Supporting Information

The Influences of Out-Of-Plane Lattice Alignment on the OFET Performances of TIPS-PEN Crystal Arrays

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Experimental Details

Material: TIPS-PEN with purity of 99.0 % was purchased from Luminescence Technology Corp. and used without further purification. Carbon disulfide (99.9%) and dichloromethane (99.5%) were obtained from Kanto Corp and Seedchem Corp. Toluene (99.5%) and chlorobenzene (99.0%) were purchased from Echo Chem Corp. and Tedia Corp.

Preparation of a PDMS slab: PDMS slab was prepared by mixing Sylgard 184 (Dow Corning) in a 10:1 ratio by mass of oligomeric base to curing agent and casting 450 mg of the mixture on the 1.8×1.8 cm^2 glass slide and then curing at 100 ℃ for 2 hrs. The thickness of the cured PDMS slab was around 1.8 mm.

The growth of crystal array:. The crystal growth of TIPS-PEN was conducted on the cleaned substrates (glass slides and SiO_2/Si substrates). The substrates were soaked in the Piranha solution (H_2SO_4 and H_2O_2 with volume ratio of 3:1) at 80^oC for 40 minutes and then sonicated in *deionized water for 40 minutes*. Finally, the substrates were cleaned with isopropyl alcohol and then exposed under the ultraviolet-ozone environment for 40 minutes. Prior to making the crystal arrays of TIPS-PEN via the PAC method, the PDMS slabs must be exposed to ultraviolet-ozone treatment for 20 minutes in the *UVO-Cleaner m*achine (*UVO-Cleaner* Jelight 42, the average intensity of 25-35 mWs/cm^2 at wavelength of 254 nm). Owing to the affinity between the PDMS slab and the TIPS-PEN, TIPS-PEN molecules were absorbed into the PDMS slab with the solvent molecules, which makes the generation of the crystal arrays difficult. Therefore, the PDMS slabs should be treated with UV-ozone to increase their surface hydrophilicity, so that the amount of absorbed TIPS-PEN can be decreased. In the PAC processing, the PDMS slab was attached on the substrate. Approximately 20 μL of TIPS-PEN solution (2mg mL^{-1}) was then dropped into the empty gap between the PDMS slab and substrate. After the crystallization of TIPS-PEN was finished, the PDMS slab was detached and leaving the crystal arrays of TIPS-PEN on the substrate. All the crystal growths of TIPS-PEN were finished at ambient condition.

General characterization: For the characterization of polarized optical microscope (POM) and the grazing incidence X-ray diffraction (GIXD), crystal arrays of TIPS-PEN were deposited on the cleaned glass slides and (2-phenylethyl)trichlorosilane (PETS)-treated SiO_2/Si substrates from their CS_2 (2 mg mL^{-1}), dichloromethane (2 mg mL^{-1}), toluene (2 mg mL^{-1}) and chlorobenzene solutions (2 mg mL^{-1}) at ambient condition. POM images

were recorded on the Leica DM2700 optical microscopy. GIXD patterns were recorded at the BL17A1 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The ring energy of NSRRC was operated at 1.5 GeV with a typical current of 300 mA. The wavelength of the incident X-rays was 1.33 Å, delivered from the superconducting wavelength-shifting magnet, and an Si(111) double-crystal monochromator. The samples were placed horizontally on a sample stage. With an incident angle of 0.2°, GIXD was conducted and the pattern was collected with a detector system that included a CMOS flat panel X-ray detector, C9728DK. The scattering wave vector, defined as $q = 4\pi \sin\theta/\lambda$ (with 2θ being the scattering angle), was calibrated using silver behenate, sodalite, and silicon powders.

Transmission Electron Microscopy (TEM) characterization: (1) The ED tilting experiments were carried out with a Philips Tecnai 12 using an accelerating voltage of 120 kV. (2) The ED scanning of an individual TIPS-PEN crystal was performed in bright-field mode and electron diffraction configuration on a JEOL JEM-2010 transmission electron microscope with an accelerating voltage of 200 kV. The TIPS-PEN crystal arrays were prepared on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) coated glass slides by the PAC method. The crystal arrays on the PEDOT: PSS film was floated onto the *surface of deionized water* and picked up by copper grids. The samples were dried under vacuum overnight before the TEM characterization.

OFET Device Fabrication and Characterization: An n-type heavily doped Si wafer with a SiO_2 layer of 300 nm and a capacitance per unit area of 11 nF cm^{-2} was used as the gate electrode and dielectric layer. By the PAC method, crystal arrays of TIPS-PEN were deposited on PETS-treated SiO_2/Si substrates from their dichloromethane, CS_2, toluene

and chlorobenzene solutions (2 mg mL^{-1}) at ambient condition. Gold source and drain electrodes (40 nm in thickness) were deposited by vacuum evaporation on the long axes of TIPS-PEN crystal arrays through a shadow mask, affording a bottom-gate, top-contact device configuration. The channel length and width were 50 μm and 1 mm, respectively. Electrical measurements of the OFET devices were carried out at room temperature under N_2(g) using a 4156C Semiconductor Parameter Analyzers, Agilent Technologies. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_G is the gate voltage.

Crystal structure modeling: Material studio 6.0 software of Accelrys was used to build up the lattice models of TIPS-PEN. The lattice models were built from the Form I crystal structures of TIPS-PEN. The unit cell parameters of Form I crystal structure were determined by crystallographic experimental data from the GIXD and ED experiments. The simulated electron diffraction patterns based on the Form I crystal structure were generated by the Cerius2 package of Accelrys.

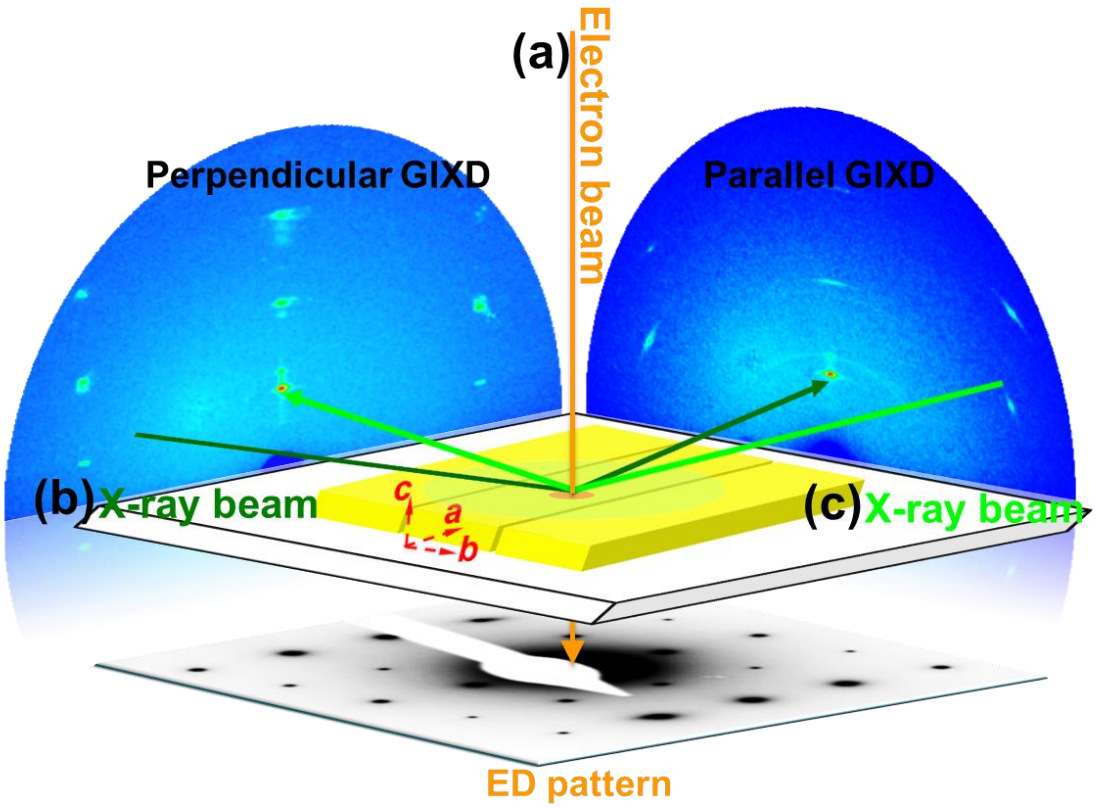

Figure S1. The schematic illustration of the construction of lattice parameters of TIPS-PEN. The two-dimensional diffraction methods including (a) Electron diffraction (ED) of transmission electron microscope (TEM), which give the top projection of reciprocal lattice. (b,c) Grazed incident X-ray diffraction (GIXD), which generates the lateral and end projection of reciprocal lattice with (b) X-ray incident beam direction perpendicular to the long axis of crystal arrays and (c) parallel to the long axis of crystal arrays respectively.

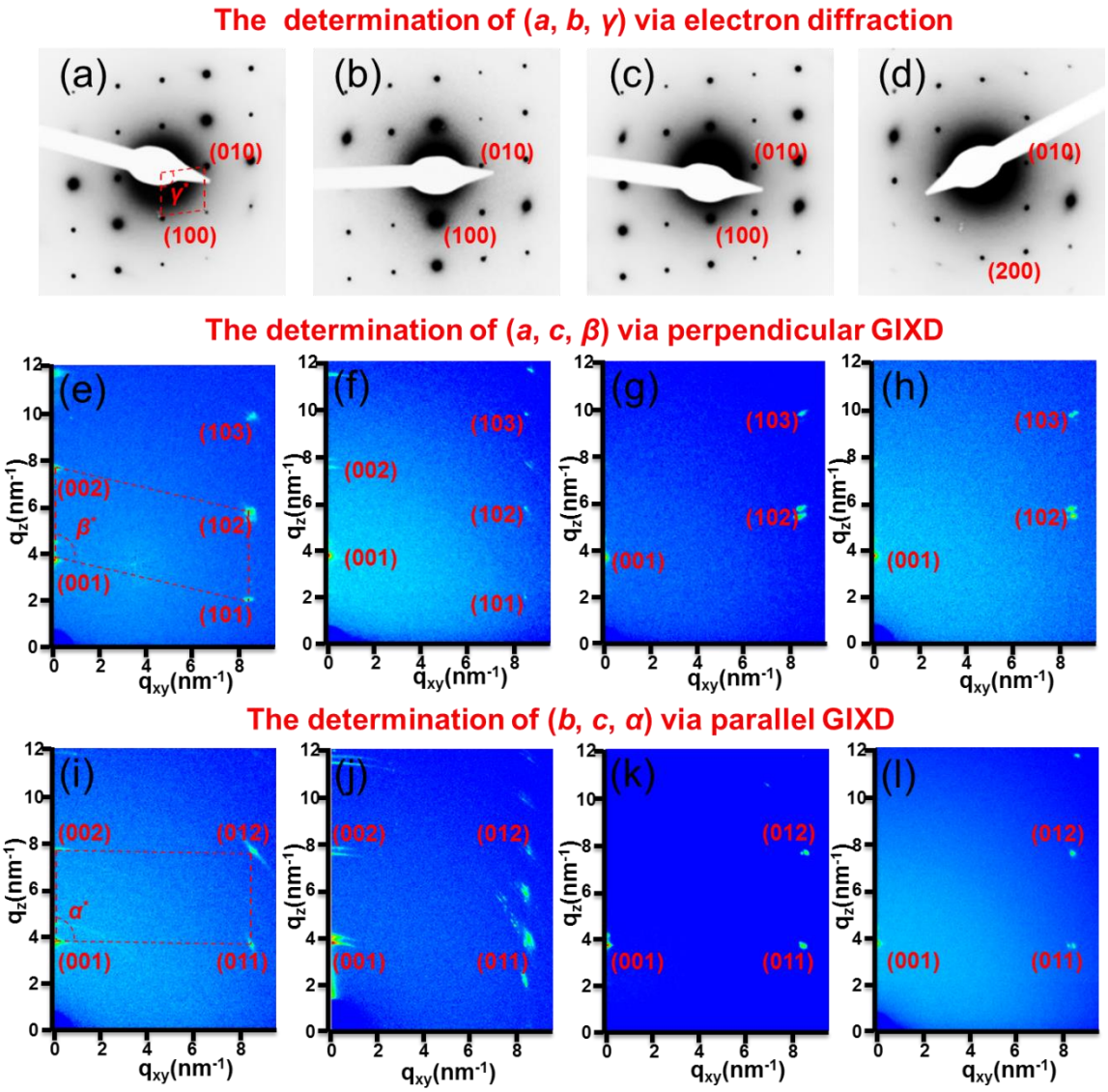

Figure S2. The extraction of lattice parameters (*a*, *b*, *c*, α, β ,γ) via ED and GIXD. The diffraction patterns of TIPS-PEN crystals generated from the crystal arrays grown from (a,e,i) DCM, (b,f,j) CS_2, (c,g,k) Tol and (d,h,l) CB. Because GIXD and ED are the two-dimensional diffraction, only two lattice constants of *a*, *b* and *c* and one corresponding angle of *α*, *β* and *γ* can be given from one direction of incident light.

Table S1. Comparison of lattice parameters of TIPS-PEN crystals grown from different solvents.

	(100)	(010)	(001)	*a* (Å)	*b* (Å)	*c* (Å)	*α* (Deg.)	*β* (Deg.)	*γ* (Deg.)
Form I [1]	7.44	7.60	16.36	7.77	7.68	16.90	87.51	75.41	81.46
DCM	7.44	7.59	16.52	7.74	7.67	17.03	88.7	76.0	82.0
CS_2	7.44	7.59	16.52	7.74	7.67	17.03	88.7	76.0	82.0
Tol	7.44	7.59	16.50	7.74	7.67	17.01	88.7	76.0	82.0
CB	7.45	7.59	16.51	7.75	7.67	17.02	88.7	76.0	82.0

Table S2. The PAC processing time in different solvent conditions

Solvent	T_b (°C)	Processing Time (min)
Dichloromethane(DCM)	40	≈ 2
Carbon disulfide (CS_2)	46	≈ 2
Toluene (Tol)	110	≈ 6
Chlorobenzene (CB)	131	≈ 6

Table S3. Orientation parameters of long axis and short axes of TIPS-PEN crystal arrays via the PAC methods with different solvents.

	DCM	CS_2	Tol	CB
f_{001} (long axis) (%)	92	93	99	99
f_{001} (short axis) (%)	88	84	97	94

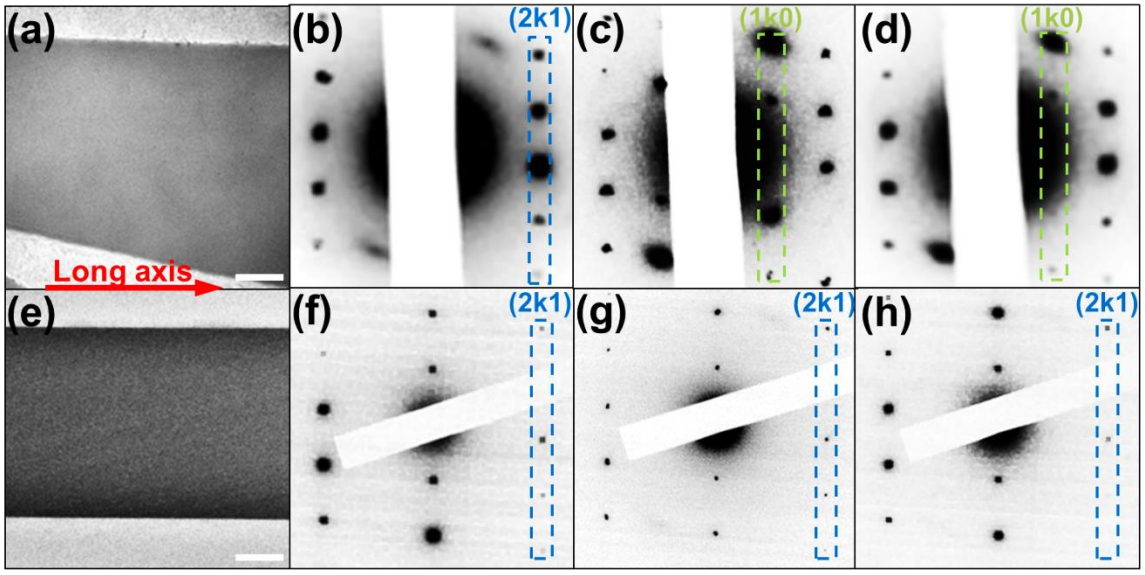

Figure S3. The TEM images of an individual crystal in the TIP-PEN crystal arrays prepared from (a) CS_2, and (e) CB. The ED patterns that were taken along the long axis of the crystal prepared from (b-d) CS_2, and (f-h) CB. In the crystal prepared from CS_2, the (2*k*1) diffractions are observed in (c), whereas the (1*k*0) diffractions are seen in (c) and (d). Thus, the pattern in (b) is denoted as ED-A, and that in (c) and (d) is denoted as ED-B. In the crystal prepared from CB, only ED-A is observed. The scale bar in (a) and (e) is 1 μm.

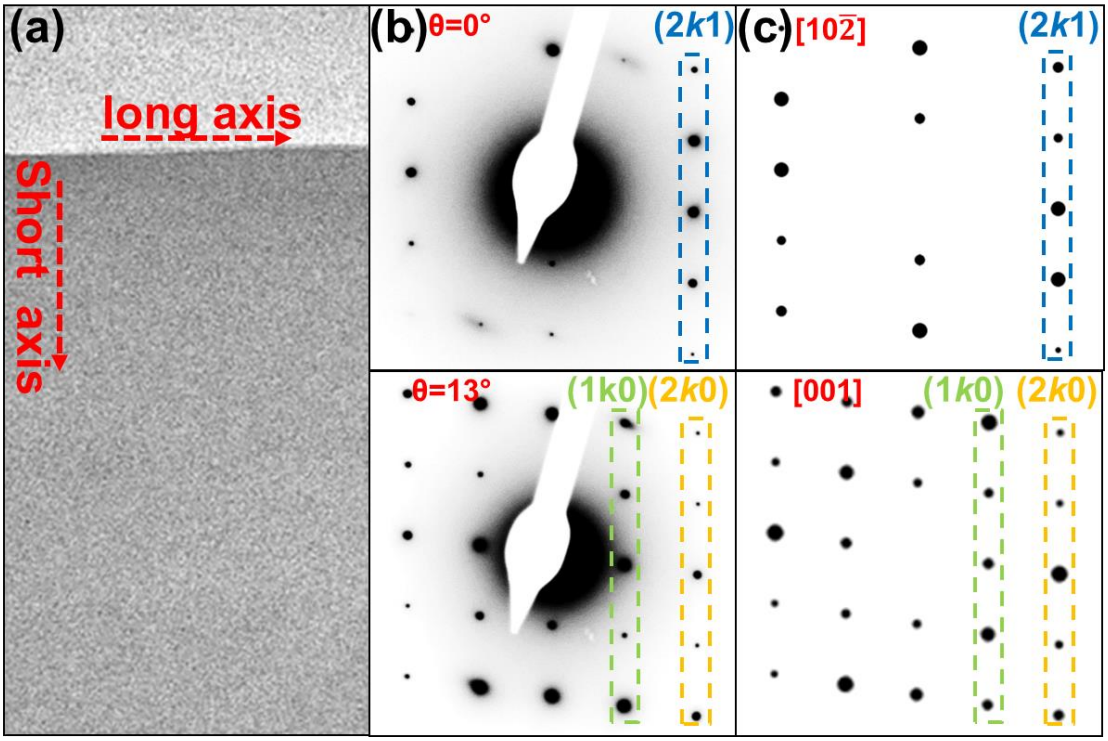

Figure S4. The confirmation of the out-of-plane misoriented angle by the ED tilting experiment: (a) TEM bright-field image of a TIPS-PEN crystal grown from Tol, (b) The diffraction patterns generated by tilting the stage with 0° and 13° tilting angle (**θ**) along its short axis, and (c) the simulated ED patterns of the Form I crystal structure generated along [001] and [10$\bar{2}$] zone and the angle between [001] and [10$\bar{2}$] zone is also 13°.

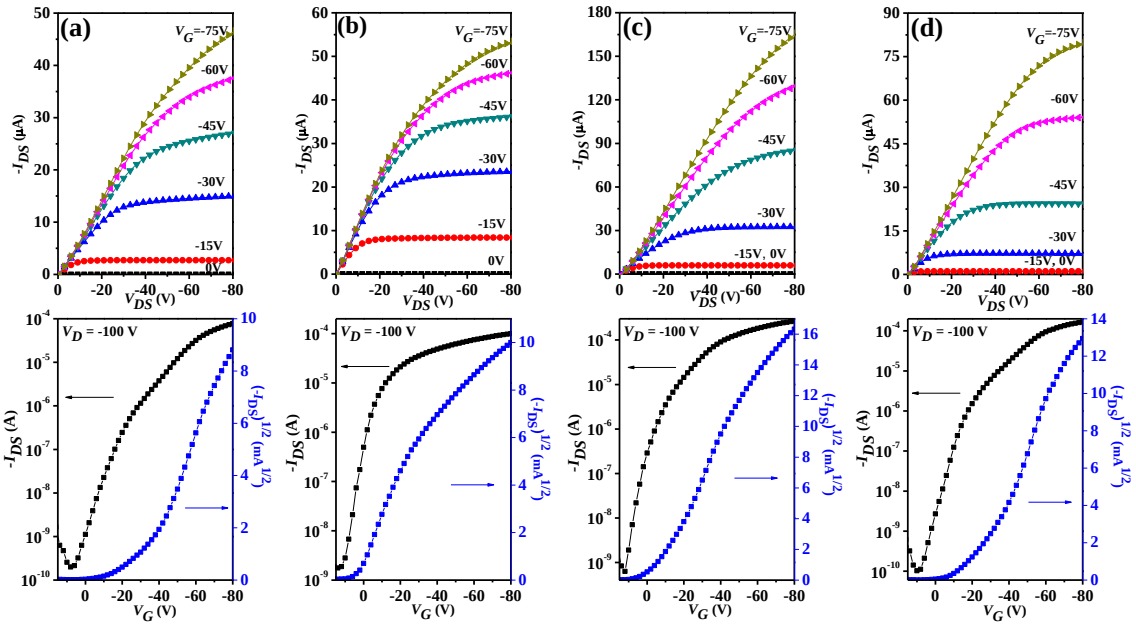

Figure S5. Output (up) and transfer (down) characteristics of the TIPS-PEN OFET devices fabricated from (a) DCM, (b) CS_2, (c) Tol and (d) CB.

Reference

(1) Diao, Y.; Lenn, K. M.; Lee, W.-Y.; Blood-Forsythe, M. A.; Xu, J.; Mao, Y.; Kim, Y.; Reinspach, J. A.; Park, S.; Aspuru-Guzik, A. n. *J. Am. Chem. Soc.* **2014**, *136*, 17046.