Supporting Information

Solution Processable Organic Field-Effect Transistors Utilising a α,α’-
Dihexylpentathiophene Based Swivel-Cruciform

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Materials

All reactions were carried out under an argon atmosphere. The solvents were used as commercial p.a. quality. $^1$H- and $^{13}$C-NMR data were obtained on a Bruker ARX 400 spectrometer. Phase transitions were studied by differential scanning calorimetry (DSC) with a Bruker Reflex II thermosystem at a scanning rate of 10 °C/min$^{-1}$ for both heating and cooling cycles. The UV-Vis and fluorescence spectra were recorded on a Jasco V-550 spectrophotometer and a Varian-Cary Eclipse spectrometer respectively. Low-resolution mass spectrometry was obtained on a Varian MAT 311A operating at 70 eV (Electron Impact, EI) and reported as m/z and percent relative intensity. FD mass measurements were carried out on a ZAB 2-SE-FDP.

**Synthesis of 2,2',5,5'-tetrabromo-3,3'-bithiophene (S1)**. 3,3'-Dithienyl (1.03g, 6.2mmol) (1) and the NBS (5.52 g, 31 mmol) were added to a pre-dried 250 ml two-neck flask and placed under an argon atmosphere. Dry THF (100 mL) was added and the reaction mixture was stirred at room temperature for 2 days. The solvent was removed and the residue taken into hexane and filtered. The solvent was removed from the filtrate and the residue was chromatographed on silica with hexane as eluent to give 2 in 31% yield. $^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 6.97 (s, 2H). $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ = 135.2, 131.6, 111.5, 111.2. LR-MS (EI, 70eV): m/z = 482 (100). Elemental analysis calculated for C$_8$H$_2$Br$_4$S: C, 19.94; H, 0.42; S, 13.31. Found: C, 19.90; H, 0.81; S, 13.23.

**Synthesis of α,α'-dihexylsexithiophene based swivel cruciform dimmer (S2)**. KOH (1.5 g, 26.7 mmol), 2 (0.2 g, 0.42 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.047 g, 0.067 mmol) were added to two-neck flask fitted a reflux condenser and a pressure equalised dropping funnel. The reaction flask degassed and filled with argon. Subsequently the flask was charged with dry THF (50 ml). The boronic ester 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-5'-N-hexyl-2,2'-bithiophene (1 g, 2.66 mmol) was placed in a schlenk tube and then dissolved in dry THF (10 ml). The solution was then added to the dropping funnel via a syringe. The mixture was heated to 60°C and the boronic ester solution added over a period of ca. 1 hour. The reaction mixture was stirred under reflux for 24 hours. After cooling to room temperature the reaction solution was diluted with chloroform and the organic phase was washed successively with water, saturated EDTA-solution and brine. The organic phase was then dried over MgSO$_4$ and the solvent was removed. The residue was chromatographed on silicagel with an 10% toluene/hexane mixture as eluent. After recrystallisation from a dichloromethane/heptane mixture the product 3 was obtained as a brown powder in 21% yield. $^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = ppm 7.04 (d, 2H, J=3.7Hz, H$_f$), 6.97 (s, 2H, H$_a$), 6.96 (d, 2H, J=3.9Hz, H$_h$), 6.92 (d, 2H, J=3.5Hz, H$_h$), 6.87 (d, 2H, J=3.9Hz, H$_b$), 6.81 (d, 2H, J=3.8Hz, H$_c$), 6.63 (d, 2H, J=3.5Hz, H$_d$), 6.55 (2H, J=3.5Hz, He), 6.29 (td, 8H, J=7.6Hz, J=22.3Hz), 1.58 (m, 8H), 1.25 (m, 24H), 0.81 (td, 12H, J=6.8Hz, J=9.3Hz). $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ = 146.31, 146.13, 138.68, 137.68, 135.33, 135.19, 134.56, 134.53, 134.21, 134.0, 132.5, 126.9, 126.3, 125.15, 125.04, 124.87, 124.03, 124.0, 123.98, 123.55, 131.73, 131.62, 31.73, 31.62, 22.71, 22.7, 14.19. FD-MS: 342.9 (100.0). Elemental analysis calculated for C$_6$H$_2$Br$_4$S: C, 66.27; H, 6.08; S, 27.64. Found: C, 66.08; H, 6.89, S, 30.27.
Scheme S1: Synthetic strategy for the preparation of DHPT-SC.
Figure S1: $^1$H NMR spectrum of DHPT-SC in C$_2$D$_2$Cl$_4$. 
Figure S2: $^1$H-$^1$H NMR COSY spectrum of the aromatic region of DHPT-SC in $\text{C}_2\text{D}_2\text{Cl}_4$. 
Figure S3: $^1$H-$^1$H NMR COSY long-range spectrum of DHPT-SC in C$_2$D$_2$Cl$_4$.
Figure S4. $^{13}$C NMR spectrum of the aromatic region of DHPT-SC in C$_2$D$_2$Cl$_4$. 
Figure S5. $^{13}$C NMR spectrum of the alkyl region of DHPT-SC in C$_2$D$_2$Cl$_4$. 
Figure S6: DSC spectrum of DHPT-SC.
Figure S7: Optical spectra of DHPT-SC in CHCl₃ solution (solid line) and thin film (dashed line).
Figure S8: Optical spectra of α,α′-hihexylpentathiophene.
Cyclic Voltammetry Measurements.

Cyclic voltammograms of DHPT and DHPT-SC were carried out in a one-compartment cell with a Pt-disk working electrode, a bare Ag-wire as reference and a Pt-wire as counter electrode. The solvent system was CH2Cl2/n-Bu4NPF6 solutions. All potentials are given versus SCE which is 0.46 V lower than $E^0$ of the ferrocene+1/0 couple used as internal reference [N. G. Connelly, W. E. Geiger, Chem. Rev., 1996, 96, 877-910].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_1^0$</th>
<th>$E_2^0$</th>
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<tbody>
<tr>
<td>DHPT</td>
<td>0.81</td>
<td>1.04</td>
</tr>
<tr>
<td>DHPT-SC</td>
<td>0.84</td>
<td>1.111</td>
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</tbody>
</table>
Device Fabrication and Thin Film Characterization.

Field effect transistors were from DHPT-SC using bottom gate geometry on highly doped n-type silicon wafers, acting as the gate electrode. A thermally grown 300 nm thick silicon dioxide layer with a capacitance of 11 nF/cm² served as the gate insulator. Prior to deposition of DHPT-SC, the surface of the substrates were carefully cleaned with several common solvents, activated with oxygen plasma and treated with hexamethyldisilazane (HMDS) for 26 h at 60 °C. The solution of DHPT-SC then spun onto the silanized Si/SiO₂ substrates, yielding layers with thickness of ca. 50 nm. Further, source and drain electrodes with interdigitating structure from Au (thickness = 100 nm) evaporated on top of the DHPT-SC thin films. Annealing was performed at 120 °C for 5 minutes followed by slow cooling with a rate of cooling = 1.3 K/min prior to the deposition of the source and drain electrodes. Output and transfer characteristics were measured using Agilent 4155C - semiconductor parameter analyzer from Hewlett Packard. All preparation processes and the characterization of the devices were performed inside a N₂-atmosphere glove box.
X-ray measurements.

The measurements were carried out using a coplanar geometry; i.e. the scattering plane is vertical to the sample surface. The symmetrical reflectivity scans (or 2:1-scans) were measured with equal incidence and exit angles with respect to the sample surface. This means we are measuring the structure parallel to the surface.