Microstructure of Oligofluorene Asymmetric Derivatives in Organic **Thin Film Transistors**

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In organic thin film transistors (OTFT), modifying the molecular chemical structure affects the molecular packing and thin film morphology, which both sensitively influence the charge carrier mobility. A detailed understanding of the interplay of molecular chemical structure, molecular packing, and thin film morphology is therefore necessary to improve OTFT performance. Fluorene-bithiophene-fluorene (FTTF) derivatives have demonstrated great potential for use as the active layer for OTFTs. A series of FTTF asymmetrically substituted derivatives were synthesized to fine-tune the film properties. In this study, the thin film microstructure details of FTTF and several FTTF derivatives with asymmetrically substituted alkyl-chains of different lengths are studied and compared with their electrical performance in thin film transistor devices. The respective unit cells were characterized using grazing incidence X-ray diffraction (GIXD), and for FTTF the detailed molecular packing was determined from the GIXD intensities in combination with packing simulation. The alignment of the FTTF core in the thin film phase was further characterized using near edge X-ray absorption fine structure (NEXAFS) spectroscopy for films prepared under different processing conditions and under different film growth stages. For well-packed asymmetric FTTF derivatives, we find that the conjugated FTTF core is in direct contact with the substrate surface, and its single alkyl chain is aligned away from that interface. The impact of the detailed microstructure in the films on the charge mobility is discussed.

Introduction

Small aromatic molecular materials are showing great potential for low-cost, large-scale electronic applications,¹⁻⁴ but the technology developments require significantly improving the performance of organic thin film transistors. It is well-known that the electronic performance of such transistor devices critically depends on the thin film's morphology and microstructure, ^{1,5–17} which can be readily tuned by the choice of the molecular side chain substituents

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and processing conditions. Thus understanding the structure-property relationship of organic thin films is essential for developing rational molecular design rules and for optimizing processing conditions. Furthermore, theoretical models for the transport in organic thin film transistor devices are dependent on the detailed knowledge of the thin film microstructure. Therefore, both a thorough and high-resolution characterization of the thin film structure at different growth stages as well as the investigation of the impact of different preparation conditions on the charge mobility are desirable.

In previous studies, grazing incidence X-ray diffraction (GIXD) was demonstrated to be a powerful tool for

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Figure 1. Chemical structure for molecules studied in this work, R = H, C_6H_{11} , C_8H_{15} , $C_{12}H_{23}$.

characterizing the thin film microstructure, identifying even subtly different film phases and accurately measuring the unit cell dimensions.^{14,17–22} Carbon K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy was found to be useful for finding the azimuthally averaged orientation of the conjugated plane of the molecule.^{23–27} This is especially useful for ultra thin films which are difficult to obtain detailed crystallography information. In addition, NEXAFS can also probe both crystallographically ordered and disordered regions of the film. The NEXAFS spectra peak positions are sensitive to the chemical environment, and thus the dichroisms of different resonance peaks may yield orientation information about different parts of a molecule.^{26,28}

In this work, we present a microstructure-property relationship study for fluorene-bithiophene-fluorene (FTTF) and its asymmetrically alkylated derivatives (see Figure 1). FTTF thin films have exhibited up to $0.3 \text{ cm}^2/(\text{V s})$ p-type charge carrier mobility in previous studies.^{29,30} Its solubility and thin film morphology can be tuned by adding different substituents.^{5,29–31} Understanding the molecular packing, molecular tilt and orientation for different FTTF derivatives helps to correlate the molecular chemical structure with the charge transport properties. Unlike the symmetrically substituted counterpart,¹⁹ the relative alignment of the asymmetrically substituted FTTF derivatives (FTTF core down and alkyl chain up, or vice versa) in a thin film phase of nearly vertical molecules is expected to have a measurable effect on the charge transport due to the exponential decay of the charge density away from the semiconductor inter-

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face.³² In our NEXAFS spectroscopy studies, we measured Auger electron yield (AEY) and total electron yield (TEY) simultaneously. Due to different degrees of surface sensitivity of the two yield signals, the comparison of peak intensities in these two spectra allows us to identify the molecular orientation near surface. By studying the thin film microstructure evolution (monolayer to 15 layer thick films) of various FTTF derivatives using GIXD, NEXAFS, and by comparison of those results to transistor performance data, we are able to correlate chemical structure, processing conditions, and microstructure with transistor performance.

Experiments

The synthesis of FTTF derivatives was reported previously.^{30,31} They were purified by three or more successive 3-zone sublimations under high vacuum (10^{-6} Torr). Thin film samples were prepared by thermal evaporation in a high vacuum chamber (base pressure $< 2 \times 10^{-6}$ Torr). During the deposition, the growth rate was monitored with a water-cooled quartz crystal microbalance (QCM) monitor and was kept constant at 0.2 Å/s. For film deposition at an elevated substrate temperature, the fluctuation of substrate temperature $T_{\rm D}$ was kept within ± 3 °C of the target temperature. The substrate preparation starts with highly doped bare Si substrates (resistivity 0.0015–0.007 Ω cm) with a layer of native oxide $(\sim 10-20$ Å). Three types of substrate surface were prepared. They are silicon oxide substrates with octadecyltriethoxysilane (OTS) and hexamethyldisilazane (HMDS) treatments using procedures as described in previous reports,³³ and a third "plain" substrate prepared by rinsing native oxide coated silicon substrates with acetone, followed by isopropyl alcohol rinse and then UV ozone cleaning for ~ 20 min.

The transistor measurements were performed in air because FTTF derivatives were found to be stable for several months in ambient conditions.^{29–31} The thin film transistors were fabricated in top-contact geometry. The transistor fabrication and measurement procedures were described in our previous report.¹⁷

GIXD measurements were performed at Stanford Synchrotron Radiation Laboratory (SSRL), beam line 11-3, with photon energy of 12.73 keV. The diffraction patterns were recorded using a 2D MAR345 image plate detector with a spatial resolution of 150 μ m $(2300 \times 2300 \text{ pixels})$. The detector-sample distance was 352 mm. The geometry of GIXD samples was rectangular (approximately 15×10 mm), with the short side aligned with the beam direction. The incidence angle was optimized such that signal-to-background ratio was maximized, and typically, the angle between the incident beam and the sample surface was chosen as 0.09-0.12°. Before data processing, the diffraction images were distortion-corrected (theta-dependent image distortion introduced by planar detector surface). The diffraction pattern obtained for a LaB₆ (Lanthanum Hexaboride) crystal was used as calibration reference. The overall resolution achieved in GIXD experiments is dominated by the sample size and estimated to be about 0.1 $Å^{-1}$.

Carbon K-edge NEXAFS spectra were collected at the wiggler beam line 10-1 of the Stanford Synchrotron Radiation Laboratory (SSRL) from 260 eV to 470 eV with an energy resolution of about 80 meV. At these photon energies, the incident X-ray beam is elliptically polarized with 80% of the intensity horizontally and 20% vertically linear polarized.²⁸ Spectra were collected by simultaneously recording the Carbon KLL Auger electron yield

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Table 1. Lattice Geometry for FTTF, C6FTTF, C8FTTF, and C12FTTF Grown on OTS Treated Substrates at 100 °C

	molecule			
	FTTF	C ₆ FTTF	C8FTTF	C ₁₂ FTTF
total length (Å)	25.12	31.79	33.14	38.34
alkyl chain length (Å)	0	6.3	10.0	15.0
d_{001} (Å)	24.02	30.01	33.14	36.86
a (Å)	5.84	5.80	5.82	5.81
<i>b</i> (Å)	8.62	8.56	8.62	8.60
<i>c</i> (Å)	24.70	30.94	34.98	39.69
α (deg)	103.5	103.0	108.6	111.6
β (deg)	90.3	94.4	92.0	92.0
γ (deg)	90.0	90.0	90.0	90.0
cell volume (Å ³)	1209.38	1491.65	1663.23	1840.24

(AEY, by means of a cylindrical mirror analyzer) and the total electron yield (TEY, by means of the sample drain current) signal as discussed in the literature.²³ The 1/e sampling depths for AEY at this energy is about 1nm.²⁸ The sampling depth of TEY is on the order of about 5 nm and thus significantly larger.²³ A detailed description of the experiment setup can be found in the literature.²⁸ In this work, Carbon K-edge NEXAFS spectra were collected at five different angles (20°, 40°, 55°, 70°, and 90°). As discussed elsewhere, NEXAS spectra were normalized to reflect the absorption spectra per average sampled carbon atom.

Results and Discussion

GIXD. GIXD was used to probe the influence of the alkyl chain substitution on the crystal packing motif and unit cell dimensions. The unit cell dimensions for FTTF and C6FTTF, C8FTTF and C12FTTF are listed in Table 1. For all compounds, the d_{001} spacing is slightly smaller than the molecular length calculated from MM2 energy minimization (MM2: molecular mechanics force field),³⁴ indicating the molecules in films are aligned in an edge-on configuration, with their long molecular axes more or less (depending on the compound) tilted away from the substrate surface normal.

The in-plane dimensions (a and b) are not only the same for all compounds, but were found to be insensitive to the different substrate surface modifications that were applied before the thin film deposition (OTS or HMDS). Within experimental error, the in-plane unit cell dimensions do not change as the film thickness changes from one monolayer (3 nm) to thicker films (50 nm). This is in contrast to other aromatic small-molecule semiconductors such as pentacene which exhibit two phases in thicker films.²⁰ We attribute the absence of a structural relaxation in thicker film samples to the large aspect ratio (length of molecule compared to the width) of FTTF compounds. For molecules adsorbing in an edge-on, nearly upright geometry on a weakly interacting amorphous substrate such as SiO_2 , as the aspect ratio of the molecule increases, the ratio between intermolecular in-plane interactions and the molecule-substrate interactions increases. Therefore, substrate-induced strained growth and consequently bulk relaxation in thicker films are less likely for high aspect-ratio molecules on inert substrates.

Figure 2 shows a representative in-plane projection of the GIXD intensity from a 50 nm C6FTTF film grown at 100 °C on an OTS treated substrate. No splitting of the (12L)



Figure 2. In-plane line scan of the GIXD signal for 50 nm C6FTTF grown at 100 °C on an OTS treated Si substrate, integrated from $Q_z = 0.0$ to 1.0 Å⁻¹. The (01L) and (10L) peak are missing, while mixed indexes such as (12L) and (12L) are present, indicating a herringbone packing that has a p2gg symmetry. No splitting for (11L) or (12L) found, indicating $\gamma = 90^{\circ}$. Colored lines are fits to the data.

and (21L) peaks was observed, indicating that the angle between a and b is very close to 90 degree. The measured unit cell volume can accommodate two molecules; this together with the absence of (10L) and (01L) diffraction peaks and the presence of (12L) and (21L) peaks indicate that there are two molecules in the unit cell arranged in a herringbone motif (approximately p2gg symmetry). This systematic absence excludes the possibility of an antiparallel mutual alignment of these two molecules (alternating alkyl chains up and down). Otherwise, (10L) and (01L) would show significant diffraction intensities. As mentioned before, the d_{001} spacing measured from GIXD is close to the MM2 energy minimized dimension of the long molecular axis. This also excludes an antiparallel alignment of molecules in adjacent (00L) planes, since otherwise the length of c axis would be a multiple of the molecular length. Similar diffraction patterns have been found in FTTF, C8FTTF, and C12FTTF. Therefore, it can be concluded that FTTF and the asymmetrically alkylated derivatives (C6FTTF, C8FTTF and C12FTTF) share the same packing motif and differ only

in that the out-of-plane unit cell axis (|c|) increases with the alkyl chain length. The addition of the alkyl chains does not lead to significantly different molecular packing. This might be due to the fact that FTTF is a much longer core, and the interaction between the FTTF cores is the dominant factor in deciding the molecular packing. Thus, the addition of alkyl chains of different lengths does not significantly change the intermolecular force balance.

We do find, however, that samples grown at different substrate temperatures differ in the degree of thin film crystallinity. Figure 3 shows diffraction images of C6FTTF and C12FTTF grown on OTS treated SiO₂ substrates at an elevated substrate temperature of $T_D = 100$ °C. The GIXD patterns are comprised of diffraction rods with well defined out-of-plane peaks, which shows the thin films form a highly textured, predominately 2D-powder diffraction, as frequently found for small molecules.

In contrast, the GIXD patterns of room temperature grown samples such as shown in Figure 4 a,c exhibit both 2D polycrystalline powder diffraction peaks and Debye rings,

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Figure 3. (a) GIXD pattern of 50 nm C6FTTF grown at 100 °C on an OTS treated Si surface, (b) GIXD pattern of 50 nm C12FTTF grown at 100 °C on an OTS treated Si surface. High temperature grown samples show out-of-plane diffraction peaks, indicating thin films are mainly composed of 2D polycrystalline powder.



Figure 4. (a) GIXD pattern of 50nm C6FTTF grown at room temperature on an OTS treated Si surface; (b) diffraction intensity distribution along Debye rings of (11L) and (02L) in (a) after background subtraction; (c) GIXD pattern of 50nm C12FTTF grown at room temperature on an OTS treated Si surfaces; (d) diffraction intensity distribution along Debye rings of (11L) and (02L) in (c) after background subtraction.

indicating the thin films are composed of both a highly textured 2D-powder and some degree of 3D polycrystallinity, i.e. unoriented crystallites whose basal planes are not oriented parallel to the substrate surface. At the same deposition temperature C6FTTF shows a better defined rod-like diffraction pattern compared to C12FTTF. This is attributed to the greater mobility of the lighter C6FTTF monomers which can then diffuse on the substrate surface during the thin film



Figure 5. Scheme showing shift disorder between adjacent shifted layers. The position of the lattice point that previously derived through the crystal translation vector \vec{c} has an extra in-plane shift in \vec{a} and \vec{b} directions.

growth and form the 2D crystallites. Thus, at the same substrate temperature, the growth of C6FTTF polycrystallites is less diffusion-limited than that of C12FTTF, leading to higher quality 2D crystallites. Figure 4 (b) shows the azimuthal scans for (11L) and (02L) Debye rings for C6FTTF and C12FTTF. The distribution of diffraction intensity in these rings has peaks appearing at 90° (see arrow) and to a larger extent in the case of C6FTTF. These peaks correspond to predominant orientations in the distribution of 3D polycrystalline orientations. A possible explanation for the occurrence of these angles may be crystallites nucleating from the facets of existing larger crystallites that grew with their basal planes parallel to the substrate surface. The crystal facets enclose characteristic angles with the substrate surface plane and may themselves serve as secondary substrate planes from which smaller crystals nucleate. The peaks around 10-40° along the Debye ring (marked with *) are most likely due to the overlap of the Debye ring intensity and diffraction from the portion of the film that is a highly oriented 2D powder.

Another finding in the GIXD pattern with room temperature-grown samples is that although the (00L) diffraction peaks are well resolved as reported previously,³¹ the high order peaks in Qz direction on the (HKL) diffraction rods are significantly broadened or cannot be observed. Possible explanations for the general broadening of all out-of-plane peaks except for the (00L) peaks are translational or rotational mis-registration between adjacent layers. Figure 5 shows a schematic, based on layering disorder, to illustrate this effect.

The diffraction intensity generated by the elastic scattering of a monochromatic X-ray beam from a quasi-crystalline slab in which the in-plane order is undisturbed while a small misregistration between subsequent crystalline sheets exists can be expressed by eqs 1 and 2 (Supporting Information).³⁵ The situation for a translational stacking fault is given by

$$I(q) \propto \left\| \sum_{l} \sum_{m,n} e^{iq((m+u_l)a+(n+v_l)\vec{b})} e^{iqlc} \right\| \times \sum_{i} f_i e^{iqr_i} \Big|^2 \propto \left\| \sum_{l} \sum_{m,n} e^{iq((m+u_l)a+(n+v_l)\vec{b})} e^{iqlc} \right\|^2 F(q)^2$$
$$|G(q)|^2 = \left\| \sum_{l} \sum_{m,n} e^{iq((m+u_l)a+(n+v_l)\vec{b})} e^{iqlc} \right\|^2 \quad (1)$$

The expression in 1 can be separated into two independent terms: the structure factor $\vec{F(q)}^2$ depends on the arrange-



Figure 6. Simulation to show the effect of the mis-registration (shift) between adjacent layers on the out-of-plane diffraction peaks. The $G^2(q)$ of (11L) is calculated by averaging the effect of forty random shifts between adjacent layers. (The $G^2(q)$ of (11L) calculated by averaging eighty random shifts gives the same result.)

ment of atoms in the unit cell and has thus the same value in all layers (q is the diffraction vector; f_i and r_i are the atom scattering factor and position vector of the atoms in the unit cell, respectively). The term $|G(q)|^2$ on the other hand is determined by the positions of the sheets comprising the crystallite. The nominal positions of a slab along the a, b, and c directions are given by the integer values m, nand l. There is a small translational offset between adjacent a,b planes (the layering disorder) which is given by the addition of small values u and v (between 0 and 1) to the in-plane unit cell indices. The function $|G(q)|^2$ is plotted in Figure 6 for both a perfectly crystalline slab (v, u = 0), and an equally large slab in which each crystalline *a*,*b*-sheet is shifted by a small random amount of up to 20% of the respective lattice constants in the *a* and *b* directions (v, u =0..0.2). In the case of a perfect crystal, the function exhibits sharp peaks at momentum values q which exactly satisfy the Bragg condition and smaller finite size peaks adjacent to these. The shape and magnitude of the Bragg maxima do not depend on the values of the HK in-plane indices. In contrast, in the pseudocrystalline slab while the (00L) peaks are unaffected by the small translational, random shift between the layers, the out-of-plane (HKL) peaks (|H| + |K|)> 0) are broadened and there is significant intensity between the Bragg peaks.

A similar effect is observed when the layering faults between adjacent layers involve layer rotations instead of translations. The simulation and results are shown in supporting materials. In reality, the interlayer disorder is probably a superposition of both translational and rotational disorder. From the qualitative correspondence between the experimental and theoretical results, we conclude that most likely the disorder between successive crystalline a-b layer sheets is responsible for the observed broadening of out-ofplane peaks that only occurs in peaks with nonzero HK indices. In particular in the case of high aspect ratiomolecules, such as those studied here, the ratio between inplane and out-of-plane intermolecular interactions is small. From an energetic point of view, this may lead to a decreasing interlayer (out-of-plane) registration between successive a-b crystal planes with increasing molecular aspect ratio.

For GIXD images of the 20 nm FTTF films grown at 100 °C, the intensities of out-of-plane peaks were measured

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Figure 7. (a) Comparison of simulated (best-fit crystallographic refinement) and experimental GIXD intensities of a 20nm FTTF thin film grown on an OTS treated Si substrate at $T_D = 100$ °C. The diffraction intensity is indicated by the area of half-circles. A satisfactory fit is achieved by fitting 9 parameters (3 angles for each molecule and the position of the second molecule with respect to first molecule) to 20 experimental peaks. (b) Molecular alignment of FTTF molecules as obtained from the crystallographic refinement calculations. The two FTTF molecules in the unit cell adopt a herringbone packing motif, their long molecular axis enclosing an angle of 67.2° with the substrate plane. In this figure, blue circles represent the carbon atom, yellow circles represent the sulfur atom and white circles represent the hydrogen atom.



Figure 8. Bragg rod profile for the 2 nm FTTF thin film grown on an OTS treated Si substrate at $T_D = 100$ °C. Also shown in the graph is the calculated diffraction profile using the crystal structure obtained from fitting the diffraction data for the 20 nm film.

and used to determine the alignment of the two FTTF molecules in the unit cell by crystallographic refinement (details reported elsewhere¹⁷). In order to make the refinement calculations computationally feasible, our approach hinges on the assumption of rigid molecules with the atomic positions within the molecule given by that for the bulk crystals. This assumption is justified for aromatic molecules which comprise a large delocalized pi-electron system³⁶ but less so for the alkyl-substituted FTTF derivatives for it is well-known that alkyl chains can adopt nonlinear conforma-



Figure 9. NEXAFS spectrum recorded for a 50 nm thin film of C6FTTF grown at $T_D = 100$ °C on an OTS treated Si substrate. The normalized total electron yield spectra (nTEY) are plotted vs the incident photon energy. The resonance peak at 285.3 eV corresponds to the $1s \rightarrow (C=C)\pi^*$ transition of the aromatic sp2-hybridized carbon atoms in benzene rings and thiophene rings. The resonance peak at 287.7 eV is from the $1s \rightarrow (C=H, C=S)\sigma^*$ transition. The resonance peaks around 292 eV is from the $1s \rightarrow (C=C)\sigma^*$ transition.²⁶



Figure 10. Dichroic ratio of the $1s \rightarrow (C=C)\pi^*$ resonance of C6FTTF (a) and C12FTTF (b) thin films of different thicknesses and growth conditions. Independent of the type of surface treatment, thin films (3 nm and 6 nm) of C6FTTF and C12FTTF have comparable dichroic ratios. However, for thick films (50 nm), C6FTTF has a significantly lower dichroic ratio than C12FTTF.

tions (e.g., Gauche defects). Therefore, crystallographic refinement calculations were only performed for GIXD data of unsubstituted FTTF films. The calculated intensities were corrected by application of appropriate Lorentz, polarization, and Debye–Waller factors (the latter estimated from available pentacene data).³⁷ The packing of FTTF molecules shows the typical herringbone motif with two molecules in the unit cell. The angle between the long molecular axis and the

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Figure 11. (a) nTEY spectra for thick (50 nm) C12FTTF grown at 25 °C on an OTS treated surface; (b) nAEY spectra for thick (50 nm) C12FTTF grown at 25 °C on an OTS treated surface; (c) nTEY spectra for thick (50 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for thick (50 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for thick (50 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for thick (50 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for thick (50 nm) C12FTTF grown at 100 °C on an OTS treated surface. A significant decrease was observed for the ratio between $1s \rightarrow (C=C)\pi^*$ and $1s \rightarrow \sigma^*$ resonance peaks for samples grown at a high substrate temperature. No significant change for this ratio was observed for samples grown at room temperature.

substrate surface is about 67.2° ; the herringbone angle that is defined by the planes of the two translationally inequivalent molecules is about 55°. The simulated diffraction intensities of 20 diffraction peaks and the corresponding experimentally obtained intensities are plotted in Figure 7.

Using the crystal-packing configuration determined from the structure refinement of diffraction data for the 20 nm film, diffraction profiles for 2 nm FTTF thin film were simulated and compared with experimental results. Figure 8 shows the calculated and measured 2 nm FTTF Bragg rod profiles. The reasonable agreement between the experimental and simulated Bragg rod profiles indicates that the molecular packing is the same in the 20 nm and 2 nm FTTF films.

NEXAFS Spectroscopy. The determination of molecular alignment within the unit cell from GIXD patterns is difficult for FTTF derivatives with long alkyl chain substituents because they lack conformational rigidity. NEXAFS spectroscopy can resolve this challenge by providing the average tilt angle over all molecules of the FTTF conjugated plane with respect to surface normal. Correlating molecular orientation to growth conditions provides insight into growth mechanics and the influence of substrate temperature. Comparing molecular orientation to that expected from the solved FTTF packing structure reveals strong similarities. Finally, a depth-sensitive comparison of NEXAFS spectra by two modes of collection reveals the surface-relative facing of the asymmetric molecules.

NEXAFS Spectrum of the Asymmetrically Substituted FTTF Series. Figure 9 shows carbon 1s K-edge NEXAFS spectra recorded by means of the TEY signal for the asymmetrically substituted FTTF derivatives studied in this work. These spectra have been recorded for a series of different X-ray incidence angles to vary the angle of the electric field vector (orthogonal to the beam) with respect to the resonance orientation. As the X-ray incidence angle moves from glancing to normal, the intensity of the $1s \rightarrow$ $(C=C)\pi^*$ resonance peak increases, indicating that the 1s \rightarrow (C=C) π^* orbital is oriented parallel to the sample surface. Since the π^* orbital is oriented perpendicular to the plane of the aromatic rings of the FTTF core, 23,26 this result indicates that the core has an edge-on preference, although it does not reveal the tilt of the core long axis. However, the d-spacing measured from GIXD is close to the molecular length, so we can conclude that the FTTF core long axis must be nearly vertical, which is self-consistent with an edgeon conjugated plane. A quantitative analysis of the angle dependence (linear dichroism) of the $1s \rightarrow (C=C)\pi^*$ peak intensity yields an azimuthally averaged molecular tilt angle (relative to the surface normal). This tilt can be expressed as a dichroic ratio, which has been defined in the previous work,²⁵ and can be calculated following the procedure

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Figure 12. (a) nTEY spectra for submonolayer (3 nm) C12FTTF grown at 25 °C on an OTS treated surface; (b) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 25 °C on an OTS treated surface; (c) nTEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface; (d) nAEY spectra for submonolayer (3 nm) C12FTTF grown at 100 °C on an OTS treated surface.

described in literature.^{25,38} The dichroic ratio varies from 0.7 for a perfectly edge-on conjugated plane to -1.0 for a perfectly flat conjugated plane. Because the dichroic ratio makes no assumption about orientation distribution, we use it to quantitatively compare the extent and direction of molecular orientation preference.

To analyze structure evolution with film thickness, substrate preparation, and substrate temperature, the conjugated plane dichroic ratio was determined for films with a thickness of 3 nm (\sim 1 monolayer), 6 nm (\sim 2 monolayer), and 50 nm, as shown in Figure 10. The TEY sampling mode is surfacesensitive, probing molecules within the topmost \approx 5 nm of the sample. Therefore, the comparison of molecular orientation from TEY spectra for films of different thickness reveals how structure develops as film thickness grows. If we assume that solidified material in underlying layers is not substantially changed when films grow thicker, then this strategy essentially provides a depth profile of orientation preference.

The greatest extents of orientation for C6FTTF and C12FTTF are observed in very thin films (1 to 2 monolayers) grown at high substrate temperatures atop OTS-modified substrates. The dichroic ratios for both materials are 0.50 to 0.55 at these conditions, indicating a pronounced edge-on preference. The similarity of the peak core dichroic ratios to each other and to that of the previously reported C12FTTFC12 core (≈ 0.50),²⁶ suggest similar core packing

regardless of the length of the alkyl substituent or the symmetry of substitution.

The persistence of molecular orientation with film growth varies strongly depending on the substrate temperature and more modestly depending on the substrate chemistry. On 140 °C substrates, the dichroic ratio remains high regardless of film thickness, indicating that the core packing observed in thin films persists to the top of 50 nm thick films. On room temperature substrates, however, the dichroic ratio falls dramatically closer to zero as film thickness increases. We do not interpret this changing dichroic ratio as the emergence of a different packing motif because the GIXD pattern of these films reveals only a single unit cell type and basal plane. The decreasing dichroic ratio must instead be due to mis-oriented crystals, consistent with the substantial arcs in the GIXD patterns of room-temperature deposited material, and may also indicate a substantial amorphous fraction. Samples grown on OTS-treated surfaces exhibit somewhat greater molecular orientation than those grown on plain Si substrates, consistent with the GIXD patterns of those samples, which reveal a higher degree of orientation for the unit cell basal plane.

The lowest dichroic ratios, which are observed atop thick films deposited at room temperature, appear to vary depending on the nature of the alkane substitution. For C12FTTF, the ratio falls to ≈ 0.25 , whereas for C6FTTF, it falls to \approx 0.10. Notably, in C12FTTFC12, the dichroic ratio observed atop analogous films was ≈ -0.20 ,²⁶ indicating a mild plane-

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Figure 13. C6FTTF (a) and C12FTTF (b) thin film transistors were fabricated using thermally evaporated 50nm thick films in top-contact configuration. Substrate temperatures during the growth were $T_D = 25$ °C, 100 and 140 °C. The thin film transistor mobility was measured in the transistor saturation region. (Also plotted in graphs for comparison is the mobility for FTTF grown at $T_D = 25$, 90, and 140 °C.³⁹) C12FTTF showed a better mobility than C6FTTF. Samples grown on an OTS-treated surface showed a better mobility than the one on a plain substrate.

on preference. These differences may be related to differences in molecular diffusivity on the sample surface during growth, and the competition between kinetically and thermodynamically preferred packing. The superior propagation of edge-on orientational order for C12FTTF is reflected in its more oriented crystal basal plane observed in GIXD patterns, and in its superior carrier mobility, as described later.

Comparing NEXAFS Core Orientation to the Solved FTTF Unit Cell. We show above that the peak dichroic ratios of C6FTTF, C12FTTF, and C12FTTFC12 all fall into a tight range of 0.50 to 0.55, suggesting similar core packing. This dichroic ratio can be compared to the calculated π^* dichroic ratio of the unsubstituted FTTF thin film unit cell that we solve in Figure 7. The orientation of the π^* resonance depends on two parameters: the molecular long axis tilt of 22.8°, and the "twist" of the short axis about the long axis, which for both molecules in the unit cell is $\approx 60^{\circ}$ away from a perfectly edge-on condition. The π^* vector for both molecules in the FTTF unit cell is therefore oriented 19.6° off surface normal, which should result in a dichroic ratio of 0.47, assuming a beamline polarization factor of 0.80. The measured dichroic ratios in films of C6FTTF, C12FTTF, and C12FTTFC12 are strikingly similar to that calculated for the solved FTTF unit cell, suggesting that the substituted molecules have core packing similar to unsubstituted FTTF. This conclusion is supported by the fact that all the compounds have monoclinic cells with nearly identical inplane a and b lattice constants.

In very thin films deposited at high temperatures, the dichroic ratios of some substituted FTTF films exceed that of unsubsituted FTTF with a difference that is beyond the uncertainty of the measurement. If we assume that substituted FTTF has the same short-axis "twist," which is supported by the similar unit cell geometry and spacings, then the long axis tilt corresponding to a dichroic ratio of 0.55 would be $\approx 17^{\circ}$. This more vertical molecular orientation could be an effect of the substitution, where the packing of the substituent chains alters the core packing geometry. It is also possible, however, that more vertical orientation is due to a monolayer phase, such as the perfect vertical packing that occurs in monolayers of pentacene.²⁰ The monolayer phase hypothesis appears more likely because extremely high dichroic ratios are not observed in 6 nm films, even on 150 °C substrates.

NEXAFS Measurement of Alignment. Unlike symmetrically substituted FTTFs, asymmetric FTTF derivatives can have an alignment (side chain-up or core-up), which is expected to be important for the respective transistor performance because it determines the proximity of the aromatic FTTF core to the dielectric interface. To probe the molecular alignment, highly surface sensitive Auger spectra (sampling depth ~ 1 nm) were collected simultaneously with the total electron yield (sampling depth > 5nm). Figure 11 shows the normalized total electron yield (nTEY) and normalized Auger electron yield (nAEY) spectra plotted vs the incidence beam energy for 50 nm C12FTTF films grown at both 100 °C and room temperature. While the dichroic ratios calculated from either resonance peak are similar, the relative intensity ratio between the two prominent resonances depends on the data channel (nAEY or nTEY). For samples grown at room temperature, the intensity ratio between the π^* resonance and σ^* resonance is comparable for both channels. However, for samples grown at a high substrate temperature, this ratio is significantly lower in nAEY than nTEY; i.e., the π^* resonance intensity is significantly decreased in the more surface-sensitive nAEY. This result suggests that in the top layer of the thick, high temperaturegrown films, the molecules are aligned with their alkyl chain atop, and the FTTF core is buried under the alkyl chains. In contrast, the room temperature grown thicker films have substantially mis-oriented crystal basal planes (see GIXD discussion above) with consequently more randomly aligned molecules in the very top layer, giving rise to the similarity in the intensity ratios as calculated from the nAEY and nTEY channels.

Even more relevant to the thin film transistor application is the orientation of the FTTF derivatives in the first monolayer adjacent to the dielectric substrate surface. Therefore, the nTEY and nAEY spectra were also simultaneously collected from the submonolayer samples (3 nm; Figure 12). The crystal basal planes are far less mis-oriented in ultrathin films, as observed from GIXD patterns. Consequently, the intensity ratio of π^* to σ^* intensity in nAEY is significantly lower than that in nTEY for submonolayer films regardless of substrate temperature. This indicates that in the first layers of films grown at either substrate temperature, the alkyl chain is pointing upward and the FTTF core is next to the dielectric substrate surface. The persistence of molecular alignment is therefore correlated to the persistence of substrate-relative orientation. At 100 °C, both persist throughout film growth, while at room temperature, both fall off dramatically.

Thin Film Transistor Mobility. As mentioned before, the in-plane a and b are the same for FTTF, C6FTTF, C8FTTF, and C12FTTF, within the measurement error margin. Furthermore, the asymmetrically substituted FTTF derivatives share the same overall crystal packing motif, apparently independent of both growth temperature and surface treatment (with the exception of different degrees of polycrystalline disorder in thick, room temperature-grown films). In a thin film transistor device and with the assumption that the FTTF core is the significant charge transport portion of the molecule, a shorter alkyl chain length should result in larger effective charge transport as on average more FTTF cores would be found within a given distance from the dielectric surface. To that end, films comprised of the FTTF derivatives with shorter alkyl chains should exhibit improved charge carrier transport properties. However, because the carrier mobility is a complicated result of the film morphology and film crystallinity/microstructure, the ultimate transistor performance depends on a number of different factors such as grain size, trap densities, etc.

The thin film transistor mobility was measured in top contact geometry and the results are summarized in Figure 13. In general, the asymmetrically substituted FTTF derivatives exhibit at least as good or more often higher holetransport mobility than their symmetrically substituted counterparts:³⁹ for example, grown at 140 °C, C12FTTF thin film devices show a mobility of $\mu = 0.16 \text{ cm}^2/(\text{V} \cdot \text{s})$ which is higher than the measured for films of its symmetric counterpart C6FTTFC6 with the same overall length ($\mu = 0.11$ $cm^2/(V \cdot s)$).³⁹ Increasing the substitute alkyl chain increases the mobility, for example, C12FTTF showed a better mobility than C6FTTF in all conditions tested. Samples grown on the OTS treated substrates showed almost twice the mobility as those grown on plain Si substrates. A high substrate deposition temperature leads to an increased mobility. These findings are consistent with structure analysis which show that films grown at a higher substrate temperature and on an OTS-treated substrates exhibit a better crystallinity, and thus most likely a lower trap density and consequently higher charge carrier mobility. Furthermore, increasing the alkyl chain length increases the molecule aspect ratio, which has previously been predicted to lead to the more favorable, large grain, layer-by-layer growth.⁴⁰

Conclusions

In summary, combined GIXD and NEXAFS studies for FTTF derivatives show that adding asymmetrical alkyl chains of C6, C8, and C12 does not alter the crystal packing motif significantly, indicating the dominant force dictating the crystal packing is the interaction between FTTF cores. However, the change of alkyl chain (molecular aspect ratio) plays a significant role in 2D and 3D polycrystallite formation, which directly affects the charge mobility. Theoretical modeling enables us to find the detailed tilt configuration in FTTF, i.e., the long axis of two molecules sitting in the same unit cell tilt almost in the same direction, i.e., $\sim 22^{\circ}$ relative to the surface normal. Using NEXAFS, no significant change was found for the tilt of the conjugated core in FTTF asymmetrical derivatives, which is consistent with the fact that GIXD shows the a and b dimensions are almost unchanged when adding different alkyl chains. The study shows that the alkyl chains point away from the interface, making the FTTF core distribution near the interface significantly different from its symmetric counterparts. The impact of the microstructure details on the charge mobility was discussed.

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Supporting Information Available: Diffraction simulation for the layering fault involving rotation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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