Supporting Information

High balanced ambipolar charge mobility in benzodipyrrolidone conjugated polymers

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General procedures, materials and instruments

All starting materials and reagents were purchased from commercial suppliers unless stated otherwise. All $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz Varian Mercury Spectrometer using deuterated solvents such as CDCl$_3$ and DMSO-d$_6$ with tetramethylsilane (TMS) as an internal standard. Values are given in ppm relative to TMS (0 ppm). UV-vis optical absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer in chloroform solutions in a quartz cell or as a thin film spin coated on glass substrates. Cyclic voltammetry (CV) was performed under an inert atmosphere using an Autolab PGSTAT30 with a three electrode setup equipped with a platinum disc working electrode, a silver counter electrode and a silver electrode coated with silver chloride (Ag/AgCl) as a quasi reference electrode. The ferrocene/ferrocenium (Fc/Fc+) couple was used as an internal standard. All polymers were measured in a 1 M electrolyte solution of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in ortho-dichlorobenzene (ODCB). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) was measured on a PerSeptive Biosystems Voyager – DE PRO spectrometer using either α-cyano-4-hydroxycinnamic acid (CHCA) and/or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrices. Molecular weights were determined by GPC using a PL-GPC 120 High Temperature Chromatograph with a Mixed-C (200 - 2.000.000 Da versus polystyrene standards) column using ODCB at 80 °C as mobile phase. XRD was measured on a Bruker D4 Endeavor diffractometer using Cu Kα radiation with a wavelength of 0.15406 nm. Scans were done from 2 – 30 degrees (2θ) with scan speed of 0.2 seconds/step and increments of 0.01 degree/step. AFM was performed in tapping mode on a Veeco Multimode SPM equipped with a Nanoscope IIIa SPM controller. PPNCH-50 aluminum coated silicon tips from Nanosensors were used with scan rates of 2 Hz.

Field-effect transistors

Field-effect transistors were fabricated on 3 x 3 cm glass substrates in a bottom-contact top-gate configuration. Substrates were cleaned prior to use with soap, demi-water and isopropanol. Gold (30 nm) electrodes were then evaporated with a preceding chromium adhesion layer (3 nm). Active layers were spin coated from a 5 mg/ml polymer chloroform solution at 1000 rpm to give approximately 30 nm active layers that were annealed at 200 °C for 30 minutes to remove solvent residues. A Cytop dielectric was applied by spin coating at 1000 rpm and annealing at 120 °C for 45 minutes to remove solvent residues and provide on average a 1350 nm thick layer. Devices were finalized by evaporation of a gold (50 nm) top gate electrode. Electric characterization was done using a vacuum probe station connected to a Keithley 2636. Channel length and width were 20 and 1000 μm respectively.
Synthesis

Scheme S1 Synthesis of BDP based polymers. (i) Chorobenzene, 125 °C, 24 h. (ii) Concentrated H₂SO₄, r.t., 15 h. (iii) 2 M KOH, hydrogen peroxide and ethanol, r.t., 2 h. (iv) 9-(Bromomethyl)nonadecane, potassium carbonate, DMF, 125 °C, 15 h. (v) 2-(4-Dodecylthiophen-2-yl)-4,5,5-tetramethyl-1,3,2-dioxaborolane, potassium phosphate tribasic, Aliquat 336, triphenylphosphine, Pd₂dba₃, toluene:water (5:1), 110 °C, 15 h. (vi) N-bromosuccinimide, DCM, 0 °C to r.t., 15 h. (vii) 2,5-Bis(trimethylstannyl)thiophene or 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, Pd₂dba₃ triphenylphosphine, toluene:DMF (10:1), 115 °C, 15 h.

**N,N’-(1,4-phenylene)bis(2-(4-bromophenyl)-2-hydroxyacetamide)** (A): 1,2,4-Trichlorobenzene (50 ml) was added to 4-bromo-DL-mandelic acid (10.0 g, 43.3 mmol) and benzene-1,4-diamine (2.1 g, 19.7 mmol) before heating the solution to 150 °C. After 2 hours the mixture was cooled and poured into methanol. The precipitate was filtered and washed with methanol to give 4.0 g (7.5 mmol, 38% yield) of the title compound after drying. ¹HNMR (400MHz, DMSO-d₆) δ (ppm): 9.88 (s, 2H), 7.59 (s, 4H), 7.58 – 7.52 (m, 2H), 7.49 – 7.41 (m, 2H), 6.50 (d, J = 4.7 Hz, 2H), 5.08 (d, J = 4.7 Hz, 2H). ¹³CNMR (100MHz, DMSO-d₆) δ (ppm): 170.85, 140.70, 134.60, 131.41, 129.13, 121.17, 120.42, 73.66.

**3,7-bis[4-bromophenyl]pyrrolo[2,3-f]indole-2,6(1H,5H)-dione** (C): To A (4.0 g, 7.5 mmol) was added concentrated sulfuric acid (100 ml) and the mixture was stirred at room temperature overnight. The solution was then precipitated in a water and ice mixture, filtered and dried to give compound B, which was subsequently used in the next reaction without further purification. The residue was re-dissolved in a mixture of ethanol, 2M KOH and hydrogen peroxide (2.5:1:1) and stirred for 2 hours at room temperature. Then water was added and the precipitate filtered off which was dried in vacuum to give 2.8 g of pale red C (5.6 mmol, 75%). The crude product was used in the next reaction as obtained.

**3,7-bis[4-bromophenyl]-1,5-bis[2-octyldodecyl]pyrrolo[2,3-f]indole-2,6(1H,5H)-dione** (1): Under an argon atmosphere C (700 mg, 1.4 mmol), 9-(bromomethyl)nonadecane (1.5 g, 4.2 mmol) and potassium carbonate (0.9 g, 7 mmol) were dissolved in DMF, heated to 125 °C and stirred at that
temperature overnight. After cooling, water was added and the mixture was extracted with ethyl acetate several times. The combined organic fractions were dried and concentrated in vacuo. Silica column chromatography with chloroform as mobile phase was used to isolate product 1, which was subsequently recrystallized from ethanol (350 mg, 330 μmol, 24%). $^1$HNMR (400MHz, chloroform-d) δ (ppm): 7.64 – 7.53 (m, 8H), 6.29 (s, 2H), 3.50 (d, J = 7.4 Hz, 4H), 1.76 (s, 2H), 1.41 – 1.15 (m, 64H), 0.87 (dt, J = 6.8, 2.7 Hz, 12H). $^{13}$CNMR (100MHz, chloroform-d) δ (ppm): 169.54, 144.29, 134.47, 132.03, 130.91, 130.00, 126.31, 123.57, 97.14, 75.59, 44.01, 37.08, 31.91, 31.88, 31.74, 29.99, 29.76 – 29.48 (m), 29.43 – 29.21 (m), 26.67, 22.78 – 22.55 (m), 14.11. MALDI-TOF m/z: 1056.66 (M⁺, 100%)

3,7-bis[4-(4-dodecylthiophen-2-yl)phenyl]-1,5-bis[2-octyldecyl]pyrrole[2,3-f]indole-2,6(1H,5H)-dione (2): To 1 (200 mg, 189 μmol) was added 2-(4-dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (180 mg, 473 μmol) and K$_2$PO$_4$ (212 mg, 1 mmol) and the mixture was put under an argon atmosphere. Toluene and water (5:1) were added with Aliquat 336 (1 ml) and argon was bubbled through for 15 minutes. Then tris(dibenzylideneacetone)dipalladium (4.3 mg, 4.7 μmol) and triphenylphosphine (4.9 mg, 18.8 μmol) were added and the mixture was heated to 115°C for 24 hours. After cooling the mixture was precipitated in methanol and filtrated. Subsequent recrystallization from chloroform:ethanol mixture gave pure 2 (186 mg, 134 μmol, 71%). $^1$HNMR (400MHz, chloroform-d) δ (ppm): 7.79 – 7.64 (m, 8H), 7.24 (s, 2H), 6.92 (s, 2H), 6.40 (s, 2H), 3.53 (d, J = 7.0 Hz, 4H), 2.68 – 2.56 (m, 4H), 1.80 (br, 2H), 1.73 – 1.57 (m, 8H), 1.44 – 1.09 (m, 96H), 0.94 – 0.78 (m, 18H).

3,7-bis[4-(5-bromo-4-dodecylthiophen-2-yl)phenyl]-1,5-bis[2-octyldecyl]pyrrole[2,3-f]indole-2,6(1H,5H)-dione (3): In DCM (20 ml) was dissolved 2 (186 mg, 133 μmol) and subsequently at 0°C N-bromosuccinimide (47.8 mg, 266 μmol) in portions. After 1 hour the mixture was allowed to warm to room temperature and stirred over night. Precipitation in methanol and filtration followed by recrystallization from chloroform:ethanol afforded the title compound (186 mg, 119 μmol, 90%) with high purity. $^1$HNMR (400MHz, chloroform-d) δ (ppm): 7.75 (d, J = 8.2 Hz, 4H), 7.60 (d, J = 8.2 Hz, 4H), 7.08 (s, 2H), 6.38 (s, 2H), 3.52 (d, J = 7.4 Hz, 4H), 1.79 (br, 2H), 2.58 (t, J = 7.8 Hz, 4H), 1.62 (p, J = 7.2 Hz, 4H), 1.45 – 1.13 (m, 100H), 0.86 (p, J = 6.8 Hz, 18H). $^{13}$CNMR (100MHz, chloroform-d) δ (ppm): 169.78, 144.10, 143.45, 142.76, 134.25, 133.98, 130.67, 130.04, 126.46, 125.45, 124.55, 109.27, 97.45, 43.96, 37.13, 31.91, 31.87, 31.80, 30.02, 29.73, 29.78 – 29.53 (m), 29.58, 29.43, 29.46 – 29.24 (m), 29.27, 26.74, 22.68, 22.67, 14.11. MALDI-TOF m/z: 1556.90 (M⁺, 100%)

**PBDPPTP:** To 1 (50 mg, 47.3 μmol) and 2,5-bis(trimethylstannyl)thiophene (19.4 mg, 47.3 μmol) under argon atmosphere was added a 10:1 toluene:DMF mixture (2 ml, anhydrous). Argon was bubbled through for 15 minutes before adding tris(dibenzylideneacetone)dipalladium (0.65 mg, 0.7 μmol) and triphenylphosphine (0.74 mg, 2.8 μmol). The mixture was heated in a sealed tube for 24 hours and then precipitated in methanol. The precipitate was subjected to Soxhlet extraction with acetone, hexanes and chloroform. The latter fraction was concentrated and precipitated in methanol again to give the desired polymer as a dark solid (36 mg, 75% yield). GPC (ODCB, 80 °C): $M_n$ = 13.9 kg/mol, PDI = 5.2. $λ_{max}$ = 615 nm.

**PBDP3TP:** To 3 (47.9 mg, 30.7 μmol) and 2,5-bis(trimethylstannyl)thiophene (12.6 mg, 30.7 μmol) under argon atmosphere was added a 10:1 toluene:DMF mixture (2 ml, anhydrous). Argon was bubbled through for 15 minutes before adding tris(dibenzylideneacetone)dipalladium (0.57 mg, 0.6 μmol) and triphenylphosphine (0.65 mg, 2.4 μmol). The mixture was heated in a sealed tube for 24
hours and then precipitated in methanol. The precipitate was subjected to Soxhlet extraction with acetone, hexanes and dichloromethane. The latter fraction was concentrated and precipitated in methanol again to give the desired polymer as a dark solid (37 mg, 80% yield). GPC (ODCB, 80 °C): $M_n = 28.9 \text{ kg/mol}$, PDI = 2.3. $\lambda_{\text{max}} = 591 \text{ nm}$.

**PBDPP4TP**: To 3 (70.0 mg, 48.4 μmol) and 5,5'-bis(trimethylstanny)-2,2'-bithiophene (23.8 mg, 48.4 μmol) under argon atmosphere was added a 10:1 toluene:DMF mixture (2 ml, anhydrous). Argon was bubbled through for 15 minutes before adding tris(dibenzylideneacetone)dipalladium (0.89 mg, 0.97 μmol) and triphenylphosphine (1.02 mg, 3.88 μmol). The mixture was heated in a sealed tube for 24 hours and then precipitated in methanol. The precipitate was subjected to Soxhlet extraction with acetone, hexanes and dichloromethane. The latter fraction was concentrated and precipitated in methanol again to give the desired polymer as a dark solid (55 mg, 78% yield). GPC (ODCB, 80 °C): $M_n = 30.6 \text{ kg/mol}$, PDI = 2.1. $\lambda_{\text{max}} = 582 \text{ nm}$. 
XRD measurements

Samples for XRD were prepared by drop casting 100 μL of a 10 mg/ml polymer solution in chloroform on to a (911) surface of a silicon wafer. Samples were measured directly as cast and after annealing by placing the samples for 15 minutes upside down on a glass plate that was placed on a 150 °C hot plate.

![XRD diffraction](image)

**Fig. S3** XRD diffraction of drop casted films of PBDPPTP, PBDPP3TP and PBDPP4TP on a silicon wafer before (black) and after annealing at 150 °C (red). All curves are normalized to the intensity at 2θ of 2.0 degrees in order to compare measurements.

**Table S1** Refraction data

<table>
<thead>
<tr>
<th></th>
<th>As cast</th>
<th>150 °C Annealed</th>
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<tbody>
<tr>
<td></td>
<td>Peak(_{\text{max}})</td>
<td>d</td>
</tr>
<tr>
<td>PBDPPTP</td>
<td>4.55</td>
<td>1.94</td>
</tr>
<tr>
<td>PBDPP3TP</td>
<td>4.20</td>
<td>2.10</td>
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<tr>
<td>PBDPP4TP</td>
<td>4.50</td>
<td>1.96</td>
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</table>
AFM measurements

Sample preparation was done using silicon wafers and a 5 mg/ml chloroform solution of polymers. Layers were spin coated at 1000 rpm and annealing was done by placing the samples directly on a 150 °C hot plate for 15 minutes.

![AFM images of spin coated layers of PBDPPTP, PBDPP3TP and PBDPP4TP on silicon substrates. In the left column as cast and in the right column annealed at 150 °C. All samples are 1 μm x 1 μm and have the height scale set between 0 - 4 nm for the as cast samples. The annealed samples differ in height scale.](image-url)
DFT calculations

**Fig. S3** Two different optimizations for P-BDP-P3TP-BDP-P. Top image shows HOMO and LUMO for the fully optimized molecule without any restrictions, bottom picture shows the results for HOMO and LUMO with fixed dihedral angles of 0° between BDP and phenyl rings.

**Fig. S4** HOMO and LUMO, LUMO+1 and LUMO+2 for the Ph-BDP-Ph-3T-Ph-BDP-Ph-3TP-BDP-Ph trimer showing the three nearly degenerate LUMO levels. LUMO+1 and LUMO+2 are respectively 0.05 and 0.06 eV higher.
Table S2 Characteristics of BDP polymers

<table>
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<tr>
<th>Donor block</th>
<th>$\lambda_{\text{max}}^\text{sol}$</th>
<th>$\lambda_{\text{max}}^\text{film}$</th>
<th>$\lambda_{\text{onset}}^\text{DFT}$</th>
<th>$\lambda_{\text{onset}}^\text{sol}$</th>
<th>$\lambda_{\text{onset}}^\text{film}$</th>
<th>$E_g^\text{sol}$</th>
<th>$E_g^\text{film}$</th>
<th>$E_{g\rightarrow0}^\text{DFT}$</th>
<th>$f_{\text{oscillator}}^\text{DFT}$</th>
<th>$\Delta E^\text{DFT}$</th>
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<tbody>
<tr>
<td>PTP</td>
<td>615 nm</td>
<td>639 nm</td>
<td>680 nm</td>
<td>720 nm</td>
<td>735 nm</td>
<td>1.72 eV</td>
<td>1.69 eV</td>
<td>1.82 eV</td>
<td>0.92 eV</td>
<td>2.08 eV</td>
</tr>
<tr>
<td>P2TP</td>
<td>-</td>
<td>-</td>
<td>713 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.74 eV</td>
<td>1.36 eV</td>
</tr>
<tr>
<td>P3TP</td>
<td>591 nm</td>
<td>655 nm</td>
<td>737 nm</td>
<td>737 nm</td>
<td>817 nm</td>
<td>1.68 eV</td>
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<td>1.49 eV</td>
<td>1.68 eV</td>
<td>1.28 eV</td>
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<tr>
<td>P4TP</td>
<td>582 nm</td>
<td>630 nm</td>
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<td>1.34 eV</td>
</tr>
</tbody>
</table>

$E_g^\text{sol/film/DFT}=\frac{1240}{\lambda_{\text{onset}}^\text{sol/film/DFT}}$, $E_{g\rightarrow0}^\text{DFT}=E_{\text{HOMO}^\text{DFT}}-E_{\text{LUMO}^\text{DFT}}$. 

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