Electronic Supplementary Information (ESI)

Controllable Growth of C_8-BTBT Single Crystalline Microribbon Arrays by Limited Solvent Vapor-Assisted Crystallization (LSVC) Method

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Experimental section：

Materials and Instrumentations:

C_8-BTBT was purchased from Sigma Aldrich and was used as received. HPLC grade toluene was purchased from commercial resources and was directly used.

OFET characteristics were measured by a Keithley 4200 SCS, which is connected with Micromanipulator 6150 probe station in a clean and shielded box. Mobility was extracted using the equation of channel current in saturation region, using the equation: $I_{DS}=W/2L\ \mu C_i(V_G-V_T)^2$, where I_{DS} is the drain-source current, W and L are the channel width and length, C_i is the dielectric capacitance, V_G is the gate voltage, and V_T is the threshold voltage.

Optical microscopy images were recorded by a Leica DM4 M.

Atomic force microscopy images were obtained by an AFM Nanoscope IIIa in tapping mode.

Transmission electron spectroscopy images was measured by JEOL JEM-1011.

Contact angles was tested on a Contact Angle Meter (DSA100, Krüss Company, Germany) by a sessile droplet method.

Theoretical calculation:

The crystal structure was optimized with VASP using LDA method and a plane-wave basis set. Van der Walls and Coulomb interaction were evaluated by using the Ewald summation method with a cutoff 600 eV;[1-3] and the convergence tolerance of energy and force is 0.00001 eV and 0.005 eV/A, respectively.

Since charge transfer process often coupled intramolecular high frequency vibration in organic semiconductors, we employed the tunneling enabled hopping model to describe the charge transport.[4-6] The transfer integral V_{fi}, and reorganization energy λ are important parameters to determine the charge transfer rate. The transfer integrals for the nearest-neighbor dimers along the transport pathways in bulk crystals were calculated using the site energy correction method.[7-9] All the calculations of transfer integral and reorganization energy were performed using density functional theory with the B3LYP

functional in combination with 6-31G* basis set using the Gaussian 09 program.[10]

The C_8-BTBT adopts herringbone stacking configuration and displays two-dimensional transport behaviour as presented in Fig. 1. From Table 1, the transfer integrals along π stacking **P1** and **P2** are much larger than the ones along other directions. Based on the transfer integral and reorganization energy parameters, the hopping rates along each pathway were estimated using the quantum charge transfer rate with short time approximation. Then, the kinetic Monte Carlo approach is adopted to simulate charge mobility in ab plane.

Substrates used:

Briefly washed SiO_2/Si: The SiO_2/Si substrates were washed successively by water, acetone and isopropyl alcohol and blow-dried under nitrogen.

Piranha-washed substrates: The SiO_2/Si substrates were washed successively by water, acetone and ethanol and blow-dried under nitrogen, then washed with piranha solution (H_2SO_4:H_2O_2 =7:3), pure water, isopropyl alcohol and blow-dried under nitrogen.

O_2 plasma treated substrates: The piranha-washed substrates were further treated with oxygen plasma for 5 min.

OTS treated substrates: O_2 plasma treated substrates were placed in a vacuumed oven at 90 ^oC for 1 hour and then a droplet of OTS was added and the oven was kept at 120 ^oC for 2 hours. Then the substrates were successively washed by hexane, chloroform and isopropyl alcohol and blow-dried under nitrogen.

BCB substrates: O_2 plasma treated substrates were spin-coated by BCB (BCB:mesitylene=1:5) at 2000 rpm, 60 s in the glove box, then annealed on hotplate at 260 ^oC for 1 hour.

The extraction of wetting envelopes:

$$\gamma_{LV}(1+\cos\theta) = 2\sqrt{\gamma_S^D}\sqrt{\gamma_{LV}^D} + 2\sqrt{\gamma_S^P}\sqrt{\gamma_{LV}^P} \quad (1)$$

Owens derived the Equation 1 from the well-known Young's equation. The equation shows the relationship between the solid surface energy (dispersion (γ_S^D) and polar (γ_S^P) components) and liquid surface energy (dispersion (γ_{LV}^D) and polar (γ_{LV}^P) components).[11] Surface energy of the adopted substrates in paper were calculated by equation 1.We took the γ_{LV}^D as a function of γ_{LV}^P, and since that

$$\gamma_{LV} = \gamma_{LV}^D + \gamma_{LV}^P \quad (2)$$

Liquid surface energy (γ_{LV}) is composed of γ_{LV}^D and γ_{LV}^P, so equation 1 can be written as:

$$\gamma_{LV}^D = \left(\pm \sqrt{\left(\frac{\sqrt{\gamma_S}}{1+\cos\theta}\right)^2 - \left(\sqrt{\gamma_{LV}^P} - \frac{\sqrt{\gamma_S^P}}{1+\cos\theta}\right)^2} + \frac{\sqrt{\gamma_S^D}}{1+\cos\theta} \right)^2 \quad (3)$$

By assuming that θ=0˚,

$$\gamma_{LV}^D = \left(\pm \sqrt{\frac{\gamma_S}{4} - \left(\sqrt{\gamma_{LV}^P} - \frac{\sqrt{\gamma_S^P}}{2}\right)^2} + \frac{\sqrt{\gamma_S^D}}{2} \right)^2 \quad (4)$$

By assuming that θ=90˚,

$$\gamma_{LV}^D = \left(\pm \sqrt{\gamma_S - (\sqrt{\gamma_{LV}^P} - \sqrt{\gamma_S^P})^2} + \sqrt{\gamma_S^D} \right)^2 \quad (5)$$

We utilized OriginLab OriginPro to draw the function plots of equation 4 and 5, which respectively represent the wetting envelope of complete wetting and critical wetting.

The funnel used:

The dimensions of the funnel are added in the manuscript, the inner diameter of the funnel is 8.5 cm, and the length of the hypotenuse is 8 cm.

Table S1 The transfer integrals V (in meV) for C_8-BTBT.

	P1	P2	P3	P4	P5	P6
C_8-BTBT	57.3747	57.3747	-31.693	-31.701	-31.685	-31.681

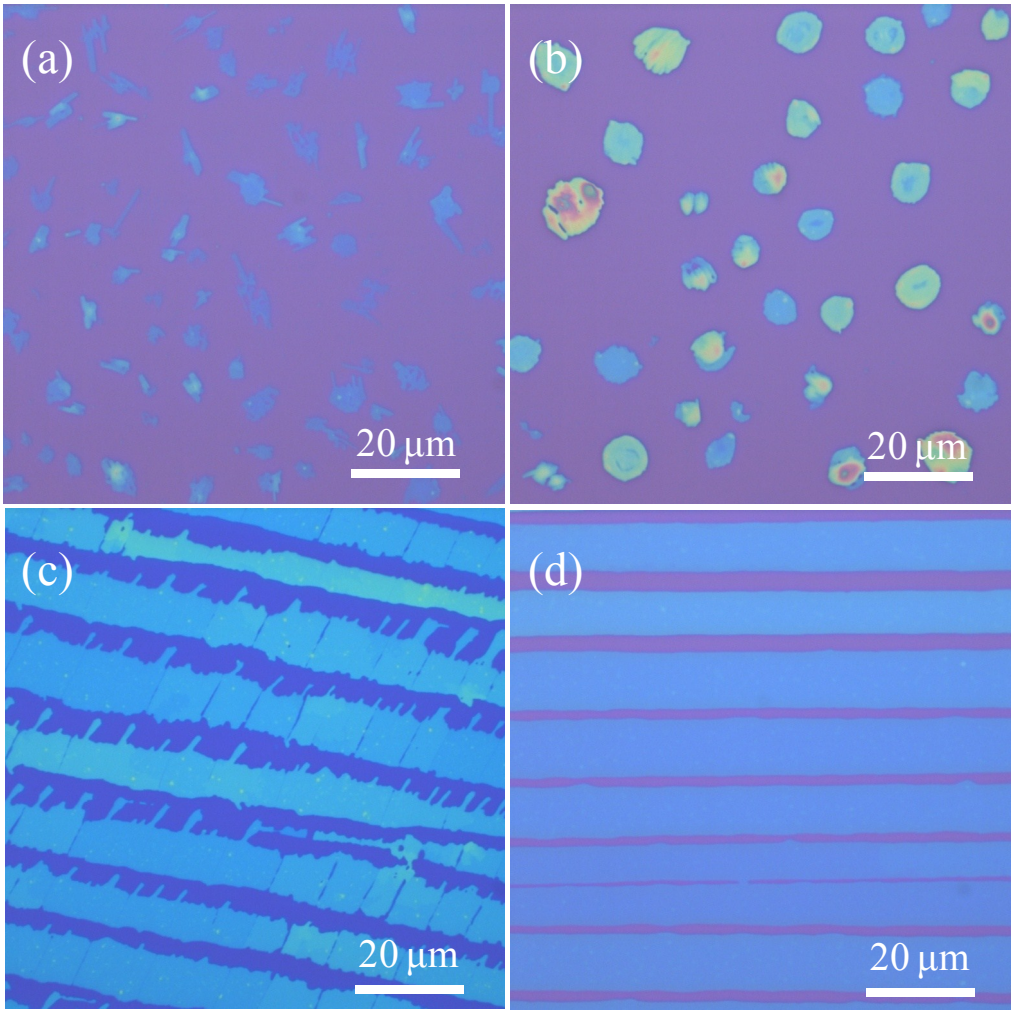

Fig. S1 (a) 0.05 mg mL^{-1} (b) 0.1 mg mL^{-1} (c) 0.2 mg mL^{-1} (d) 0.5 mg mL^{-1} C_8-BTBT in toluene on SiO_2 with substrate temperature of 40 ^oC.

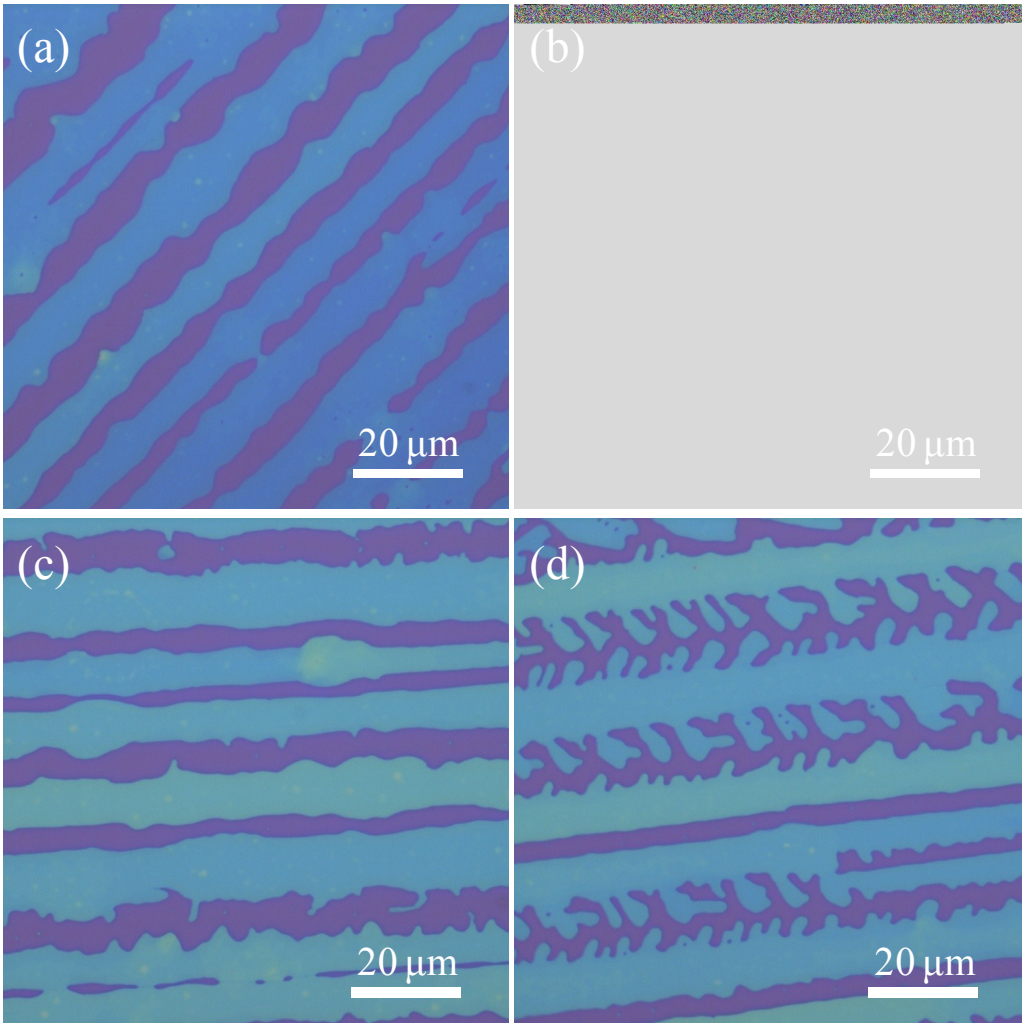

Fig. S2 0.5 mg mL^{-1} C_8-BTBT in toluene crystallized on SiO_2 heated at different temperatures: (a) 30 °C (b) 40 °C (c) 50 °C and (d) 60 °C hot plates.

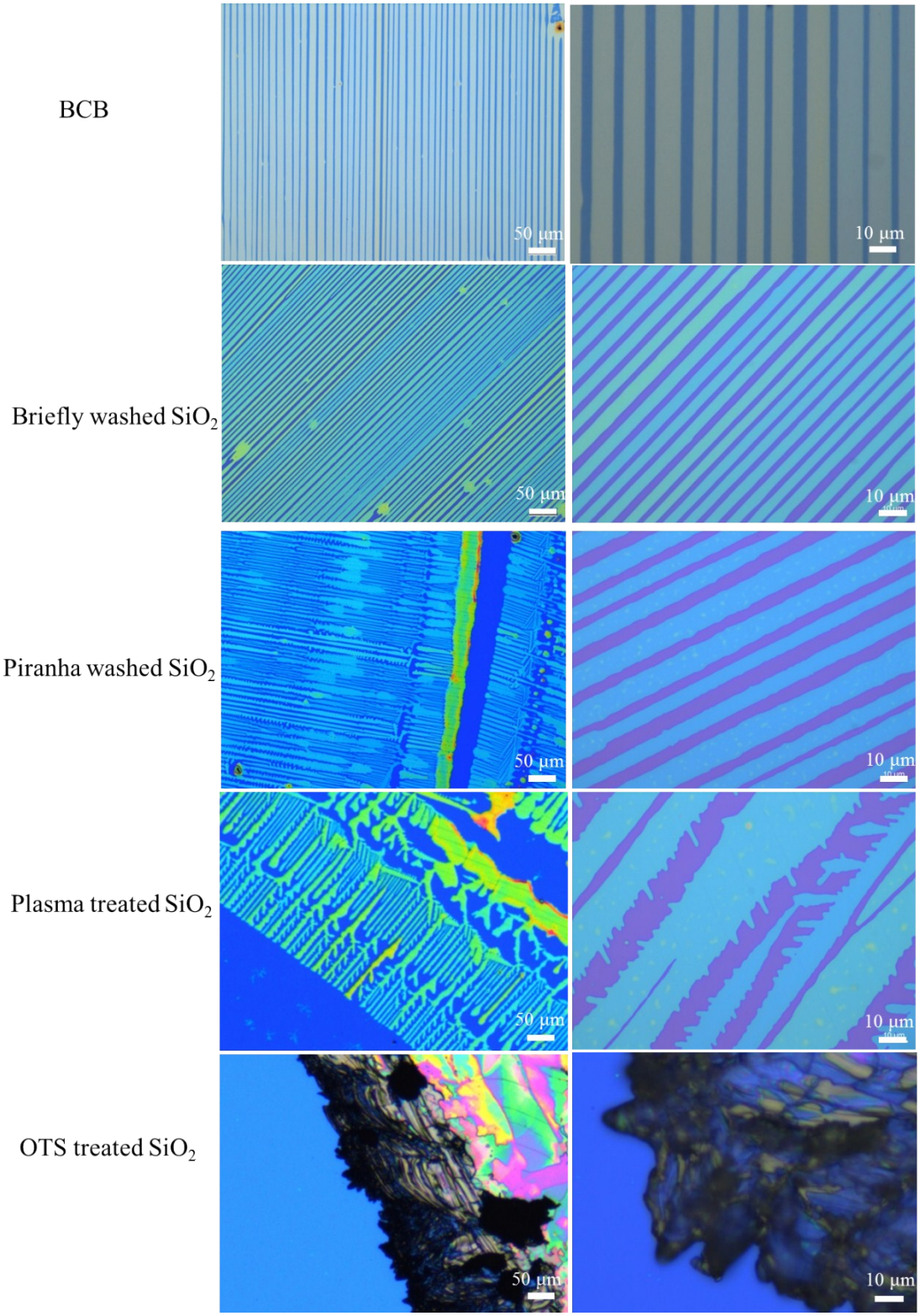

Fig. S3 OM images of C_8-BTBT grown on different substrates, showing the varied coverage fraction and alignment quality.

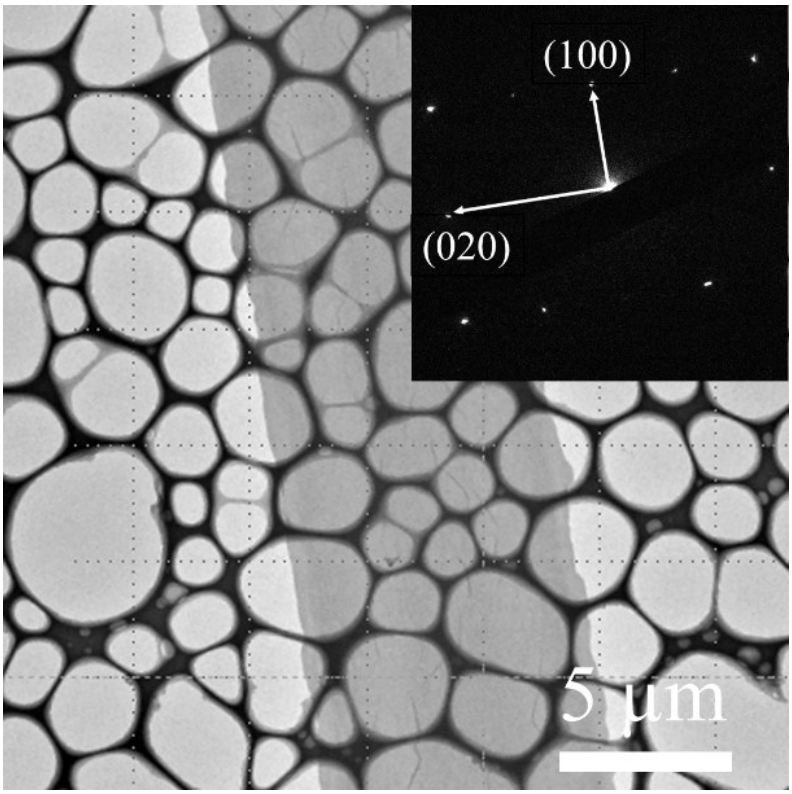

Fig. S4 TEM image and corresponding SAED patterns (inset) of C_8-BTBT ribbon crystals.

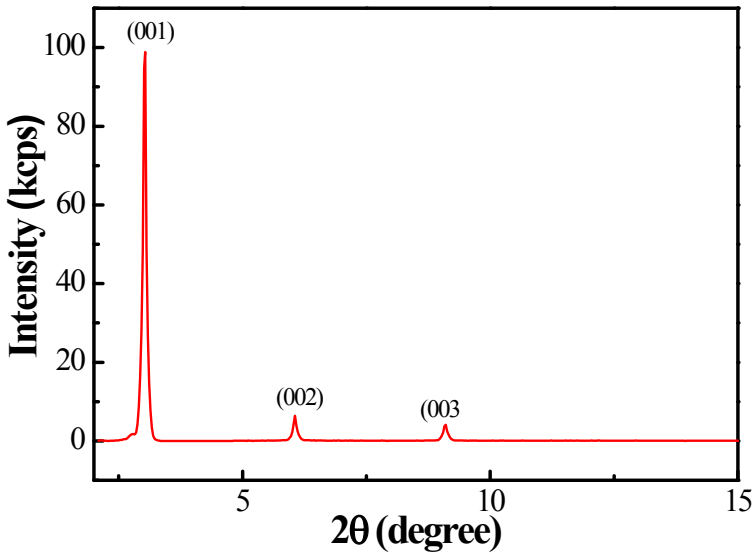

Fig. S5 Powder XRD pattern of the oriented crystals grown on SiO_2/Si subsrates.

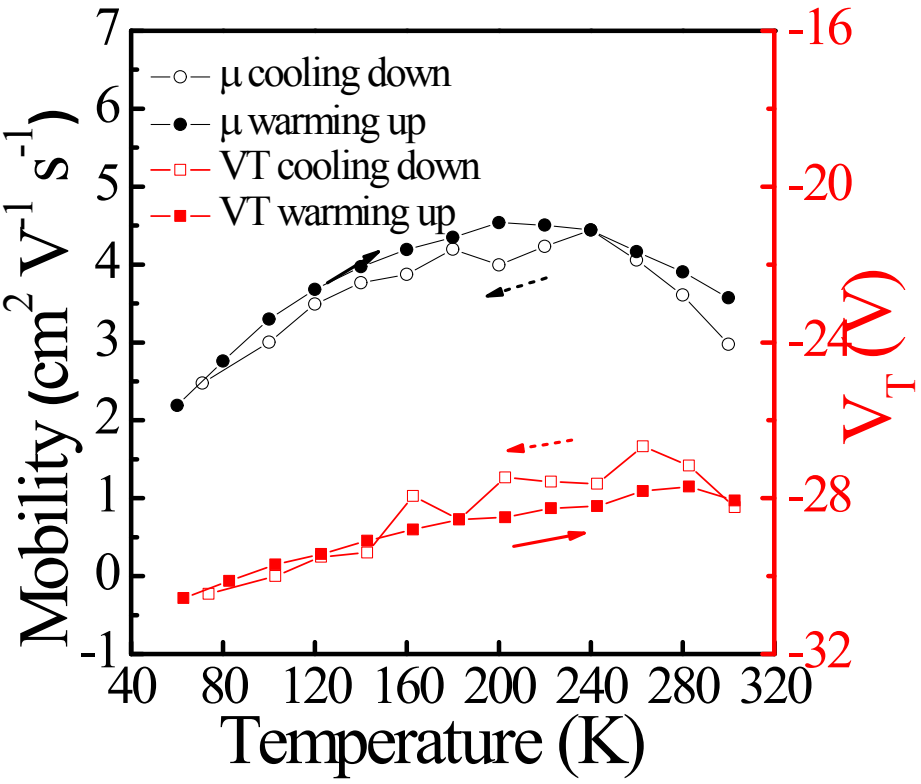

Fig. S6 Temperature dependence of mobilities and threshold voltages. Mobility (black) and threshold voltage (red) measured during warming up (solid) and cooling down (open) and the arrows indicate the scan direction of the temperature.

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