Electronic Supplementary Information

Improving the electrical performance of solution processed oligothiophene TFTs via structural similarity blending

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Table of Contents

| 1. Grazing incident X-Ray Diffraction patterns and UV-Vis absorbance spectra of | S2 |
|---|----|
| films produced from DH4T/DH2T blends | |
| 2. Electrical characterization | S3 |
| 3. Optical Microscope imaging | S6 |
| 4. Ambient UV photoelectron spectroscopy (PESA) measurements | S7 |

1. Grazing incident X-Ray Diffraction patterns and UV-Vis absorbance spectra of films produced from DH4T/DH2T blends

Grazing incident X-Ray Diffraction patterns and UV-Vis absorbance spectra of films produced from DH4T/DH2T blends do not highlight a change in crystalline structure upon addition of small amounts of DH2T compared to a film produced from a pristine DH4T solution.



Fig. S1. 2D GIXD patterns of films drop-cast on bare Si. (a) Pure DH4T dropcasted from dichlorobenzene ; (b) DH2T/DH4T blend containing 2% DH2T and 98% DH4T.



Fig. S2. Normalized absorbance spectra of DH4T dissolved in DCB (black), and of dropcasted films containing pristine DH4T (red), 1% DH2T in DH4T (blue), and 5% DH2T in DH4T (green).

2. Electrical characterization

In order to investigate charge injection in different films produced from blends of DHnT molecules, output curves plots are reported in this section (Figure S3 and S4). Electrical characterization presented in Fig. S5 highlights the similarity in terms of V_{TH} and I_{off} of films fabricated using DH4T solutions with up to 50% DH6T. At 90% DH6T, the I_{off} is increased by 3 orders of magnitude with an unchanged threshold voltage. Table S1 recapitulates the electrical characteristics of the most important films discussed in the manuscript. Figure S6 compares mobilities of films produced from blends of DHnT using chloroform as solvent.



Fig. S3. Output curves of $L = 20 \ \mu m$ transistors of blends of DH4T and DH2T in chloroform. Films consist of (a) pure DH4T; (b) 99 wt% of DH4T; (c) 95 wt% of DH4T.



Fig. S4. Output curves of $L = 20 \mu m$ transistors of blends of DH4T and DH6T in chloroform. Films consist of (a) pure DH4T; (b) 90 wt% of DH4T; (c) 50 wt% of DH4T; (d) 10 wt% of DH4T; (e) 2 wt% of DH4T; (f) pure DH6T.



Fig. S5. Threshold voltages (a) and off currents (b) as a function of the amount of DH6T added to DH4T. All the transfer curves are recorded in devices with with $L = 10 \mu m$ and W = 10 mm.

Table S1. Electrical performances of DH4T blends drop-cast from a chloroform solution. All films were drop-cast on HMDS-treated SiO_2 and untreated gold electrodes.

| Blend | Blending ratio | Average field-effect mobility [cm ² /Vs] ^[a] | I_{on} / I_{off} |
|-----------|----------------|---|----------------------------------|
| Pure DH4T | / | 3.4±1.1 ×10 ⁻⁵ | 10 ³ -10 ⁴ |
| Pure DH6T | / | 4.3±4.2 ×10 ⁻⁶ | 10 ¹ -10 ² |
| DH4T:DH2T | 98:2 | 2.8±1.5 ×10 ⁻⁵ | 10 ³ |
| DH4T:DH2T | 95:5 | 1.7±1.0 ×10 ⁻⁵ | 10 ³ |
| DH4T:DH6T | 10:90 | 6.6±0.5 ×10 ⁻³ | 10 ³ -10 ⁴ |
| DH4T:DH6T | 50:50 | 8.6±6.5 ×10 ⁻⁵ | 10 ⁵ -10 ⁶ |

[a] Average over 8 tested devices



Fig. S6. Mobility as a function of DH4T wt% in a blend with either DH6T or DH2T. Fieldeffect mobility values were obtained from transfer curves (average over 8 transistors with $L = 2.5 \mu m$; 5 μm ; 10 μm ; 20 μm).

3. Optical microscope images

Optical Microscope images were taken to investigate aggregation at the scale of the channel for blends of DH4T and DH6T. Films were similar for DH4T contents up to 50 wt%, but even small additions of DH4T lead to important changes in the film.



Fig. S7. Optical microscope images of devices whose active layer is a DH4T/DH6T blend in chloroform. Films consist of (a) pure DH4T; (b) 90 wt% of DH4T; (c) 50 wt% of DH4T; (d) 10 wt% of DH4T; (e) 2 wt% of DH4T and (f) pure DH6T [W= 10 mm, L = 20μ m].

4. Ambient UV photoelectron spectroscopy (PESA) measurements

Ambient UV photoelectron spectroscopy (PESA) measurements were performed in order to investigate the composition of the suface of the film as well as the vertical phase segregation in the film. It reveals a largely DH4T composed top surface up to 90 wt% DH4T in the blend. Large error bars at such a ratio indicate high vertical phase segregation, with different ionization energy values for different measurements.



Fig. S8. Ionization energy as a function of the amount of DH6T added to DH4T.