

## Supporting Information

# Tuning the charge injection of P3HT-based organic thin-film transistors through electrode functionalization with oligo-phenylene SAMs

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### Materials

PT was purchased from Aldrich, BPT and TPT were synthesized by lithiation of 4-bromobiphenyl and 4-bromo-p-terphenyl respectively, followed by a nucleophilic substitution with sulfur and subsequent protonation.<sup>1</sup>

*Synthesis of [1,1'-biphenyl]-4-thiol (BPT):* All chemicals were directly used for the syntheses without purification, dry solvents were purchased from Fluka. The solvents for extractions were distilled before use. Characterizations were performed with the following instruments: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX-NMR (400 MHz), the J values are given in Hz. Mass spectra were recorded on a finnigan MAT 95Q for Electron Impact (EI) measured in m/z (%). The elementary analyses were measured on a Analysator 240 from Perkin-Elmer. 4-Bromobiphenyl (200 mg, 0.858 mmol, 1.00 equiv.) was weighed into a preheated 25 ml Schlenktube under argon atmosphere. The tube was evacuated and backfilled with argon three times. Then the solid was dissolved in 5 ml THF (crown-cap) and cooled to -78 °C. Afterwards tBuLi (1.13 mL, 1.6 M in pentane, 1.80 mmol, 2.10 equiv.) was added drop wise and the resulting pale brown suspension was stirred at -78 °C for 1 h. Afterwards the suspension was allowed to warm to rt and then finely ground sulfur (30.3 mg, 0.944 mmol, 1.10 equiv.) was added in 5 portions over a period of half an hour. The brown reaction mixture was stirred for 3 h at rt and then quenched with 1 M aq. HCl (2 mL). The mixture was diluted with demin. water (10 mL) and the phases were separated. The aqueous one was extracted twice with EtOAc (25 mL each). Afterwards the combined organic layers were made alkaline with 1 M aq. NaOH (5 mL) and extracted three times with demin. water (50 mL each). The pH of the collected aqueous phases was then adjusted to pH 6 with 1 M aq. HCl (12 mL). After extraction with EtOAc (3 × 75 mL), the combined organic layers were washed with brine and demin. water, dried over sodium sulfate, filtered and concentrated. The obtained yellow solid was further purified by vacuum sublimation (52 %). mp 110 – 111 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ): 7.63 (d, J = 7 Hz, 2H, Ar H), 7.55 (d, J = 8 Hz, 2H, Ar H), 7.43 (t, J = 7 Hz, 2H, Ar H), 7.38 (d, J = 8 Hz, 2H, Ar H), 7.34 (t, J = 7 Hz, 1H, Ar H), 5.53 (s, 1H; SH); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>, δ): 139.4 (Cq), 136.6 (Cq), 131.7 (Cq), 128.8 (Ct), 128.7 (Ct), 127.2 (Cq), 127.2 (Ct), 126.2 (Ct); EIMS (m/z (%)): 187 (16), 186 (100) [M<sup>+</sup>], 185 (69) [M<sup>+</sup> - H], 153 (8) [C<sub>12</sub>H<sub>9</sub><sup>+</sup>], 152 (21); Anal. calcd for C<sub>12</sub>H<sub>10</sub>S: C 77.38, H 5.41; found: C 77.15, H 5.65.

*Synthesis of [1,1':4',1''-terphenyl]-4-thiol (TPT):* The terphenylthiol was synthesized according to procedure described for BPT using 4-bromo-p-terphenyl (200 mg, 0.647 mmol, 1.00 equiv.). After quenching with 1 M aq. HCl the precipitate formed was filtered off and washed with EtOAc (100 mL). The workup was continued with the filtrate as described above to afford TPT as a white solid (35 %). mp 217 – 218 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ): 7.75 (s, 4H, Ar H), 7.72 (d, J = 7 Hz, 2H, Ar H), 7.62 (d, J = 8 Hz, 2H, Ar H), 7.48 (t, J = 7 Hz, 2H, Ar H), 7.40 (d, J = 8 Hz, 2H, Ar H), 7.38 (t, J = 7 Hz, 1H, Ar H), 5.56 (s, 1H; SH); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>, δ): 138.3 (Cq), 136.0 (Cq), 132.9 (Cq), 131.5 (Cq), 130.6 (Cq), 128.9 (Ct), 128.8 (Ct), 128.6 (Ct), 127.1 (Ct), 127.0 (Ct), 126.7 (Ct), 126.4 (Ct); EIMS (m/z (%)): 263 (20), 262 (100) [M<sup>+</sup>], 261 (25) [M<sup>+</sup> - H], 282 (10).

### Contact Angle (CA) and Cyclic Voltammetry (CV) measurements

The wettability of the modified surfaces was determined by static water contact angle (CA) measurements. The obtained values were 82.1 ± 1.4°, 78.7 ± 1.8°, 84.5 ± 5.4° for the TPT, BPT and TP respectively (see Table I), in agreement with previously reported data.<sup>2</sup> The highest occupied molecular orbital (HOMO) level of the P3HT was determined experimentally by cyclic voltammetry measurements.<sup>3, 4</sup> The CV was carried out in dry acetonitrile and 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte (vs. Ag/AgCl). A P3HT solution in chloroform was drop-cast on a gold substrate which was used as the working electrode. The HOMO level was calculated from the first onset oxidation

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potential (eV) ( $E_{\text{HOMO}}$  (eV) =  $-e(E_{\text{onset}}^{\text{ox}} + 4.7)$ ),<sup>3</sup> and the LUMO level could be obtained from the difference of the  $E_{\text{HOMO}}$  and the optical band gap ( $E_{\text{g}}^{\text{op}}$ ) (1.92 eV), which was determined from the absorption spectrum lower energy edge of a P3HT film. The HOMO and LUMO levels were determined to be -4.96 and -3.04 eV, respectively.

#### Macroscopic Kelvin Probe measurements

All the measurements were performed with the Ambient Kelvin Probe Package from KP Technology Ltd. equipped with a 2 mm diameter tip amplifier under an argon environment. All work function ( $\Phi_m$ ) values reported herein were obtained as an average from different samples and long acquisition time measurements, with a standard deviation lower than 0.02 eV. The absolute  $\Phi_m$  values measured on thermally evaporated gold substrates for PT, BPT and TPT SAMs were 5.05, 4.90, and 4.87 eV respectively (see Table I). The work function of the bare gold substrate (thermally evaporated at the same time and conditions as the others, thus having the same crystallinity order) was also experimentally determined as 5.12 eV.

#### Self-Assembled Monolayers preparation

For the SAMs preparation, freshly cleaned gold substrates (from Arrandee) were immersed in a 5 mM solution of PT and BPT and in a saturated solution of TPT in degassed chloroform. After 48 hours the samples were removed from the solution and rinsed vigorously with CHCl<sub>3</sub> and ethanol to remove the physisorbed material.

#### Film thickness measurement

The film thickness (15 nm) was measured by Atomic Force Microscopy (AFM), Digital Instruments Dimension 3100 AFM, under ambient conditions in tapping mode.

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