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# Supramolecular Design and Assembly Engineering toward High-Performance Organic Field-Effect Transistors

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Article Recommendations

**CONSPECTUS**: Supramolecular assembly describes the dynamic processes in which molecules of a system organize themselves into ordered patterns or structures through noncovalent interactions. Among these systems, single-crystalline organic semiconductors (OSCs) in electronic devices, such as organic field-effect transistors (OFETs), represent a class of semiconductive molecules that can form regular lattices. These organic nature of these OSCs allows for precise design of the superstructure and compact arrangement through intermolecular interactions, such as  $[\pi \cdots \pi]$ , van der Waals, and polarity—polarity interactions. As a result, they exhibit exceptional carrier mobilities and stability in solid-state aggregations, making them ideal for electronics research and production. However, it is important to note that defects and disorders are unavoidable in spontaneous and rapid supramolecular assembly processes. They will hinder charge-carrier transport as scattering sites and thus impair device performance. On the other hand, by utilizing different processing methods, OSCs can be prepared into variant aggregated forms, such as amorphous, liquid-crystalline, or single-crystalline films. The

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performance of devices that use these materials relies heavily on the specific properties of the assembled components. Therefore, the regulation of supramolecular assembly in solid aggregations is necessary to achieve high-performance devices as well as scaled electronic production with controllable cost, particularly in emerging fields, such as flexible electronics, wearable devices, and low-cost sensors. Currently, researchers are actively exploring the fundamental mechanism to regulate and enhance the performance of OSC aggregations as well as developing novel materials that broaden their potential applications. However, investigation on mechanisms and functions pertaining to molecule-level arrangements in solid-state OSCs remains underdeveloped, necessitating indepth investigation and summarization.

In this Account, we first provide an overview and analysis of the supramolecular assembly process and the underlying mechanisms, focusing on three key dimensions, i.e., (i) molecular design, (ii) intermolecular interaction, and (iii) macroscopic morphology control. Then, we highlight our research on the morphology regulation and optimization of OSC films. Three strategies have been summarized and discussed to achieve high-quality OSCs and high-performance OFETs. These include: (i) molecular engineering of OSCs to install supramolecular assembly properties, (ii) thermal annealing optimization on OSCs films to increase crystallinity, and (iii) strain engineering processing on OSCs to install device functionalization. Their design rationales for target applications were analyzed. By deliberation on these issues, the fundamental underpinnings of material investigation are elucidated, thereby affording readers a comprehensive survey of the methodologies and strategies employed in the realm of single-crystalline semiconductors. To conclude, the main challenges and future perspectives toward the forthcoming development and commercialization of high-performance functional OFETs are discussed to inspire more novel material designs and regulation methodologies.

# 1. INTRODUCTION

Many hierarchically complex systems, either living or nonliving, can be traced back to their assembly for distinctively larger scales than their components.<sup>1–3</sup> Among them, the active organic semiconductors (OSCs) represent a typical assembled system benefiting from tailored molecular design and controlled processing methods, which makes them flourishing and promising candidates for functional electronic devices including organic field-effect transistors (OFETs), particularly in the emerging fields of flexible electronics, wearable devices, and low-cost sensors.<sup>4–6</sup>

An OFET is a three-terminal active electronic device composed of source, drain, and gate electrodes, organic

semiconductor layers, and dielectric layers. Based on the selected device configuration, OFETs can be categorized into four distinct types as illustrated in Figure 1: the bottom gate bottom contact (a), the bottom gate top contact (b), the top gate top contact (c), and the top gate bottom contact (d).

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Figure 1. Four types of OFETs. (a) Bottom gate/bottom contact, (b) bottom gate/top contact, (c) top gate/top contact, and (d) top gate/ bottom contact.

OFET uses an external electric field through the gate electrode to control the current flow in the OSC channel. When a positive gate voltage is applied, it attracts negatively charged carriers (electrons) or repels positively charged carriers (holes), resulting in the formation of a conducting channel or depletion region, respectively.<sup>4</sup> The performance of an OFET can be modulated by the assembly nature of OSCs, and eventually determined by the practical film quality, which depends on the degree of crystallinity, impurity doping and interface conditions.<sup>4,7</sup> Three key parameters are selected to evaluate the OFET performance: charge carrier mobility  $(\mu)$ , threshold voltage ( $V_{\rm th}$ ), and on/off ratio ( $I_{\rm on}/I_{\rm off}$ ). The process of assembly and interaction at various scales, from molecular interaction to supramolecular assembly and film morphology, plays a crucial role in the overall construction of the system, thereby ultimately determining OFET performance (Figure

2a).<sup>8,9</sup> For example, in the realm of nanoscale, the widely adopted solution processing methods under quasi-equilibrium conditions will inevitably introduce point defects, polycrystalline grain boundaries, and solvent residues to the film of OSCs.<sup>10,11</sup> On the other hand, tailored intermolecular interactions, such as  $[\pi \cdots \pi]$ , van der Waals, and polaritypolarity interactions, have the ability to govern the supramolecular assembly process, thereby giving rise to variations in crystal grain size, orientation, phase separation and maturation behavior.<sup>1,12</sup> These underlying concerns can impact the quality of the OSC films, which in turn affect the performance of the OFETs. In addition to the inherent characteristics of molecules, various processing methods using identical OSCs could result in considerable differences in supramolecular assembly behaviors, i.e., amorphous, liquid-crystalline, and single-crystalline forms, depending on the level of molecular arrangement precision (Figure 2b).<sup>1,12-14</sup> In order to improve the performance of OFETs, the precise control of supramolecular assembly assumes paramount significance in governing the operational efficiency of functional OFETs. Particularly, it is crucial to precisely manage the formation of solid states that arise from conventional processing techniques, with the ultimate goal of optimizing the OFET performance.

In this Account, we highlight our ongoing endeavors concerning the conception and governance of supramolecular assemblies to achieve superior performance in OFETs. Three practical regulation strategies and their working principles are summarized and discussed at different scales, i.e., (i) molecular engineering of OSCs to install supramolecular assembly properties, (ii) thermal annealing optimization on OSCs films to increase crystallinity, and (iii) strain engineering processing on OSCs for compact molecular packing. The discussion will answer key inquiries related to the regulation of supramolecular assembly applied to OFETs and provide



Figure 2. Interactions and aggregations for OSCs in OFETs (a) Spatial scales of supramolecular interactions. (b) Schematic illustration of an organic field-effect transistor (OFET). Inset shows three typical aggregation forms of organic semiconductor films, namely, amorphous, liquid-crystalline, and single-crystalline films. Figure 2b was reproduced with permission from refs 15 and 21. Copyright 2017 The Authors and Copyright 2022 The Authors.



**Figure 3.** Intermolecular interactions and resultant aggregation morphology. (a) Three-component model of OSCs that can be used to regulate the supramolecular assembly through the manipulation of various intermolecular interactions. (b) Schematic illustration showing the formation of micelle (left) and bilayer sheet (right) structures resulting from the aggregation of the engineered molecules. Reproduced with permission from ref 23. Copyright 2019 The Authors.

important insights ranging from the design principles of crystalline OSCs to the effective regulation of functionalization through molecular arrangement adjustments in solid aggregations. It will also clarify the governing principles and influential factors that exert an impact on the processing and preparation of crystalline OSCs. The rationales of design and regulation strategies toward target application will also be summarized. Ultimately, the remaining challenges and future perspectives in the design and application of supramolecular assembly regulation in OSC aggregates will be provided with the aim of providing new ideas for novel material development and processing-method improvements for high-performance OFETs.

# 2. MOLECULAR ENGINEERING OF OSCs TO INSTALL SUPRAMOLECULAR ASSEMBLY PROPERTIES

Molecular engineering focuses on the systematic investigation and manipulation of molecular properties, noncovalent interactions, and assembly behaviors to achieve specific functionalities.<sup>14,16</sup> In the realm of molecular engineering, new compounds equipped with distinctive architectures and characteristics have been synthesized in order to achieve the desired functionalities. This intricate pursuit encompasses the modification of pre-existing molecules or the creation of entirely unprecedented ones. Given the fact that structure plays a pivotal role in determining the material properties, the strategy of molecular engineering emerges as the fundamental starting point for the bottom-up design of OSCs, serving as the very essence of regulating supramolecular-assembly.<sup>17,18</sup> Drawing on these empirical observations, we summarize our endeavors on the regulation of supramolecular assembly, by bringing up a three-component OSC model with (i) a conjugated  $\pi$  core, (ii) an alkyl linker, and (iii) a polar head (Figure 3a).<sup>19-22</sup> In particular, the conjugated  $\pi$  core was chosen to facilitate charge-carrier transport in OSCs through efficient  $[\pi \cdots \pi]$  stacking. The head groups are grafted for further functionalization by involving noncovalent interactions. The linker, typically alkyl chains, plays an important role in

establishing the connection between the  $\pi$  core and head components, modulating the intra/intermolecular interactions, as well as increasing the solubility of OSCs. Their various noncovalent interactions, including hydrogen bonding, van der Waals force, dipole–dipole, and  $[\pi \cdots \pi]$  interactions, can facilitate ordered supramolecular assembly with regular morphologies (Figure 3b).

Based on the three-component structural model, we have developed a series of amphiphilic OSCs, specifically phosphonate-modified benzo [b] benzo [4,5] thieno [2,3-d]thiophene ( $C_n$ **P-BTBT**, where n = 3-11, with  $C_7$ **P-BTBT** illustrated in Figure 3a left), in order to examine the evolutionary supramolecular assembly of their solid aggregates on two-dimensional surfaces at ambient conditions.<sup>23</sup> This design harnesses the robust  $[\pi \cdots \pi]$  interactions amidst the BTBT components to promote the formation of highly crystalline semiconducting films from their amorphous precursors. The polar and fluidic characteristics of amphiphilic phosphonate segments encourage molecules to display rapid lateral diffusion across the layer through weak noncovalent interactions of hydrophobic linkers. Furthermore, the linker with various lengths fine-tunes the spatial distance between BTBT and phosphonate segments, harmoniously balancing the inherent rigidity of the  $\pi$ -cores with the graceful fluidity of the phosphonate portions.<sup>24</sup> Consequently, the phase transition of  $C_n$ **P-BTBT** is confined to a narrow temperature range (~50-60  $^{\circ}$ C) as observed in differential scanning calorimetry (DSC) measurements, fostering the spontaneous solid-solid phase transformation into highly organized aggregates via intricate micelle structures that serve as mass carriers in extensive migration between distinct domains (Figure 4a). Moreover, we find that a short linker (n = 3 and 4) can lead to strong intermolecular coupling between BTBT and phosphonate segments, as indicated by the absence of transition peaks in DSC, while a long linker (n = 10 and 11) may separate them as independent segments, diminishing their functionality on account of the pronounced liquid crystal property of the alkyl chains. As a result, C7P-BTBT with a moderate linker



Step 1: Flattening; Step 2: Coalescence; Step 3: Spinodal decomposition; Step 4: Ostwald ripening; Step 5: Layer growth



**Figure 4.** Self-evolutionary crystallization of OSC films. (a) Evolutionary selection growth approach and time-lapse sequence of representative AFM images showing the morphological evolution of the OSC precursors. (b) Time evolution of film X-ray diffraction (XRD) patterns showing the transition of crystalline phases. (c) Peak intensity evolutions extracted from the peaks of ~12.6° and ~13.0°, which can be divided into three stages of crystallization. (d) Schematic illustration showing the nanocluster-involved nonclassical nucleation mechanism. (e) High-resolution AFM images showing evidence of the spherical molecular cluster as mass transport carriers on the surface. Green and red arrows mark two nanoclusters; white dashed arrows mark the moving directions. (f, g) Output (f) and transfer characteristics (g) of an OFET device employing  $C_7P$ -BTBT nanowire as the conductive channel. Reproduced with permission from ref 23. Copyright 2019 The Authors.

length was chosen for its superior self-assembly properties, as substantiated in Figure 4.

In order to investigate the supramolecular assembly behaviors, the growth trajectory of the  $C_7P$ -BTBT films was imaged using a real-time in situ atomic force microscope (AFM). The evolutionary assembly process can be divided into three stages (Figure 4a). First, prenucleation occurs in Stage 1. Small droplets (0 h) on the surface vanish and collapse into desolvated nanoplates (0.07 h) and eventually a loosely covered amorphous base film (0.22 h). Second, in Stage 2, the base film undergoes nucleation and demixing into thick and thin separated islands, which is followed by thermodynamically driven Ostwald ripening, allowing the expansion of dense islands at the cost of thin islands via long-range migration of organic clusters on the surface (2.32 h). Third, in Stage 3, thick islands undergo self-reorganization and layer growth when they become separated beyond the small molecules' diffusion distance, ultimately leading to the formation of mature superstructures of single-crystalline films or single-crystal microwires (18.13 h).

In order to track the changes in the crystal lattice associated with the assembly process, quantitative analyses of real-time in situ film XRD experiments were performed. As observed in Figure 4b, the peaks associated with the (040), (060), (080), (0100), and (0120) planes exhibit noteworthy intensity variations. By extraction of the (060) peak intensity evolutions, the growth path can also be divided into three stages (Figure 4c), aligning harmoniously with the AFM observations (Figure 4a). Additionally, the (0k0) Bragg peaks undergo a remarkable shift from a  $2\theta$  angle of approximately 12.6° (indicative of a metastable state) to a value of approximately 13.0° (indicative of an equilibrium state). This observation reveals a reduced

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**Figure 5.** Thermal annealing of OSC films. (a) Molecular designs for thermal annealing optimization. (b) Schematic illustration showing melt and cold crystallization used to fabricate the OSC films with different superstructure morphologies. (c) Monolayer FET fabricated on melt-crystallization-based polycrystalline films. (d) Crystalline nanowire FET array fabricated on cold-crystallization-based single-crystal array. Reproduced with permission from ref 19. Copyright 2022 Wiley-VCH GmbH.

intermolecular spacing along the (010) direction in the equilibrium state, which will facilitate the carrier transport in OSCs and benefit the OFET performance.

We have proposed a mass transport mechanism to elucidate the evolutionary growth process. This phenomenon entails the creation of a nanoscopic mass carrier (Figure 4d), as revealed by the high-resolution in situ AFM investigations conducted between two neighboring regions (Figure 4e). As the metastable thin film detaches from the edges, the amphiphilic C<sub>7</sub>P-BTBT molecules reorganize in a 3D fashion. The crystallization of the BTBT backbone promotes the formation of spherical structures through collective effects of dipoledipole interactions of phosphonate heads, hydrophobic interaction of alkyl chains, and  $[\pi \cdots \pi]$  interactions of **BTBT** units. This work demonstrates the regulation of supramolecular assembly through molecular engineering toward high-performance OFETs. OFETs were fabricated (Figure 4f inset), achieving an average hole mobility up to  $\sim$ 5.3 cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$  and a high on/off ratio of ~10<sup>5</sup> (Figure 4f and g).<sup>25</sup> This design principle emulates the self-assembly behaviors of phospholipid bilayers, which exhibit a thermodynamic preference for the formation of spherical liposome or micelles structures. It supplements the traditional crystallization theory based on solution systems and provides experimental insights for the development of postprocessing-free OSCs.<sup>26,27</sup> Furthermore, the art of molecular engineering, serving as the core strategy, constitutes the bedrock of novel material investigations and the advancement of supramolecular assembly methodologies.

# 3. THERMAL ANNEALING OPTIMIZATION ON OSC FILMS TO INCREASE CRYSTALLINITY

Thermal annealing represents a widely adopted postprocessing technique employed for the manipulation of OSCs. By thermal incubation, this strategy serves the purpose of liberating the intrinsic stress and regulating the morphology, thereby enhancing the overall quality and performance of OSCs.<sup>16,28</sup> Generally, the deposition of the OSCs films from solution engenders an array of imperfections, including point defects, amorphous regions, or disordered packing, all of which synergistically leads to substantial detriments on device performance.<sup>28</sup> As shown in Figure 5b, heating the film allows for structural rearrangements and desirable reorganization, which results in compact molecular packing and long-range order. This order morphology with compact molecular packing, in turn, facilitates the free movement of charge carriers in OFETs and results in improved carrier mobility (Figure 5c and d). Thermal annealing has additional positive impacts on the morphology of the fabricated organic films. Heating the films to elevated temperatures can promote trapped molecules of solvents to be removed and cracks to be healed, thereby resulting in seamless microstructures such as single-crystalline monolayers and microwires of OSCs (Figure 5b). In this section, we focus on the examination of two thermal annealing methods, namely, melt crystallization and cold crystallization, alongside an investigation into their corresponding OSC compounds (Figure 5a).

# 3.1. Melt Crystallization

Melt crystallization is a refining and purification methodology that has found substantial applications in the realms of



**Figure 6.** Melt crystallization of OSC films. (a) Differential scanning calorimetry (DSC) thermogram of M-2. Cr, crystal. LC, liquid crystal. Lq, liquid. (b) Polarized optical image (POM) image for M-2 liquid crystal. (c) XRD patterns of a M-2 film before and after annealing. (d) Molecular packing of the core-cladding liquid-crystalline pentathiophene M-4 monolayer. (e, f) Output (e) and transfer characteristics (f) of an OFET device employing liquid-crystalline M-4 film as the semiconductor layer. (g) Schematic illustration showing a monolayer OFET with a microfluidic channel for real-time detection of melamine in water; (h) Schematic of the sensing mechanism (top) and the energy-level diagram for the M-4/ melamine interface (bottom). (i) Real-time electrical measurements with different concentrations of melamine. Reproduced with permission from refs 30 and 31. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim and Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

chemical, pharmaceutical, and food industries, among others. Interestingly, this technique is now gathering attention as a promising approach in the fabrication of high-performance OFETs.<sup>29</sup> The fundamental concept underlying melt crystallization can be elucidated in a subsequent manner. The material to be thermally annealed is (i) heated above its melting point, which is then (ii) followed by controlled cooling to allow for the internal rearrangement of molecules, inducing nucleation and crystal growth and ultimately (iii) culminating in the establishment of a highly organized crystalline structure within the OSC film. Melt-crystallization is a promising strategy for high-performance OFET and shows great potential in material universality and scalable possibility for industrial production. In order to harness the benefits of meltcrystallization, we modify traditional oligothiophene backbones by incorporating long alkyl side chains.<sup>30</sup> The side chains, on one hand, can increase the solubility of OSCs, thus improving their solution processability. On the other hand, they can promote the supramolecular assembly by integrating selfhealing capabilities of liquid crystals into oligothiophenes. The seamless integration allows for the spontaneous formation of a highly ordered molecular stacking of OSCs during thermal annealing. We present two types of liquid crystalline

oligothiophene derivatives (M-1, M-2 and M-3, M-4), whose liquid crystalline characteristics were observed in DSC studies (Figure 5a top).<sup>30,31</sup> In Figure 6a, the DSC thermogram for M-2 exhibits two endothermic peaks at approximately 135 and 160 °C, which represent the transitions from the crystalline to liquid crystalline phase and from the liquid crystalline to the isotropic phase, respectively. The Maltese crosses in the polarizing optical microscopy image further prove the smectic liquid crystalline phase incubated in the temperature range between these two endotherm peaks (Figure 6b).

Revealed by XRD measurements in Figure 6c, distinctive and highly crystalline XRD patterns, assigned to the equidistant (00*n*) reflection family (Figure 6c inset), were found after thermal annealing, which indicates that the annealing process results in the formation of highly regular lamellar  $\pi$ stacks perpendicular to the substrate surface. Furthermore, the interlayer spacings (*d*-spacing) of 40.2 and 47.2 Å for **M-1** and **M-2**, respectively, are slightly greater than the molecular lengths of 34.8 and 38.7 Å when the alkyl groups are fully extended in an all-*anti* conformation, which implies that side chain interdigitation forms due to the strong interchain van der Waals forces in the as-cast solid films. Thus, the designs of thermally annealed **M-1** and **M-2** are able to self-assemble into

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Figure 7. Cold crystallization of OSC films. (a, b) DSC curves of C-1 (a) and C-3 (b). (c) Schematic illustration showing the temperature-triggered supramolecular assembly explained using the Tetris strategy as an analogy. (d) Solid-state X-ray (super)structures of C-3 revealing the (super)structural basis for the temperature-triggered supramolecular assembly mechanism. (e) 2D peak intensities associated with variable-temperature XRD patterns showing the temperature-triggered supramolecular assembly. Reproduced with permission from ref 19. Copyright 2022 Wiley-VCH GmbH.

a highly crystalline, lamella-like layered structure with optimized stacking, which promotes charge transport for better device performance. M-2 exhibits the top hole mobilities of 0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for air-stable thin-film and 6.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for single crystal. In order to improve the assembly capability, we grafted two additional long alkyl chains on the other side of the oligothiophene core, as M-3 and M-4 depicted in Figure 5.<sup>31</sup> As shown in Figure 6d, taking M-4 as an example, the engineered molecule exhibits an upright orientation and possesses the capability to assemble into core-cladding condensed monolayers, driven by the  $[\pi \cdots \pi]$  and van der Waals interactions. Furthermore, the top two C<sub>12</sub>-alkoxyphenyl moieties may also contribute to the hydrophobic nature of the surface, thereby preserving the internal conductive core for diverse applications such as aquatic environment sensing. The bottom two C12-alkoxyphenyl moieties form a protective layer that eliminates the scattering/trapping sites from the dielectric surface. The holistic design of OSCs also offers the conformational flexibility, enabling molecules to surmount the rough surface while maintaining optimal stacking. Collectively, these outer alkoxyphenyl-coating layers supply a unique insulating barrier on each side, restricting charge carriers to a one-dimensional (1D) path.

Crystalline semiconducting monolayers were obtained by concentration control in spin-coating. Consequently, mono-

layer field-effect transistors (MFETs) were fabricated on these dense defect-free two-dimensional (2D) monolayers of M-4 exhibiting a comparable performance to traditional thin film transistors, with hole mobility  $\mu = \sim 8.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and  $I_{\rm on}/I_{\rm off}$  = ~10<sup>5</sup> (Figure 6e and f). These MFETs enable ultrasensitive detection in a rough environment on account of the protective core-cladding design and large signal-to-noise ratio from quasi-2D structures. As illustrated in Figure 6g, a microfluidic channel was incorporated into the MFET system to enable real-time measurements. The analyte melamine absorbed in the monolayer could increase the conductivity by electron transfer and capacitive coupling (Figure 6h). As demonstrated by the real-time results in Figure 6i, the MFET device exhibited significantly enhanced sensitivity, as low as 0.01 ppm, which is at least 3 orders of magnitude greater than the sensitivity (10 ppm) of conventional bulk thin-film transistor sensors. These findings offer novel perspectives on the integration of molecular engineering, chemical selfassembly, and materials fabrication methods to attain the desired characteristics for device applications.<sup>32,33</sup>

## 3.2. Cold Crystallization

Cold crystallization represents another crystallization process accompanying exothermal occurs anomaly when a material is heated within a temperature range below its melting point.<sup>34,35</sup> Intrinsically, the temperature-triggered supramolecular assem-



**Figure 8.** Solvent vapor annealing (SVA) of the OSC films. (a) Process of fabricating an array of oriented single-crystalline OSC films through epitaxial growth on an oriented iPP substrate in combination with an SVA process. (b) Time-dependent structural evolution of **C8-BTBT** by SVA on an oriented iPP substrate revealed by POM. The inset shows the statistics of the crystal orientation. The white arrows indicate the iPP orientation. (c) Configuration of the single-crystal FET array. Inset shows the image of the channel region in a single device. (d) Hole-mobility statistics of working single-crystal FETs. Reproduced with permission from ref 48. Copyright 2020 Royal Society of Chemistry.

bly starts with reorganizations in partial segments, which could further trigger systematic self-assembly and crystallization. Taking advantage of this cold-crystallization strategy, a molecular design (C-3 in Figure 5a bottom), exhibiting a temperature-triggered supramolecular assembly, was proposed in order to achieve packing regulation in solid-state films.<sup>19</sup> C-1, C-2, and C-4 were designed with similar structures as comparison points for supramolecular assembly behavior analysis.

The thermal properties were primarily investigated by DSC experiments. C-1 with a rigid  $\pi$ -core and flexible  $\sigma$ -substitution, and C-2 with small trimethylsilyl group exhibit typical melt crystallization features (Figure 7a). C-3 is composed of three components, i.e., (i) a conjugated  $\pi$ -core, (ii) a diphenylsilyl docker, and (iii) a carbon–carbon triple bond. In the case of C-3 (Figure 7b), the cold crystallization properties were revealed by the exothermic peak at ~57 °C during the heating process, while no crystallization peaks were observed during the cooling process. The self-assembly of C-4 could be more complicated than that of C-3 as evidenced by multiple

endothermic peaks during the heating cycle.<sup>31</sup> The observed difference can be ascribed to the presence of a soft bridge between the bulky docker and the  $\pi$ -core, which grants the molecule increased flexibility in adjusting its conformation during the heating process.

The thermodynamic behavior of C-3 was analyzed. From the perspective of the C-3 structure, the diphenylsilyl docker can rotate around the axis determined by the triple bond (as illustrated in Figure 7c, top right) when heated. This results in (i) a modification in the diphenylsilyl dockers' orientation, (ii) the alignment of the colored (red and blue) phenyl rings with the conformations of adjacent molecules, (iii) the subsequent formation of a dimer due to the  $[\pi \cdots \pi]$  interactions among the diphenylsilyl dockers, and (iv) the eventual development of long-range ordered superstructures (Figure 7c, bottom). These behaviors can be validated through the solid-state X-ray (super)structures depicted in Figure 7d. The backbones of C-3 are almost coplanar from the Si atom to the alkyl chain end. This 3D superstructure arises from a dual-level assembly process, encompassing (i) the interaction between adjacent



**Figure 9.** Responsive strain-engineering of OSC films. (a) Conversion of *trans* and *cis* conformations of **AZO-BTBT-8** upon irradiation with ultraviolet (UV) or visible (vis) light. (b) GIXD pattern sequentially for the pristine, UV-irradiated, and vis-irradiated samples. (c) Current decay (dots) and fitting curves (lines) obtained from a conductive atomic force microscope (cAFM). (d) Schematic diagram for the distribution of molecular conformation and strain in the **AZO-BTBT-8** film after UV irradiation. Green and yellow lines represent the molecules with *cis* and *trans* conformations, respectively. (e) Calculated spatial distributions of the strain along the *x*-axis within the OSC film. (f) Layered structures of the OFET arrays. From bottom to top: Indium tin oxide (ITO)-coated PET substrate, 200 nm-thick  $Al_2O_3$  film, 100 nm-thick **AZO-BTBT-8** film, Au electrodes, 100 nm-thick HfO<sub>2</sub> arrays, and Au electrodes. The left-top inset shows the magnified structure of the top three layers in one pixel, and the left-bottom is the SEM image of an individual pixel. (g, h) Top-view photograph (h) and corresponding current mapping (h) of a smiling cartoon sun (garland) mask. Reproduced with permission from ref 21. Copyright 2022 The Authors.

layers, maintained by  $[\pi \cdots \pi]$  associations between BTBT pairs with 3.5 Å plane-to-plane separations, and (ii) supplementary interlamellar assembly reinforced by  $[\pi \cdots \pi]$  interactions with 3.6 Å plane-to-plane separations between the phenylene rings in the bulky dockers. Conversely, the dominant interactions in C-4 are  $[C-H\cdots\pi]$  and  $[C-H\cdotsS]$  types, which are weaker than  $[\pi\cdots\pi]$  in C-3 and insufficient to lock the molecular conformations during the heating process to yield long-range ordered superstructures.

In situ variable-temperature X-ray diffraction experiments (VT-XRD, Figure 7e) were conducted in order to investigate the crystallization behaviors on silicon substrates toward device fabrication. C-3 was first heated above its melting point at ~96.2 °C into an isotropic liquid. There were no diffraction peaks until ~60 °C in the heating process in the second cycle. At this time, the crystalline sample displayed an increased number of reflection peaks, signifying that the cold crystallization process resulted in a higher degree of crystallinity compared to the initial state. We further fabricated

OFETs based on single-crystalline microwires of C-3 resulting from cold crystallization (Figure 5 right bottom). The maximum hole mobilities were determined to be 1.2 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, along with an on/off ratio surpassing 10<sup>5</sup>, achieved without the need for additional optimization. This OFET performance ranks among the top records for 1D organic nanofiber transistors.<sup>36–38</sup> Temperature-triggered supramolecular assembly in cold crystallization provides a method that approaches more precise control over assembled structures, presenting a vast scope for exploration of the development of a new generation of supramolecular electronics.

# 4. STRAIN ENGINEERING ON OSCs FOR DEVICE FUNCTIONALIZATION

Strain engineering serves as an effective approach in semiconductor production to improve device performance, which is originally rooted in the reorganization of inorganic materials' atomic packing structures under mechanical stress.<sup>39,40</sup> In emerging fields, such as flexible electronics and wearable electronics,<sup>5,41,42</sup> the application of strain engineering has been expanded from traditional inorganic semiconductors to OSCs, where impressive performance improvements are found.<sup>43–45</sup>

It is important to note that, owing to differences in material structure, the strain effect exhibits significant distinctions between inorganic semiconductors and OSCs, which deserves more in-depth investigation. In view of the characteristics of OSCs, we categorize the strain-engineering strategy into external and self-strained regulation according to the stress sources. Their working mechanisms and principles are discussed accordingly.

## 4.1. Strain Engineering by External Regulation

Strain engineering is frequently conducted by exerting external stress during the fabrication of films or directly on assembled structures. The resultant lattice under strain in these methodologies exhibits heightened packing density and regularity, rendering strain engineering a general strategy employed in enhancing the device performance of OSCs.<sup>40,46</sup> For example, Bao et al. achieved strain-enhanced mobility in OSCs by solution blade-shearing, where a substantial mobility improvement is achieved.<sup>47</sup>

Utilizing the interfacial stress from lattice mismatch between amorphous 2,7-dioctyl[1]benzothieno[3,2-b]benzothiophene (C8-BTBT) and oriented isotactic polypropylene (iPP), we prepared highly oriented OSC single-crystal arrays by epitaxial growth under a solvent vapor annealing (SVA) approach.<sup>48</sup> As shown in Figure 8a, an amorphous C8-BTBT film was first casted on the melt-drawn oriented iPP and annealed by SVA. As the solvent vapor diffuses, C8-BTBT obtains a higher degree of freedom, which allows for its assembly into crystalline microstructures driven by the noncovalent interactions, including  $[\pi \cdots \pi]$  interactions and van der Waals force. During this process, the interfacial stress from the lattice strain was generally released with the epitaxial growth driven by the van der Waals force between the oriented iPP template and octyl group in C8-BTBT.<sup>49</sup> As shown in Figure 8b, the amorphous C8-BTBT film evolved into an oriented singlecrystal array evidenced by the statistical diagram of the crystalorientation distribution, where approximately 78% of crystals on iPP films were found to be oriented in the molecular chain direction, with an angular deviation of  $\pm 15^{\circ}$ . On this basis, an OFET array can be fabricated with electrode deposition through masks (Figure 8c). As shown in Figure 8d, the devices within the array demonstrate a high yield of up to 81%, an average hole mobility of 2.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with the best mobility reaching 9.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and an on/off ratio of  $10^7$ . The significant difference in device yield (less than 10% effective on an OTS-modified isotropic substrate) and the comparable hole mobilities of devices on oriented iPP and isotropic OTSmodified substrates demonstrate the reliability of single-crystal OFET array fabrication using oriented epitaxial growth.

### 4.2. Self-Strained Regulation

In contrast to strain-engineering by application of an external force, self-responsive strain-engineering entails the emergence of strain within solid films of OSCs in response to external stimuli, such as light.<sup>16</sup> This strategy enables the postregulation of supramolecular assembly and can even bring macroscopic changes in material properties.

When the photoisomerization group is incorporated, the rearrangement of the packing in OSCs can induce intrinsic strain within the material, a phenomenon that has been exploited in light-responsive actuators.<sup>50,51</sup> It is reasonable to

hypothesize that the light-induced strain in OSCs should also be capable of light-strain modulation. On this basis, we designed and synthesized a new OSC material named AZO-BTBT-8 (Figure 9a), where the incorporation of azobenzene endows it with photoisomerization properties.<sup>21</sup> The photoisomerization can be validated by grazing incidence X-ray diffraction (GIXD) and in situ conductive AFM. In GIXD diffraction (Figure 9b), the intensities and positions of Bragg rods (110) and (020) can reversibly switch upon UV and vis irradiation, indicating packing regulation in regularity and intermolecular distance in the xy plane. The conductive AFM (Figure 9c) scan shows a significant and instant current increase upon UV irradiation, which can be attributed to the enhanced packing regularity through the trans-cis conformation transition. Then, a gradual current decay at room temperature in the dark was observed as a result of the reversed isomerization under thermal effect.

Upon examination of the strain-distribution calculations in Figure 9d, it was noted that following UV exposure, the strain accumulated along the x-axis before eventually dispersing at the film's edge. As the film depth increases, the strain gradually diminishes and ultimately reaches the interface between the dielectric and semiconductor layers, influencing the device output through the optimized packing of interfacial molecules. In our thin-film OFET device, the top surface is primarily responsible for photoisomerization, while the bottom surface largely contributes to the electrical conductivity. Consequently, isomerization occurring at the top surface can induce consistent lattice strain within the bulk semiconductors, thereby modulating the device output (Figure 9e). A comprehensive investigation of the properties of the OFET device was conducted. The hole mobility of the annealed device on polyethylene terephthalate (PET) rose from ~0.015 to ~0.141 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, maintaining a fixed on/off ratio of  $10^5$ and demonstrating an average 9.4-fold increase as a result of molecular stacking optimization under UV irradiation. Subsequently, a large-scale, flexible  $33 \times 40$  array was developed by directly depositing patterned electrodes onto a designated flexible substrate, as depicted in Figure 9f. The optical pattern was achieved by exposing the array to top UV illumination through a garland mask (Figure 9g and h). The available evidence indicates that OFET array devices are reversible, programmable, and scalable, presenting promising potential for applications in various fields, including portable displays, flexible sensors, wearable devices, health care, and tissue detection.<sup>4–6,41,42</sup>

## 5. CONCLUSION AND PERSPECTIVES

In summary, we have extensively discussed the design principles and the working mechanisms of supramolecular assembly toward functional OFETs at different scales. Three practical strategies applied in OSC assembly regulation were summarized as (i) molecular engineering of OSCs to install supramolecular assembly properties, (ii) thermal annealing optimization on OSCs films to increase crystallinity, and (iii) strain engineering processing on OSCs for compact molecular packing. Among them, the traditional thermal annealing method is rejuvenated with strategical design, and some underexplored topics, such as evolutionary organic crystals and self-strained molecular crystalline films, were carefully discussed. This account provides a comprehensive overview of supramolecular assembly and attracts broad interest in account of their potential applications not only in organic electronics but also in other functional devices and microsystems, such as flexible devices and wearable systems. Despite the tremendous advancements achieved in recent times, more endeavors are essential to promote the potential application and commercialization of ordered OSCs- and OFET-based technologies. Herein, we also highlight the remaining challenges for achieving this goal, hoping to arouse the interest and thinking of a broad readership.

Materials design. Although organic semiconductor materials have experienced unprecedented development on account of their strong designability and processability, their design principles remain unclear, which reduces the efficiency of material design and development.8,52 Changes and modifications in molecular structure for functionality often lead to the loss of original assembly properties or even new issues at different scales, such as complicated interfaces/boundaries, poor film formation, and low structural stability. For instance, in order to achieve evolutionary self-assembly with molecular aggregations, the phase transition temperature is adjusted to the room temperature window, which exacerbates the impact of thermal effects on the device stability. Therefore, the development of high-performance materials is not a simple addition of structures but rather a structural balance and property compromise at different scales, and the design principles and rules in target-molecular engineering need to be carefully investigated in future research. Encouragingly, with the booming development of artificial intelligence, it has become possible to explore the use of advanced computational methods and machine learning algorithms to predict and optimize the performance of OSCs.<sup>5</sup>

**Stability and tunability.** Supramolecular assembly of OSCs intrinsically works based on noncovalent interactions, making it susceptible to external interference that can impair the device stability.<sup>55,56</sup> For example, during investigation of strain engineering, deformation of a flexible device can also induce strain in OSC films, resulting in fluctuation of OFET performance besides the in situ strain generated by photo-isomerization. Moreover, OSCs in condensed states usually exhibit a low response tunability due to the significant steric hindrance and lack of degrees of freedom. Therefore, for assembly strategies based on external stimuli, investigations on improving the sensitivity to effective signals and amplifying the response amplitude are of great significance to device functionalization.

Large-scale production and commercialization. Largescale production is a critical step of OSCs in the practical application toward commercialization.<sup>57</sup> However, frequently adopted assembly regulation strategies are developed from laboratory methodologies, lacking stable and efficient production techniques and experience. Taking thermal annealing as an example, it is challenging to ensure a uniform annealing temperature and consistent duration over a large area, which is crucial for assembly quality and macroscopic morphology control. The emerging strategies, such as molecular engineering and strain engineering, could provide opportunities to solve these problems. Reasonable material design can even directly obtain the required high-performance OSC morphology. Moreover, stress engineering can achieve high-performance device preparation through controllable light irradiation. These two methods simplify the manufacturing process and provide the possibility of the preparation of stable and highperformance OFET devices. However, commercialization is systemic engineering, which also requires low cost, compatibility with other materials and systems, performance stability, etc. Therefore, significant investments are still needed to bring high-performance OFETs into daily life.

Overall, despite the unprecedented development of material systems and regulation strategies based on supramolecular assembly, the remaining critical issues from bottom to top still need to be carefully addressed in future research.

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J.T., X.G., and H.C. conceived and designed this Account. M.R. wrote Section 3 Thermal annealing optimization. M.L. drafted the rest of the account. All the authors discussed and commented on the manuscript. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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