Electronic Supplementary Information

Self-assembly and electrical properties of a novel heptameric thiophene-benzothiadiazole based architectures

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S1
1) Synthesis

General.

Compounds 1 and 2 were prepared by adapting already reported procedures.1,2

All $^1$H and $^{13}$C NMR spectra were recorded with a Varian Mercury 400 spectrometer operating at 400 MHz ($^1$H). Chemical shifts were calibrated using the internal CDCl$_3$, acetone-$d_6$ or CD$_2$Cl$_2$ resonance that were referenced to TMS. Mass spectra were collected on an ion trap Finningan Mat GCQ spectrometer operating in electron impact (EI) ionization mode. Each sample was introduced to the ion source region of GCQ via a direct exposure probe (DEP). The melting points were determined with a Bühchi 510 apparatus.

Bis-2,5′′-[4-(2-hexyl-thien-5yl)-2,1,3-benzothiadiazole-7yl]-5,2′:5′,2′′terthiophene, (T-BTZ-T)$_2$-T, 3:

To a refluxing toluene solution (10 ml) of compound 1 (150 mg, 0.4 mmol), in situ-prepared Pd(AsPh$_3$)$_4$ (5 mol%, i.e. 9.0 mg of Pd$_{2}$dba$_3$ and 22 mg of AsPh$_3$) at 80°C under N$_2$ atmosphere, stannyl derivative, 2 (150 mg, 0.18 mmol) in toluene (5 ml), was added dropwise. The solution was refluxed for 7 h then the solvent was removed under vacuum and the crude product purified by flash chromatography on silica gel by using warm toluene as eluent. Repeated crystallization from toluene/pentane afforded 3 as a dark-red powder.

m.p. 181 °C, MS (70 eV, EI): m/z 848 (M$^+$), $^1$H NMR (CDCl$_3$ + CS$_2$, TMS/ppm): 8.07 (d, 3$^J$=4.0 Hz 2H), 7.98 (d, 3$^J$=3.6 Hz 2H), 7.83 (d, 3$^J$=7.6 Hz 2H), 7.78 (d, 3$^J$=8.0 Hz 2H), 7.26 (d, 3$^J$=4.0 Hz 2H), 7.22 (s, 2H), 6.86 (d, 3$^J$=3.6 Hz 2H), 2.90 (t, 4H), 1.77 (m, 4H), 1.44 (m, 4H), 1.37 (m, 8H), 0.94 (t, 6H). $^{13}$C NMR (CDCl$_3$, TMS/ppm diagnostic signals): 14.1, 15.3, 22.6, 28.8, 29.7, 30.3, 31.6, 124.8, 125.0, 125.3, 125.4, 127.7, 127.8, 128.1.

Anal. calcd for C$_{48}$H$_{44}$S$_7$ C, 68.20; H, 5.25. Found C, 68.29; H, 5.35

2) Cyclic Voltammetries (CVs)

Redox potentials have been evaluated by cyclic voltammetries performed at room temperature in CH$_2$Cl$_2$ (Carlo Erba RPE, distilled over P$_2$O$_5$ and stored under Ar
pressure) with 0.1 mol-L⁻¹ (C₄H₉)₄NClO₄ (Fluka, puriss. crystallized from CH₃OH and vacuum dried). BTZ is partially soluble in this electrolyte and its concentration has been estimated about 0.7 mmol-L⁻¹. Potential scans have been imposed by using an AMEL electrochemical system model 5000 with rates ranging from 0.02 to 0.2 V·s⁻¹. Working electrode was semi-spherical Pt (area 0.05 cm²), auxiliary electrode Pt wire, and reference electrode aqueous KCl Saturated Calomel Electrode (SCE), both separated from the working electrode compartment by a liquid bridge containing the same electrolyte solution. $E^\circ_{\text{Fc/Fc}^+} = 0.47$ V vs. SCE, $E_{\text{Fc/Fc}^+} = -5.15$ eV.

3) Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was performed by using a Thass DSC-XP-10 instrument under nitrogen atmosphere.

The thermogram shows a crystallization peak centered at 169°C followed by melting to a liquid crystalline state at 184.7°C. Additional transitions were observed at 334.9°C and 346.7°C corresponding to LC-LC transitions and to the clearing point (i.e. transition to isotropic liquid).

Accordingly, the cooling curve shows three transitions centered at 341.2°C, 328.6°C and 152.5°C respectively.
Figure S1. DSC thermograms of (T-BTZ-T)$_2$-T recorded at 10 °C/min in air. (a) second heating run and b) second cooling run.

4) Hot stage polarized microscopy (POM)

Hot stage polarized microscopy (POM) was performed by using a Nikon Eclipse 80i optical microscope with a Leika microsystem hot stage (WETZIAR GMDH). The images were recorded with a digital color camera Nikon Digital Sight DS-2Mv. Glass substrates were furnished by Knittel gläser and were washed with Acetone spectroscopic grade before use. Powder samples were sandwiched between two untreated glass plates.

According to DSC, liquid crystalline behavior was observed by POM in the range 175°-288°C. Figure S2 shows the Shlieren texture observed at 245°C.
Figure S2. POM micrographs of (T-BTZ-T)$_2$-T (crossed polars). Textures of the liquid crystalline mesophase observed at 245 °C. Image size 800x800 µm.

5. OFETs based on spin-coated (T-BTZ-T)$_2$-T films

Bottom-gate bottom contact transistors featuring 230nm thermally grown oxide on n$^{++}$-doped silicon (Fraunhofer Institute, capacitance 1.5 x 10$^{-8}$ F/cm$^2$) were prepared by spin-coating (T-BTZ-T)$_2$-T solutions.

Several experimental conditions varying solvent polarity and solution concentrations were tested to optimize the deposition process. The best device performance was obtained for a 1 mg/ml solution in toluene. A warm solution (100°C) was spin-cast on bare SiO$_2$ which although leading to a non-homogenous film due to fast precipitation, showed the highest mobility. The measured hole mobility (highest) was 2 x 10$^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for a device with channel length (L) =10 µm and channel width (W) =10 mm (data not shown here).
Table S1. Summary of charge carrier mobilites obtained for different sample preparation procedures.

Solv.: solvent; Dep.: deposition method; Funct.: functionalization of the dielectric; Mob. (samples), best device: the average mobility is extracted from the number of samples detailed in brackets, the best mobility is also detailed. h: hole mobility and e: electron mobility.

All mobilities were extracted from saturation regime.

<table>
<thead>
<tr>
<th>Solv.</th>
<th>Dep.</th>
<th>Funct.</th>
<th>Anneal T</th>
<th>Mob. (samples); best device</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>DC</td>
<td>OTS</td>
<td>--</td>
<td>4.8 x 10^{-4} cm^2/Vs (4); 7.3 x 10^{-4} cm^2/Vs</td>
</tr>
<tr>
<td>DCB</td>
<td>DC</td>
<td>OTS</td>
<td>100°C, 5h</td>
<td>h: 9.5 x 10^{-4} cm^2/Vs (4); 1.1 x 10^{-3} cm^2/Vs; e: 2.0 x 10^{-6} cm^2/Vs (4); 2.2 x 10^{-6} cm^2/Vs</td>
</tr>
<tr>
<td>DCB</td>
<td>DC</td>
<td>--</td>
<td>200°C, 1h</td>
<td>6.7 x 10^{-5} cm^2/Vs (4);</td>
</tr>
<tr>
<td>DCB</td>
<td>DC</td>
<td>--</td>
<td>--</td>
<td>5.1 x 10^{-5} cm^2/Vs (3)</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>--</td>
<td>--</td>
<td>1.8 x 10^{-5} cm^2/Vs (3)</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>--</td>
<td>200°C, 1h</td>
<td>9.4 x 10^{-4} cm^2/Vs (4); 1.4 x 10^{-3} cm^2/Vs</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>--</td>
<td>200°C, 15h</td>
<td>1.7 x 10^{-3} cm^2/Vs (3); 2.5 x 10^{-3} cm^2/Vs</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>HMDS</td>
<td>100°C, 5h</td>
<td>h: 2.7 x 10^{-4} cm^2/Vs (4); e: 3.6 x 10^{-7} cm^2/Vs (only short channels)</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>HMDS</td>
<td>150°C, 2h</td>
<td>h: 4.6 x 10^{-4} cm^2/Vs (4); 9.0 x 10^{-4} cm^2/Vs; e: negligible</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>HMDS</td>
<td>200°C, 1h</td>
<td>1.1 x 10^{-3} cm^2/Vs (4); 1.5 x 10^{-3} cm^2/Vs</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>OTS</td>
<td>--</td>
<td>3.8 x 10^{-6} cm^2/Vs (3); 5.9 x 10^{-6} cm^2/Vs</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DC</td>
<td>OTS</td>
<td>100°C, 5h</td>
<td>h: 1.3 x 10^{-3} cm^2/Vs (3); 2.5 x 10^{-3} cm^2/Vs; e: 2.8 x 10^{-6} cm^2/Vs (3); 6.9 x 10^{-6} cm^2/Vs</td>
</tr>
</tbody>
</table>

DCB: dichlorobenzene; CHCl₃: chloroform; DC: drop casting; OTS: Octadecyltrichlorosilane; HMDS: hexamethyldisilazane.
7. AFM images of (T-BTZ-T)$_2$-T fibers on SiO$_2$.

**Figure S3.** a) Topographic (Z scale: 232 nm) and c) phase AFM images (intermittent contact mode “tapping”) of a (T-BTZ-T)$_2$-T fiber. b) Height profiles: 1 and 2 are used to correlate the height profile with the corresponding lines (1 and 2) depicted in a) on the fiber.
8. Transfer characteristics for the drop-casted film.

![Graph showing transfer characteristics for a drop-casted film.]

**Figure S4.** Transfer characteristics for a drop-casted film (from solution in CHCl₃) on an OTS-treated substrate annealed for 5h at 100°C. p-channel (red) / n-channel (blue) have been measured at V_D = ±40V. µ was extracted at V_D = 40 V.

9. Fibers based device preparation

100 µl of the solution containing the fibres was first drop-cast on non-treated SiO₂ substrate (same substrates used for the bottom-gate bottom-contact transistors without the patterned electrodes) in a glove box environment and then once dried, the samples were transferred (being exposed to air) to the thermal evaporator chamber for the top gold electrodes evaporation. Transmission electron microscopy grids were used as shadow masks.

10. Photoelectron spectroscopy

In order to quantify the ionization energy (IE) of the different structures, ultraviolet ambient photoelectron spectroscopy measurements were performed by sampling in each measurement an area of about 4 mm² (beam size) by using a Photoelectron Yield Spectrometer operating in Air (PYSA), Model AC-2 from Riken Keike Co., Ltd.

11. Laser scanning confocal fluorescence microscopy

Fluorescence imaging was performed on an inverted Nikon A1 laser scanning confocal microscope equipped with a CW argon ion laser. Confocal fluorescence imaging exciting at 488 nm was carried out on the samples at room temperature measuring fluorescence with a PMT featuring a bandpass filter centred at 700 nm
(bandpass width of 40 nm). The images were collected using a Nikon PLAN APO VC 60× NA 1.40 oil immersion objective. Pixel dimension for the xy plane corresponds to 0.1×0.1 µm. Pinhole dimension was set to 0.7 au corresponding to an optical thickness of ca. 230 nm. Spectral imaging was done with Nikon 32-PMT array detector with resolution of 6 nm for each PMT.

**Figure S5.** Confocal fluorescence microscopy image of the (T-BTZ-T)$_2$-T unstructured casted film (1mg/ml, toluene, rt, on SiO$_2$).

12. **X-ray diffraction analysis was carried out by means of a PANalytical X’Pert** diffractometer equipped with a copper anode (λ mean = 0.15418 nm) and a fast X’Celerator detector. Step 0.05° (2theta scale), counting time 300 sec.

13. **Scanning Electron Microscopy (SEM) Secondary Electrons (SE)** images were obtained with a ZEISS 1530 instrument equipped with a Schottky emitter and operating at 10 keV, an Energy Dispersive X-Ray Spectrometer (EDX) for X-Ray microanalysis, and two different SE detectors, the InLens (IL) and the Everhart-Thornley detectors (ETD).
References:
