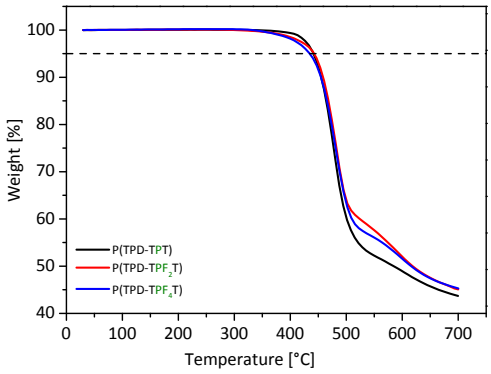


Figure S1. Thermogravimetric analysis of the PTPDs with the decomposition onset ($T_{5\%}$).

3.2 Flash-Differential Scanning Calorimetry (DSC)

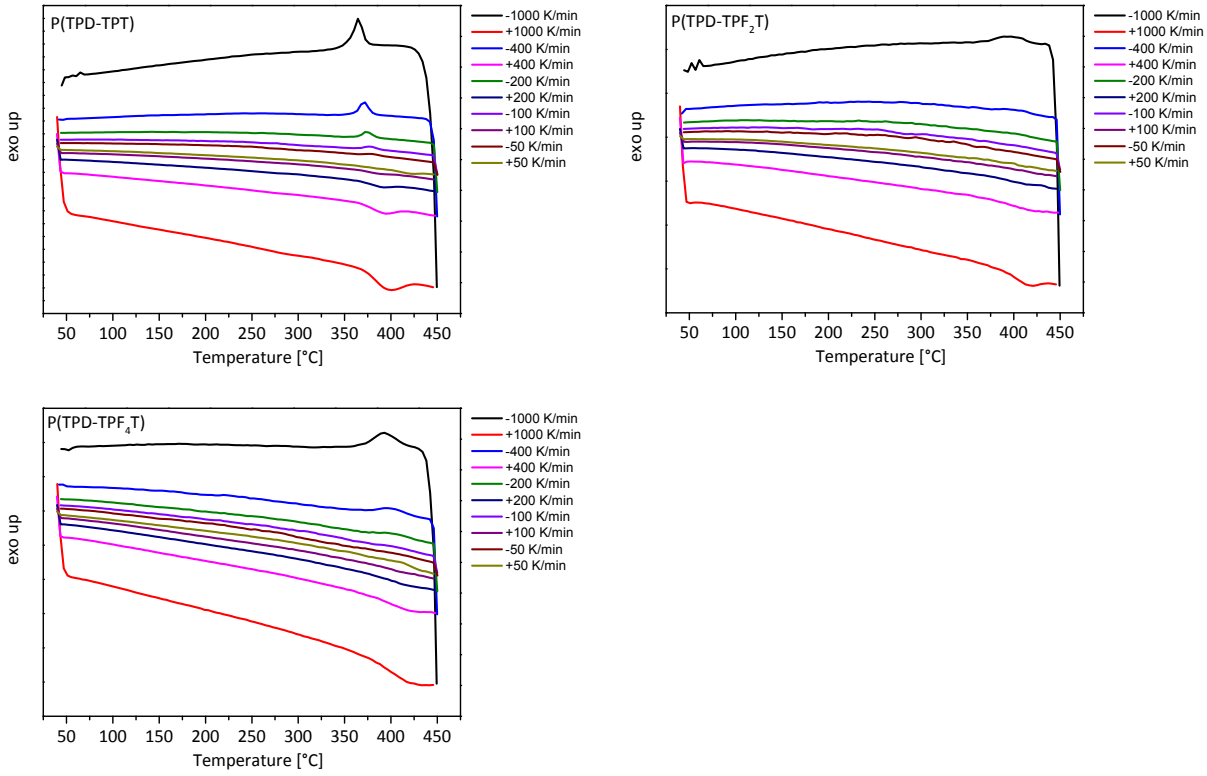


Figure S2. Flash-DSC analysis of the PTPDs with scanning rates from 50-1000 K/min.

4 UV-Vis and fluorescence spectroscopy

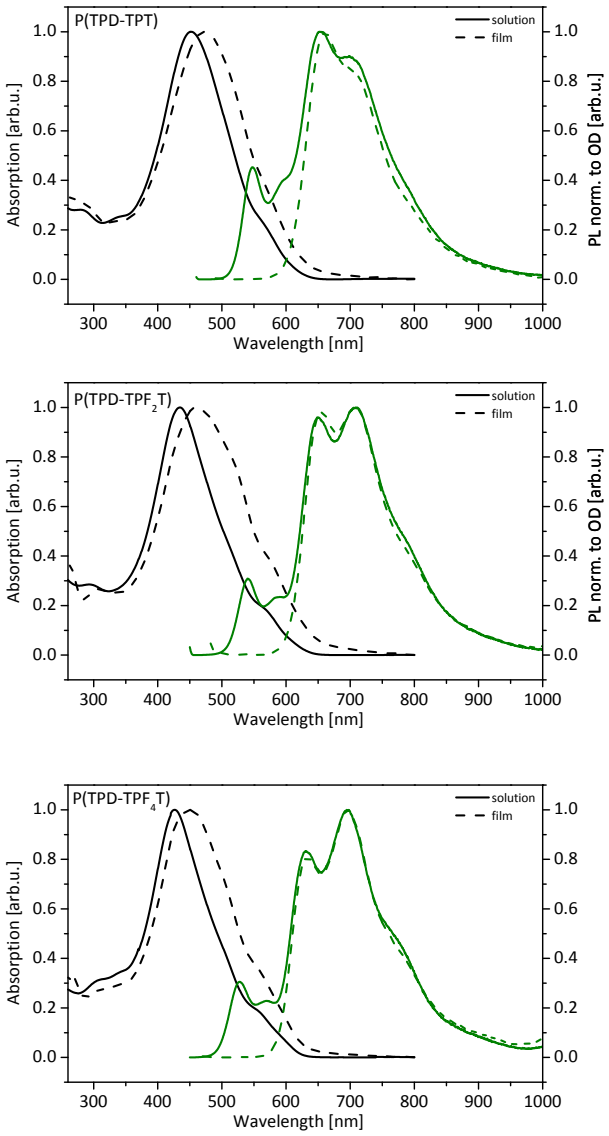


Figure S3. UV-Vis and photoluminescence spectra in solution and thin films for each PTPD.

5 OFET *I-V* curves

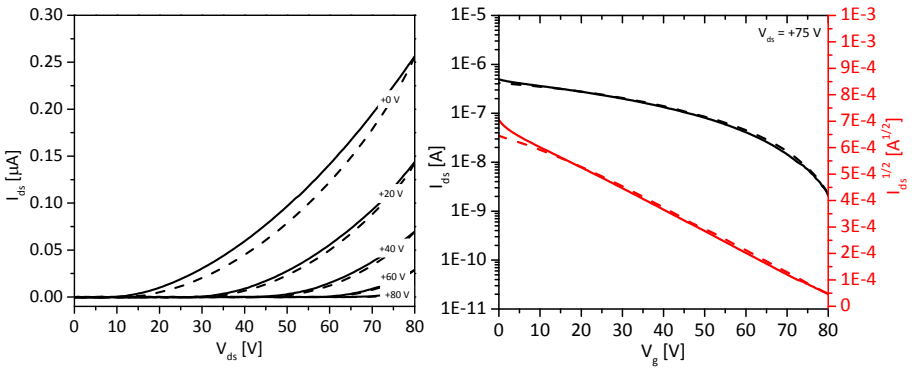


Figure S4: OFET output (left) and transfer (right) characteristics: n-channel operation of P(TPD-TPT) in the as cast state. Solid lines represent forward scans and dashed lines reversed scans.

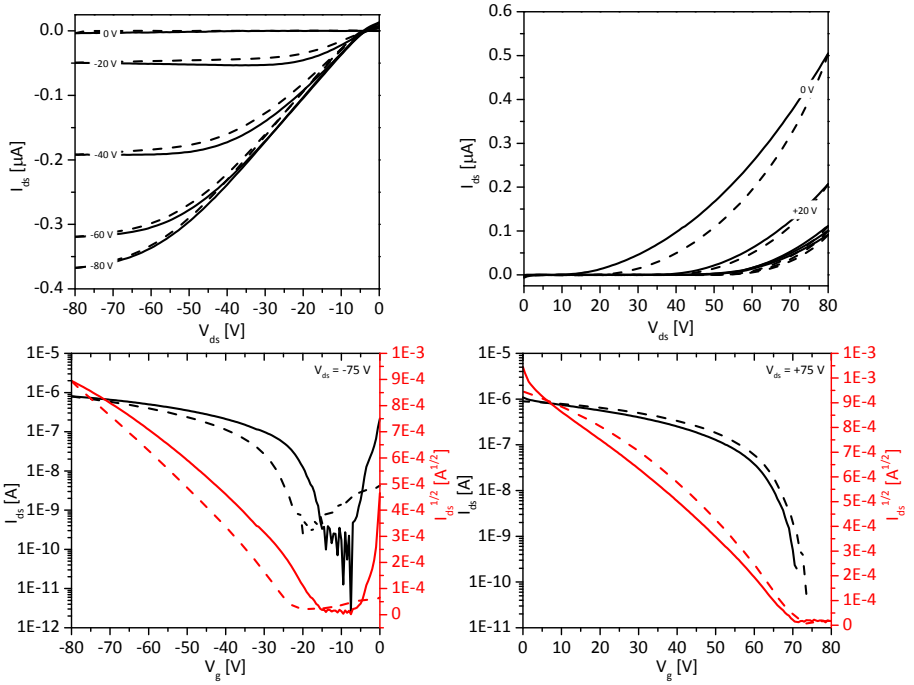
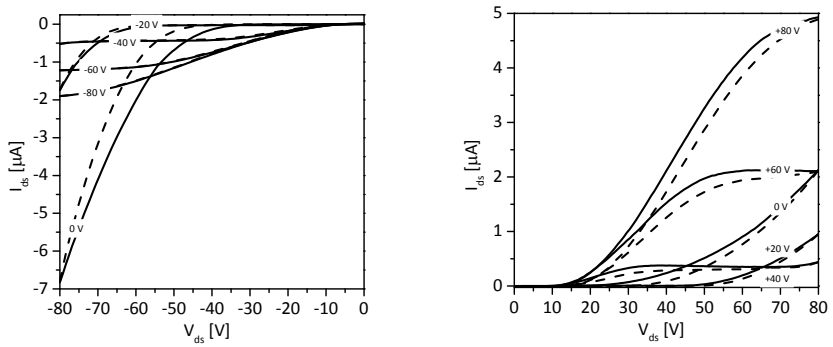


Figure S5: OFET output (top) and transfer (bottom) characteristics: p-channel operation (left) and n-channel operation (right) of P(TPD-TPF_2T) in the as cast state. Solid lines represent forward scans and dashed lines reversed scans.



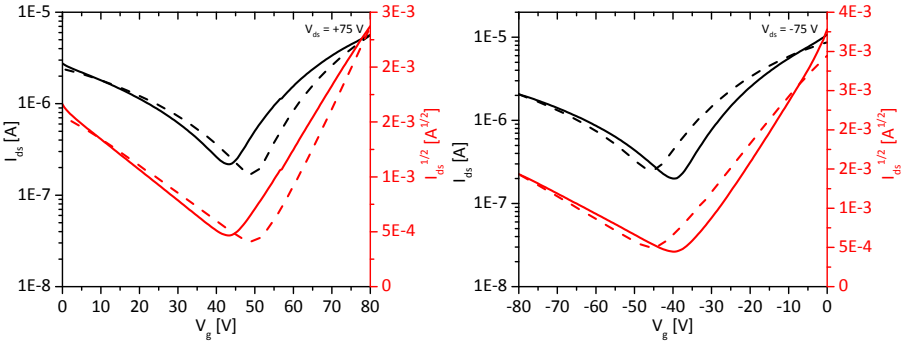


Figure S6: OFET output (top) and transfer (bottom) characteristics: p-channel operation (left) and n-channel operation (right) of P(TPD-TPF_2T) after thermal annealing. Solid lines represent forward scans and dashed lines reversed scans.

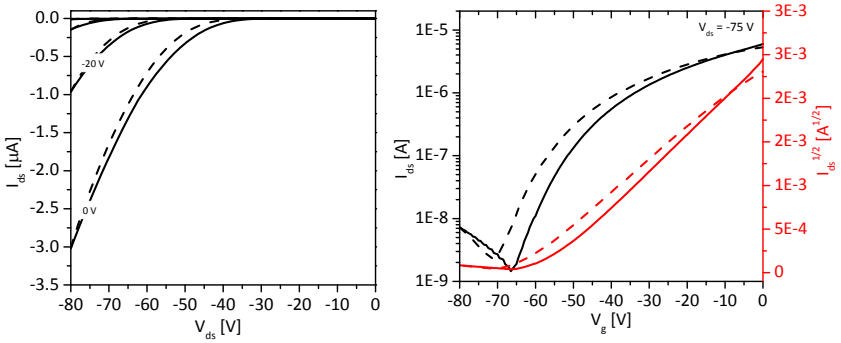


Figure S7: OFET output (left) and transfer (right) characteristics: p-channel operation of P(TPD-TPF_4T) after thermal annealing. Solid lines represent forward scans and dashed lines reversed scans.

Table S1: OFET hole and electron mobilites as well as corresponding threshold voltage for as-cast films and after thermal annealing at 250 °C for 15 min under nitrogen.

	as-cast		annealed			
	μ_h [a]	V_T	μ_h [a]	V_T	μ_e	V_T
	[$cm^2V^{-1}s^{-1}$]	[V]	[$cm^2V^{-1}s^{-1}$]	[V]	[$cm^2V^{-1}s^{-1}$]	[V]
P(TPD-TPT)	(2.5 ± 0.8) x 10^{-5}	4	(0.4 ± 0.1) x 10^{-4}	-14.0	(1.1 ± 0.1) x 10^{-4}	49.8
P(TPD-TPF_2T)	(5.0 ± 1.9) x 10^{-5}	8	(1.1 ± 0.5) x 10^{-4}	-30.3	(3.4 ± 1.5) x 10^{-4}	43.5
P(TPD-TPF_4T)	-	-	-	-	(3.7 ± 1.6) x 10^{-4}	28.3

6 GIWAXS data

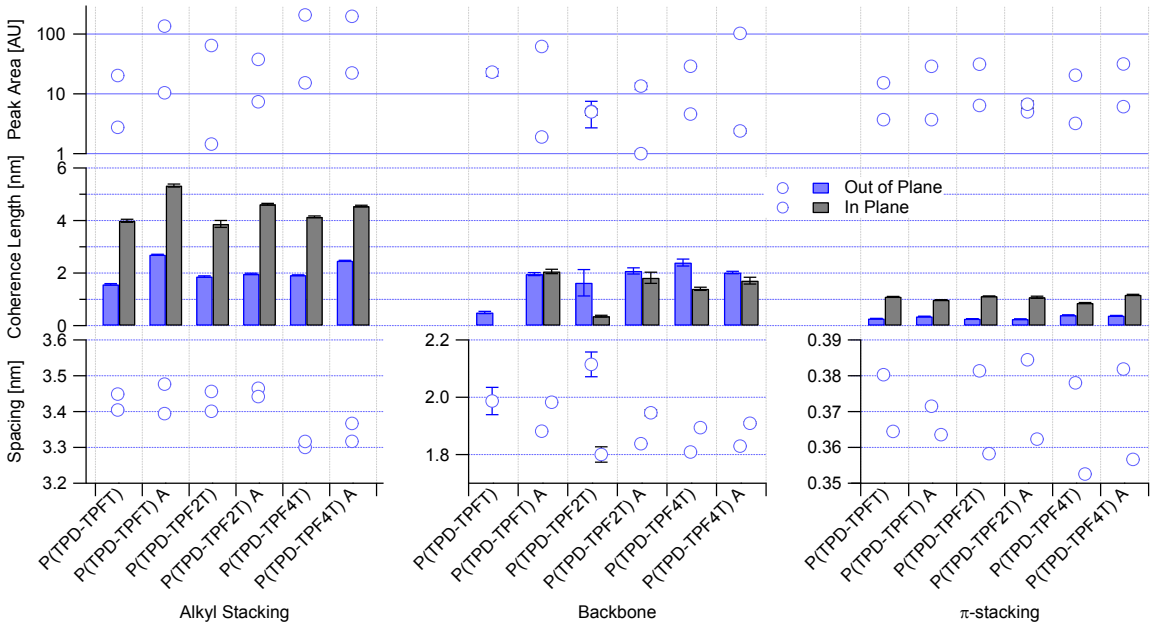


Figure S8: Graphical summary of peak fitting analysis of the out-of-plane and in-plane scattering profiles.

7 References

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