Kinetic Versus Thermodynamic Orientational Preferences for a Series of Isomorphic Molecular Semiconductors

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ABSTRACT: Due to the anisotropic nature of charge transport through most organic semiconductors, the orientation of the conjugated backbone is of great relevance because it may affect final device properties. Herein, we present a set of four nearly isostructural molecular organic semiconducting materials whose orientation changes drastically with a two-atom change in the conjugated framework. We investigate the X-ray diffraction patterns of these materials in the thin film, both as-deposited from solution and following melt-annealing. Following melt-annealing of the films, crystallites of all four materials orient edge-on with respect to the substrate, which indicates that this orientation is thermodynamically preferred. We can infer that the initial face-on orientation of some of the materials is due to kinetic trapping during the spin-coating process. Previous observations from the literature suggest that the edge-on orientation is the thermodynamically preferable state for many organic semiconducting materials. However, a cohesive explanation for this phenomenon remains elusive.

INTRODUCTION

The orientation of molecular organic semiconducting materials is important due to the anisotropic nature of charge transport through π−π stacking, which can impact device performance. For applications such as organic field-effect transistors (OFETs), edge-on orientation relative to the substrate may be preferable. However, for applications in which charges move in the direction normal to the substrate surface (e.g., diodes, organic light-emitting diodes, organic photovoltaics), it is beneficial for the materials to orient face-on, as the π−π stacking is in the direction of charge transport. However, orientation with respect to the substrate is not the single determining factor of charge carrier mobility in a given direction. Factors, such as crystal structure, formation of connected networks, grain boundaries, and intermolecular electronic coupling, play a role, as well. Even though the degree by which orientation impacts charge carrier mobility is under examination, the forces and molecular features that impact the preferred orientation have not been fully elucidated.

Previous reports demonstrated that material orientation relative to the substrate can be controlled by processing conditions. For the small molecule donor p-SIDT(FBTTTh)2, spin-coating the material with or without the solvent additive diiodooctane results in face-on or edge-on crystallites of the donor, respectively. In bilayer devices, improved performance is due to an increase in open circuit voltage from 0.69 V to 0.84 V, attributed to improved π orbital overlap with the acceptor, [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM). The widely studied polymer N2200 has also been shown to change orientation following annealing above its melting point. In the as-cast film, N2200 crystallites orient face-on and flip to edge-on when melt-annealed. There have been several examples of this behavior in the literature, but no unifying mechanism exists so far. Other reports, in which poly(3-alkylthiophene) polymers were studied, suggest that higher crystallinity and preaggregation in solution favor the edge-on orientation; however, no chemical explanation for this phenomenon is given.

In summary, it is understood that orientation of a material can be controlled by processing conditions, yet there is no explanation for the relationship between chemical structure and the final organization obtained from solution. Given the absence of modeling tools, a priori knowledge or other approaches that allow one to predict molecular orientation, this question remains open to investigation.

We previously reported four isomorphic organic semiconductors, Scheme 1 (full chemical structures in Scheme S1), whose crystallite orientation in the as-cast film depends on the
position of the pyridylthiadiazole (PT) acceptor fragment within the conjugated backbone. It was found that the molecules with benzothiadiazole (BT) acceptors in the inner positions assume an edge-on orientation, whereas those with PT units at the same positions show face-on orientation. The difference in crystallite orientation, especially in the isomers N2a and N2b, raises the question of the origin of this phenomenon.

It is important to consider that the differences in orientation arise from very small (single atom) changes in chemical structure. Are the face-on crystallites the thermodynamically preferred orientation, or is it a case of kinetic trapping? This question is relevant due to the impact of crystallite orientation on the preferred direction of charge transport in the solid state, especially since a molecule in this group has been shown to be able to withstand significant thermal stress in an organic field-effect transistor (OFET) device architecture. Although previous studies relied on processing conditions to modify crystallite orientation, we present a system in which the solid state, especially since a molecule in this group has been shown to be able to withstand significant thermal stress in the melt-annealing. The stacking distances corresponding to the peaks discussed earlier have not changed significantly. The \( \pi-\pi \) stacking distance remains at 3.6 Å, and the lamellar stacking distance changes from 15.5 Å to 16.0 Å, possibly due to unfolding of the alkyl chains or a change of inclination of the molecules relative to the substrate normal.

Compared to Figure 1a, the diffraction pattern of Figure 1c indicates a higher degree of order within the crystallites or throughout the film. For instance, the full width half-maximum of the lamellar and \( \pi-\pi \) stacking peaks changed from 0.06 Å\(^{-1}\) to 0.03 Å\(^{-1}\) and 0.12 Å\(^{-1}\) to 0.07 Å\(^{-1}\), respectively. This corresponds to a change in the crystalline correlation length \( L_C \) from 95 Å to 171 Å for the lamellar stacking peak and 47 Å to 82 Å for the \( \pi-\pi \) stacking peak. It is unclear whether this increase in the \( L_C \) is due purely to improved order within the crystallites or to larger crystallites as well. There is also less intensity dependence with respect to \( \chi_c \), indicating that the orientation of the crystallites has become more uniformly edge-on. After melt-annealing, the off-axis area displays distinct peaks, attributed to improved order within the crystallites, likely due to the extra thermal energy and crystallization time afforded by melt-annealing the film. There is also a new peak at 0.5 Å\(^{-1}\) along the \( q_z \) axis, which is indicative of a secondary lamellar stacking distance of 13.7 Å.

Figure 1. GIWAXS diffraction patterns of N0 as-cast (a), in the melt (b) at 250 °C and melt-cooled (c).
stacking peak at [1.7, 0.4] \((q = 1.8 \text{ Å}^{-1})\) suggests that there may be two coexisting polymorphs, supported by the presence of multiple endotherms in the DSC heating traces\(^{19}\) and a second lamellar stacking peak. However, without the crystal structure, it is difficult to attribute these new peaks to any specific interactions or changes in local packing.

Similar observations can be made for films of N2a. Figure 2a shows the diffraction pattern of the as-cast N2a film. The lamellar stacking peak is at 0.4 Å\(^{-1}\) along the \(q_z\) axis, along with its overtones, and the \(\pi-\pi\) stacking peak is located at 1.8 Å\(^{-1}\) along the \(q_{xy}\) axis. Some diffuse scattering is also visible in the off-axis area. The melt diffraction pattern of the N2a film is not shown as it is the same as that of the N0 film (i.e., no visible scattering peaks). The lamellar stacking distance in the melt-
cooled film (Figure 2b) increases from 14.6 Å to 16.3 Å and the π−π stacking distance does not change from 3.4 Å. As with the melt-annealed N0 films, the $L_c$ increases from 97 Å to 182 Å for the lamellar stacking and 67 Å to 109 Å for the π−π stacking. There is also less disorder along $\chi$, indicating more uniform orientation of the crystallites relative to the substrate. The diffraction pattern of the melt-annealed N2a film also shows the appearance of two groups of off-axis peaks. The first group of peaks ($q_{yi} < 0.5 \text{ Å}^{-1}$) is well defined along the $q_{y}$ and $q_{z}$ axes and has multiple overtones. This indicates that the reflections of the unit cell responsible for this diffraction have a low degree of disorder. The second group of off-axis peaks ($0.5 < q_{yi} < 1.5 \text{ Å}^{-1}$) is well defined in the $q_{y}$ plane, but appears poorly defined in the $q_{x}$ direction, indicating a higher degree of stacking disorder in the out-of-plane direction.

As previously discussed in the Introduction, the as-cast diffraction pattern of the N2b film (Figure 3a) is noticeably different from those of the previously discussed materials, N0 and N2a. The face-on orientation of as-cast N2b crystallites is consistent with previously reported data. The linecuts in Figure 3 show that following melt-annealing, the lamellar and π−π stacking peaks have shifted by 90° so that the π−π stacking peak is located along the $q_{y}$ axis, whereas the lamellar stacking peak is located on the $q_{z}$ axis. Although the axes along which the stacking peaks appear have changed, their $q$ values have not. The π−π stacking peak is at 1.8 Å$^{-1}$ and the lamellar stacking peak is at 0.4 Å$^{-1}$. The diffraction peaks from the as-cast N2b film are relatively broad and show some dependence of intensity with respect to $\chi$. Following melt-annealing, the new edge-on crystallite peaks are located at 1.7 Å$^{-1}$ along the $q_{x}$ axis (π−π stacking) and 0.4 Å$^{-1}$ along the $q_{y}$ axis (lamellar stacking). As with N0 (Figure S2), there is also a new lamellar stacking peak that appears at 0.5 Å$^{-1}$ along the $q_{x}$ axis. Similarly to the previous materials, the π−π stacking distances do not change significantly, increasing from 3.6 Å to 3.4 Å, whereas the lamellar stacking distance decreases slightly from 17.6 Å to 15.7 Å. The new lamellar stacking distance (13.8 Å) is also consistent with that of N0 (13.7 Å). As observed with the other melt-annealed samples, the degree of disorder decreases compared to the as-cast films. The $L_c$ for the π−π and lamellar stacking peaks increases from 24 Å to 94 Å and from 36 Å to 175 Å, respectively. Off-axis peaks also appear following melt-annealing, indicating improved intracrystalline order. Melt-annealing of the molecule N2b, which has interior PT acceptor fragments, therefore produces a drastic change in the diffraction pattern of the film. The main diffraction peaks reorient and resemble the melt-annealed diffraction patterns of N0 and N2a.

N4 exhibits the same behavior as N2b, both in the as-cast film and following melt-annealing. In the as-cast diffraction pattern (Figure 4a), the π−π stacking peak is located at 1.8 Å$^{-1}$ along the $q_{x}$ axis and the lamellar stacking peak is located at 0.4 Å$^{-1}$ along the $q_{y}$ axis. Both peaks appear broad and show intensity dependence with $\chi$, indicating some disorder in the crystallite orientation. Following melt-annealing (Figure 4b), the crystallite orientation flips from face-on to edge-on. The π−π stacking diffraction peak is now located at 1.7 Å$^{-1}$ along the $q_{y}$ axis, and the lamellar stacking peak is located at 0.4 Å$^{-1}$ along the $q_{x}$ axis. Stacking distances do not change significantly. There is no change in the π−π stacking distance, and the lamellar stacking distance decreases from 17.9 Å to 17.7 Å. The $L_c$ increases from 26 Å to 122 Å for π−π stacking and from 34 Å to 131 Å for lamellar stacking. A secondary, much less intense, lamellar stacking peak is observed at 0.40 Å$^{-1}$ along the $q_{y}$ axis, corresponding to a stacking distance of 15.8 Å. As observed in the previous examples, the azimuthal dependence of the peaks decreases significantly, indicating more uniform crystallite orientation with respect to the substrate. Off-axis peaks also start to appear, though they are not sharp or intense enough to characterize. This suggests that the degree of ordering is improved as compared to the as-cast film, but not to the same extent as in the other materials.

The reorientation of N2b and N4 crystallites following melt-annealing of the films indicates that the initial (as-cast) face-on crystallite orientation is kinetically trapped. In the as-cast films, the relative population of edge-on to face-on crystallites of N2b and N4 films is very high, whereas the relative population of face-on to edge-on crystallites is significantly smaller (Figure S3 and Table S1). The lower relative population of face-on crystallites in the as-cast N2b and N4 films suggests that the face-on orientation is not as favorable as the edge-on crystallites in the as-cast N0 and N2a films. Following melt-annealing, the relative population of edge-on to face-on crystallites is at least 8:1 in all four films, indicating that crystallites of all four materials significantly prefer the edge-on orientation. Although the mechanism for kinetic trapping into face-on orientation of crystallites is not yet completely understood (see relevant system in N2200), the possibility of there being a kinetic trap during spin-coating is not out of the question. When comparing the lattice parameters of the sets of materials...
Å and 17.9 Å, respectively. The lattices of as-cast N2b and N4 are larger than the equilibrium distance: 15.5 Å and 14.6 Å, respectively. On the other hand, the lamellar stacking distances of the as-cast N0 and N2a lattices are slightly shorter than the equilibrium distance: 15.5 Å and 14.6 Å, respectively. These differences indicate that face-on orientation may be a quenched metastable state. The degree of variation in the crystallites are also approximately twice as large as those of the as-cast N2b and N4 crystallites, which suggests that there is a larger degree of disorder in the latter. These differences indicate that face-on orientation may be a quenched metastable state. The degree of variation in the primary lamellar stacking distances of all the materials converge to approximately 16 Å. This suggests that the structural similarity of the four conjugated backbones.

Table 1. Spacing Distances and LC Derived from GIWAXS Diffraction Peaks

| diffraction peak | as-cast | melt-annealed | % change |
|------------------|---------|---------------|----------|
|                  | d-spacing (Å) | LC (Å) | d-spacing (Å) | LC (Å) | d-spacing (Å) | LC (Å) |
| N0 lamellar      | 15.5    | 95.0          | 16.0      | 171.3 | 3.7        | 80.4 |
|                  | π−π     | 3.6           | 3.6       | 81.7  | 1.8        | 75.8 |
|                  | π−π 2   | 46.5          | 48.2      |       |            |       |
| N2a lamellar     | 14.6    | 96.7          | 16.3      | 182.0 | 11.6       | 88.2 |
|                  | π−π     | 3.4           | 3.4       | 109.4 | 0.3        | 61.9 |
|                  | π−π 2   | 67.6          |           |       |            |       |
| N2b lamellar     | 17.6    | 36.4          | 15.7      | 174.8 | −11.1      | 380.2 |
|                  | π−π     | 3.6           | 3.7       | 93.5  | 1.8        | 288.9 |
|                  | π−π 2   | 24.0          |           |       |            |       |
| N4 lamellar      | 17.9    | 34.6          | 17.7      | 130.8 | −1.2       | 278.2 |
|                  | π−π     | 3.6           | 3.6       | 122.1 | 1.6        | 367.8 |
|                  | π−π 2   | 26.1          |           |       |            |       |

(kinetically trapped and edge-on) in Table 1, it is important to note that there are some consistent trends, which could correlate to the observed behavior. Following melt-annealing, the (primary) lamellar stacking distances of all the materials converge to approximately 16 Å. This suggests that the thermodynamically preferred lamellar stacking distance of all four materials does not vary significantly. However, the as-cast lamellar stacking distances are different. The lamellar stacking distances of as-cast N0 and N2a lattices are slightly shorter than the equilibrium distance: 15.5 Å and 14.6 Å, respectively. On the other hand, the lamellar stacking distances of the lattices of as-cast N2b and N4 films are almost 2 Å longer: 17.6 Å and 17.9 Å, respectively. The LC of the as-cast N0 and N2a crystallites are also approximately twice as large as those of the as-cast N2b and N4 crystallites, which suggests that there is a larger degree of disorder in the latter. These differences indicate that face-on orientation may be a quenched metastable state. The degree of variation in the π−π stacking distance is very small: a range of only 0.3 Å (approximately 2%). This is likely due to the relatively stronger π−π interactions and the structural similarity of the four conjugated backbones.

- **CONCLUSIONS**

In conclusion, we have shown that even though the four N series molecules have different orientational preferences relative to the substrate when kinetically trapped during spin-coating, their thermodynamically preferred orientation is the same. As demonstrated by in situ GIWAXS measurements, the molecules with inner BT units (N0 and N2a) are able to achieve the thermodynamically preferred orientation during spin-coating. However, the molecules with inner PT acceptor units (N2b and N4) are kinetically trapped in the face-on orientation during spin-coating. After annealing these films to the melt and then cooling, the resulting crystallites are oriented edge-on relative to the substrate. Although there is not yet a mechanistic explanation for the kinetically determined orientational preferences observed in these organic semiconductors, it is worth noting that crystallite orientation has been shown to depend on processing conditions. This study shows such changes within a series of closely chemically related materials, especially for two isomers: N2a and N2b. Furthermore, the N series of molecular semiconductors presents a well-defined, monodisperse system to study crystallite reorientation that has previously been observed in polydisperse systems. An understanding of the degree to which organizational preferences under kinetic control can be preprogrammed through the chemical structure of molecular semiconductors remains a formidable challenge. However, it is worth re-emphasizing that such control would open opportunities to optimize the charge carrier transport in the bulk and thereby relevant electronic device properties.

- **EXPERIMENTAL SECTION**

Silicon substrates (with native oxide) were cleaned by sonication in piranha solution (3:1 H2SO4/H2O2), acetone, and isopropanol for approximately 5 min each. The substrates were subsequently dried in an oven at 130 °C and cleaned via UV−ozone treatment for 30 min each. The substrates were then brought into a glovebox under N2 atmosphere, where the films were deposited via spin-coating at 1500 rpm for 60 s from chloroform solutions (10 mg/mL) of each material. GIWAXS measurements were taken at beamline 11-3 of the Stanford Synchrotron Radiation Lightsource using a charge coupled device detector with a beam energy of 12.4 keV. The films were melt-annealed by heating the stage above the melting point of the material (confirmed by no X-ray diffraction) and then allowing it to cool back down to ambient temperature.

- **ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01435.

- Full chemical structures of the N series of molecules;
- linecuts of N0, N2a, and N4; analysis of populations of face-on and edge-on crystallites in the thin films (PDF)

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Notes
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