## Supporting Information

## Shear aligned large-area organic semiconductor crystals through extended $\pi$ - $\pi$ interaction

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Fig. S1. Typical transfer curves for BGTC device made of shear-coated TIPS-PPP on plasmatreated SiO<sub>2</sub>/Si substrate.



Fig. S2. Polarized optical microscope images for shear-coated TIPS-PPP crystals using a concentration of 3 mg/ml, 5 mg/ml, and 8 mg/ml. The inset shows rotated images at 13°, and the scale bar is 500 um.



Fig. S3. In-situ UV-vis spectra for drop-casted (a,b) TIPS-PEN and (c,d) TIPS-PPP solutions within two minutes. The absorption intensity at 672 nm (TIPS-PEN) and 830 nm (TIPS-PPP) is plotted versus drying time to show the onset of significant  $\pi$ - $\pi$  stacking behavior.



Fig. S4. Indexed GIWAXS image of a TIPS-PPP thin film. The GIWAXS image is obtained by combining a parallel and perpendicular measurement to obtain a complete diffraction pattern. On the left the unit cell obtained from the GIWAXS measurements is used to index the peaks, whereas on the right the literuature unit cell is used to index the peaks.



Fig. S5. Observed and calculated GIWAXS image of a TIPS-ppp thin film. The image on the right was calculated from the crystal structure reported by Jousselin-Oba et al. The procedure for the calculation of the GIWAXS image is described in REF 22.



Fig. S6. GIWAXS patterns for shear-coated TIPS-PPP crystals upon in-situ heating. (a,d) 25 °C, (b,e) 150 °C, (c,f) 200 °C.



Fig. S7. Polarized optical microscope image of patterned gold electrodes on TIPS-PPP crystals.



Fig. S8. Representative output characteristics of BGTC device.



Fig. S9. DFT simulation of mobility anisotropy for TIPS-PPP and TIPS-PEN. (a) A bottom view of the molecule backbone. The 0 degree means along the backbone direction and 90 degrees means perpendicular to the backbone direction. (b) Polar plot of simulated mobility for TIPS-PPP. (c) Polar plot of simulated mobility for TIPS-PEN. Note that the scales of the y-axes in (b) and (c) differ.



Fig. S10. Grain boundary effect on the OFET device performance. (a, b) Representative polarized optical microscope images under 13° rotation. (c) Transfer curves for representative four devices. (d) Extracted mobility over gate voltage. BGTC devices are fabricated with a channel length of 50 um and a channel width of 1000 um. A clear grain boundary can be observed in device 3 and 4.



Fig. S11. Coating speed effect on OFET device performance. Representative transfer characteristics of BGTC devices at (a) 0.01 mm/s, (b) 0.1 mm/s, and (c) 1 mm/s. BGTC devices are fabricated with a channel length of 50 um and a channel length of 1000 um. The extracted mobility along the perpendicular direction is 1.87, 0.86, and 0.0025 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, and the mobility along the parallel direction is 0.57, 0.46, and 0.03 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. BGTC devices are fabricated with a channel length of 50 um and a channel width of 1000 um.



Fig. S12. Device geometry effect on the OFET performance. (a) Polarized optical microscope image of shear-coated TIPS-PPP film on top of  $SiO_2/Si$  substrate with evaporated Cr/Au electrode. (b-c) Representative transfer curve and extracted mobility versus gate voltage. (d) Output curve for TGBC devices. (e, f) Representative transfer curve and extracted mobility versus gate voltage in the linear region for TGBC devices. The channel length is 50 um, and the width is 2000 um.

Unit Cell	GIWAXS fitting	Single crystal XRD
a /(Å)	7.58	7.5635
b /(Å)	8.38	8.3244
c /(Å)	18.60	18.5700
α /(°)	100.98	102.515
β /(°)	92.49	94.641
γ /(°)	99.45	98.308
Area /(Å <sup>2</sup> )	62	62.3
Volume /(Å <sup>3</sup> )	1141	1121.8

Table S1. Comparison of fitted unit cell parameters from GIWAXS and single crystal X-ray diffraction (XRD).