

Template-Free Orientation Selection of Rod-Like Molecular Semiconductors in Polycrystalline Films

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S Supporting Information

ABSTRACT: Many organic semiconductors (OSCs) feature strong optical anisotropy that can be exploited to increase the efficiency of optoelectronic devices. We demonstrate that for the technologically relevant, rod-like OSCs diindenoperylene (DIP), pentacene (PEN), and α -sexithiophene (6T) deposited on silicon oxide surfaces it is possible to prepare polycrystalline thin films in which the long molecular axis is oriented parallel to the substrate plane in a template-free fashion. In films grown by organic molecular beam deposition at room temperature or higher, the molecules are oriented upright standing (σ -orientation). Instead, the here-presented growth at low temperatures followed by slow annealing up to a temperature near molecular desorption has the effect of "freezing" the molecules with their long axis oriented parallel to the substrate plane (λ -orientation) while conferring them crystalline long-range order. We discuss the huge impact on the optical anisotropy of the films observed as a consequence of the orientation transition. Finally, we propose a mechanism for explaining the achieved λ -orientation, which is stable under environmental conditions.



The efficiency of optoelectronic devices based on thin layers of organic semiconductors¹ (OSCs) can be substantially improved by controlling thin film structure and molecular orientation. Although this has been achieved for polymers to some extent,^{2,3} their high molecular weight and inherent high number of degrees of freedom render the selfassembly processes highly dependent on the preparation method. Employing small-molecule OSCs allows superior control over thin film structure due to the reduced degrees of freedom of the molecular components. Additionally, the use of organic molecular beam deposition⁴ (OMBD) allows one to rule out solvent effects on intermolecular interactions and structure-formation processes compared to deposition from solution.

Employing OMBD to grow thin films of $OSCs^{5-7}$ allows the use of several strategies to affect the growth itself. For instance, illumination with polarized monochromatic light during the growth of the OSC tetracene has been recently shown to induce a biaxially anisotropic alignment of the crystalline domains.⁸ More common approaches that have been explored to some extent include changes of the growth rate⁹⁻¹¹ and substrate temperature,^{12,13} interrupted growth,¹⁴ and combinations of them.¹⁵ In all cases, the relevant parameters are manipulated *during* the growth processes.

Various strategies for post-growth manipulation of polycrystalline films of OSCs have also been exploited. For instance, solvent-vapor annealing can promote further film crystallization and improve the performance of optoelectronic components.^{16,17} The effects on thin film morphology can be quite dramatic, with strong dewetting of the material on the substrate surface and a possible change of the average molecular orientation. $^{17-19}$ Thermal annealing, in turn, can be conveniently carried out in situ on as-grown films in order to improve their degree of crystallinity in the direction perpendicular to the substrate surface.^{20,21} However, the overall effect of possible structural reorganizations on charge transport properties depends critically on temperature and duration of the thermal annealing treatment.^{22,23} Interestingly, post-growth thermal annealing can also induce crystallization of amorphous layers of OSCs.²⁴ This suggests that if the molecules exhibit a preferred orientation already in a poorly ordered film providing thermal energy to the system can promote crystallization and turn the solid into a polycrystalline, uniaxially ordered film in which the molecular orientation is inherited from the disordered material.

It is important to stress here the role of molecule-molecule and molecule-substrate interactions responsible for crystallization processes during the growth of thin films of OSCs. For a given material, such interactions render substrate-independent control of molecular orientation in crystalline films very difficult. Indeed, apart from possible reorientation effects,^{25,26}

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Figure 1. (a,c) Ex situ X-ray diffraction patterns measured in grazing-incidence geometry for uniaxially oriented, polycrystalline DIP films in (a) σ and (c) λ -orientation, both on a native Si oxide substrate. The expected positions of the Bragg peaks were simulated using the unit cell of the 423 K polymorph of DIP from ref 32, which corresponds to its thin film phase. The Miller indices of the strongest Bragg peaks are shown, with the circles having a diameter proportional to the expected intensity. The insets illustrate the different orientations of the DIP unit cell and the contact plane with the substrate used to reproduce the measured diffraction patterns. (b,d) Extinction coefficient obtained using VASE on the same DIP films as those in (a) and (c). Sketches illustrating the overall orientation of the molecules and of the TDM are shown.

the crystal packing of the initial nuclei determines to a large extent the structure and molecular orientation of the subsequent layers. Our approach consists of frustrating the effectiveness of strong intermolecular interactions by suppressing the growth dynamics.

The possibility to use annealing to turn a disordered into a polycrystalline solid exhibiting a molecular orientation "locked" in the as-grown film has obviously important consequences on its optical properties. Indeed, due to the typically strong intrinsic anisotropy of molecular semiconductors, the efficiency of light absorption along a given direction as well as the emission depends on the orientation of the absorber/ emitter.^{27,28} For uniaxially ordered thin films of small molecules, this has the obvious consequence that spatial decomposition of the extinction coefficient, k, in the directions parallel (k_{xy}) and perpendicular (k_z) to the substrate plane shows pronounced anisotropy. This was illustrated for polycrystalline thin films of the molecular semiconductor diindenoperylene (DIP) exhibiting an upright standing orientation (σ -orientation): the HOMO-LUMO transition dipole moment (TDM) of DIP is oriented parallel to the long molecular axis; therefore, the in-plane absorption is much lower than the out-of-plane absorption.²⁹

In the present work, we deposited thin films of three rodshaped OSCs: DIP, pentacene (PEN), and α -sexithiophene (6T). For each material, deposition was carried out simultaneously on native and 121 nm thermally grown Si

oxide wafers employing a portable vacuum chamber,³⁰ which allows control of the sample holder temperature by liquid N₂ cooling as well as resistive heating. For all three materials, the substrates were cooled down to 123 K and their temperature (T_{sub}) was kept at 123 K during the deposition. The base pressure before starting the cooling was 5×10^{-8} mbar. The growth rate was around 0.3 nm/min for a total film thickness set to 20 nm on the thickness monitor. After growth, all films were annealed at a rate of ~2 K/min up to temperatures compatible with their thermal stability, namely, 413 K for DIP, 353 K for PEN, and 393 K for 6T. The final temperature was then kept for ~90 min. For all three materials, we carried out ex situ X-ray scattering experiments. For DIP, the experiments were also carried out in situ. In the following, we first focus on the results obtained for DIP. Subsequently, we summarize the results for PEN and 6T, highlighting similarities and differences with DIP.

X-ray diffraction patterns measured in situ in grazingincidence geometry for a DIP film right after film deposition on native Si oxide at $T_{sub} = 123$ K are reported in the Supporting Information (SI). They show a diffraction feature from weakly ordered DIP domains, corresponding to molecules exhibiting their long axis roughly parallel to the substrate plane (λ -orientation). Therefore, even at this low temperature (LT), some nuclei with short-range order are formed having a lateral coherent grain size of ~4.5 nm, which



Figure 2. Ex situ X-ray diffraction patterns and extinction coefficient for PEN (a,b,e,f) and 6T (c,d,g,h) films in standing-up (σ) and lying-down (λ) molecular orientations, respectively. The symbols and Miller indices overlaid on the PEN and 6T diffraction patterns belong to the PEN substrateinduced polymorph (ref 35) and to the 6T low-temperature bulk polymorph (ref 36), respectively. The sketches reported for the *k* data summarize the thin film optical properties, as detailed in the text.

corresponds approximately to the length of three molecules in λ -orientation.

X-ray scattering and variable angle spectroscopic ellipsometry (VASE) experiments were further carried out ex situ. A DIP film grown at RT was compared with a film grown at LT (123 K). Both samples were annealed up to 413 K and then cooled down to RT. The X-ray diffraction pattern measured ex situ for the film grown at RT is shown in Figure 1a, and it is compared with the corresponding data for the film grown at 123 K (Figure 1c). The X-ray diffraction pattern of the RT film matches the well-known thin film phase with molecules standing nearly upright.¹² The weak diffraction ring at $Q_{tot} =$ 0.375 Å⁻¹ stems from some DIP domains exhibiting a nearly random orientation.³¹ Correspondingly, $k_z > k_{xy}$ in the visible range up to 3 eV (Figure 1b).

The situation is very different in the case of the LT film. Here, the DIP unit cell is tilted by 90° around the crystallographic *a*-axis with the (020) plane parallel to the substrate (Figure 1c). The long molecular axis is then also parallel to the substrate plane, and the molecules exhibit a tilted edge-on configuration (inset Figure 1c). From the position of the strong Bragg reflection at $Q_{\rm II} = 0$ Å⁻¹ and $Q_z \approx 1.5$ Å⁻¹, it is evident that the (020) plane is parallel to the substrate. Note that there is no trace of the σ -orientation of DIP in the diffraction pattern.

The appearance of the two truncation rods (1k0) and (1k1) at $Q_{\parallel} = 0.88$ and 0.97 Å⁻¹ for the LT film in Figure 1c is an indication of the overall high coherence length of the crystallites in the direction perpendicular to the substrate. A broader distribution of crystallite orientations for the film grown at RT is evident by the comparably broader Bragg peaks, i.e., the LT film exhibits a higher mosaicity than the RT film. The mosaicity calculated from the Bragg peaks belonging to the (1k1) truncation rod is $\pm 7^{\circ}$ (see the SI). Remarkably, the presence of the (00*l*) series of sharp Bragg peaks along Q_{\parallel} at $Q_z = 0$ Å⁻¹ indicates a high coherence of the crystallites in

the direction parallel to the substrate surface, with a coherent grain size of \sim 50 nm estimated from the width of the (001) peak (see the SI).

In agreement with the molecular tilt, the in-plane absorption of DIP in λ -orientation is much stronger than the out-of-plane absorption, i.e., $k_{xy} \gg k_z$ (Figure 1d). The long-range order of the DIP crystallites in λ -orientation is further supported by the VASE data in Figure 1d. Indeed, the highest-energy mode at around 2.8 eV has been assigned to the combination of localized as well as delocalized excitations, and its intensity relative to the other transitions indicates intermolecular interactions in structurally ordered aggregates.^{29,33}

We have shown that vacuum deposition of DIP films lacking long-range order followed by thermal annealing to induce crystallization is an efficient method to obtain a molecular λ orientation in the polycrystalline films. Selecting the orientation of DIP between σ and λ consequently allows the thin film optical absorption to be inverted between the in-plane and out-of-plane directions, respectively (Figure 1b,d). The use of small-molecule OSCs as light harvesters in solar cells calls for maximization of the absorption in the direction parallel to the bottom/top contacting substrates, where often indium tin oxide (ITO)³⁴ or other transparent conductive oxides are used as electrodes. Similar requirements for the orientation of molecular emitters apply to organic lightemitting diodes (OLEDs). To demonstrate that the abovepresented growth scheme allows for the fabrication of thin films with molecular λ -orientation for other technologically relevant OSCs than DIP, we present results also on PEN and 6T.

In Figure 2, the diffraction pattern of a PEN film in σ orientation (Figure 2a) differs strongly from that of a PEN film in λ -orientation obtained with the growth procedure illustrated above (Figure 2b). Nearly perpendicular orientations of the unit cell of the substrate-induced polymorph of PEN³⁵ have been used to index the observed diffraction features, as detailed in the SI.

The HOMO–LUMO TDM of PEN is parallel to the short molecular axis; therefore, $k_{xy} \gg k_z$ in thin films of PEN in σ orientation (Figure 2e and ref 37). For the PEN film in λ orientation, k_{xy} and k_z have similar strength. Interestingly, one observes that the low-energy (LE) Davydov component of the fundamental HOMO–LUMO transition³⁸ at ~1.88 eV is oriented mostly in-plane, whereas the high-energy (HE) Davydov component at ~1.99 eV is oriented mostly out-ofplane (Figure 2f). The spatial decomposition of the Davydov components has already been observed in PEN single crystals,³⁹ and in our polycrystalline film, it is a direct consequence of the particular orientation of the herringbone stacking relative to the substrate.

We obtained similar results for 6T. The unit cell of the lowtemperature (low-*T*) bulk polymorph of $6T^{36}$ is rotated by 90° around the *c*-axis for the two prepared samples (Figure 2c,d). Notice in particular the (h00) series of sharp in-plane Bragg reflections for the λ -orientation, which denotes well-defined stacking of the 6T molecules in the direction parallel to the substrate. However, the mosaicity is higher compared to that of DIP and PEN in λ -orientation.

Quantification of the anisotropy of the optical properties by VASE for these 6T films is difficult due to the pronounced island-like morphology, which generates a strong scattering background (see the SI). The data reported in Figure 2g,h represents nevertheless a qualitative estimation of the optical anisotropy. Because the HOMO–LUMO TDM of 6T is parallel to the long molecular axis, k_z is larger than k_{xy} for the 6T film in σ -orientation⁴⁰ and vice versa for the 6T film in σ -orientation, the optical anisotropy for the 6T film in λ -orientation, which we ascribe to the higher mosaicity in 6T.

We note that a λ -orientation of molecular OSCs in crystalline films has already been observed in the literature for other material—substrate combinations.^{25,41–56} Specifically for DIP, some in situ investigations have shown that by deposition via OMBD on amorphous Si oxide at $T \leq 300$ K it is possible to obtain crystalline domains with λ -orientation,^{12,31,57,58} although a coexistence with crystalline domains in σ -orientation was always observed. For PEN grown on Si oxide at $T_{sub} = 210$ K, a recent work⁵⁹ demonstrates the growth of thin films in which the molecular domains exhibit both σ - and λ -orientation. In contrast, for both DIP and PEN, our work demonstrates the complete suppression of the σ -orientation in favor of the λ -orientation in crystalline films.

Furthermore, for noncrystalline systems of OSCs known as "anisotropic organic glasses",⁶⁰ the average molecular orientation in vapor-deposited films can be tuned to some extent. In particular, for rod-shaped molecules, lowering of the deposition temperature leads to a reduction of the average tilt angle between the long molecular axis and the substrate. Such average tilt is then preserved after film annealing.^{61,62}

The mechanism that explains the results we obtained seems to primarily involve suppression of molecular dynamics. The molecules landing on the bare substrate adopt a λ -orientation in order to maximize the van der Waals interactions with the Si oxide surface. However, due to the low T_{sub} , they lack the necessary thermal energy for a collective transition to a σ orientation,^{63,64} which would allow one to maximize the interactions per unit area. The same scenario holds for molecules landing on top of an already formed organic layer. The molecules within "buried" layers additionally experience hindrance to motion from the material deposited on top. In the end, the molecular aggregates in the as-deposited film exhibit an overall λ -orientation with no long-range order.

Upon film annealing, the molecular units receive enough thermal energy such that crystallization processes are triggered, which seemingly occur via minimal structural reorganization thanks to the initial "compact" (though disordered) packing of the film. When cooling down to RT, the formed crystallites are already kinetically trapped in the λ -orientation, which does not change further upon exposure to atmospheric conditions.

In summary, we have shown that vacuum deposition of the three rod-like OSCs DIP, PEN, and 6T at T_{sub} = 123 K followed by annealing in vacuum leads to the formation of uniaxially aligned films where the crystalline domains consist of molecules exclusively oriented with their long axis parallel to the substrate. The films are mostly polycrystalline with longrange order, although some material-dependent differences in film texture are recognized. The optical properties of the thin films change according to the molecular orientation. In particular, for materials having their HOMO-LUMO TDM parallel to the long molecular axis, light absorption efficiency in the direction parallel to the substrate plane is greatly enhanced. Importantly, the horizontal molecular orientation and crystallinity of the films are conserved after exposure to atmospheric conditions. The alignment of the long molecular axis of rodshaped OSCs parallel to the substrate plane on Si oxide without the use of specific templating surfaces, together with the pronounced crystalline coherence of the uniaxially anisotropic thin films, had so far, to the best of our knowledge, not been achieved. Such a combination of properties has great potential for optoelectronic devices where high light-harvesting efficiency and high charge carrier mobility are demanded. We expect that, although this report shows results for three materials on amorphous Si oxide, the above-outlined mechanism is general for rod-shaped OSCs on a variety of substrates, both amorphous and (poly)crystalline.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.9b00304.

Additional experimental details, additional grazingincidence X-ray scattering data of a DIP film in λ orientation, additional comments on the structural data for PEN and 6T films, AFM data of 6T films, and UV– vis absorption and photoluminescence spectra for all films in both σ - and λ -orientation (PDF)

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Notes

The authors declare no competing financial interest.

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