

Mechanics-Guided Layer-by-Layer Transfer of Molecular Bilayer Semiconductors

Shunto Arai,* Mariko Shimokawa, Takayuki Harada, and Toshiki Higashino

Cite This: *ACS Appl. Mater. Interfaces* 2026, 18, 49581–49589

Read Online

ACCESS |



Metrics & More



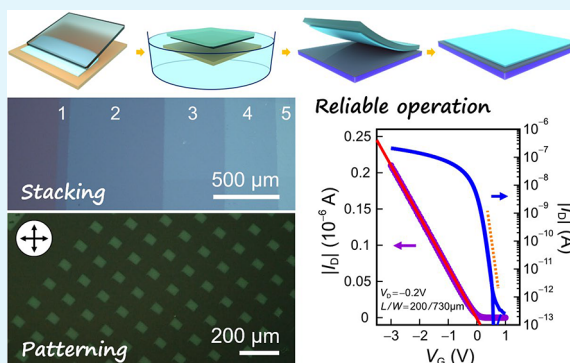
Article Recommendations



Supporting Information

ABSTRACT: Layer-controlled organic thin films are essential components of organic electronic devices. Although layer-transfer methods are effective for device prototyping, managing crack formation during this process is challenging. In this study, we investigate the fracture mechanics of bilayer-type organic semiconductor (OSC) films as a model for developing a crack-suppressed transfer methodology. We find that crack formation is strongly dependent on film thickness and is suppressed when the film is reduced to a single molecular bilayer (SMB) thickness. The observed crack directionality in thick films is clearly correlated with the crystallographic orientation. These fracture behaviors can be qualitatively explained by combining a macroscopic elasticity model with calculations of intermolecular interaction energies. Based on this understanding, we successfully fabricate highly ordered multilayered artificial lattices through sequential SMB transfers. Furthermore, by expanding the π -electron core to tune intermolecular interactions, we achieve the direct patterning of OSC films, even on lyophobic substrates, providing a suitable interface for organic thin-film transistors (OTFTs). OTFTs incorporating crack-suppressed SMBs exhibit sharp on/off switching with a subthreshold swing of less than 150 mV dec^{-1} and a relatively high device mobility exceeding $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These findings pave the way for molecular layer engineering for surface tailoring and organic device manufacturing.

KEYWORDS: organic semiconductors, molecular bilayers, layer-by-layer assembly, fracture mechanics, organic thin-film transistors



1. INTRODUCTION

Two-dimensional (2D) layered semiconductors provide an ideal platform for electronic applications based on their flexibility and unique electrical properties. In such systems, film-transfer techniques offer a powerful methodology for creating artificial heterostructures with tailored optoelectronic properties, as exemplified by graphene and transition-metal dichalcogenides.^{1–3} For these atomic layer systems, various film-transfer methods have been developed, enabling the fabrication of artificially stacked crystals that do not form spontaneously in nature, which have been conceptualized as “2SD materials”.⁴ Such stacking degrees of freedom are expected to support the development of novel heterostructures for organic systems, offering immense potential for rapid prototyping and the tailoring of material properties.⁵

For this purpose, various approaches have been proposed to transfer organic semiconductors (OSCs), including the dry transfer of bulk single crystals and scooping of self-assembled films from liquid surfaces, such as Langmuir–Blodgett films.^{6–8} However, achieving molecular-level thickness uniformity while maintaining crystallinity over large areas is difficult. Alternative techniques have been developed to form large-area, uniform-thickness thin films, detach them from their initial substrates,

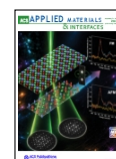
and transfer them to other substrates. One such approach involves the formation of a film on a hydrophilic substrate and the immersion of the entire setup in water.⁹ Following immersion, water molecules penetrate the interface and naturally detach the film from the substrate. Although the structural stability of OSCs on the water surface is required, this method has been successfully applied to organic thin-film transistors (OTFTs) using materials with rigid π -electron frameworks (π -cores), such as dinaphtho[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (DNBDT) derivatives. However, the direct transfer of molecular layers often induces film damage, even in atomic layer systems.^{10,11} To mitigate film fracture, the OSC layer can be encapsulated by an additional protective layer, enabling damage-free transfer as part of a stacked structure^{12,13} (see Table S1 in the Supporting Information for a comparison

Received: June 18, 2026

Revised: August 18, 2026

Accepted: August 25, 2026

Published: September 2, 2026



of these representative film-transfer methods). Although such methods are useful for fabricating prototype devices, establishing more versatile transfer technologies requires a fundamental understanding and control of the crack formation induced by deformation during the transfer process. Therefore, it is necessary to clarify the roles of molecular layer thickness and crystallographic orientation in crack formation.

As a model system for investigating such properties, a class of OSCs has been reported in which π -core is asymmetrically substituted with an alkyl chain.^{14–18} Such asymmetric OSCs typically provide bilayer-type molecular packing, where molecules separately form a semiconductive π -core layer and an inert alkyl chain layer. These layers couple to form an alternating antiparallel alignment, resulting in tail-to-tail (head-to-head) contact for the alkyl chain (π -core) layers. It has been discussed that the separate formation of 2D semiconductive π -core and alkyl chain layers should enhance layered crystallinity, supporting the formation of single-crystalline thin films with large crystalline domains.¹⁹ This layered crystallinity even enables the formation of single molecular bilayers (SMBs) of OSCs by mixing molecules with different alkyl chain lengths.^{20,21} In mixed crystallization from a solution, longer alkyl chains create protrusions on the film surface, which suppress stacking crystallization as a result of the “geometric frustration effect.” The resulting SMB-based OTFTs exhibit sharp on/off switching characteristics,²² suggesting the formation of 2D molecular crystal OSC layers with few defects. With their tunable thickness (or layer numbers) and π -core interactions, such asymmetric OSCs serve as an ideal platform for systematically investigating how film thickness and specific intermolecular forces govern the mechanical behavior of molecular thin films during transfer.

In this study, we examined a film-transfer technique for asymmetric OSCs utilizing a water immersion technique assisted by a polydimethylsiloxane (PDMS) protective layer. This PDMS layer can also be used as a stamp for film transfer owing to its film-release capability, which mitigates mechanical damage to the OSC layer during delamination. By employing phenyl/alkyl-substituted [1]benzothieno[3,2-*b*][1]benzothiophene (Ph-BTBT- C_n) as a benchmark material,^{14,18,23,24} we find that while thick films exhibit directional cracking during transfer, mechanical failure is considerably suppressed in ultrathin SMBs. Such thickness-dependent anisotropic crack propagation can be qualitatively explained using a continuum elasticity model combined with quantum chemical calculations of the anisotropic intermolecular interaction energies. Based on this physical framework, we fabricate artificial organic superlattices via sequential SMB transfer. Furthermore, by employing benzothieno[6,5-*b*]benzothieno[3,2-*b*]thiophene derivatives (Ph-BTBTT- C_n) with an extended π -core backbone, we demonstrate that tuning intermolecular interactions allow for successful direct SMB patterning, even on lyophobic substrates. The resulting OTFTs exhibit sharp switching characteristics and high reproducibility. This study provides fundamental insights into the interfacial mechanics of layered OSCs and offers rational design principles for manufacturing advanced flexible electronics.

2. RESULTS

2.1. Molecular Semiconductor Layer Transfer

The film transfer process is schematically illustrated in Figure 1. First, OSC films were prepared on freshly cleaved mica

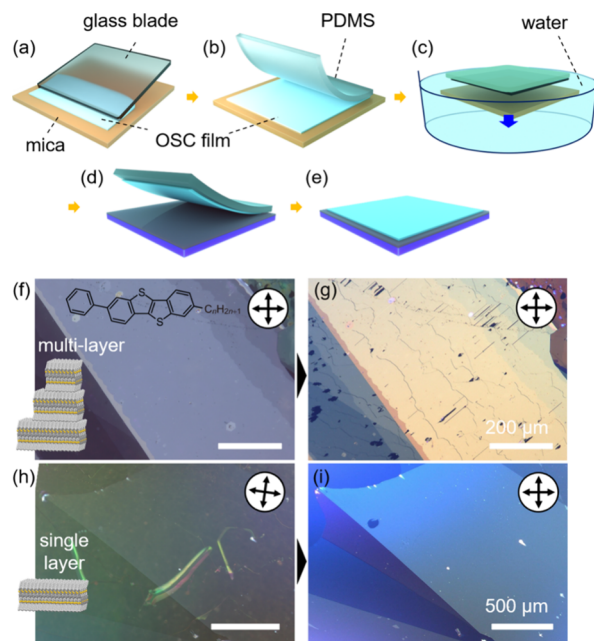


Figure 1. Transfer of organic semiconductor (OSC) films. (a–e) Procedures for transferring OSC films. (a) Blade coating of the OSC film on a mica substrate. (b) Covering the OSC film with a PDMS sheet. (c) Exfoliation of the OSC film from the mica substrate upon immersion in water. The blue arrow indicates the spontaneous sinking of the mica substrate. (d) Transferring the OSC film onto a different substrate using the PDMS stamp. (e) Transferred films on the target substrate. (f–i) Typical polarized optical microscopy (POM) images of multilayered ($\phi_{\text{long}} = 0.0$) (f, g) and SMB ($\phi_{\text{long}} = 0.5$) (h, i) films, observed before (f, h) and after (g, i) transfer onto Si/SiO₂ substrates. Scale bars are 200 μm for (f, g) and 500 μm for (h, i), respectively.

substrates (Figure 1a). Mica was chosen as the growth substrate based on its atomically flat surface and pronounced hydrophilicity (water contact angle $< 5^\circ$), which are essential for subsequent water-assisted delamination. We used Ph-BTBT- C_n ($n = 10$ and 12) as the benchmark material for the asymmetric OSCs.¹⁴ The blade-coating method was used to create continuous single-crystalline films of Ph-BTBT- C_n . To control the film thickness via the geometric frustration effect, we used solutions of Ph-BTBT- C_{10} and Ph-BTBT- C_{12} mixed at various volume ratios, ϕ_{long} (volume fraction of the longer-chain component in the mixed solution; see the Experimental Section for details).

The blade-coated films were laminated with a thin PDMS sheet, as shown in Figure 1b. The flexible PDMS stamp adhered well to the film surface without external pressure, conforming to any slight roughness of the substrate. Next, the substrate was immersed in water to exfoliate the PDMS/OSC layer from the mica substrate via the penetration of water into the hydrophilic surface, as shown in Figure 1c. The sheet was utilized as a sticker for the OSC layers, which were transferred onto various substrates (see Figure 1d,e).

Figure 1f–i present typical polarized optical microscopy (POM) images of the fabricated films. The as-grown film on the mica substrate consists of large crystal domains that grow in the blade-coating direction (Figure S1a). Although most of the film was successfully delaminated and transferred onto Si/SiO₂ substrates (see Figure S1b), the structural integrity

was highly dependent on the film thickness. Specifically, when a relatively thick film (over approximately 15 nm) was transferred, significant crack formation was induced across the entire area, as shown in Figure 1g, whereas no such cracks were present in the as-coated film on the mica substrate, as shown in Figure 1f. These cracks compromised the structural integrity of the transferred crystals, which is expected to impede efficient charge transport. In striking contrast, crack formation was suppressed by reducing film thickness. As shown in Figure 1h,i, the SMB film transferred using the same procedure exhibited a continuous and crack-suppressed morphology over a large area. Furthermore, the microscopic analyses presented in Figure S2, including angle-dependent POM and optical interference color observations, reveal that crystalline orientation and thickness uniformity were maintained even after the transfer process. Notably, the magnified optical images confirm that no directional cracks were present in the transferred SMBs, as shown in Figure S2d,e. Figure S3 shows that the atomic force microscopy (AFM) height profiles of the transferred films rarely contain submicrometer cracks. This confirms that the larger-area optical images provide sufficient information to evaluate crack formation. We thus observed the film-thickness dependence of crack formation, as shown in Figure S4. These results demonstrate a clear correlation between film thickness and the integrity of the transferred film, revealing that a bilayer-type OSC film can be transferred without mechanical failure by reducing its thickness to the SMB level.

We also investigated the film morphology at each stage of the transfer process to identify the onset of crack formation. While apparently no cracks are observed in the as-coated films, they are occasionally generated during the handling of the freestanding PDMS/OSC stack. We find that cracks are formed not only under tensile strain but also under compressive strain (Figure S5). However, the results indicate that the susceptibility to crack formation under compression is lower than that under tensile stretching.

2.2. Crack Anisotropy in the Transferred Multilayer Films

We first focus on the crack patterns observed in the transferred thick multilayered films. A notable feature of these cracks is that they do not propagate randomly but instead follow specific, regular directions, as shown in Figure 2a. This directional preference is independent of the directionality of film transfer and is unaffected by the alkyl chain length of the OSCs. This orientational propensity strongly suggests a direct correlation with the underlying arrangement of rigid π -cores. Figure 2b illustrates intralayer herringbone-type packing, with the crack directions indicated by dotted lines. This fracture anisotropy should arise from the anisotropy of the intermolecular interactions between adjacent π -cores (see also Figures S6 and S7). To confirm this, we calculated the intermolecular interaction energies within the plane (see the Experimental Section and Figure 2c). Specifically, we analyzed the fracture within a single layer, given that the π -cores in both the upper and lower layers within the bilayer packing exhibit an almost identical arrangement, as shown in Figure S8. The interaction energies in the slipped parallel configuration (e_1 and e_4) are approximately two-thirds of those in the T -shaped configuration (e_2 , e_3 , e_5 , and e_6). For simplicity, we denote the values of the interaction energies in the slipped parallel and T -shaped configurations as e_P and e_T , respectively (i.e., $e_P = e_1 = e_4$ and $e_T = e_2 = e_3 \sim e_5 = e_6$). Figure 2d–f present three possible crack directions along the low-index crystallographic planes, which require a low energy cost to cleave. The actual fracture surface in Figure 2d exhibits a higher flatness than the planes perpendicular to the x_{HB} or y_{HB} directions, as indicated in Figure 2e,f, respectively. This flatness should minimize the total number of bond breakages per unit length of macroscopic crack propagation, thereby suppressing alternative pathways. Additionally, assuming that interactions with the nearest-neighbor molecules are primarily responsible for the energy cost of creating a particular fracture surface, we conclude that the experimentally observed cracks shown in Figure 2d are energetically favorable because the breakage of weaker e_P bonds

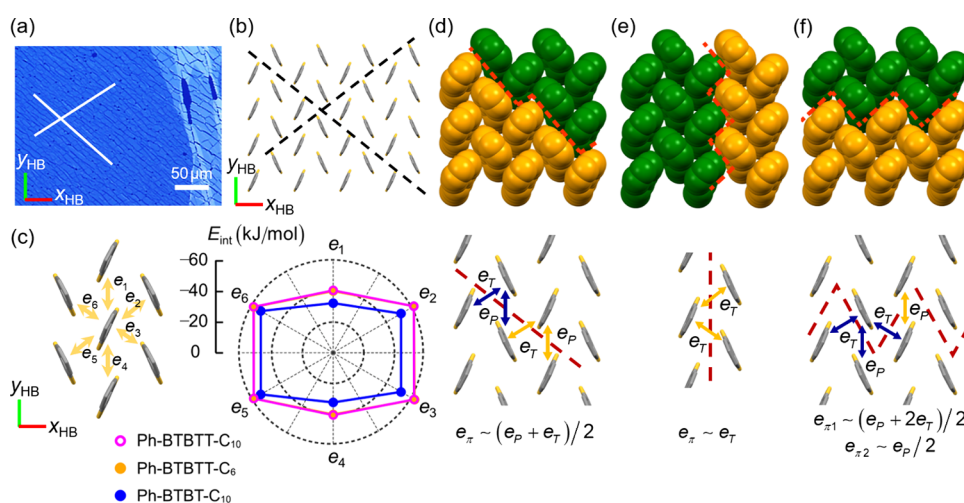


Figure 2. Crack direction analysis for multilayered film transfer. (a) Optical microscopy image of typical cracks in the multilayer film ($\phi_{long} = 0.0$). White lines indicate the directions of crack propagation. The color contrast is adjusted to increase the visibility of cracks in the film. Scale bar is 50 μ m. (b) Experimentally observed crack orientation is shown in the π -core arrangement within the crystal. (c) Schematic of the herringbone packing motif (left) and calculated interaction energies between π -cores for T -shaped (e_2 , e_3 , e_5 , and e_6) and slipped-parallel (e_1 and e_4) contacts (right). (d–f) Possible crack orientations (top) and their estimated energy cost per molecule, approximated from the nearest neighbor interactions (bottom). (d) Experimentally observed crack orientation. (e,f) Model cleavages along planes perpendicular to the (e) x_{HB} or (f) y_{HB} direction.

minimizes the overall energetic cost compared with disrupting the stronger e_T bonds. The net interactions were evaluated for crystallographically independent molecules, as indicated by the blue and yellow arrows in the bottom panels of Figure 2d–f. It should be noted here that the directional preference for the most stable axes becomes gradually less pronounced in thicker multilayers, as shown in Figure S7. This behavior occurs because the low fracture threshold obscures the energetic anisotropy, thereby diminishing the exclusive directional selection of crack propagation.

This result indicates that the anisotropy of the intermolecular interactions between adjacent π -cores also contributes to crack propagation. For example, DNBDT derivatives, which are known for their robust transfer characteristics,⁹ exhibit not only stronger overall π -core interactions owing to their extended π -electron backbone but also smaller anisotropies between their e_p and e_T values, as shown in Figure S9. This reduced energetic anisotropy indicates that there is no single energetically favorable path for crack propagation, which should suppress preferential cleavage and enhance rigidity during the transfer process.

2.3. Modeling of Thin-Film Fracture

The contributions of film thickness and intermolecular interactions to crack propagation can be understood qualitatively via mechanical modeling. Note that the contribution of surface effects should be negligible in this system, since the film surface is composed of alkyl-chain layers,²⁰ ensuring an identical interfacial environment regardless of the thickness. We consider a thin film (thickness h , Young's modulus E_{film}) laminated onto a soft PDMS stamp (Young's modulus E_{sub}). A crack that penetrates through the entire thickness of the thin film and propagates in a long, straight line is referred to as a "channeling crack," and the theoretical aspects of such cracks have been studied extensively.^{25,26} Following this framework, we consider a single crack formed when the film adheres to the PDMS stamp under tensile stretching (Figure S10a) and ignore multiple cracking modes.^{27,28} By utilizing the Dundurs parameter α , which reflects the elastic mismatch between the film and substrate, the energy release rate G can be expressed using a dimensionless function $Z(\alpha)$ as follows (see Supporting Information for details):

$$G \sim U_{\text{film}} h \sim E_{\text{film}} h Z(\alpha) \varepsilon^2, \quad (1)$$

where ε represents the total strain.

Fracture is expected when G reaches the intrinsic fracture energy of the material at a critical strain. For a molecular crystal, this fracture energy can be approximated by the cohesive energy of the adjacent π -cores per unit area (e_π), rather than flexible alkyl chains. Therefore, the fracture conditions can be expressed as follows:

$$\varepsilon_c \sim \sqrt{\frac{e_\pi}{E_{\text{film}} h Z(\alpha)}}. \quad (2)$$

Although eq 2 is derived from elasticity theory, which is recognized as a macroscopic approximation for discrete molecular systems, the model predicts that when the film thickness h is small, the critical strain is large. This relationship explains why SMBs can be transferred without cracks, whereas thicker films experience severe fracture. This model also incorporates the

effects of the underlying support material. For a stiffer support (higher E_{sub}), the elastic mismatch is reduced, effectively increasing the critical strain. It has been reported that a rigid substrate can be used to prevent damage to films caused by deformation during transfer.²⁹ Figure S11 shows the optical microscopy images of the films transferred using a PDMS stamp with reduced thickness. While the thinner support increased the structural flexibility and difficulty of manual handling, the SMBs can be successfully transferred without significant damage, confirming the mechanical robustness of our film-transfer process against variations in support rigidity. Although the above discussion is limited to channeling cracks under tensile film deformation, cracks may also arise from buckling under compressive strain,^{30,31} as shown in Figure S10b (see also Figure S5). Regardless, as described in the Supporting Information, thinner films are inherently more prone to buckling.³² However, the local strain concentrated at the buckled apex decreases in thinner films. Consequently, reduced thickness effectively mitigates crack formation, suggesting that thickness dependence becomes even more prominent.

2.4. Fabrication of Artificial Superlattices via Sequential SMB Transfer

The mechanistic understanding presented above suggests a methodology for constructing thick yet crack-suppressed multi-layered structures based on the sequential transfer of SMBs. Figure 3a presents an optical micrograph of five stacked SMBs of Ph-BTBT- C_n transferred onto a Si/SiO₂ substrate. We intentionally shifted the edge positions of each SMB layer to present differences in film thickness based on color. The film color changes as a result of multilayer interference, as reported previously.^{20,23} The AFM height profile of this five-bilayer stack, shown in Figure 3b, reveals a total thickness of approximately 27 nm, which is consistent with the thickness estimated from the c -axis lattice constant (or bilayer thickness) of Ph-BTBT- C_{10} . Notably, this multilayer film is crack-suppressed, in contrast to a film of a similar thickness produced in a single transfer step (Figures 2a and S4). This result demonstrates that a layer-by-layer transfer approach circumvents the fracture associated with the release of large amounts of elastic energy in thick films.

Out-of-plane X-ray diffraction (XRD) measurements were conducted to assess the structural quality and uniformity of the multilayer films on a macroscopic scale. We prepared multi-stacked films by transferring SMBs three and five times. The resulting XRD patterns exhibit sharp Bragg peaks corresponding to the interlayer spacing ($\Delta q \approx 0.11 \text{ \AA}^{-1}$), as shown in Figure 3c. Notably, in the magnified view of the obtained XRD patterns (Figure 3d), a series of well-defined satellite peaks, known as Laue fringes, is clearly observable between the main peaks. The number of fringes changes with the number of stacked layers, and their distinct appearance is the hallmark of a highly ordered superlattice with a uniform layer thickness and flat interfaces.^{23,33,34} These results confirm that the sequential transfer technique enables the fabrication of uniform artificial molecular superlattices.

2.5. Intermolecular Interaction Tuning and Patterning of SMBs

In the previous subsections, we have demonstrated that reducing the thickness of molecular films effectively suppresses channeling cracks. Considering the application of these films as active layers in OTFTs, it is desirable to tune inter-core

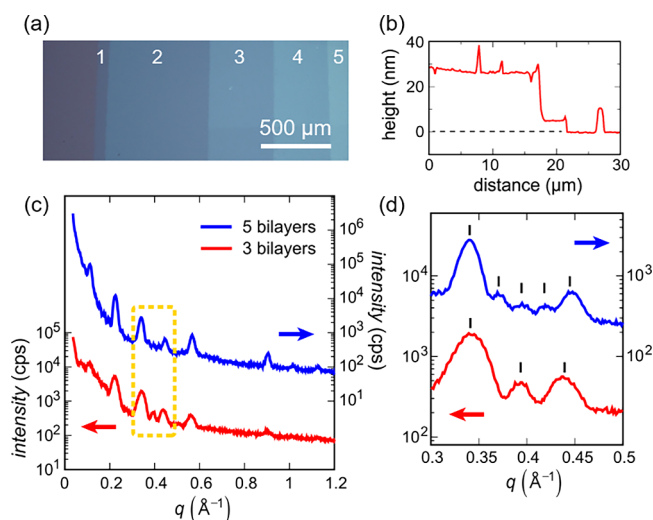


Figure 3. Layer-by-layer transfer of SMBs of Ph-BTBT- C_n . (a) Optical microscopy image of a multistacked transferred film with a five-bilayer thickness. Each SMB was fabricated with $\phi_{\text{long}} = 0.5$. Scale bar is 500 μm . (b) Height profile of the film measured after trimming the edge. (c) XRD patterns of the multi-stacked transferred films. (d) Magnified view of the XRD patterns shown in (c) indicated by the dotted orange region.

interactions to improve structural and mechanical processability. In bottom-gate, bottom-contact (BGBC) transistor architectures, we have previously demonstrated that Ph-BTBT-based devices are susceptible to degradation as a result of structural instability at semiconductor/metal/dielectric ternary interfaces.³⁵ Therefore, to improve durability further, we used Ph-BTBTT- C_n as an OSC with an extended π -system.^{18,24} This material has a five-ring backbone incorporating an additional thiophene ring attached to the BTBT core, which enhances the interaction energy between adjacent π -cores within the layer (e_π), as shown in Figure 2c. This increase in cohesive energy should enhance fracture resistance during processing according to eq 2, despite the core extension indirectly increasing the Young's modulus.

To assess mechanical processability, we first explored multilayer formation via sequential SMB transfer. Figure S12 presents high-quality multilayer structures, demonstrating that the enhanced cohesion energy e_π does not impede the layer-by-layer assembly process. Next, we investigated the tolerance of the patterning procedure, as shown in Figure 4. In this process, a continuous SMB is “die-cut” by a structured SiO_2 substrate before being transferred to a target substrate, as shown in Figure 4b. This lithography-free process creates a grid-like patterned film, as shown in Figure 4a. The successful formation of the die-cut film suggests that enhanced cohesive energy effectively relieved the mechanical stress along the template boundaries, maintaining the structural integrity of the molecular film during processing. The peeling force can induce a local strain exceeding the critical strain of the molecular layers, leading to mechanical damage at the pattern boundaries. Regardless, Figure S13 shows the optical microscopy images of the patterned films fabricated using a metal mask template with curved geometry. The selective transfer was successfully achieved regardless of the pattern curvature or the crystallographic orientation. These results indicate that Ph-BTBTT- C_n films enable

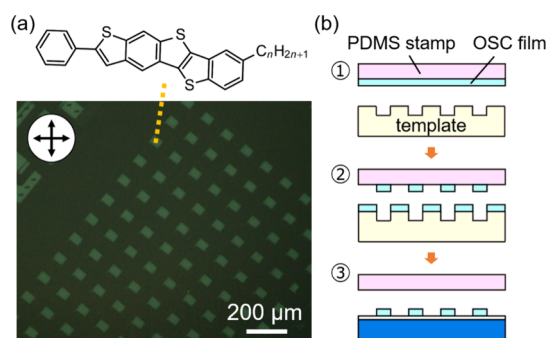


Figure 4. Transfer patterning of Ph-BTBTT- C_n SMBs. (a) Chemical structure of Ph-BTBTT- C_n (top) and polarized optical microscopy image of the patterned film (bottom). SMB was fabricated with $\phi_{\text{long}} = 0.5$. Scale bar is 200 μm . (b) Schematics of the procedure for producing patterned OSC films.

the processing of both vertical and lateral patterning. The high processability and structural stability of this material demonstrate its excellent potential for electronic applications.

2.6. OTFT Characteristics When Using Transferred SMBs

To examine the electrical performance of the transferred SMBs, BGBC OTFTs were fabricated as shown in Figure 5a. The surfaces of the source/drain electrodes were modified using pentafluorobenzenethiol (PFBT) to improve carrier injection.^{36,37} We also covered the surface of the SiO_2 gate insulating layer with CYTOP to reduce carrier-trapping agents and achieve sharp switching characteristics.^{22,38} Notably, this dry transfer method can be used to form SMBs over a large area on a liquid-repellent CYTOP surface, whereas thin films cannot be formed directly via simple blade coating.

Figure 5b–d present the typical transfer and output characteristics of the fabricated TFTs. Low-voltage operation (below 3 V) was achieved, along with sharp on/off switching, a small threshold voltage (V_{th}) or turn-on voltage (V_{on}) of approximately 0 V, and negligible hysteresis. The highest device mobility measures are approximately 5.8 and 5.9 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the linear and saturation regimes, respectively. These values are slightly lower than those reported for single-crystal-based top-contact devices using the same material,^{18,24} which is partly explained by the fact that the current channel does not consist of a single-crystal domain. Notably, Figure 5e reveals that the device mobilities in the linear and saturation regimes are almost identical, indicating that charge injection occurs smoothly even under a low applied voltage in the linear regime ($V_D = -0.2 \text{ V}$), just as in the saturation regime. Furthermore, the mobility exhibits negligible V_G dependence for the Ph-BTBTT- C_n -based OTFTs. In contrast, Figure S14 reveals that the Ph-BTBT- C_n -based TFTs exhibit a decrease in mobility at high voltages, originating from contact resistance,³⁹ suggesting a possible structural disorder at the ternary interface due to weak inter-core interactions, as discussed previously.³⁵

While maintaining device mobility without a significant reduction in BGBC geometry for both materials, the devices exhibit sharp on/off characteristics. Typical TFTs using Ph-BTBTT- C_n and Ph-BTBT- C_n can provide subthreshold swing (SS) values of approximately 135 mV dec^{-1} and 85 mV dec^{-1} in the linear regime, respectively (see Figures 5b and S14a). Such sharp switching characteristics, which were obtained

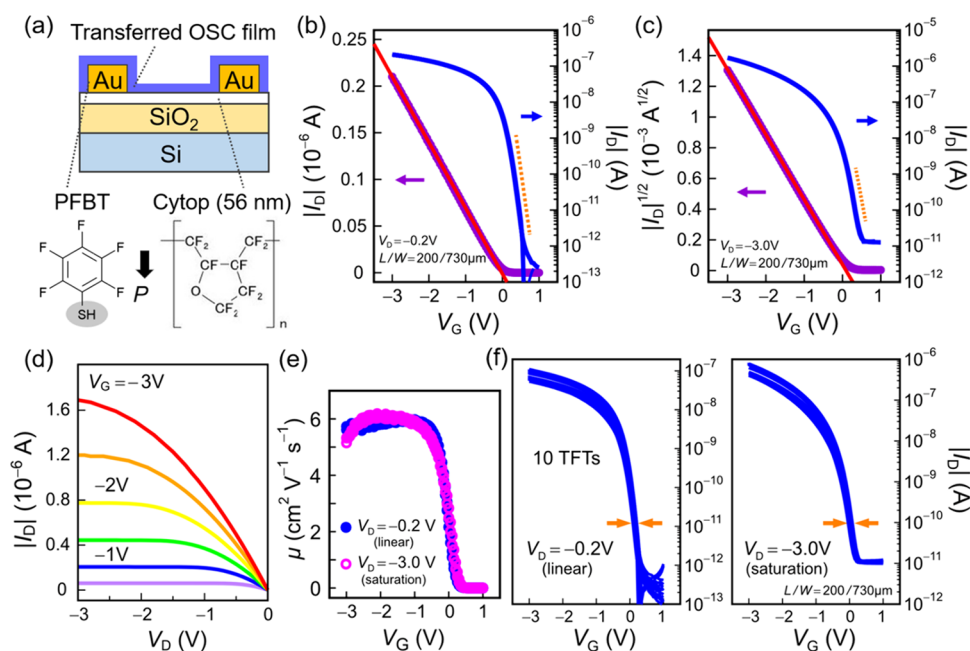


Figure 5. Typical performance of the OTFTs using the stamp-transferred Ph-BTBTT- C_n SMB fabricated with $\phi_{\text{long}} = 0.5$. (a) Schematic cross section of a bottom-gate bottom-contact (BGBC) TFT. (b,c) Typical transfer characteristics in the (b) linear regime ($V_D = -0.2$ V) and (c) saturation regime ($V_D = -3.0$ V). The channel length and width are $L = 200$ μm and $W = 730$ μm , respectively. (d) Typical output characteristics. (e) Gate-voltage dependence of the device mobility in the linear and saturation regimes. (f) Distribution of transfer curves for 10 TFTs fabricated on the same substrate, observed in the (left) linear and (right) saturation regimes.

despite the small capacitance (~ 16.5 nF cm^{-2}) owing to the relatively thick dielectric layer (Figure S15), suggest an extremely low density of interfacial trap states, indicating that our crack-suppressed film transfer technique successfully preserved the high crystalline quality of the SMB. Sharp switching properties were also confirmed using different types of insulating layers, where the SiO_2 surface was modified with fluorinated self-assembled monolayers, as shown in Figure S16 (also see the Experimental Section). These findings indicate that SMBs can be transferred to various surfaces without incurring severe damage.

We also examined the distribution of the transfer curves for 10 TFTs fabricated on the same substrate, as shown in Figure 5f. Uniform subthreshold characteristics were observed in both the linear and saturation regimes, regardless of the channel orientation relative to the crystal growth direction. The results exhibit a small variation in V_{on} for each regime, leading to minimal fluctuations in the subthreshold characteristics, as indicated by the orange arrows in the figure. It should be noted that while the device-level variation in the same substrate remains small, the average V_{on} can shift when using different substrates, even when covered by a CYTOP layer (see Figure S17). Given that both the device mobility and SS values are unaffected by substrate differences, this shift is likely attributable to extrinsic factors, such as adsorbed molecules and fixed charges near the surface of the dielectric layer, rather than the transfer process itself. This result implies that further optimization of the dielectric surface and passivation techniques is expected to enhance overall uniformity when using transferred SMBs.

To further investigate the vertical interlayer transport properties across the transferred interfaces, we also fabricated top-contact OTFTs incorporating a double-transfer SMB channel, as shown in Figure S18. The resulting output characteristics

showed negligible access resistance, indicating that the vertical interlayer electronic coupling remains robust even across artificial stacked interfaces. This behavior is consistent with that of naturally grown multilayers,²³ suggesting that the vertical transport is predominantly governed by the intrinsic interlayer structure rather than the in-plane crystallographic alignment.

Furthermore, Figure S19 shows the long-term stability of the fabricated OTFTs under ambient conditions. The Ph-BTBTT-based OTFT maintains the device mobility even after 100 days of storage in air at room temperature, while the Ph-BTBT-based device shows slight decrease in the mobility. This robust ambient stability was reproducible across multiple evaluated devices, confirming the chemical and structural durability of the transferred SMBs. The reliable formation of crack-suppressed ultrathin OSC layers demonstrates the potential of our approach as a versatile platform for device engineering, contributing to fundamental studies on molecular-scale electronics.

3. CONCLUSIONS

In this study, we have investigated the mechanical aspects of transferring bilayer-type OSC films. We found that crack formation can be suppressed by reducing film thickness to an SMB. Furthermore, we observed that cracks propagate in specific crystallographic directions. These behaviors can be explained by elasticity theory combined with anisotropic intermolecular interaction energies. Based on this concept, multilayer films were fabricated through multiple SMB transfers. The artificially stacked films exhibited clear Laue fringes, indicating the uniformity of the transferred layers. We also successfully fabricated patterned SMBs without lithography techniques using extended π -core molecules. It should be noted that increasing inter-core interactions can potentially compromise solvent solubility and

the resulting solution processability. Therefore, the development of extended π -cores with a five-ring backbone, such as BTBTT derivatives, could be an effective strategy for balancing the competing requirements of processability and stability.

The electrical quality of films prepared using these methods was evaluated by fabricating BGBC TFTs. By tuning the inter-core interactions using Ph-BTBTT- C_n , the fabricated OTFTs exhibited reliable operation with sharp switching characteristics, demonstrating that our transfer methodology can produce high-quality films with favorable interfacial properties suitable for device applications. These findings should provide a rational basis for designing both materials and processes, thereby contributing to the advancement of manufacturing techniques for flexible organic electronics.

4. EXPERIMENTAL MATERIALS AND METHODS

4.1. Thin-Film Fabrication

Powdered Ph-BTBTT- C_6 and Ph-BTBTT- C_{10} were synthesized and purified according to a previous report.²⁴ We purchased Ph-BTBTT- C_{10} and Ph-BTBTT- C_{12} from Tokyo Chemical Industry Co., Ltd. These materials were used as received without further purification. We prepared 0.02 and 0.1 wt % solutions of Ph-BTBTT- C_n and Ph-BTBTT- C_n in chlorobenzene (Wako Special Grade; Fujifilm Wako Pure Chemical, Japan), respectively. To produce SMBs, solutions with different chain lengths were mixed at a volume ratio of 7:3 or 5:5 (i.e., $\phi_{\text{long}} = 0.3$ or 0.5). The results were not affected when ϕ_{long} was varied between 0.1 and 0.5. The OSC film was fabricated using the blade-coating method, in which a solution was unidirectionally swept using a thin glass blade covered with CYTOP (CTL-809 M; AGC Inc., Japan). The coating speed was controlled at $1.0 \mu\text{m s}^{-1}$ for Ph-BTBTT- C_n and $4.0 \mu\text{m s}^{-1}$ for Ph-BTBTT- C_n via a stepping motor (SHOT-302GS; Sigma Koki Co. Ltd., Japan) under ambient conditions.

4.2. Transfer Procedures of Molecular Films

Mica was selected as the hydrophilic substrate for preparing the molecular layer. The mica substrate was cleaved to obtain a fresh surface before preparing the OSC films. A molecular layer was formed on this surface using the blade-coating method and then covered with a PDMS sheet. We used a 200- μm -thick PDMS sheet (CSCRIE, Japan), and the tensile strength of the film was 8.0 MPa. To examine the effect of PDMS thickness, we also used a 100- μm -thick PDMS sheet purchased from the same supplier. Owing to the flexibility of the PDMS sheet, it could cover the substrate even if it was slightly rough. The entire substrate was immersed in water at ambient temperature, allowing the molecular layer to be exfoliated while attached to the PDMS sheet. The OSC layer was transferred to a target substrate by placing the composite on it and subsequently peeling off the PDMS sheet. This process was repeated to obtain multilayer structures. For patterning, the OSC film on the PDMS stamp was brought into contact with a micro-structured SiO_2 template to selectively remove unwanted regions prior to the final transfer onto the target substrate.

4.3. Structure Evaluation of the Films

The thickness profile of the OSC film was measured using a tapping-mode AFM (MFP-3D, Oxford Instruments, U.K.). The crystallinity of the OSC film was characterized using a crossed Nicols polarized microscope (VHX-8000; Keyence Co. Ltd., Japan). We also measured XRD patterns using a thin-film diffractometer (Empyrean 3, Malvern Panalytical, U.K.) with monochromated $\text{CuK}\alpha 1$ radiation. The diffraction intensity was recorded using a proportional detector under ambient conditions.

To analyze crack-angular preference, the contrast of the optical microscopy images was enhanced, followed by a fast Fourier transform (FFT) to extract the characteristic crack orientations. Then, the bright

spots in the resulting FFT profiles were systematically counted along each direction. Due to the orthogonal relationship between real-space lines and Fourier-space peaks, a 90° angular correction was applied to the extracted data prior to plotting. Note that this counting method provides an approximate orientational preference rather than a strict number distribution.

4.4. Calculation of Intermolecular Interaction Energies

We evaluated the intermolecular interaction energies between two molecules using the Gaussian16 program.⁴⁰ We used the atomic coordinates for each molecular packing obtained from X-ray single-crystal structure analyses. The intermolecular interaction energies were calculated at the B3LYP/6-311G** level using Grimme's D3 dispersion correction.⁴¹ The basis set superposition error⁴² was corrected using the counterpoise method.⁴³ Note that this calculation provides reasonable estimates of the interaction energies between aromatic hydrocarbons and heterocycles.⁴⁴ The contributions of core-core interactions were evaluated using the fragment structures in the crystals. The dangling bonds in the fragments were capped with hydrogen atoms.

4.5. OTFT Performance

We used a heavily *p*-doped silicon wafer covered with a 100 nm thermally grown silica layer for device fabrication. The substrates were cleaned via 3 min sequential sonication in deionized water, acetone, isopropanol, and deionized water. The Si/ SiO_2 substrate was covered with either CYTOP (CTL-809M, AGC Inc., Japan) or 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFD-TES; Sigma-Aldrich Co. LLC, USA). We prepared a CYTOP solution diluted using the solvent (CT-Solv.180; AGC Inc., Japan) at a volume ratio of 1:4 and formed a gate dielectric layer on the silica surface by spin coating at 2000 rpm for 60 s. Subsequently, the CYTOP layer was cured at 80°C for 15 min at 0.02 MPa and 180°C for 60 min at 0.02 MPa. We prepared PFD-TES vapor in a metal container, placed the substrate in it, and heated it at 150°C for at least 2 h. After the substrate had absorbed the vapor, it was rinsed with isopropanol and heated at 120°C for 20 min to form the fluorinated self-assembled monolayer on the silica surface. After drying, the source and drain electrodes were fabricated through the thermal deposition of 25 nm thick gold layers through a shadow mask. The electrode surfaces were then modified using chemical vapor treatment with PFBT (>98.0%; Tokyo Chemical Industry Co., Ltd., Japan) in a closed container. For the double-transfer SMB channel devices, the SMBs were sequentially transferred onto the Si/ SiO_2 substrate. Subsequently, the top-contact Au electrodes were fabricated using the same evaporation conditions and thickness as those for the single-layer devices. For accurate mobility evaluation, the parts of the thin films outside the channel were trimmed using a homemade micromanipulator. The conventional two-probe characteristics of bottom-gate bottom-contact OTFTs were measured under ambient conditions using a semiconductor device analyzer (B1500A; Agilent Technologies Co. Ltd., USA). For the long-term stability evaluation, the fabricated devices were stored under ambient conditions in air. The frequency-dependent dielectric constant was measured using an impedance measurement setup combining a digital impedance analyzer (MFIA, Zurich Instruments) and a material impedance analyzer interface (MIA, Toyo Corporation). The measurements were performed with an AC amplitude of 50 mV and a DC bias of 0 V over a frequency range from 0.1 Hz to 100 kHz using a probe station (TOP-400G, Toyo Corporation).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c12628>.

Modeling of thin-film fracture, Table S1, and Figures S1–S19 (DOCX)

AUTHOR INFORMATION

Corresponding Author

Shunto Arai – National Institute for Materials Science (NIMS),
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan;
orcid.org/0000-0002-0055-3006; E-mail:
ARAI.Shunto@nims.go.jp

Authors

Mariko Shimokawa – National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Takayuki Harada – National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Toshiki Higashino – National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan; orcid.org/0000-0002-9227-8207

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsami.6c12628>

Author Contributions

S.A. conceived and designed the study. S.A. conducted data curation with the help of M.S. T.Hi. provided the powdered Ph-BTBTT-C_ns material. S.A. and M.S. contributed to film formation, evaluation, and the fabrication and characterization of OTFTs. T.Ha supported the XRD measurements. S.A. performed the calculation of intermolecular interaction energies. S.A. wrote the paper with input from all authors. All authors have approved the final version of the manuscript.

Notes

This study was partly supported by JSPS KAKENHI (grant nos. JP21H05234, JP25K24862, and JP26K01381) and JST PRESTO (grant no. JPMJPR23N1) and CREST (JPMJCR24A2), Japan. S.A. would like to thank the MEXT Leading Initiative for Excellent Young Researchers (grant no. JPMXS0320220012).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Takeo Minari for allowing us to use the vacuum deposition system and the electrical measurement system. We also appreciate Ms. Kanako Suda for the experimental support for AFM measurements.

ABBREVIATIONS

2D	two-dimensional
OSC	organic semiconductor
DNBDT	dinaphtho[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene
π -cores	π -electron cores
SMB	single molecular bilayer
OTFT	organic thin-film transistor
PDMS	polydimethylsiloxane
Ph-BTBT-C _n	phenyl/alkyl-substituted [1]benzothieno[3, 2-b][1]benzothiophene
Ph-BTBTT-C _n	phenyl/alkyl-substituted benzothieno[6,5-b]benzothieno[3,2-b]thiophenes

AFM	atomic force microscope
XRD	X-ray diffraction
SS	subthreshold swing
PFD-TES	1H,1H,2H,2H-perfluorodecyltriethoxysilane

REFERENCES

- (1) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. Large-scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. *Nature* **2009**, *457*, 706–710.
- (2) Jain, A.; Bharadwaj, P.; Heeg, S.; Parzefall, M.; Taniguchi, T.; Watanabe, K.; Novotny, L. Minimizing residues and strain in 2D materials transferred from PDMS. *Nanotechnology* **2018**, *29*, 265203.
- (3) Ahn, J.-H.; Kim, H.-S.; Lee, K. J.; Jeon, S.; Kang, S. J.; Sun, Y.; Nuzzo, R. G.; Rogers, J. A. Heterogeneous three-dimensional electronics by use of printed semiconductor nanomaterials. *Science* **2006**, *314* (5806), 1754–1757.
- (4) Ago, H.; Okada, S.; Miyata, Y.; Matsuda, K.; Koshino, M.; Ueno, K.; Nagashio, K. Science of 2.5 dimensional materials: paradigm shift of materials science toward future social innovation. *Sci. Technol. Adv. Mater.* **2022**, *23*, 275–299.
- (5) Zou, D.; He, Z. F.; Chen, M.; Yan, L. Z.; Guo, Y. F.; Gao, G. Y.; Li, C.; Piao, Y. Z.; Cheng, X.; Chan, P. K. L. Dry Lithography Patterning of Monolayer Flexible Field Effect Transistors by 2D Mica Stamping. *Adv. Mater.* **2023**, *35* (20), 2211600.
- (6) Briseno, A. L.; Mannsfeld, S. C. B.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. Patterning organic single-crystal transistor arrays. *Nature* **2006**, *444*, 913–917.
- (7) Xu, C.; He, P.; Liu, J.; Cui, A.; Dong, H.; Zhen, Y.; Chen, W.; Hu, W. A General Method for Growing Two-Dimensional Crystals of Organic Semiconductors by “Solution Epitaxy.” *Angew. Chem., Int. Ed.* **2016**, *55* (33), 9519–9523.
- (8) Xie, Y.; Zong, H.; Zhou, F.; Luo, X.; Zhou, Z.; Peng, J.; Zhou, G. Transfer Printing of Two-Dimensional Molecular Crystals for Low-Voltage, High-Performance, and Degradable Transistors. *Nano Lett.* **2025**, *25* (16), 6574–6582.
- (9) Makita, T.; Kumagai, S.; Kumamoto, A.; Mitani, M.; Tsurumi, J.; Hakamatani, R.; Sasaki, M.; Okamoto, T.; Ikuhara, Y.; Watanabe, S. High-performance, semiconducting membrane composed of ultrathin, single-crystal organic semiconductors. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117*, 80–85.
- (10) Chen, Y.; Gong, X.-L.; Gai, J.-G. Progress and Challenges in Transfer of Large-Area Graphene Films. *Adv. Sci.* **2016**, *3* (8), 1500343.
- (11) Ma, L.-P.; Ren, W.; Cheng, H.-M. Transfer Methods of Graphene from Metal Substrates: A Review. *Small Methods* **2019**, *3* (7), 1900049.
- (12) He, Z. F.; Dai, D. S. H. S.; Chen, M.; Zou, D.; Chik, G. K. K.; Rafael, R.; Lee, K. H.; Piao, Y. Z.; Zhang, S. M.; Cheng, X. Van der Waals Assembled Solution-Processed Organic Monolayer Single-Crystal Transistor for Electrocardiograph Sensing. *Adv. Funct. Mater.* **2022**, *32* (41), 2205129.
- (13) Wang, X. R.; Li, S. C.; Sheng, Q. Y.; Liu, Z. Z.; Peng, B. Y.; Li, H. Y. A Dry-Transfer Method for Molecular Monolayer Crystals toward Flexible High-Performance Organic Field-Effect Transistors. *ACS Mater. Lett.* **2024**, *6* (9), 4240–4247.
- (14) Iino, H.; Usui, T.; Hanna, J. Liquid crystals for organic thin-film transistors. *Nat. Commun.* **2015**, *6*, 6828.
- (15) Minemawari, H.; Tanaka, M.; Tsuzuki, S.; Inoue, S.; Yamada, T.; Kumai, R.; Shimoi, Y.; Hasegawa, T. Enhanced Layered-Herringbone Packing due to Long Alkyl Chain Substitution in Solution-Processable Organic Semiconductors. *Chem. Mater.* **2017**, *29*, 1245–1254.
- (16) Inoue, S.; Shinamura, S.; Sadamitsu, Y.; Arai, S.; Horiuchi, S.; Yoneya, M.; Takimiya, K.; Hasegawa, T. Extended and Modulated Thienothiophenes for Thermally Durable and Solution-Processable Organic Semiconductors. *Chem. Mater.* **2018**, *30*, 5050–5060.
- (17) Higashino, T.; Arai, S.; Inoue, S.; Tsuzuki, S.; Shimoi, Y.; Horiuchi, S.; Hasegawa, T.; Azumi, R. Architecting Layered Molecular Packing in

Substituted Benzobisbenzothiophene (BBBT) Semiconductor Crystals. *CrystEngComm* **2020**, *22*, 3618–3626.

(18) Higashino, T.; Inoue, S.; Arai, S.; Matsui, H.; Toda, N.; Horiuchi, S.; Azumi, R.; Hasegawa, T. Architecting Layered Crystalline Organic Semiconductors Based on Unsymmetric π -Extended Thienoacenes. *Chem. Mater.* **2021**, *33*, 7379–7385.

(19) Higashino, T.; Inoue, S.; Sadamitsu, Y.; Arai, S.; Horiuchi, S.; Hasegawa, T. Bilayer-type Layered Herringbone Packing in 3-*n*-Octyl-9-phenyl-benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophene. *Chem. Lett.* **2019**, *48*, 453–456.

(20) Arai, S.; Inoue, S.; Hamai, T.; Kumai, R.; Hasegawa, T. Semiconductive Single Molecular Bilayers Realized Using Geometrical Frustration. *Adv. Mater.* **2018**, *30*, 1707256.

(21) Arai, S.; Morita, K.; Tsutsumi, J.; Inoue, S.; Tanaka, M.; Hasegawa, T. Layered-Herringbone Polymorphs and Alkyl-Chain Ordering in Molecular Bilayer Organic Semiconductors. *Adv. Funct. Mater.* **2020**, *30*, 1906406.

(22) Kitahara, G.; Inoue, S.; Higashino, T.; Ikawa, M.; Hayashi, T.; Matsuoka, S.; Arai, S.; Hasegawa, T. Meniscus-Controlled Printing of Single-Crystal Interfaces Showing Extremely Sharp Switching Transistor Operation. *Sci. Adv.* **2020**, *6*, eabc8847.

(23) Hamai, T.; Arai, S.; Minemawari, H.; Inoue, S.; Kumai, R.; Hasegawa, T. Tunneling and Origin of Large Access Resistance in Layered-Crystal Organic Transistors. *Phys. Rev. Appl.* **2017**, *8*, 054011.

(24) Higashino, T.; Inoue, S.; Arai, S.; Tsuzuki, S.; Matsui, H.; Kumai, R.; Takaba, K.; Maki-Yonekura, S.; Kurokawa, H.; Inoue, I. Effects of Thiophene-Fused Isomer on High-Layered Crystallinity in π -Extended and Alkylated Organic Semiconductors. *Chem. Mater.* **2024**, *36*, 848–859.

(25) Beuth, J. L. Cracking of Thin Bonded Films in Residual Tension. *Int. J. Solids Struct.* **1992**, *29*, 1657–1675.

(26) Hutchinson, J. W.; Suo, Z. Mixed-Mode Cracking in Layered Materials. *Adv. Appl. Mech.* **1992**, *29*, 63–191.

(27) Delannay, F.; Warren, P. On Crack Interaction and Crack Density in Strain-Induced Cracking of Brittle Films on Ductile Substrates. *Acta Metall. Mater.* **1991**, *39*, 1061–1072.

(28) Thouless, M. D. Crack Spacing in Brittle Films on Elastic Substrates. *J. Am. Ceram. Soc.* **2005**, *73* (7), 2144–2146.

(29) Chen, L.; Niu, Y.; Liu, C.; Fan, R.; Liu, P.; Ma, D.; Zhang, X.; Liu, C.; Duan, H. Reliable transfer enabled by UV-curable stamp with tunable rigidity. *Surf. Interfaces* **2024**, *55*, 105348.

(30) Liu, N.; Sun, Q. C.; Yang, Z. S.; Shan, L. N.; Wang, Z. Y.; Li, H. Wrinkled Interfaces: Taking Advantage of Anisotropic Wrinkling to Periodically Pattern Polymer Surfaces. *Adv. Sci.* **2023**, *10*, 2207210.

(31) Meng, Y. C.; Xiang, H. G.; Zhang, J. Q.; Yin, J.; Li, L. Q.; Zhang, Z. H.; Guo, W. L. The Universal Scaling Law for Wrinkle Evolution in Stiff Membranes on Soft Films. *Matter-Us* **2023**, *6*, 1964–1974.

(32) Huang, Z. Y.; Hong, W.; Suo, Z. Nonlinear Analyses of Wrinkles in a Film Bonded to a Compliant Substrate. *J. Mech. Phys. Solids* **2005**, *53*, 2101–2118.

(33) de Oteyza, D. G.; Barrena, E.; Sellner, S.; Ossó, J. O.; Dosch, H. Molecular structure and growth morphologies of pentacene/fluorinated copper-phthalocyanine heterostructures. *Thin Solid Films* **2008**, *516* (21), 7525–7529.

(34) Krauss, T. N.; Barrena, E.; Zhang, X. N.; de Oteyza, D. G.; Major, J.; Dehm, V.; Würthner, F.; Cavalcanti, L. P.; Dosch, H. Three-Dimensional Molecular Packing of Thin Organic Films of PTCDI-C₈ Determined by Surface X-ray Diffraction. *Langmuir* **2008**, *24* (22), 12742–12744.

(35) Murata, K.; Kitahara, G.; Inoue, S.; Higashino, T.; Matsuoka, S.; Arai, S.; Kumai, R.; Hasegawa, T. Stability of Ternary Interfaces and its Effects on Ideal Switching Characteristics in Inverted Coplanar Organic Transistors. *Phys. Rev. Appl.* **2024**, *21*, 024005.

(36) Hong, J.-P.; Park, A.-Y.; Lee, S.; Kang, J.; Shin, N.; Yoon, D. Y. Tuning of Ag work functions by self-assembled monolayers of aromatic thiols for an efficient hole injection for solution processed triisopropylsilylethynyl pentacene organic thin film transistors. *Appl. Phys. Lett.* **2008**, *92* (14), 143311.

(37) Kim, S. H.; Kang, I.; Kim, Y. G.; Hwang, H. R.; Kim, Y.-H.; Kwon, S.-K.; Jang, J. High performance ink-jet printed diketopyrrolopyrrole-based copolymer thin-film transistors using a solution-processed aluminium oxide dielectric on a flexible substrate. *J. Mater. Chem. C* **2013**, *1* (13), 2408–2411.

(38) Blülle, B.; Häusermann, R.; Batlogg, B. Approaching the Trap-Free Limit in Organic Single-Crystal Field-Effect Transistors. *Phys. Rev. Appl.* **2014**, *1*, 034006.

(39) Uemura, T.; Rolin, C.; Ke, T.-H.; Fesenko, P.; Genoe, J.; Heremans, P.; Takeya, J. On the Extraction of Charge Carrier Mobility in High-Mobility Organic Transistors. *Adv. Mater.* **2016**, *28* (1), 151–155.

(40) *Gaussian 16 Rev. C.01*; Wallingford, CT, **2016**.

(41) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(42) Ransil, B. J. Studies in Molecular Structure. IV. Potential Curve for the Interaction of Two Helium Atoms in Single-Configuration LCAO MO SCF Approximation. *J. Chem. Phys.* **1961**, *34*, 2109–2118.

(43) Boys, S. F.; Bernardi, F. D. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.

(44) Tsuzuki, S.; Uchimaru, T. Accuracy of Intermolecular Interaction Energies, Particularly Those of Hetero-Atom Containing Molecules Obtained by DFT Calculations with Grimme's D2, D3 and D3BJ Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2020**, *22*, 22508–22519.