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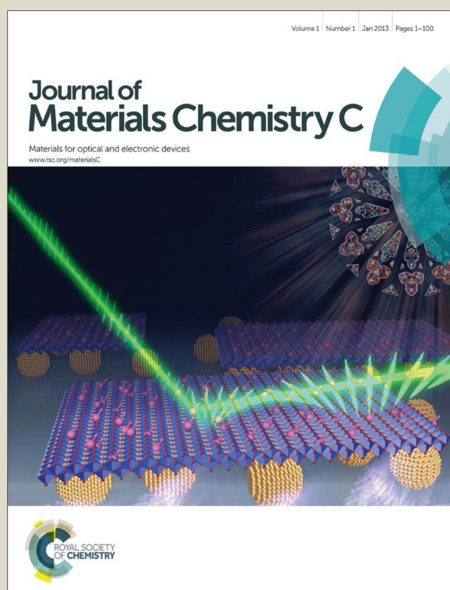

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COMMUNICATION

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

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Long-range order at multiple length scales in small molecule semiconductors is critical to achieve effective electrical charge transport. As a consequence, processing strategies are often important for the fabrication of high-performance devices, such as thin-film transistors. We demonstrate that melting followed by quenching at a fixed temperature can obviate prior processing, control the crystallization process, and lead to enhanced charge mobilities in thin-film transistors based on 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene active layers. Melting followed by quenching to 80 °C yields films with higher degrees of orientational order, and therefore charge mobilities in devices that are higher by a factor of five over films annealed at the same temperature directly after film casting.

Charge transport in small molecule organic semiconductors is governed by the coupling between adjacent molecules in the unit lattice and connectivity between grains in crystalline materials[1-7]. As a consequence, the crystallization of small molecule semiconductors in the active layer of organic thin film transistors (OTFTs) can significantly affect charge mobilities of devices. In some cases, promoting crystallization simply provides percolating pathways for low-resistance charge conduction, while in others the types of grain boundaries are perturbed to maximize charge hopping between grains[8-11].

Several processing methods have been proposed to control the morphology of the active layer in small molecule OTFTs[12-21]. Single crystals of 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT) have been demonstrated with inkjet printing of two solvents, one a good solvent for C8-BTBT carrying the molecule and a second poor solvent to induce crystallization[13]. Using a blade patterned with an array of micropillars, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) crystals have been aligned to demonstrate a two order of magnitude increase in charge mobility in the direction of alignment when compared to active layers with isotropic films[12, 18, 22]. Depositing or annealing organic semiconductors at temperatures above the melting temperature but below the liquid crystal to isotropic transition leads to enhanced order in the active layer and improved device performance.[23, 24] These studies demonstrate promising processing approaches aimed at controlling the crystallization of organic semiconductors.

Here we demonstrate that melting films prior to annealing at a specific quench temperature can control the crystallization in C8-BTBT films. Melt and quench experiments demonstrate a local order enhancement in polycrystalline films. Such films also exhibit higher charge mobilities over the films annealed below the melting temperature. By erasing the processing history prior to annealing, this approach leads to systematic control of crystallization through control of the quench temperature.

Bottom-gate, bottom-contact thin film transistors with C8-BTBT films spun cast as active layers were fabricated to extract charge mobilities as previously described. Briefly, approximately 100 nm thick gold electrodes were printed using conventional lithography on a clean 300 nm thick thermally grown silicon dioxide wafer comprising highly doped silicon on the bottom as a gate electrode (C = 10.6 nF cm^{-2}, Process Specialties, Inc.). We spun-cast hexamethyldisilazane (HMDS) (99 %, Sigma-Aldrich) at 4000 rpm on patterned substrates to functionalize the surface[25, 26].

As received C8-BTBT (Lumtec) was purified through recrystallization from toluene[27]. Concentrated 75 mg/ml C8-BTBT solutions were made in anhydrous toluene (99.99 %, Sigma-Aldrich) at 50 °C. Solutions were further heated to 60 °C to ensure complete dissolution. The solutions were cooled to ca. 5 °C for approximately five hours to induce crystallization. C8-BTBT crystals were recovered through filtering, and the final product is white, instead of a slight yellow prior to purification. Purified C8-BTBT was then put under vacuum at room temperature for 24 hours to minimize residual solvent. The yield for recrystallization is approximately 25%. Solutions of purified C8-BTBT were made at a 10 mg/mL concentration in anhydrous toluene. The solutions were stirred at ambient temperature inside a glovebox for 1 hour before spin casting. Films were cast on patterned SiO_2 substrates by spin-coating C8-BTBT solutions at 700 rpm, resulting in approximately 45 nm thick active layers.

Differential scanning calorimetry (DSC) data shows a melting temperature of 109 °C for C8-BTBT (Figure S1 of the Supplementary Information). A second peak is visible in the DSC data near 124 °C that could indicate melting of a small population of more stable crystals or a liquid crystal to isotropic transition. Nevertheless, we first melt the active layer in C8-BTBT devices on a

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hot plate at 109 °C for one minute. Although it is possible that the sample is not fully melted, higher temperatures lead to rapid dewetting (Figure S2 of the Supporting Information). The melted samples were then rapidly quenched to different temperatures by transferring to an adjacent hot plate at the desired quench temperature. Solution processing and quenching take place inside a nitrogen-purged glove box. Melting, or at least partial melting, of C8-BTBT films will minimize effects of prior processing. Moreover, we hypothesize that quenching C8-BTBT films at different temperatures enables us to control crystallization kinetics, thereby controlling the degree of order in the film[28, 29].

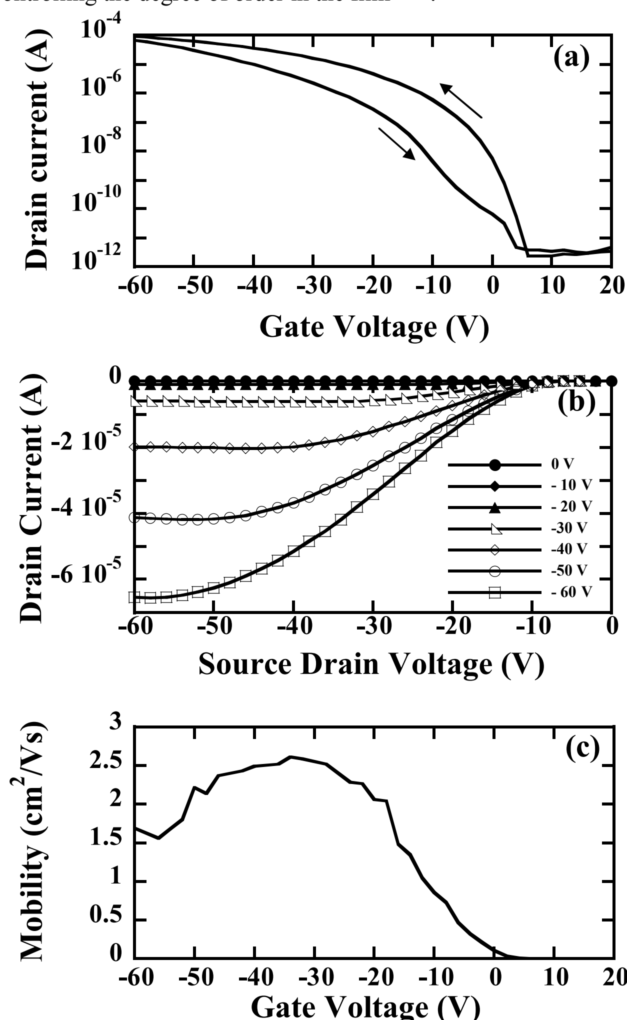

Fig. 1: a) Transfer characteristics, b) output characteristics, and (c) hole mobility for a C8-BTBT device that was annealed at 109 °C for one minute and subsequently quenched to 80 °C for 3 min.

The electrical properties of C8-BTBT OTFTs were measured inside a nitrogen glovebox using a Keithley 2636A Sourcemeter. Figure 1 shows electrical characteristics of a typical device quenched at 80 °C and annealed at that temperature for 3 min. Transfer characteristics at a source-drain voltage of -60 V (Figure 1a) of the device show minimal hysteresis, on/off current ratios above 10^6, and threshold voltages near zero. Even though some contact resistance issues are evident in output characteristics (Figure 1b), the device appears to reach saturation at high source-drain voltages. The mobilities extracted in the saturation regime as a function of gate voltage are shown in Figure 1c. Mobilities increase as the gate voltage becomes more negative and the device turns on, then mobilities saturate and begin to decrease. The decrease at high negative gate voltages is likely indicative of the device falling out of saturation as the magnitude of the gate voltage exceeds the magnitude of the source-drain voltage plus the threshold voltage. Thus, we take the hole mobility for devices as the average of mobilities between V_G of -20 V and -50 V. In Figure 1c, the mobility we extract is 2.5 $cm^2V^{-1}s^{-1}$.

Figure 2 shows the hole mobilities extracted from devices where the active layer was melted and then quenched at various temperatures for 3 min. Approximately 15 devices were tested for each condition. Mobilities are highest for devices where C8-BTBT films were melted at 109 °C and recrystallized at 80 °C. Lowering the quench temperature by 5 °C decreases charge mobilities by almost a factor of two. Increasing the quench temperature by 10 °C also decreases charge mobilities for C8-BTBT devices by a factor of two.

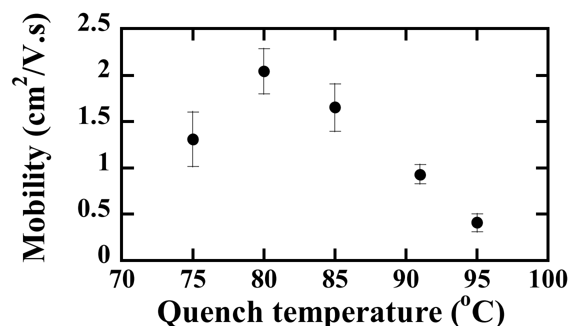

Fig. 2: Charge mobilities of thin film transistors after melting C8-BTBT active layers at 109 °C and quenching at the indicated temperature for three minutes. Error bars are the standard deviation obtained from measuring approximately 15 devices.

As a control, we also annealed C8-BTBT devices at 80 °C for three minutes directly after solvent casting. Devices annealed at 80 °C after casting exhibit charge mobilities of 0.40 ± 0.10 $cm^2V^{-1}s^{-1}$, while devices with as-cast C8-BTBT active layers exhibit charge mobilities of 0.20 ± 0.01 $cm^2V^{-1}s^{-1}$. The on/off ratio for all devices is near 10^6, while the threshold voltage decreases from about 5 V for as-cast and annealed devices to -3 V for quenched devices (Figure S3 of the Supplementary Information). Annealing after melting the C8-BTBT active layer leads to higher device charge mobilities than annealing directly after casting.

We hypothesize that enhanced charge mobilities in quenched C8-BTBT films are due to different C8-BTBT thin film morphologies. We examined the microstructure of C8-BTBT films after various processing conditions using grazing-incidence wide angle X-ray scattering (GIWAXS) at Beamline 7.3.3 of the Advanced Light Source (X-ray energy of 10 keV). The diffraction data for all samples shown in Figure 3 suggest that C8-BTBT crystallites are strongly oriented with the crystallographic *c* axis along the substrate normal[30, 31]. The similarities in the film texturing and location of diffraction peaks suggest the same polymorph is observed in all samples. Nevertheless, C8-BTBT films quenched at 80 °C shows sharper diffraction features compared to both as-cast and C8-BTBT films annealed at 80 °C after casting, potentially indicating stronger long-range order.

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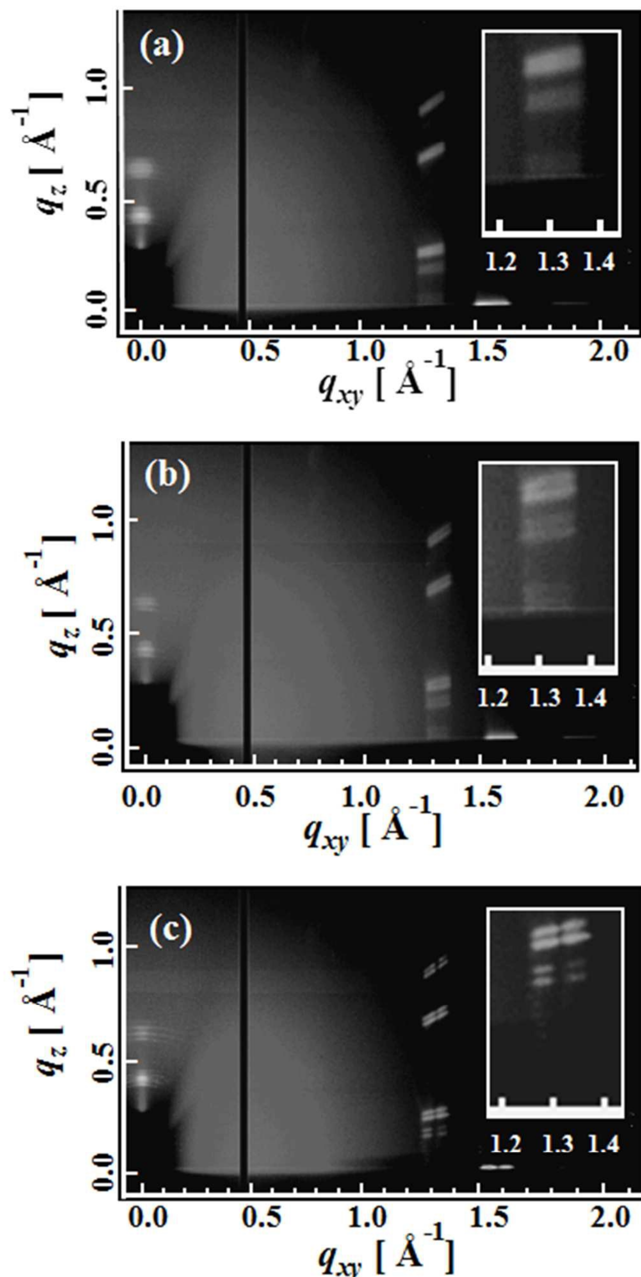

Fig. 3: GIWAXS data taken at an incident angle of 0.175 degrees for thin films of C8-BTBT. (a) Not annealed, (b) annealed at 80 °C, and (c) melted at 109 °C and quenched to 80 °C. C8-BTBT films after melting and quenching exhibit sharper diffraction peaks, as shown in the insets.

The crystallite orientations of C8-BTBT films were quantified through pole figures obtained from rocking curves around the (300) reflection using a Rigaku DMAX-Rapid II Microdiffractometer. We chose the (300) peak because of the low reflectivity background near q_z = 0.7 Å^{-1}. Table S2 of the Supplementary Information shows that melting and quenching films at 80 °C leads to slightly larger coherence lengths (~15 nm) than for as cast films (~14 nm) or after annealing films at 80 °C (~13 nm), as obtained from the full-width at half maximum intensity of the (300) reflection[32]. Intensities at the (300) reflection as a function of azimuthal angle are shown in Figure 4. As-cast films and films annealed at 80 °C for three minutes have similar crystallite orientations. Films of C8-BTBT that were melted and quenched at 80 °C have narrower crystallite orientation distributions compared to as-cast samples and samples annealed at 80 °C without melting. As shown in Figure S4 and Figure S5 of the Supplementary Information, Atomic Force Microscopy images reveal well-defined molecular steps and polarized optical microscopy images show stronger liquid crystalline order for samples that were melted and quenched, supporting our conclusion that order is enhanced through this protocol.

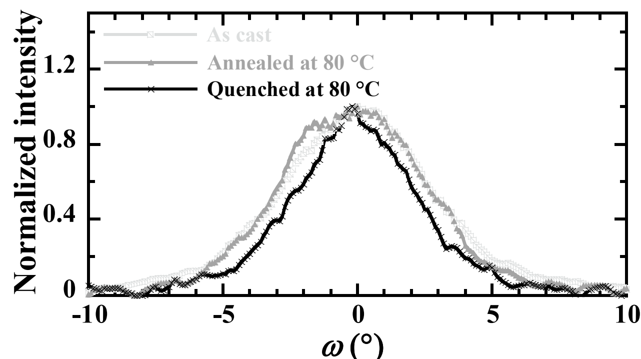

Fig. 4: Rocking scan intensities as a function of azimuthal angle ω for C8-BTBT films. Intensities are normalized to the maximum intensity for each sample. Narrower distributions of crystallite orientations are apparent in C8-BTBT films that were melted and quenched to 80 °C when compared to as-cast films and films annealed at 80 °C.

We hypothesize that the sharper GIWAXS peaks shown in Figure 3 for C8-BTBT films quenched at 80 °C are indicative of stronger crystallite texturing, which is apparent in the narrower crystallite distribution shown in Figure 4. We also hypothesize that a narrower distribution of crystallite orientations leads to higher charge mobilities in thin film transistors[33]. Figure 5 compares the full width at half maximum (FWHM) in ω of the active layer with thin film transistor mobilities. A trend is apparent, where broader orientation distributions in the active layer lead to lower device mobilities. An exception is found for films quenched at 95 °C, where the device mobilities are low for the apparent narrow distribution of crystallite orientations. We speculate that quenching at this high temperature may compromise film continuity, as suggested by optical micrographs shown in Figure S2 and Figure S4 of the Supplementary Information. Overall, melting films prior to annealing leads to more oriented crystallites and consequently, higher charge mobilities in devices.

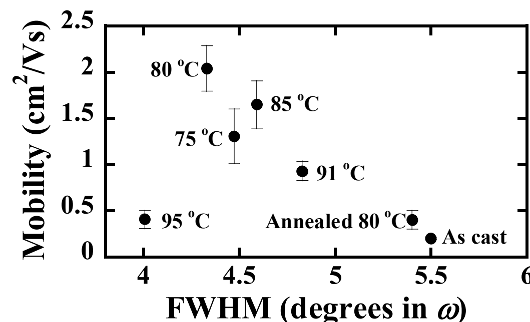

Fig. 5: Device mobilities versus orientational order from rocking scans in terms of the FWHM in degrees of azithumal angle ω. Samples are labelled with either the quenching temperature, with As cast for un-annealed samples, or with Annealed at 80 °C for samples annealed directly after spin casting.

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We speculate that melting and quenching increases the orientational order by controlling the crystallization process. Furthermore, the DSC data shown in Figure S1 of the Supplementary Information suggests a liquid crystalline phase exists above the crystal melting temperature. Thus, it is possible that annealing for 1 min at the melting temperature may induce liquid crystalline order in the active layer, which has been shown to enhance organic thin film transistor mobilities.[23, 24] Nevertheless, the dependence of the film structure and device mobilities on the quench temperature suggests that control of the crystallization process in the active layer is crucial for device performance and afforded by melting prior to thermal annealing.

In summary, we can enhance crystal texturing by melting and quenching C8-BTBT films. The stronger orientational order in the active layer of thin film transistors leads to an increase in hole mobilities by a factor of five. A distinct advantage of melting films prior to annealing is obviating the effects of processing history prior to thermal annealing. Varying the quench temperature should affect crystallization kinetics by controlling the thermodynamic driving force for crystallization, thus providing a systematic approach to control the structure in the active layer of organic thin film transistors.

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