Electronic Supplementary Information

Enhanced mobility in P3HT-based organic thin-film transistors upon blending with a soluble phenylene-thiophene-thiophene-phenylene small molecule

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1. Synthesis and NMR

The molecule 5,5'-bis(4-hexylphenyl)-2,2'-bithiophene (dH-PTTP) was synthesized by BASF laboratories according to reference [1].

Here is reported the NMR data:

\[ ^1H \text{ NMR (400 MHz, CDCl}_3, \delta): 7.55 \text{ (d, } J = 8.0 \text{ Hz, 4H, Ar H), 7.23 \text{ (m, 6H, Ar H and thiophene), 7.12 \text{ (d, } J = 4.0 \text{ Hz, 2H, thiophene), 2.65 \text{ (t, } J = 7.6 \text{ Hz, 4H, CH}_2, 1.66 \text{ (m, 4H, CH}_2, 1.35 \text{ (m, 12H, CH}_2, 0.92 \text{ (t, } J = 6.8 \text{ Hz, 6H, CH}_3); } ^{13}C \text{ NMR (100 MHz, CDCl}_3, \delta): 143.2, 142.6, 136.3, 131.5, 128.9, 125.5, 124.3, 123.2, 35.7, 31.7, 31.3, 28.9, 22.6, 22.6, 14.1.} \]

2. Electrical characterization details

Organic thin-film transistors were prepared starting from n++-Si/SiO₂ substrates exposing pre-patterned interdigitated gold source and drain electrodes (IPMS Fraunhofer). After an accurate cleaning of the substrates, the solutions (in different ratios) were drop-cast onto the substrates. Electrical characterization was performed in an inert environment (glovebox, with water and oxygen levels lower than 2 ppm) by means of an electrometer, Keithley 2636A, interfaced by LabTracer™ software.

The following equations, 1 and 3, correlate the drain current of a p-type thin-film transistor with the applied bias voltages to the gate and the drain electrode respectively while the source electrode is grounded. [2]

In particular considering that the following equation 1

\[ I_D = -\frac{1}{2} \mu_{sat} C_i \frac{Z}{L} (V_G - V_m)^2 \] (1)
holds in the saturation regime, where \( V_{DS} \geq (V_G - V_{th}) \),
where \( I_D \) is the drain current, \( V_G \) is the gate voltage, \( V_D \) is the drain voltage, \( L \) is the channel length, and \( C_i = 1.5 \times 10^{-8} \text{ F cm}^{-2} \) is the capacitance of the gate dielectric per unit area, the field-effect mobility in the saturation regime can be extracted from

\[
\mu_{\text{SAT},p} = \frac{2 \left( \frac{\partial I_D}{\partial V_G} \right)^2}{C_i \frac{W}{L}}
\]  

If one considers the expression of the drain current in the linear regime, where \( V_{DS} \leq (V_G - V_{th}) \),

\[
I_D = -\mu_{\text{LIN}} C_i \frac{Z}{L} [(V_G - V_{th})V_{DS}]
\]  

then the threshold voltage values can be extracted by plotting the \( I_D \) vs. \( V_G \) curve and then extracting the intercept with the voltage axis of the line which fits the linear part of the curve.

**Figure S1** Variation of the threshold voltage \( V_{th} \) (linear regime) for different percentage of dH-PTTP in the blend (W/L=10000\( \mu \text{m}/20\mu \text{m} \))
3. Atomic Force Microscopy experimental details

The film morphology shown in Figure 3 within the main text was imaged by Atomic Force Microscopy (AFM), Digital Instruments Dimension 3100 AFM, under ambient conditions in tapping mode.

The films were realized by spin-coating hot (100 °C) solutions (0.5mg/mL in p-xylene) in the above-mentioned weight ratios at 1500 rpm.

4. Ultraviolet Ambient Photoelectron Spectroscopy

The work-function change upon addition of dH-PTTP in the blend was monitored by an Ultraviolet Photoelectron Spectrometer, AC-2, by RKI Instruments working at ambient conditions. The imaged films were realized following the same experimental procedures as those employed in the realization of FET devices in order to ensure full consistency with the electrically characterized films.

5. Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) and XRD

GIWAXS measurements were performed using a custom setup consisting of rotating anode X-ray source (Rigaku Micromax, operated at 42kV and 20mA), Osmic confocal MaxFlux optics and a three pin-hole collimation system (JJ X-ray). Samples on the top of approx. 1.5×1.5 cm² silicon platelets were irradiated at the incident angle (αi) of 0.20°. Diffraction patterns were recorded for 3h on a MAR345 image plate detector. Finally, the data was processed and imaged using Datasqueeze 2.2.5 program. For one-dimensional XRD, a 0-0 Siemens D500 Kristalloflex with a graphite-monochromatized CuKα X-ray beam was used.
Figure S2 GIWAXS patterns of drop-cast films of a) P3HT, b) dH-PTTP/P3HT blend (50%) and c) dH-PTTP.

Figure S3 XRD of drop-cast dH-PTTP, P3HT and dH-PTTP/P3HT blend film (50%).
Figure S4 GIWAXS patterns of drop-cast dH-PTTP/P3HT blend films with a P3HT fraction of a) 95%, b) 75%, c) 25% and d) 5%.

6. Literature
