**Printed, cost-effective and stable poly(3-hexylthiophene) electrolyte-gated field-effect transistors**

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**SUPPLEMENTARY INFORMATION**

1. **Determination of the ink surface tension**

We have carried out surface tension measurements of the ink formulation (P3HT in ODCB, 2.6 mg/ml) using an OCA 15EC video-based optical measuring instrument, together with the SCA 21 software. The pendant drop method was used: droplets of known volume (\textbf{Figure S1}) have been created with a dispenser and a syringe (needle inner diameter = 0.525 mm). Their shape was captured via an optical camera, interpolated and used to numerically solve the Young-Laplace equation.

In the \textbf{Table S1} below all the parameters used for the definition of the surface tension are reported. The droplet volume has been maximized in order to achieve a shape as different as possible from a sphere, and the ink density was set to be the same as for the pure solvent, due to the very low OSC concentration. The surface tension for our ink formulation is 32.5 mN/m.

\textbf{Table S1:} Pendanto drop method parameters

| **Temperature** | **Liquid density** | **Air density** | **Droplet Volume** | **Surface Tension** |
|-----------------|--------------------|-----------------|--------------------|--------------------|
| 25 °C           | 1.30 g/cm³         | 1.2931 kg/m³    | 3.3 µL             | 32.5 mN/m          |

\textbf{Figure S1:} P3HT in ODCB (2.6 mg/ml) ink droplet for surface tension measurement
2. **Waveforms used for the printing processes**

**Figure S2**: Waveform settings for the P3HT ink (a) and for the SU8 ink (b). The Level indicates the percentage of the firing voltage applied to the nozzles for each segment. The typical waveform of the Dimatix DMP2831 is divided into four segments, each with adjustable settings: Level, Slew rate and Duration. The Level (in percentage) is the amplitude of the firing voltage (in this specific case: 40 V for P3HT ink and 34 V for SU8 ink) applied to the operating nozzle, the Slew rate, in a scale of 0 to 2 (arbitrary units), indicates how fast is the shift between two consecutive segments, and the duration (in μs) is the time of the application of the firing voltage for each segment.
3. Transfer and output curves of the ink-jet printed devices realized for this study.

In Figure S3a are reported the transfer curves of the ink-jet printed P3HT EGOFETs realized for this study. All the four ink-jet printed P3HT devices worked properly after their preparation. In particular, three devices on four exhibited a value of $I_{D_{\text{max}}}$ $> 1 \, \mu\text{A}$ already applying a $V_G < -0.4 \, \text{V}$. Interestingly, the passivation of the tracks, connecting source and drain electrodes, with the SU8 layer allowed to reach gate leakage current $I_G$ three orders of magnitudes lower compared with $I_{D_{\text{max}}}$ in all the devices. As an example, the output curve of one EGOFET (namely Dev_002 of Figure S3a) is displayed in Figure S3b. All devices exhibited a modest ON/OFF ratio just after their preparation but, owing to the shift in the threshold voltage $V_T$ associated to the aging, this parameter raised to values higher than $10^2$. This trend can be clearly seen in Figure S4, where it is reported the effect of the cycling (acquisition of 200 transfer curves over a period of 8 days) on a second device (Dev_002). The decrement in the $I_{D_{\text{max}}}$ measured for this EGOFET was -36 $\%$, a value comparable with the one related to the device reported in the main text (-33 $\%$).

**Figure S3:** (a) $I_D$ and $I_G$ curves registered for the ink-jet printed P3HT EGOFETs realized for this study. The fifth device is the one reported in main text. (b) Typical output curve ($I_D$ vs. $V_D$) for an ink-jet printed P3HT EGOFET (namely Dev_002 in Figure S3a).
Figure S4: Effect of the aging on a second ink-jet printed P3HT EGOFET (namely Dev_002 in Figure S3a). Interestingly the two studied transistors showed the almost the same relative current decrement (-36%) as a consequence of the aging, confirming the reproducibility of the printing technique.

4. Long-term Stability.

The EGOFET reported in the main text has been stored in water and in the dark for about two months. In Figure S5 are reported the average $I_{D\text{ max}}$ measured on the same device 34 and 52 days after that the study on the stabilization was concluded. The value of currents reported in the Figure S5 are the average values obtained upon the acquisition of twenty transfer curves applying a delay of one hour between each acquisition. The EGOFET maintained almost unaltered its behaviour (the small variations can also be associated to changes of the water used as electrolyte), confirming the extremely high stability of the ink-jet printed P3HT-based EGOFETs.

Figure S5: Evaluation of the long-term stability of an ink-jet printed P3HT EGOFETs. In the graph are reported the average value of $I_{D\text{ max}}$ exhibited by the device 34 and 52 days after its stability characterization.
5. List of the fitting parameters of the $I_D^{\text{max}}$ decay and of the physical-based modelling.

**Table S2:** Fitting parameters of the $I_D^{\text{max}}$ as a function of measurement time for ink-jet printed and spin-coated P3HT EGOFETs. In both cases $R^2 > 0.99$.

| $I_D^{\text{max}}$ (ink-jet) | $A_1$ (A) | $\tau_1$ (h) | $A_2$ (A) | $\tau_2$ (h) | $y_0$ (A) |
|-----------------------------|-----------|--------------|-----------|--------------|-----------|
| $I_D^{\text{max}}$ (spin-coated) | $1.59 \times 10^{-6} \pm 5.4 \times 10^{-8}$ | $2.62 \pm 0.13$ | $1.65 \times 10^{-6} \pm 1.1 \times 10^{-8}$ | $59.81 \pm 1.05$ | $3.03 \times 10^{-7} \pm 7 \times 10^{-10}$ |

**Table S3:** Geometrical and physical parameters of the drain current model.

| Parameters | spin-coated | ink-jet printed | note |
|------------|-------------|----------------|------|
| Channel width ($W$) | 10560 µm | 10500 µm | Measured |
| Channel length ($L$) | 5 µm | 5 µm | Measured |
| Temperature ($T$) | 293 K | 293 K | Measured |
| P3HT permittivity ($\varepsilon_p$) | $26.55 \times 10^{-14}$ F cm$^{-1}$ | $26.55 \times 10^{-14}$ F cm$^{-1}$ | Ref. 1 |
| HOMO hole mobility ($\mu_H$) | $1.8 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ | $1.8 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ | Ref. 1 |
| HOMO energy level ($E_{\text{HOMO}}$) | 5.1 eV | 5.1 eV | Ref. 1 |
| LUMO energy level ($E_{\text{LUMO}}$) | 3.2 eV | 3.2 eV | Ref. 1 |
| Density of HOMO states ($N_{\text{HOMO}}$) | $1.4 \times 10^{18}$ cm$^{-3}$ | $1.4 \times 10^{18}$ cm$^{-3}$ | Ref. 2 |
| Density of localized states ($N_{t}$) | $4.90 \times 10^{19}$ cm$^{-3}$ | $8.65 \times 10^{19}$ cm$^{-3}$ | Fitted |
| Energy disorder ($E_t$) | $28.3 \times 10^{-3}$ eV | $26.7 \times 10^{-3}$ eV | Fitted |
| EDL capacitance per unit area ($C_{\text{EDL}}$) | $2 \times 10^{-6}$ F cm$^{-2}$ | $2 \times 10^{-6}$ F cm$^{-2}$ | Fitted |
| Threshold voltage at cycle #1 ($V_T$) | $-252 \times 10^{-3}$ V | $-5 \times 10^{-3}$ V | Fitted |

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