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Supplementary Information for

Direct Printing of Soluble Acene Crystal Stripes by Programmed Dip-Coating Process for Organic Field-Effect Transistor Applications

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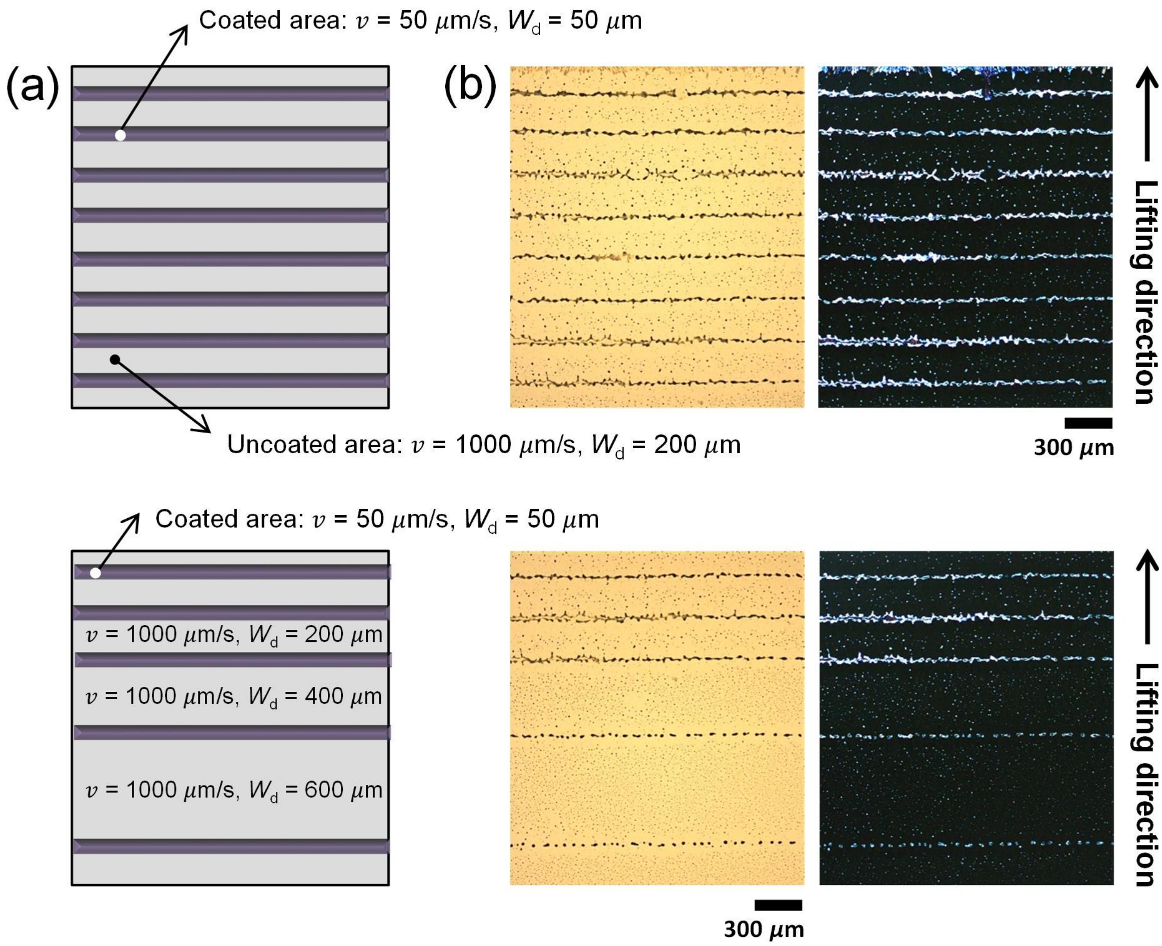


Figure S1. Programmed dip-coating processes with chloroform as the solvent: (a) Schematic illustration of the programmed information to print TIPS-PEN by the dip-coating process. (b) OM (left) and POM (right) images of the patterned TIPS-PEN formed by the programmed dip-coating processes corresponding to the procedure described in (a) (all images share the scale bar).

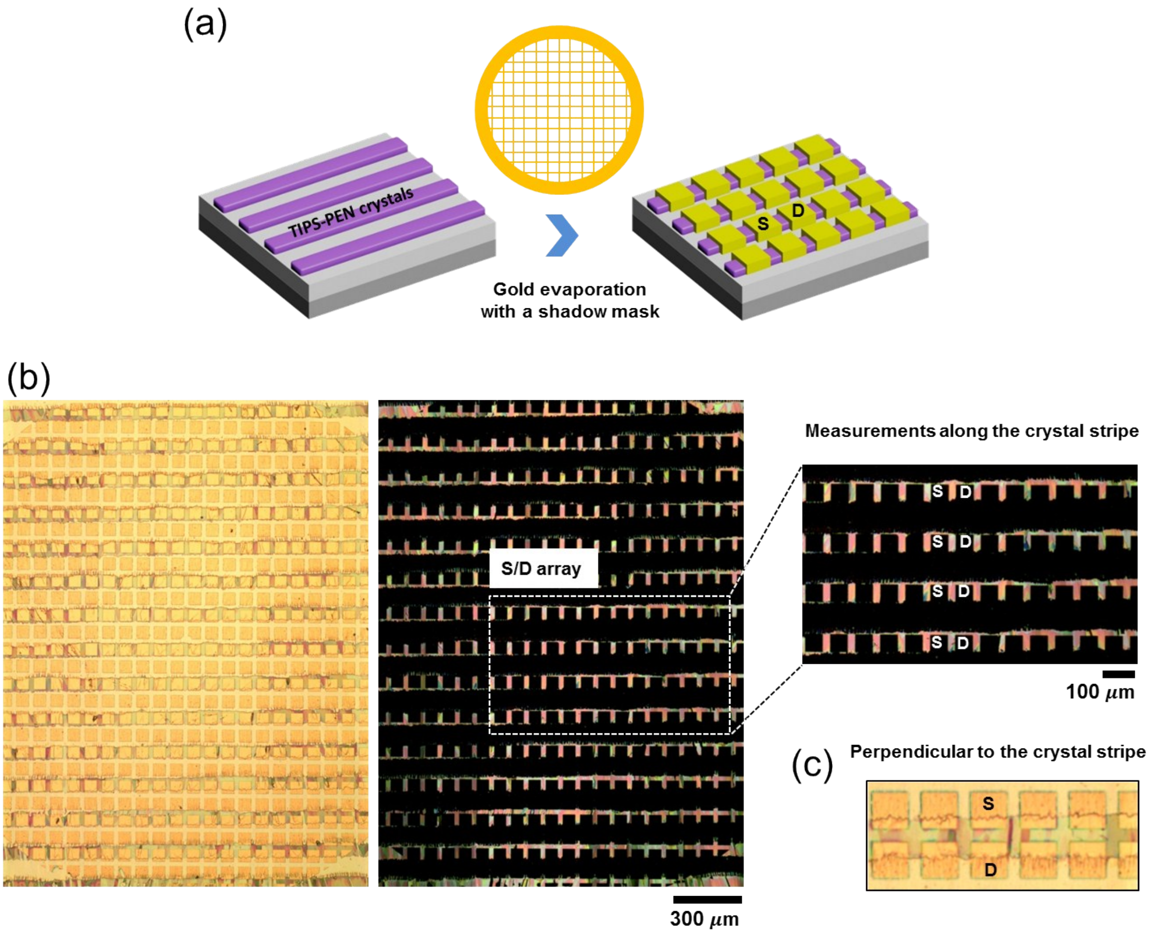


Figure S2. (a) Schematic illustration of the fabrication process and device structures of the patterned TIPS-PEN OFETs. (b) OM and POM images of the OFETs using the patterned TIPS-PEN crystal stripes formed by the programmed dip-coating process (both images share the scale bar: 300 μm). The right inset shows the magnified POM image. (c) OM image of the OFETs perpendicular to the patterned TIPS-PEN stripes.

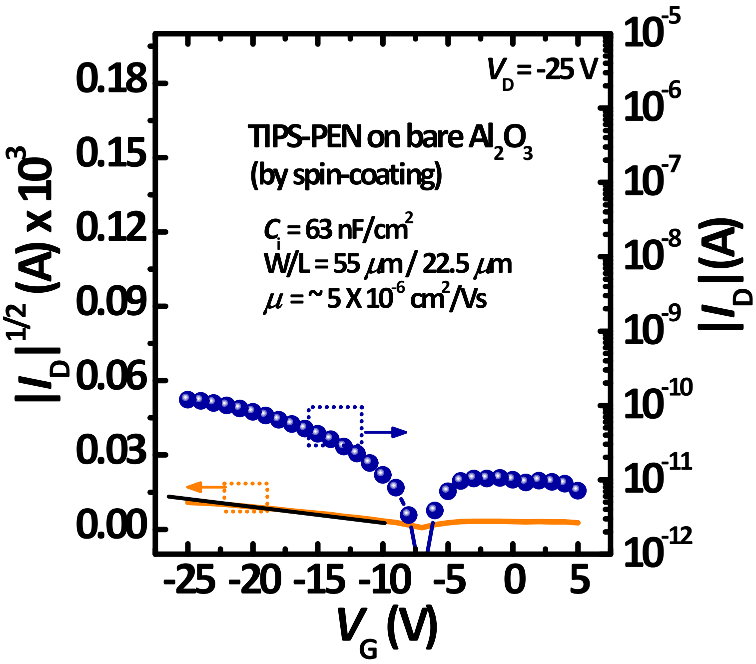


Figure S3. Transfer characteristics in the saturation regime ($V_D = -25$ V) of spin-coated TIPS-PEN OFETs using bare (untreated) Al_2O_3 gate dielectrics.

TIPS-PEN OFETs using bare Al_2O_3 gate dielectrics exhibited very low electrical performances with carrier mobility of ~ 5 × 10^{-6} cm^2/V·s. Since this value of mobility was too low, it was not appropriate to consider those devices as the representative control device. Therefore, we selected HMDS-treated TIPS-PEN OFETs as the control sample of spin-coating technique and compared them to the patterned TIPS-PEN OFETs.

(a)

1) Programed dip-coating: coating rate (v), width (W_d) (This work)

- Crystal stripe perpendicular to the coating direction
- Thin-film morphologies (similar with spin-coated films)
- Relatively lower OFET performance (μ = 0.22 $cm^2/V{\cdot}s$)
- Can control the inter-stripe spacing (patterned)

2) Continuous dip-coating: a constant coating rate of 150 μm/s (Adv. Funct. Mater. 2012, 22, 1005)

- Crystal growth along the coating direction
- Almost single crystal-like & higher OFET performance (μ = 0.85~1.3 $cm^2/V{\cdot}s$)
- Cannot control the gap spacing (un-patterned)

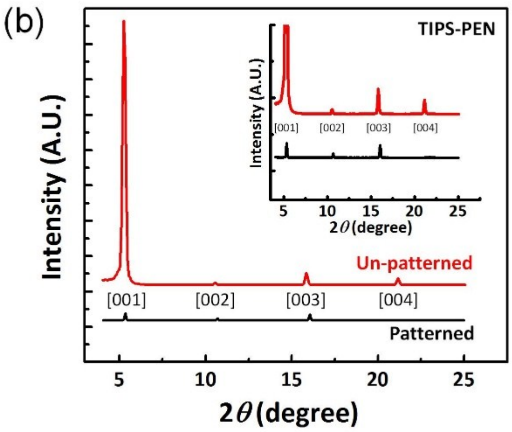
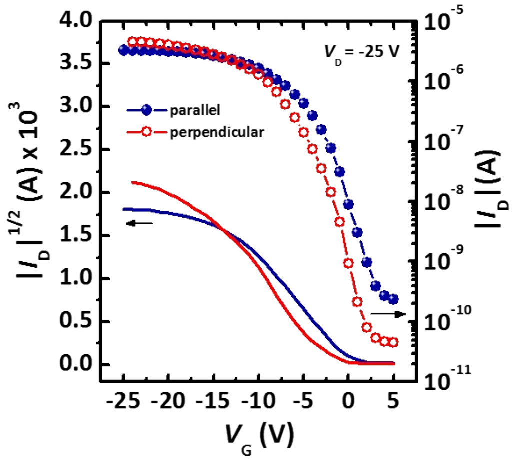


Figure S4. (a) Comparison between important features of (1) the programmed dip-coating (present work) and (2) continuous dip-coating (Adv. Funct. Mater. 2012, 22, 1005). (b) θ–2θ mode out-of-plane XRD patterns of patterned TIPS-PEN crystal stripes formed by a programmed dip-coating process and un-patterned TIPS-PEN crystal arrays formed by a continuous dip-coating process (λ = 1.07 A). The inset shows magnified spectra of the XRD patterns. The intensities of the XRD patterns were normalized according to the probed material volume and X-ray exposing time.

As summarized in Fig. S4a, we found in our previous work that when TIPS-PEN was continuously dip-coated at a constant coating speed, dozens of millimeters-long acene crystals were grown along the coating direction (*Adv. Funct. Mater.*, 2012, **22**, 1005–1014). These crystals were found to be almost single crystal-like and showed superior electrical performances with the mobility values of 0.85–1.3 $cm^2/V{\cdot}s$ to those of the patterned TIP-PEN FETs fabricated using the programmed dip-coating technique (0.22 ± 0.09 $cm^2/V{\cdot}s$) in this present study.

Although we could achieve high performance and single crystal-like crystal arrays from the continuous dip-coating, we could not control the gap space of the crystals from this approach. This became the motivation of current work. To enable the control over the gap space of the crystals, we introduced the programmed dip-coating process and demonstrated its feasibility. However, we observed a reduction of the carrier mobility for achieving the patternability. In other word, direct printing of TIPS-PEN stripes and obtaining their patterns (i.e. control over the crystal gap spacing) require some sacrifice in OFET performances. As we can see in Figs. 1 and 2, the patterned TIPS-PEN obtained by the programmed dip-coating process did not show single crystal-like crystal arrays but formed rather thin-film-type crystal stripes perpendicular to the coating direction. In other words, the patterned TIPS-PEN stripes showed completely different microscale morphologies from the un-patterned TIPS-PEN arrays by the continuous dip-coating process. Rather, the morphology of crystal stripes by the programmed dip-coating process looks similar with that of spin-coated films. This was why we compared the characteristics of our patterned TIPS-PEN stripes to those of spin-coated films.

Figure S4b shows θ–2 mode out-of-plane XRD patterns of the patterned TIPS-PEN stripes formed by the programmed dip-coating and un-patterned TIPS-PEN arrays formed by the continuous dip-coating processes. Both samples were prepared at a lifting rate (v) of 150 μm/s, the optimal lifting rate to achieve TIPS-PEN crystals, and the resulting thickness were found to be similar, approximately 95 ± 10 nm. The significantly higher [00*l*] peak intensities of the un-patterned sample imply that the patterned TIPS-PEN stripes exhibited lower degree of out of plane order compared to un-patterned TIPS-PEN crystal arrays obtained from the continuous dip-coating. This might be because the patterned crystals were all close to the nucleation (*Sci. Adv.* 2017, **3**, e1602462). For this reason, we think that the patterned films exhibited lower electrical performaces compared to the un-patterned crystal arrays.



	OFETs parallel to the TIPS-PEN stripes	OFETs perpendicular to the TIPS-PEN stripes
Mobility [cm²/V·s]	0.22 ± 0.09	0.26 ± 0.07

Figure S5. Comparison of transfer characteristics in the saturation regime ($V_D = -25$ V) of the OFETs whose S/D alignments were parallel and perpendicular to the patterned TIPS-PEN stripe. The right table summarizes average mobilities of the OFETs.

Figure S5 shows the comparison of transfer characteristics between representative OFET samples whose S/D electrodes alignments were perpendicular and parallel to the TIPS-PEN stripe. The OFET devices perpendicular to the TIPS-PEN stripes exhibited an average mobility value of 0.26 ± 0.07 cm^2/V·s, which was not seriously different from those of the devices parallel to the TIPS-PEN stripes. In other words, the mobility anisotropy between parallel and perpendicular OFET devices seems not significant in our system. We think that this result might be due to the polycrystalline nature of our crystal stripes, where the effects of grain boundary are more dominant than those of crystal anisotropy.

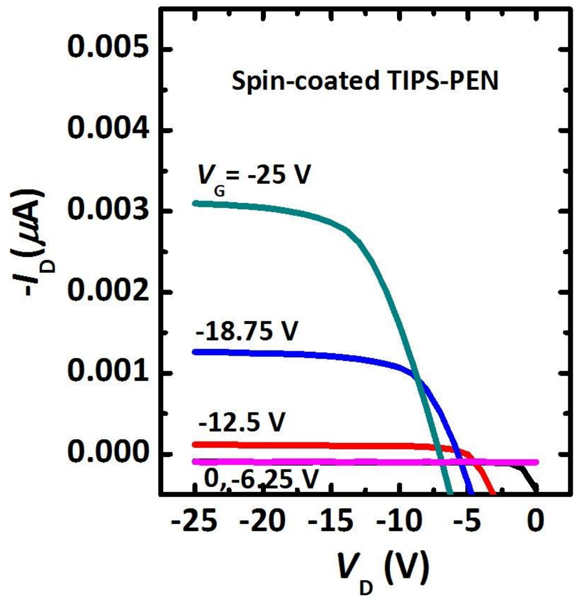


Figure S6. Output characteristics of the spin-coated TIPS-PEN OFETs.

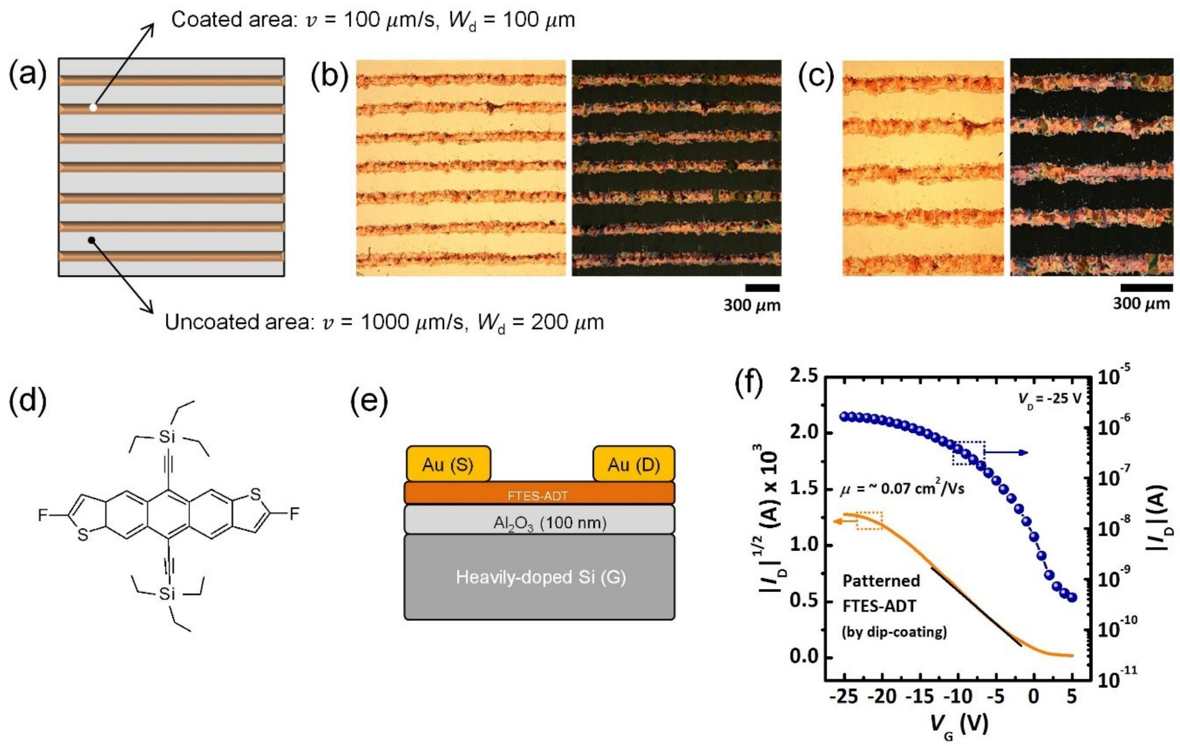


Figure S7. Programmed dip-coating processes for printing FTES-ADT: (a) Schematic illustration of the programmed information for printing FTES-ADT in a dip-coating process. (b) OM (left) and POM (right) images of the patterned FTES-ADT formed corresponding to the procedure described in (a) (both images share the scale bar). (c) Magnified images of (b). (d) Chemical structure of FTES-ADT. (e) Schematic illustration of the cross-sectional device structure of the FTES-ADT OFET. (f) Transfer characteristics in the saturation regime (V_D = −25 V) of the patterned FTES-ADT OFETs.