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Supplementary information for

Controlling Crystallization to Improve Charge Mobilities in Transistors Based on 2,7-Dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene

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1. Differential scanning calorimetry (DSC) result of C8-BTBT

Differential scanning calorimetry results of C8-BTBT are shown in Figure S1. The crystallization temperature (T_C) and melting temperature (T_m) for C8-BTBT are 98 °C and 109 °C, respectively. Another peak at approximately 124 °C is also apparent, which is likely due to a liquid crystal to isotropic transition.

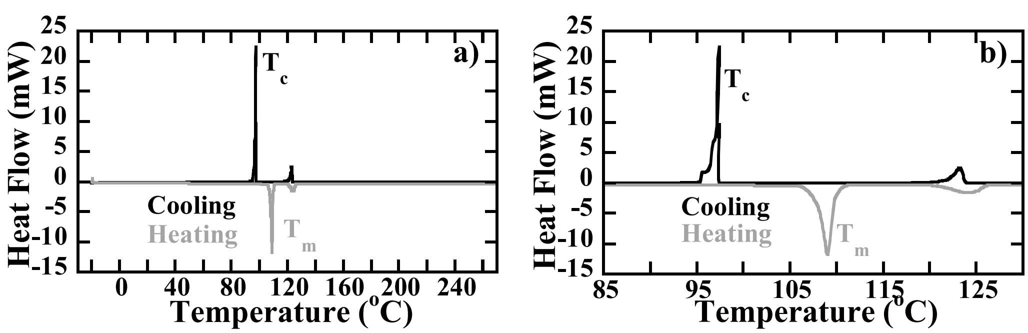


Figure S1. Differential scanning calorimetry results for C8-BTBT. (a) Two peaks are apparent in heating scans, a melting temperature (T_m) at 109 °C and a liquid crystal to isotropic transition at 124 °C. (b) Same as (a) with a narrower temperature range.

2. Polarized optical micrographs (POM) as a function of temperature

Using a polarized optical microscope equipped with a heating stage, bright field and cross-polarized images of C8-BTBT films were taken at various temperatures. Figure S2 shows evidence of birefringence at 109 °C, suggesting a liquid crystalline phase. As the temperature increases beyond 109 °C, birefringence decreases and dewetting becomes apparent.

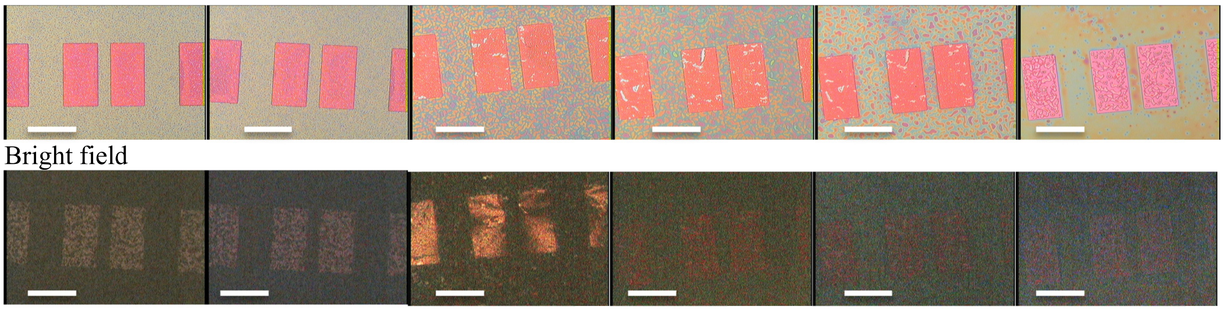
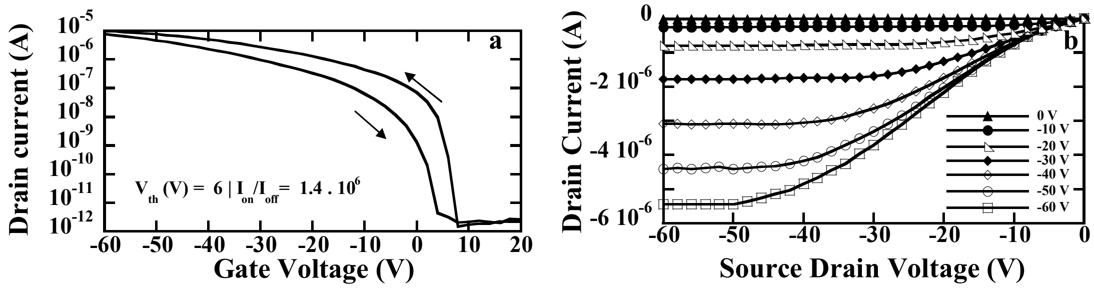


Figure S2. Optical micrographs of C8-BTBT films as a function of temperature. Bright field (top) and cross-polarized (bottom) optical microscopy images as a function of temperature. From left to right: 25 °C, 80 °C 109 °C, 115 °C, 125 °C and 135 °C respectively. Scale bar is 100 μm.

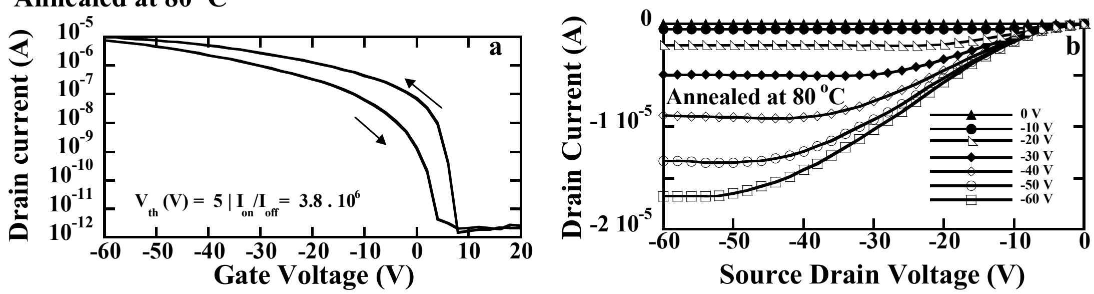
3. Device characteristics for C8-BTBT thin film transistors

Transfer and output characteristics of transistor devices processed with different conditions are shown in Figure S3. The on/off ratio is high for all devices, near 10^6, but contact resistance and hysteresis are evident. The threshold voltage moves to negative voltages for devices that were melted at 109 °C prior to annealing.

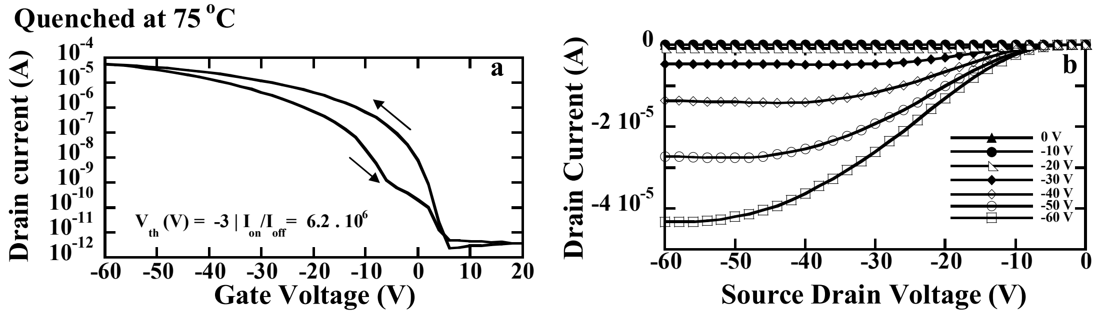
As cast



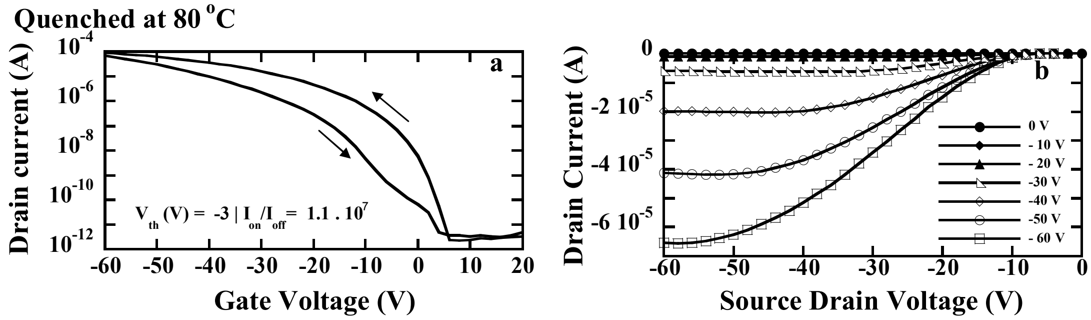
Annealed at 80 °C



Quenched at 75 °C



Quenched at 80 °C



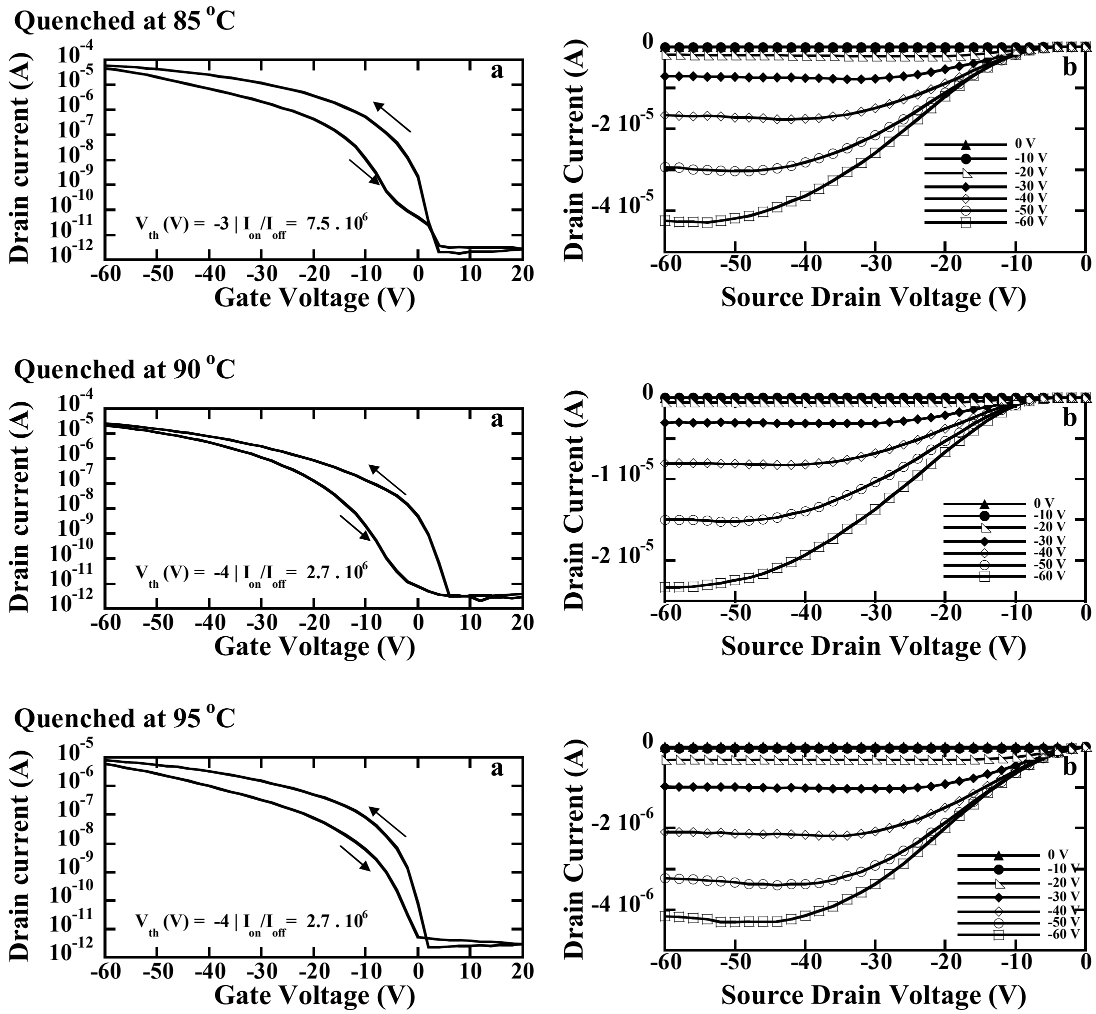


Figure S3. Device performance of C8-BTBT thin film transistors. a) Transfer characteristics and b) Output characteristics of devices where the active layer was as cast, annealed at 80 ^{o}C, or melted and quenched at various temperatures. V_{th} is threshold voltage, and I_{on}/I_{off} is the on/off ratio.

4. Quantifying the coherence lengths and distribution of crystallite orientations of C8-BTBT films

Using the X-ray rocking scan data, the full width at half maximum (FWHM) in scattering vector q of the (300) reflection in Scherrer's equation (with a shape factor of 1) yields the coherence lengths of C8-BTBT films under various processing conditions shown in Table S1. We can also quantify the breadth of the distribution of crystallite orientations by taking the FWHM in azimuthal angle ω of pole figures obtained from rocking scans around the (300) reflection using a Rigaku DMAX-Rapid II Microdiffractometer. The coherence lengths and FWHM in ω of the active layer are compared to the thin film transistor mobilities in Table S1. Films that were melted and quenched at 80 ^{o}C show a slightly larger coherence length and smaller FWHM in ω than films processed at other conditions.

Table S1. FWHM of rocking scan intensities and charge mobilities of thin film transistors for various processing conditions

Processing condition	Coherence length (nm)	FWHM (degrees in ω)	Mobility ($cm^2V^{-1}s^{-1}$)
As-cast	14.1	5.5	0.20 ± 0.01
Annealed at 80 ^oC	12.7	5.4	0.40 ± 0.10
Quenched at 75 ^oC	13.5	4.5	1.3 ± 0.3
Quenched at 80 ^oC	14.8	4.3	2.0 ± 0.2
Quenched at 85 ^oC	13.9	4.6	1.7 ± 0.3
Quenched at 90 ^oC	13.7	4.8	0.93 ± 0.10
Quenched at 95 ^oC	12.9	4.0	0.41 ± 0.10

5. Optical microscopy and AFM images of C8-BTBT thin films

Figure S4 shows optical microscopy (OM) and atomic force microscopy (AFM) images of C8-BTBT films after various processing conditions. The OM micrographs appear to show more holes in the channel regions after quenching at high temperatures (90 and 95 ^oC). All films show evidence of molecular terracing in AFM images, although the terracing is more apparent in quenched films. The step height is 2.9 nm, which corresponds to the interlayer distance in the crystallographic *c*-axis[1, 2]. Polarized optical microscopy (POM) images in Figure S5 show some features for quenched films that suggest the presence of domains aligned over large distances, and that are consistent with a liquid crystalline structure.

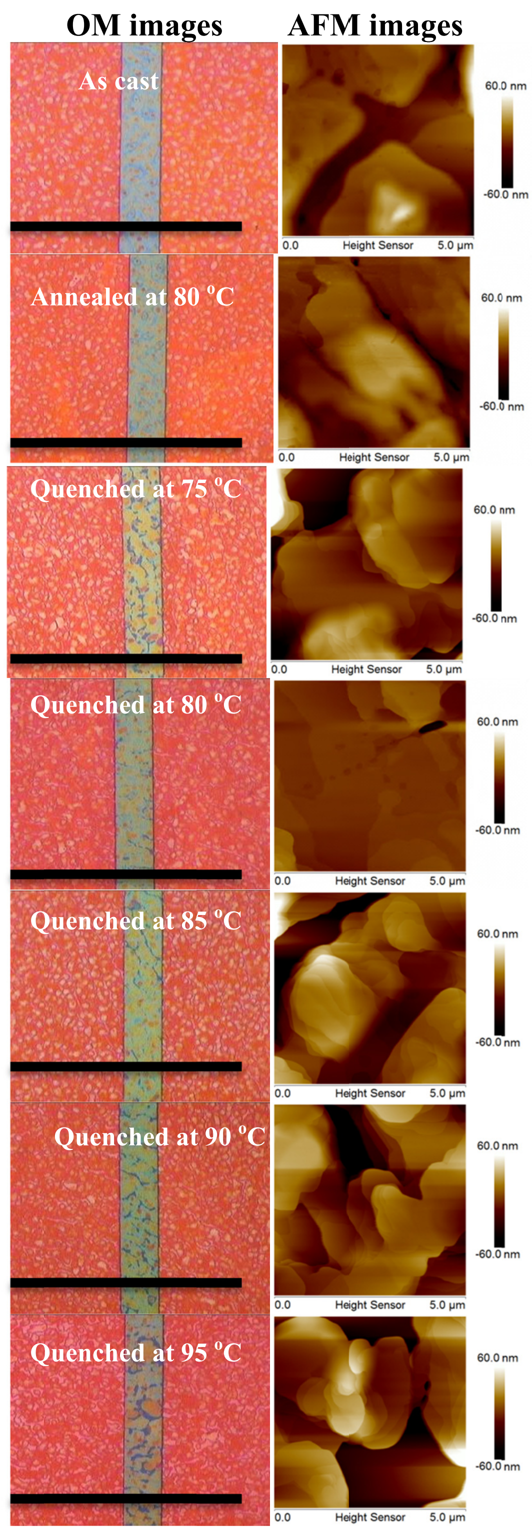


Figure S4. Optical microscopy (left) and AFM images (right) for C8-BTBT films after various processing conditions. Scale bar is 50 µm in the optical micrographs.

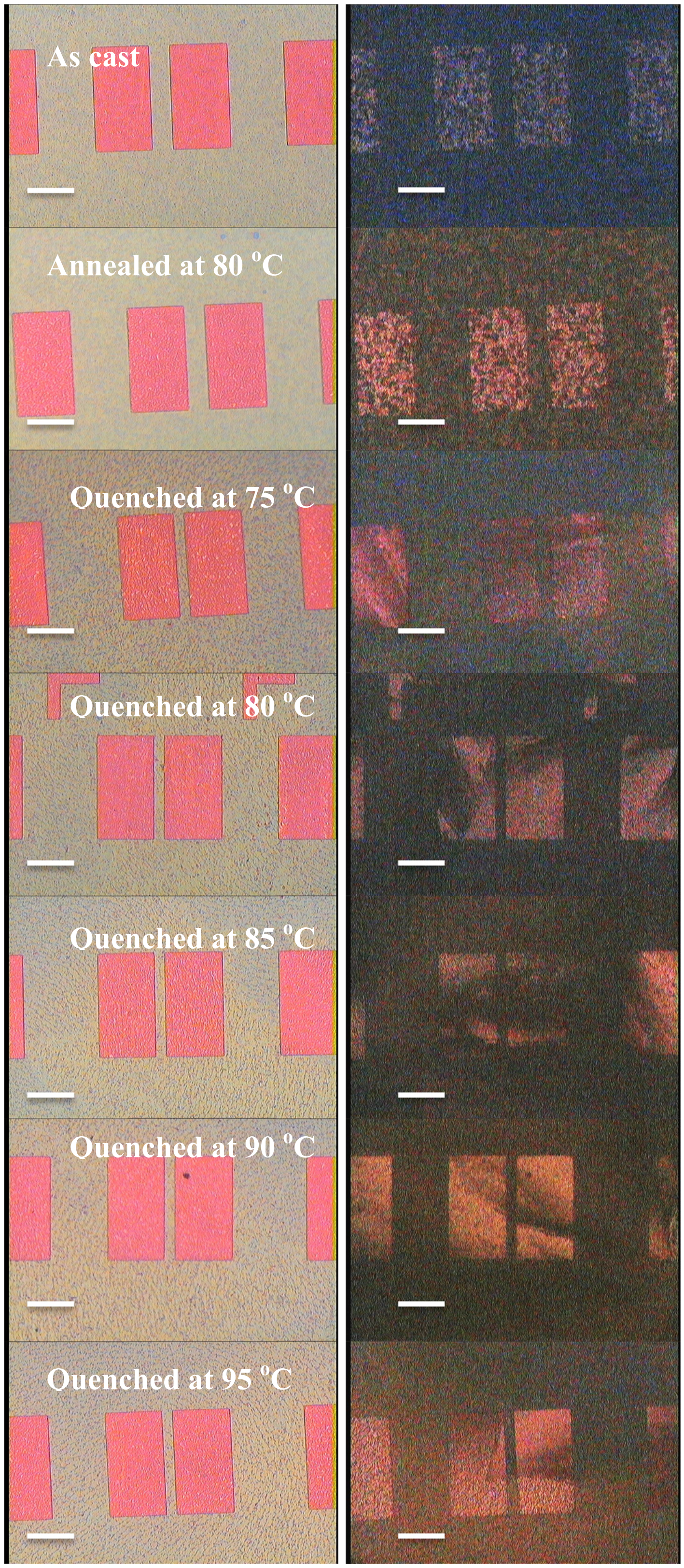


Figure S5. Bright field (left) and polarized optical microscopy (right) images of C8-BTBT film after various processing conditions. Scaler bar is 100 μm.

6. References

1. T. Izawa, E. Miyazaki and K. Takimiya, *Advanced Materials*, 2008, 20, 3388-3392.
2. H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara and T. Yui, *Journal of the American Chemical Society*, 2007, 129, 15732-15733.