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**Syntheses.**

**9-(Iodomethyl)nonadecane.** A flask was charged with 23.9 ml (67.08 mmol, 1.0 eq.) 2-octyldodecan-1-ol, 21.20 g (80.45 mmol, 1.2 eq.) triphenylphosphine and 5.48 g (80.49 mmol, 1.2 eq.) imidazole, separately dissolved using in total 115 ml DCM. At 0 °C 19.56 g (77.07 mmol, 1.15 eq.) iodine was added in portions and the mixture was stirred for 17 h before it was washed with aqueous Na$_2$S$_2$O$_3$ solution, water and brine and dried over MgSO$_4$. To remove triphenylphosphine oxide, the solution was concentrated under reduced pressure, the white residue suspended in hexane and the mixture passed through a silica gel plug. After two cycles the product was obtained as colorless oil (27.12 g, 99 %). $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ [ppm] = 3.27 (d, 2 H), 1.46 - 1.17 (m, 32 H), 1.13 (m, 1 H), 0.89 (t, 6 H). $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ [ppm] = 38.76, 34.42, 31.92, 31.89, 29.73, 29.62, 29.59, 29.55, 29.34, 29.29, 26.51, 22.68, 16.77, 14.09.

**3,6-Di(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.** A mixture of 60 ml (0.55 mol, 13.7 eq.) anhydrous 2-methyl-2-butanol, 40 mg (0.25 mmol, 0.01 eq.) anhydrous iron(III) chloride and 3.45 g (0.15 mol, 3.8 eq.) sodium pieces were stirred at 90 °C until complete conversion of sodium. Afterwards 10.93 g (0.10 mol, 2.5 eq.) 2-thiophenecarbonitrile were added in one portion and 5.84 g (0.04 mol, 1.0 eq.) dimethyl succinate in 5 ml 2-methyl-2-butanol dropwise over 60 min. After stirring for 2 h at 90 °C the reaction mixture was cooled to 50 °C, diluted with 50 ml methanol and acidified using 15 ml glacial acetic acid. After refluxing for 5 min the mixture was poured into 500 ml ice water, the precipitates were collected by filtration, thoroughly washed with water and warm methanol and dried in vacuum at 40 °C overnight (7.21 g, 60 %). $^1$H-NMR (DMSO-d$_6$, 500 MHz) $\delta$ [ppm] = 11.21 (s, 2 H), 8.21 (dd, 2 H, $^3$J = 3.7 Hz, $^4$J = 1.1 Hz), 7.95 (dd, 2 H, $^3$J = 5.0 Hz, $^4$J = 1.1 Hz), 7.30 (dd, 2 H, $^3$J = 5.0 Hz, $^3$J = 3.7 Hz). $^{13}$C-NMR (DMSO-d$_6$, 125 MHz) $\delta$ [ppm] = 161.67, 136.20, 132.67, 131.31, 130.85, 128.74, 108.61.
2,5-Bis(2-octyldodecyl)-3,6-di(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione. A solution of 7.61 g (25.34 mmol, 1.0 eq.) 3,6-di(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, 0.34 g (1.27 mmol, 0.05 eq.) 18-crown-6 and 12.26 g (88.68 mmol, 3.5 eq.) anhydrous potassium carbonate in 150 ml anhydrous DMF was stirred 2 h at 125 °C. Then, 27.89 g (68.28 mmol, 2.7 eq.) 9-(iodomethyl)nonadecane was added over 1 h and the mixture was stirred for 20 h at 125 °C. After cooling water and EtOAc were added, the solvents removed under reduced pressure, the residue dissolved in EtOAc, washed with water, dried over MgSO$_4$ and concentrated under reduced pressure. The raw product was purified by column chromatography (SiO$_2$/hexane to 10 % diethyl ether/hexane) and the product isolated as dark red solid (9.02 g, 41 %). MALDI-TOF-MS: [M]$^+$: 860.6 (th. [M]$^+$: 860.63). $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ [ppm] = 8.86 (dd, 2 H, $^3$J = 3.8 Hz, $^4$J = 1.1 Hz), 7.61 (dd, 2 H, $^3$J = 5.0 Hz, $^4$J = 1.1 Hz), 7.26 (dd, 2 H, $^3$J = 5.0 Hz, $^3$J = 3.8 Hz), 4.02 (d, 4 H, $^3$J = 7.8 Hz), 1.91 (m, 2 H), 1.46 - 1.03 (m, 64 H), 0.87 and 0.86 (2 t, 12 H). $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ [ppm] = 161.76, 140.43, 135.16, 130.39, 129.87, 128.36, 108.00, 46.25, 37.75, 31.91, 31.86, 31.21, 30.00, 29.63, 29.61, 29.54, 29.34, 29.28, 26.22, 22.67, 22.64, 14.08.

3,6-Bis(5-bromothiophene-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione. To a solution of 5.62 g (6.52 mmol, 1.0 eq.) 2,5-bis(2-octyldodecyl)-3,6-di(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione in 435 ml chloroform at 0 °C was added 2.77 g (15.56 mmol, 2.39 eq.) N-bromosuccinimide and stirred overnight protected from light. The mixture was washed with water and brine, dried over MgSO$_4$ and the crude material was purified by column chromatography (SiO$_2$/hexane to 10 % diethyl ether/hexane) yielding a dark purple solid (5.85 g, 88 %). MALDI-TOF-MS: [M]$^+$: 1016.4 (th. [M]$^+$: 1016.45). $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ [ppm] = 8.61 (d, 2 H, $^3$J = 4.3 Hz), 7.21 (d, 2 H, $^3$J = 4.3 Hz), 3.92 (d, 4 H, $^3$J = 7.9 Hz), 1.88 (m, 2 H), 1.44 - 1.05 (m, 64 H), 0.88 and 0.86 (2 t, 12 H). $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ [ppm] = 161.41, 139.39, 135.28, 131.43, 131.22, 118.93, 108.06, 46.38, 37.78, 31.92, 31.88, 31.22, 29.99, 29.64, 29.56, 29.49, 29.36, 29.29, 26.20, 22.69, 22.67, 14.10.
$^1$H-NMR spectrum of the polymer P(DPP2OD-TT)

**Figure S1.** High-temperature $^1$H-NMR spectra of P(DPP2OD-TT) in C$_2$D$_2$Cl$_4$ at 120 °C.
Figure S2. GPC curves of P(DPP2OD-TT) in CHCl₃ at 40 °C.

Figure S3. HT-GPC curves of P(DPP2OD-TT) in 1,2,4-TCB at 150 °C.
**Figure S4.** TGA measurements of P(DPP2OD-TT) under nitrogen.

**Figure S5.** DSC analysis of P(DPP2OD-TT) under nitrogen with applied heating-cooling-heating cycle up to 350 °C (top) and one maximum heating scan with a new P(DPP2OD-TT) sample.
GIWAXS diffractograms of P2 and P3

**Figure S6.** 2D GIWAXS diffractograms of P2 and P3 as cast and annealed at 200°C.
Figure S7. 2D X-ray diffraction patterns obtained with the beam slightly tilted to the normals of free standing P1 films (a) as cast and (b) annealed at 300 °C. Respective radially averaged patterns along (c) the meridian, and (d) the equator. (e) XRD curves obtained from GIWAXS of thin P1 film showing the (h00) series at the indicated temperatures. (f) Extracted lamellar spacing, d_{100}, and full width at half maximum of the (100) reflection as a function of temperature.
Figure S8. Cyclic voltammograms of dopants in 0.1 M \(n\)-Bu₄NPF₆ acetonitrile solution at 50 mV·s⁻¹ scan rate externally referenced to ferrocene/ferrocenium redox couple (\(E_{1/2}\) adjusted to 0.0 V).

Figure S9. Cyclic voltammetry scans of thin P(DPP2OD-TT) films at a scan rate of 50 mV/s using 0.1 M \(n\)-Bu₄NPF₆ acetonitrile solution and externally referenced to ferrocene/ferrocenium redox couple (\(E_{1/2}\) adjusted to 0.0 V).
<table>
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<tr>
<th></th>
<th>$E_{\text{onset,red}}$ [V]</th>
<th>$E_{1/2,\text{red}}$ [V]</th>
<th>$E_{\text{LUMO}}$ [eV]</th>
<th>$E_{\text{onset,ox}}$ [V]</th>
<th>$E_{\text{HOMO}}$ [eV]</th>
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<td><strong>F$_4$TCNQ</strong></td>
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<td><strong>F$_6$TCNNQ</strong></td>
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<tr>
<td><strong>P(DPP2OD-TT)</strong></td>
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<td>-</td>
<td>-3.84$^c$</td>
<td>0.45</td>
<td>-5.54$^d$</td>
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$^a$First half-wave reduction potentials ($E_{1/2,\text{red}} = (E_{pR,\text{red}} + E_{pA,\text{red}})/2$). $^b$For electrochemically reversible dopants $E_{\text{LUMO}} = -(5.09 + E_{1/2,\text{red}})$[eV]. $^c,d$For electrochemically irreversible P(DPP2OD-TT): $E_{\text{LUMO}} = -(5.09 + E_{\text{onset,red}})$[eV] and $E_{\text{LUMO}} = -(5.09 + E_{\text{onset,ox}})$[eV].