Solvent-Free Directed Patterning of a Highly Ordered Liquid Crystalline Organic Semiconductor via Template-Assisted Self-Assembly for Organic Transistors

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In the past few years, small organic semiconductors (OSCs) have found applications in numerous emerging low-cost and disposable electronic devices because of their highly ordered packing and high crystallinity and have begun to be considered as replacements for typical conjugated polymers such as poly(3-alkylthiophenes) (P3HT) and poly(2,5-bis(3-alkylthiophene-2-yl)thieno(3,2-b)thiophene) (PBTTT) [1,2]. One urgent requirement for the realization of devices using small molecules is the development of technologies for the simple fabrication of flexible, large-area, low-cost, and high electrical performance devices. Thus, a variety of methods for the preparation of solution-processable OSCs have been developed such as spin-coating, drop-casting, solvent evaporation methods, and inkjet printing [3]. The control of the nucleation and growth of OSC materials from solution to produce single-crystalline OSC patterns requires mastery of various factors, including the boiling temperature of the solvent, the solution wettability of the substrate, and the affinity of the solvent with the OSC materials. [4,5]. However, during solidification the nucleation of small molecules is difficult to control, so it is almost impossible to fabricate single crystals that are uniform in size and shape. [5] In order to fabricate more uniform active layers of small molecules, recent research has focused on controlling their morphology by defining nucleation locations and inducing directional growth. [6,9] Such methods require relatively complex tools, many process steps, or have limitations on their control of crystal shape. [3,7] Above all, most solution-processed organic-printed electronics exhibit significant drawbacks, resulting from the poor solvent resistance of other components, such as the polymeric substrates, gate insulators, and other active materials. The solvent used in the preparation of one component frequently dissolves or otherwise affects other previously prepared components. [8] In order to overcome the problems of solution processing for printed electronics, in this study we aimed to test the usefulness of the liquid crystallinity of a small OSC molecule, which enables its direct printing without the use of solvents. In recent years, many liquid crystalline OSC materials such as thiienoacene-based, terthiophene-based, and discotic (including various p-conjugated cores) molecules have been shown due to their high degree of crystallinity in thin film and particular molecular structure to provide outstanding electrical performance. [9,10] In particular, thiienoacenes consist of fused thiophene rings in a ladder-type molecular structure and have been intensively studied as potential OSCs for high-performance organic field effect transistors (OFETs). [9] Most thiienoacene-based materials exhibit smectic liquid crystalline phases. [11] In this study, we selected a liquid crystalline small molecule based on thiienoacene, 2,7-didecylobenzothienobenzothiophene (C_{10}-BTBT), as shown in the center of Figure 1. Derivatives of benzothienobenzothio-phene (BTBT) are well known to be air-stable p-type organic semiconductors and to exhibit liquid crystallinity; the best mobility in FETs is that of single-crystal C_{8}-BTBT with over ~31 cm^{2}/V·s achieved by using double-shot inkjet printing. [34] In addition, the Hana group has firstly reported the superior availability of liquid crystallinity of OSC in solution processing for FETs. [12] They obtained devices with enhanced electrical properties by preparing solution-cast thin films in the temperature range of the smectic liquid crystalline phases of C_{10}-BTBT and dioctylterthiophene (8-TTP-8). [12]

In this study, we fabricated highly ordered organic semiconductor micropatterns of the liquid crystalline small molecule, C_{10}-BTBT, by using a simple method based on template-assisted self-assembly (TASA). The self-alignment properties of the smectic liquid crystal phase of C_{10}-BTBT enable the solvent-free processing of well-defined micropatterns for printed OFETs. The orientation of the liquid crystalline OSC material was directed by using a topographically pre-patterned polymeric template. The nucleation and directional growth of C_{10}-BTBT via TASA was investigated with X-ray diffraction as well as optical and electron microscopy. We then fabricated high-performance organic transistors with an a mobility of ~1.7 cm^{2}/V·s based on the highly ordered small molecule micropatterns. We used a polyimide organic dielectric layer in the FETs instead of typical SiO, gate insulators to realize all-organic FET devices.

The TASA technique makes use of directed confined geometries to control the dimensions and arrangements of nano- and microstructures of soft materials and colloid particles. [14]
Figure 1. A schematic illustration of the micropattern and OFET fabrication process. Center: molecular structure of C\textsubscript{10}-BTBT. a) A pre-patterned PDMS template and a polyimide gate insulator coated ITO substrate were prepared. PDMS template is placed in conformal contact with substrate. b) The crystalline powder of C\textsubscript{10}-BTBT was placed at the entrance of trenches. c) The trenches were filled with liquid crystalline materials (C\textsubscript{10}-BTBT) by capillary action at the above Tiso (122 °C). After the PDMS template was carefully detached, C\textsubscript{10}-BTBT line patterns were generated. d) Gold electrodes with 50 nm were thermally evaporated to form the source and drain contacts of OFETs.

This technique, which is currently attracting great interest in the fields of nanotechnology and materials science, uses a combination of bottom-up self-assembly and top-down fabrication with lithographic templates. Recently, it was shown that liquid crystals in microconfined systems can form regular arrays with well-ordered molecular structures. Unlike previously reported self-assembled building blocks such as block copolymers, colloid particles, and surfactants, liquid crystals have the significant advantage of very rapidly forming highly ordered structures due to the reversible and non-covalent interactions between the liquid crystal molecules. This capacity for rapid rearrangement is, for example, exploited in liquid crystal displays, which have response times on the order of milliseconds under electric field. Furthermore, the molecular orientation of a liquid crystal can easily be controlled by surface anchoring, which is a very simple and cost-effective mechanism that is well suited to mass production. A schematic illustration of the fabrication process based on TASA is shown in Figure 1. We used polydimethylsiloxane (PDMS) to prepare a pre-patterned template, which acts as a topographic mold. This PDMS template was replicated from a pre-patterned photoresist master mold fabricated with conventional photolithography. The PDMS template was set in conformal contact with the substrate to obtain line patterns, as shown in Figure 1a. Indium tin oxide (ITO)-coated glass was used as the gate substrate. A 300 nm synthetic polyimide (KPI-C\textsubscript{18}) film was prepared on an ITO-coated glass substrate as an organic gate insulator (OGI) (see Figure S1, Supporting Information). The C\textsubscript{10}-BTBT crystalline powder was placed on the substrate and then heated to above the isotropic phase temperature of C\textsubscript{10}-BTBT (T\textsubscript{iso} = 122.1 °C, Figure S2, Supporting Information) in order to fill the confined geometry by capillary action, as shown in Figure 1b. At this high temperature, capillary forces drive the isotropic liquid phase of C\textsubscript{10}-BTBT into the void space of the PDMS template, which results in a negative copy of the mold. The sample was then rapidly cooled to room temperature at a rate of 10 °C/min. When the PDMS template is carefully detached from the substrate, C\textsubscript{10}-BTBT lines are generated on the substrate, as shown in Figure 1c. Small LC materials have high mobility and respond rapidly in the smectic phase, so LC molecular arrangement occurs very fast in this confined geometry. We have found that the growth of a C\textsubscript{10}-BTBT line pattern over a centimeter scale requires only a few seconds. However, the nucleation of domains can occur randomly during the cooling process, so C\textsubscript{10}-BTBT lines consisting of several single crystalline domains can arise even when the LC molecules are confined within the template. We found that topographical confinement can be combined with the use of a thermal gradient to produce a single crystalline domain in each line. By elevating the entrance of the trench on the hot stage to tilt the sample by 2 mm, a thermal gradient is produced in the sample from the entrance to the end of the trench. The direction of crystalline growth follows the long axis of the trench. Thus, there are several single crystalline domains in each line in randomly nucleated samples, whereas the line patterns in thermally graded samples consist of almost a single crystalline domain, as shown in Figure S3. We fabricated bottom gate, top contact transistors by thermally evaporating gold electrodes onto the C\textsubscript{10}-BTBT line patterns, as shown in Figure 1d.

The series of polarized optical microscopy (POM) images in Figures 2a–c show the dimensional control of the C\textsubscript{10}-BTBT line patterns. The widths, spacings, and thicknesses of the line patterns are the same as those of the PDMS templates, which have widths of 10, 5, and 0.6 μm; the C\textsubscript{10}-BTBT lines are 800 nm thick with spacings equal to each width. The long axis of the molecule is slightly tilted (approx. 4 degrees) along the optical axis of the polarized light, so the line patterns are dark under POM observation when the long axis of the line pattern is parallel or vertical with respect to the axis of the cross-polarizer. Thus, the long axis of the line pattern (or the crystal growing...
that the molecules stand upright and are packed so that their π orbitals are parallel to the substrate. The height of step match well with the layer d-spacing with 3.33 nm analyzed by XRD study for C10-BTBT thin film. \[11\] And this 2D-layered structure is consistent with the cross-sectional SEM results in Figure 2d.

In order to confirm the molecular ordering and crystal-line structures of the transferred C10-BTBT micropatterns, 2D-grazing incidence X-ray diffraction (2D-GIXD) was performed with the synchrotron X-ray source at Pohang Accelerator Laboratory. A schematic illustration of the GIXD experimental set-up is shown in Figure 3a. Figure 3b shows the 2D-GIXD pattern of a 50 nm thick C10-BTBT thin film spin-coated onto a polyimide gate insulator. The spin-coated film produces diffuse intensities around the \((00l)\) diffraction peaks along the Debye rings, which indicates that the spin-coated films have a polycrystalline layered structure with an interlayer distance of 3.37 nm, as is consistent with previously reported results. \[20\] Further, there were no specific reflection peaks through the in-plane. In other words, the self-aligned C10-BTBT crystals prepared with the TASA technique generate many reflection spots in the direction of \(q_z\) (out-of-plane) at a given \(q_{xy}\) (in-plane), as shown in Figure 3c, which indicates that the 3D crystal structure of the C10-BTBT film is well-ordered in both vertical and lateral directions. High-order spots are present in Figure 3c in the direction of \(q_z\) at 3.38, 1.66, and 1.12 nm and are attributed to the \((001)\), \((002)\), and \((003)\) reflections for the C10-BTBT crystal structure, respectively. A clear spot corresponding to the \([110]\) and \([020]\) reflections at the in-plane of 2D-GIXD can be seen in Figure 3c. Figure 3d shows the 1D diffraction profile with respect to the out-of-plane direction extracted from the 2D-GIXD results in Figure 3c.

The cross-sectional scanning electron microscopy (SEM) image in Figure 2d reveals the internal structure of the C10-BTBT line patterns on the SiO\(_2\)/Si substrate. The inset shows the internal layered structure resulting from the stacking of smectic layers. The layers are flat and parallel to the bottom of the substrate. Some deviations of the layers from ideal smectic layers could be caused by the fracturing of the samples. Further, the wide region atomic force microscopy (AFM) images in Figure 2e show that the C10-BTBT lines are uniformly patterned, 10 μm wide, 800 nm thick, and spaced 10 μm apart. As shown in the AFM image and surface profile in Figure 2f and Figure S4, Supporting Information, the top surface of the film is molecularly flat and exhibits only a few steps with an average height of ~3.4 nm, the molecular length, which implies that the molecules stand upright and are packed so that their π orbitals are parallel to the substrate. The height of step match well with the layer d-spacing with 3.33 nm analyzed by XRD study for C10-BTBT thin film. \[11\] And this 2D-layered structure is consistent with the cross-sectional SEM results in Figure 2d.

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spots corresponding to the single crystal were mainly observed vertically at a given \(q_{xy} (>0)\) and were indexed to \(\{1, \pm 1\}\) and \(\{0, \pm 2\}\). However, when we rotated the sample so that the axis of the \(C_{10}\)-BTBT line pattern was parallel to the direction of the X-ray beam, the in-plane reflection spots shown in Figure 3c were no longer evident, as shown in Figure S5, Supporting Information. We conclude that our \(C_{10}\)-BTBT crystals are oriented with the [100] direction almost perpendicular to the walls of the PDMS templates and that the [010] direction is the same as the growth direction, as was inferred from the thermal gradient direction shown in Figure S3, Supporting Information.

Note that this result is in contrast with the diffuse diffraction patterns shown in Figure 3b for spin-coated polycrystalline films with uncontrolled growth direction. Thus, the patterned \(C_{10}\)-BTBT lines prepared without solvents by using the liquid crystallinity (or self-alignment) of \(C_{10}\)-BTBT on the polyimide dielectric layer provide crystalline structures that are suitable for high performance FETs.

In order to demonstrate that the \(C_{10}\)-BTBT line patterns act as organic semiconductors in devices, we fabricated bottom gate, top contact OFETs on a 300 nm thick polyimide (KPI-C18)
gate dielectric layer on an ITO/glass substrate. A micropatterned active layer was prepared by using the TASA technique on the polyimide gate insulator. Gold electrodes for the devices were evaporated from the bottom through a shadow mask so that the direction of the channels was parallel to that of the crystal growth in the [010] direction, as shown in Figure 4a. The magnified POM image in the inset of Figure 4a clearly shows there is uniform texture that indicates single crystal structure in the channel region of the FET. Figure 4b shows typical output characteristics of a device on the organic gate insulator/ITO substrate, which indicate well-saturated performance. Figure 4c shows the transfer characteristics of the same device in the linear and saturation regions; the average mobility ($\mu$) of 20 FET devices was estimated to be 1.74 cm$^2$ V$^{-1}$ s$^{-1}$ ± 0.22 by using the MOSFET standard model in the saturated regime, $I_D = \frac{W}{2L} C_i \mu (V_G - V_T)^2$, where $W$ is the width of the channel, $L$ is the length of the channel between the source and the drain contacts, $C_i$ is the areal capacitance of the dielectric layer, and $V_T$ is the threshold voltage. This value is higher than typical values for conventional spin-coated and vacuum evaporated polycrystalline devices on the same gate insulator, [17] which are approx. 0.3 cm$^2$ V$^{-1}$ s$^{-1}$, due to the good molecular packing and high crystallinity of the C$_{10}$BTBT semiconductor films. Representative electrical characteristics of C$_{10}$BTBT FETs prepared with various methods, including the field-effect mobility, off-current, on/off current ratio, threshold voltage, and sub-threshold slope (S-slope), are summarized in Table 1. These FET devices were fabricated with same structure except the preparation method of OSC layer. And it was found that varying the dimensions of the micropatterns of C$_{10}$BTBT results in no significant differences in the electrical characteristics of the FETs, even though the surface textures of the micropatterned films do vary slightly with the dimensions of the templates, as shown in Figure S6, Supporting Information. Unfortunately, the mobilities of these devices are much lower than the highest mobility for C$_{10}$BTBT reported in the literature (31.3 cm$^2$ V$^{-1}$ s$^{-1}$).[3c] We can suggest some reasons for this reduced electrical performance. Firstly, the measured mobilities of our OFETs do not represent the intrinsic mobility of C$_{10}$BTBT since the output curves reveal a noticeable contact resistance. The HOMO level of C$_{10}$BTBT is located at ~5.5 eV with respect to vacuum, so there is a large energy barrier to hole injection from Au into C$_{10}$BTBT.[11] Some groups have tried to reduce the energy barrier between OSCs, particularly BTBT derivatives, and source/drain electrodes.[12,17,21] Secondly, the large film thickness of the OSC, approx. 800 nm, could be a limitation, because the active channel formed within several nanometers from the substrate and in the top contact geometry, holes have to cross the thick semiconducting layer to reach the channel. This effect means that the contact resistance increases with increasing semiconductor thickness.[22] However, it should be noted that we made no effort to optimize device geometry or contact resistance, as such optimization was beyond the scope of this study. Furthermore, charge transport in our system occurs along the [010] direction, whereas, in previously reported devices using single crystal C$_{10}$BTBT, transport occurs along the [100] direction, which is thought to provide stronger intermolecular electronic coupling.[12,20] Because most OSC materials involve planar $\pi$-conjugated structures with specific molecular arrangement

![Figure 4.](image-url)
In conclusion, we have demonstrated a method for the fabrication of highly ordered micropatterns of crystalline C_{10}-BTBT as an organic semiconductor; the sizes of these micropatterns are easily controlled by using the TASA technique and the intrinsic liquid crystallinity of C_{10}-BTBT. The microsized PDMS template produces a well-defined C_{10}-BTBT pattern with ordered crystal structure by guiding the molecular packing on the molecular scale. Although the micropatterns are not composed of single crystalline structures, we were able to control the crystalline orientation and degree of crystallinity over large areas. The C_{10}-BTBT micropatterns were found to act as high-performance active layers in OFETs with a mobility of ~1.7 cm^2 V^{-1} s^{-1}. The generality of this approach was demonstrated with other typical liquid crystalline or crystalline OSCs, including dicycletetrithiophene (8-TTP-8), and 2,7-dioctylbenzo[4,5-b]thiophene (FA-C_{8}-BTBT) as shown in Supporting Information, Figure S8–S10. This method can be scaled up to produce high quality crystalline arrays over the desired regions of a substrate. Furthermore, our solvent-free process is sufficiently general to enable the printing of other organic electronics, such as organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs), as well as OFETs, without the use of solvents.

**Experimental Section**

**Materials and Pattern Formation:** C_{10}-BTBT was prepared following previously reported synthetic routes. The polyimide (KPI-C_{18}) gate insulator was synthesized by using 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), p-phenylenediamine (p-PDA), 1,3,5-triethylbenzene (TTEE) and 3,5-diethylbenzene (DIEB), and the procedure of our previous study. A Sylgard 184 elastomer kit was purchased from Dow Corning and pre-patterned photoresist master molds were fabricated with standard photolithography; their width was of 10, 5, and 0.6 μm with spacing equal to each width and their height (0.5–1 μm) was determined by the thickness of the photoresist. The PDMS templates were then fabricated by curing a mixture of PDMS precursor and curing agent (Sylgard 184, Dow Corning Corp) at a ratio of 10:1 (w/w). The mixture was poured onto a pre-patterned photoresist master and then cured at 60 °C for 8 h in a convection oven. After the PDMS template was fully cured, it was simply peeled off the master mold. To fabricate the C_{10}-BTBT micropatterns, the PDMS templates were set in conformal contact with the insulating polyimide coated ITO substrate. The C_{10}-BTBT crystalline powder was placed on the substrate and then heated to the temperature corresponding to the isotropic phase (with an Inspect HCS600XY hot-stage and a M2K1000 controller) in order to fill the confined geometry by capillary action. The sample was then cooled to room temperature at a rate of 10 °C min^{-1}. The widths, spacings, and thicknesses of the line patterns are the same as those of the PDMS templates.

**Microstructure Characterization:** Polarized optical microscopy (POM) (Nikon Eclipse LV50-POL), atomic force microscopy in height mode (AFM) (Bruker, Multimode-8), and scanning electron microscopy (SEM) were used to examine the line micropatterns of C_{10}-BTBT. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) measurements were performed by using the synchrotron source on the 9A U-SAXS beamline at the Pohang Accelerator Laboratory (PAL) in Korea. Samples with dimensions of 10 mm × 10 mm were prepared, and guided into a focused X-ray beam of energy 11.146 keV and size 70 μm (vertical) by 400 μm (horizontal). The sample-to-detector distance (SDD) was 258.5 mm and the diffraction patterns were mostly acquired for 1–10 s with a two-dimensional charge-coupled device (2D CCD) detector. (Rayonix Inc. USA).

**Device Fabrication and Characterization:** To assess the electrical performance of the C_{10}-BTBT line patterns, bottom gate and top contact OFETs were fabricated on a 300 nm thick spin-coated polyimide (KPI-C_{18}) film (C_{18} = 88% NF) on top of an indium tin oxide (ITO) coated gate electrode following the method of our previous study. 50 nm thick source and drain gold electrodes were deposited by thermal evaporation onto the semiconductor layer through a shadow mask, creating transistors with a channel length (L) and a width (W) of 50 and 1000 μm respectively. The transfer (I_{ds} vs. V_{gs}) characteristics of the FET devices were measured with an Agilent E5272 semiconductor parameter analyzer. All electrical measurements were performed in dark ambient conditions.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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