## **Supplementary Material**

# Preparation of highly oriented single crystal arrays of C8–BTBT by epitaxial growth on oriented isotactic polypropylene

Mingliang Li,<sup>a,b</sup> Tingcong Jiang,<sup>e</sup> Xiaoge Wang,<sup>c</sup> Hongliang Chen,<sup>f</sup> Shuo Li,<sup>a,b</sup> Feng Wei,<sup>a,b</sup> Zhongjie Ren,<sup>e</sup> Shouke Yan,<sup>\*e</sup> Xuefeng Guo<sup>\*c,d</sup> and Hailing Tu<sup>\*a,b</sup>

<sup>a</sup>GRIMAT Engineering Institute Co., Ltd, Beijing 101407, P. R. China.

<sup>b</sup>State Key Laboratory of Advanced Materials for Smart Sensing, General Research Institute for Nonferrous Metals, Beijing 100088, P. R. China. <sup>c</sup>Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

<sup>d</sup>Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China. <sup>e</sup>State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China. <sup>f</sup>Department of Chemistry. Northwestern University. Evanston. IL 60208, USA

#### Section 1. General materials and methods.

**NMR:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker–400 MHz NMR ARX400. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR signals were quoted to tetramethylsilane ( $\delta = 0.00$  ppm) and CDCl<sub>3</sub> ( $\delta = 77.00$  ppm) as internal standards, respectively. Mass spectra (MS) were recorded on a Bruker APEX IV mass spectrometer.

Polarized optical microscopy (POM): POM images were obtained on silicon substrates by using Nikon Eclipse LV100 POL in reflection mode.

Scanning electron microscope (SEM): Mode S4800 was used with a scan voltage of 1.0 kV. Cross section SEM was conducted on ZEISS Merlin Compact with a scan voltage of 5.0 kV.

Atomic force microscopy (AFM): The morphology of thin films was investigated by a ScanAsyst model AFM (Bruker Dimension Icon with Nanoscope V controller) under ambient conditions.

Film X-ray diffraction: Film X-ray diffraction data were collected on PANalytical high resolution PXRD.

Transmission electron microscope (TEM): Field-emission High Resolution TEM was conducted on JEM-2100F of JEOL.

#### Section 2. Synthesis procedure and designed apparatus for SVA and melt-draw technique

2,7-dioctyl[1]benzothieno[3,2-b][1] benzothiophene (C8-BTBT) was synthesized according to the literature.<sup>1,2</sup>

C8–BTBT: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.76 (d, 2H, *J* = 5.4 Hz), 7.70 (s, 1H), 7.26 (d, 2H, *J* = 6.3 Hz), 2.75 (t, 4H, *J* = 5.1 Hz), 1.68 (m, 4H), 1.30 (m, 20H), 0.88 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 142.45, 140.09, 132.58, 131.24, 125.85, 123.34, 121.08, 36.15, 31.91, 31.72, 29.51, 29.35, 29.28, 22.68, 14.10. EI–MS: Calcd. for [M]<sup>+</sup>: 464.25659. Found: 464.25748.



Fig. S1 Schematics of the designed apparatus for SVA.



Fig. S2 Schematics of the apparatus for melt-draw technique for highly oriented iPP thin film

**Melt–draw technique:** Dissolve the 0.5 wt. % solution of iPP with xylene as solvent by heating at 200 °C, drop the solution on a preheated 140 °C hot stage with a glass dropper, and spread the solution evenly on the hot stage with a glass rod. After the xylene is volatilized, a film is formed on the hot stage. Then, quickly pulled on the hot stage, using a motorized roller with a rotational speed of about 20 cm s<sup>-1</sup>. A highly oriented film is obtained. The film is removed by a self–made collecting bracket and covered on the surface of the clean silicon wafer.



Fig. S3 The topographical image of AFM for the highly oriented iPP film.





Fig. S4 POM images for as-cast films(a) and SVA crystals(b) on OTS motified silicon wafer.



Fig. S5 (a-b) AFM images of crystals after SVA and their corresponding height plots based on colours (down).

### Section 4. Characterization and statistics of crystal electronic devices

FET Characterization: FETs were measured under ambient conditions using Keithley 4200 semiconductor parameter analyzer.  $\mu_{\text{FET}}$  and  $V_{\text{th}}$  were extracted from transfer characteristics in the saturated regime by Equ. S1.  $I_{t} = -C_{t} \mu_{\text{FET}} (V_{cc} - V_{tb})^{2}$ 

$$V_{d} = \frac{1}{2L} C_{i} \mu_{FET} (V_{GS} - V_{th})^{2}$$
(S1)

 $C_i$ , capacitance per unit area measured by capacitance-voltage measurement is  $4.2 \times 10^{-5}$  F m<sup>-2</sup> at 50 Hz. *W* and *L* are channel width and channel length, respectively.





Fig. S7 (a) Configuration of the single–crystal FET arrays on OTS–modified substrate; (b) An invalid device failing to bridge the electrodes; (c) A working device with both ends of the crystal connected to the electrodes.



**Fig. S8** (a) Transfer characteristics of a typical OTS-modified silicon substrate device ( $\mu_{\text{FET}}$  of 6.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, on/off ratio 10<sup>6</sup>) operated at -60 V drain voltage in air. The effective channel length is  $L = 49 \ \mu\text{m}$  and channel width is  $W = 12.7 \ \mu\text{m}$ . (b) Output characteristics with gate voltage ( $V_{\text{GS}}$ ) ranged from 0 to -60 V in -15 V steps.

#### References

- 1. M. Saito, I. Osaka, E. Miyazaki, K. Takimiya, H. Kuwabara and M. Ikeda, Tetrahedron Letters, 2011, 52, 285.
- 2. H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara and T. Yui, *Journal of the American Chemical Society*, 2007, **129**, 15732.