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Modelling of Grazing-Incidence X-ray Diffraction from Naphthyl End-capped Oligothiophenes in Organic Field-Effect Transistors

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Abstract

The structure of two naphthylene-capped oligothiophene, 5,5'-bis(naphth-2-yl)-2,2'-bi- and tri- thiophene, thin-film field-effect transistor assemblies has been studied using modeling in conjunction with grazing incidence x-ray diffraction. Although the well known herringbone molecular packing motif is observed in these films for both compounds, density functional calculations and molecular mechanics modeling give evidence for a local polymorphic ordering in which these molecules can be flipped 180° about the long axis. In one case, that of the oligothiophene trimer, a disordered surface induced phase is observed. Prospective structural models are tested and refined using

various supercell constructions optimized by molecular mechanics prior to structure refinements of the thin-film scattering data.

Introduction

Deciphering the structure within organic thin films remains an important goal for fully understanding the behavior of organic electronic (OE) devices¹ including organic field-effect transistors² (OFETs), organic photovoltaics (OPVs) and diverse OFET based sensors.³ Knowledge of the bulk structure often provides a useful reference point but the actual structural ordering in thin-film OE devices can differ in very important ways.⁴ This result should not be surprising given that interfacial interactions are more important in thin films. Ever present in OEs is the inherent anisotropy of the molecular level forces combined with non-equilibrium growth conditions.⁵ This gives rise to a variety of effects including so called surface induced phases (SIPs) and polymorphism.^{6,7} Working devices may even undergo evolution in the structural order during device operation.⁸

From a structural standpoint the family of dinaphthylene terminated oligothiophenes (NaTx's, with $x = 2$ and 3 shown in Fig. 1 respectively) represents a limiting case of a very stiff rod-like moiety with respect to the intramolecular structure in combination with much weaker Van der Waal (VdW) intermolecular interactions. Both the thiophene dimer (NaT2) and trimer (NaT3) compounds form single crystals in bulk suitable for crystal refinement.⁹ NaT2 yields a classic structure¹⁰ in which the long axes of near neighbors are aligned parallel to yield a two-dimensional layer structure along the b - c plane as depicted in the top panel of Fig. 2. Locally, within each layer, two molecules pack into a repeating herringbone motif. NaT2 is found to be monoclinic with $P2_1$ symmetry. NaT3 is more complicated¹¹ and this single-crystal refinement identifies an unusually large three layer repeat in which the middle layer adopts a slightly different tilt angle of the NaT3 long axis in comparison to that in the two adjoining layers. This outcome may be due the distinct differences in

the intrinsic molecular anisotropy between NaT2 and NaT3. As Fig. 1a shows NaT2, with an even number of thiophene rings, has a fundamentally different molecular symmetry from those NaTx compounds having an odd number of rings (such as NaT3 shown in Fig. 1b). Planar NaT2 has inversion symmetry with respect to the black dot signifying the geometric center while NaT3 has mirror symmetry about the axis which bisects the central thiophene ring. The red arrows are intended to further visualize this distinction with regards to the core thiophene units.

Figure 1: Sketches of the molecular structures for NaT2 (top) and NaT3 (bottom) according to single crystal refinements.⁹ The red arrows specify the orientation of the thiophene rings and, in combination with the vertical dashed line, show the different symmetry of NaTx molecules having an even or odd number of thiophene rings.

Thin films, the typical configuration for both OFETs and OPVs, are more difficult to assess by direct methods. There are recent reports¹² highlighting the use molecular modeling in combination with refinement of novel structures in polymer OE thin films. Notable in Ref. 12 is the observation of an SIP having triclinic symmetry and a unit cell containing just a single molecule. To validate this model the authors employed density functional theory (DFT) calculations in tandem with a more traditional structure refinement (SR). In their SR the individual lattice reflections and their intensities were initially tabulated and then refined using a conventional crystallographic *R*-factor with appropriate constraints in the molecular geometry. This method is certainly sound but has limited use in cases where the crystallite sizes become small, the unit cell lattice parameters are large and/or there is appreciable structural disorder. At issue is the appearance of overlapping peaks and broad scattering features. In principal prospective structures and refinements could employ the

1
2
3 full 2D grazing-incidence x-ray diffraction (GIXRD) intensity maps but this approach can be
4
5 computationally cumbersome and requires considerable effort to effectively treat background
6
7 contributions and other experimental scattering artifacts.
8

9 In this paper we report detail structural analyses of NaT2 and NaT3 thin-films in OFETs
10
11 using both molecular modeling and a customized refinement of the GIXRD data with 1D
12
13 “layer-line” scans of the 2D detector data. This work extends prior characterization and
14
15 device studies of NaT2^{13,14} and NaT3.¹⁵ NaT2 thin films adopt a structure similar to that
16
17 of the reported bulk phase whereas NaT3 thin films yield a much more disordered layer
18
19 structure which we identify here as a substrate SIP. Molecular modeling calculations indicate
20
21 that local intermolecular packing disorder is an important complicating factor in this class
22
23 of compounds. Model DFT calculations are used to validate two distinct molecular packing
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25 motifs that are very close in their total energy. The only difference is that, with respect to
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27 near-neighbor pairs forming the classic herringbone motif, one molecule is flipped 180° about
28
29 its long axis.
30

31 To accommodate this proposed alternative packing into subsequent structural refine-
32
33 ments we employ a preliminary step whereby various supercell (SC) model structures are
34
35 first optimized via empirical force-fields in a zero temperature molecular mechanics (MM)
36
37 calculation. These starting structures are then used in the subsequent refinements of the
38
39 GIXRD 2D data. GIXRD 2D maps are computationally simulated and then compared di-
40
41 rectly to the intensities along individual 1D $k\ell$ “layer-lines” (because of cylindrical powder
42
43 averaging these line are really cylinders which appear as lines because of the projection of the
44
45 Ewald sphere onto the area detector). The structure factor (SF) refinements yield reason-
46
47 ably good agreement with the experimental data. A major observation is that introduction
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49 of local disorder in NaT2 can actually improve the agreement slightly and this structure is
50
51 sound from an energetic standpoint as well. Likely consequences of this disorder within the
52
53 unit cell with regards to OFET transport properties are discussed. For NaT3 we are able to
54
55 substantiate a qualitative thin-film model with a molecular packing closer to NaT2 rather
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than that of NaT3 crystals.

Figure 2: Top: The unit cell packing of bulk NaT2 (Model A). Bottom: A proposed NaT2 (or NaT3) packing polymorph (Model B) which, according to molecular modeling and density functional theory calculations, is nearly degenerate in energy. The red arrows and letter designation (i.e., U and D) show the relationships between these two structure. All that is needed is to flip one molecule 180° among the pair about its long axis.

Results and Discussion

Experimental Grazing Incidence XRD

Experimental room temperature GIXRD 2D maps for NaT2 and NaT3 are shown at top in Figs. 3 and 4 respectively. These figures are composite images from two separate 2D maps recorded at differing detector angles as noted previously. We first discuss the NaT2

1
2
3 results. The NaT2 thin films exhibit a textured crystalline structure with peak positions
4 and intensities comparable to those reported for the bulk crystal. All films exhibit a strong,
5 uniaxial alignment so that the reciprocal a^* -axis is parallel to the q_z axis (i.e., perpendicular
6 to the substrate surface) and perpendicular to the b - c plane of the conventional molecular
7 unit cells. There is an isotropic ordering of these crystallites about this a^* axis. With this
8 texture all (hkl) peaks with nonzero h or k actually form concentric rings of scattering about
9 the q_z axis. A very modest arcing of the reflections is also seen and results from crystalline
10 regions not perfectly parallel to the film surface.

11
12 The observed Bragg peaks are noticeably anisotropic in their relative peak widths along
13 various scattering directions. Parallel to the film surface they are much sharper than in the
14 perpendicular direction. The corresponding crystal size anisotropy is even more pronounced
15 because of the significant contributions by the beam and film widths in the q_{xy} direction.¹⁴
16 For NaT2, using a simple application of the Scherrer formula $\xi = 5.66/\Delta q$ where Δq is
17 the full width at half maximum of a scattering peak, yields nominal crystallite coherence
18 lengths ξ in excess of 200 Å for the b - c plane (in-plane) and just 70 Å along the a^* direction
19 (out-of-plane). The in-plane NaT3 coherence length is similar to that of NaT2. Detailed
20 assessments of crystal sizes for NaT2 and NaT3 samples are reported in Table 3 in Ref.
21 14 and in Table 1 of Ref. 15 respectively. These crystal sizes are generally insensitive to
22 film thickness. The overall extent of crystallinity is high, perhaps over 90%, but without a
23 quantitative analysis this is only an estimate.

24
25 For NaT2, given the overall molecular length, this implies that a nominal crystal domain
26 of just four or so repeats along the a -axis and, notably, this is on the order of the film surface
27 roughness. With such a small number of layers there will be considerable lattice fringing
28 and so underlies the relatively large wings of scattering as seen along the q_z direction.

29
30 These well-defined, distinct Bragg peaks are superimposed on a characteristic background
31 which includes weaker diffuse scattering from the thermal motion and static disorder of the
32 oligothiophenes. Finally there are very weak scattering intensities suggestive of a second

Figure 3: Top: A typical room temperature NaT2 GIXRD 2D composite image is shown in which images at two detector positions have been merged (at $q_{xy} = 1.40 \text{ \AA}^{-1}$). The various “layer-lines” are labeled with their respective Miller indices. Bottom: Simulated NaT2 2D GIXRD image from refinement of the $8 \times 1 \times 1$ NaT2 “no flip” model (see text) at room temperature. The area to the left of the yellow dashed lines is typically not observable in the experimental 2D maps. In both cases the image color scales are based on the square root of the scattering intensities.

Figure 4: Top: A typical room temperature NaT3 GIXRD 2D composite image using the procedure as stated in Fig. 3. Bottom: Simulated NaT3 2D GIXRD image from refinement of a $6 \times 2 \times 2$ supercell (with $\beta = 101.0^\circ$) containing a large amount of disorder in the form of 180° flips about the long axis of the molecule. The area to the left of the yellow dashed lines is typically not observable in the experimental 2D maps. In both cases the image color scales are based on the square root of the scattering intensities.

orientation of the NaT2.

Simulated 2D images and the explicit GIXRD data comparisons from this sample at elevated temperatures, at 343 K (70 °C) and at 393 K (120 °C), are included in the supporting materials (i.e., series C, D shown in S10-S15 and G shown in S18-S23). The only noticeable changes are the monotonic shifts in the lattice constants consistent with a nominal thermal expansion within this VdW bonded solid. Thus, with respect to room temperature, most peaks shift to lower wavevector but, because there are also changes in the unit cell angle β , some peaks actually shift to higher wavevector. The full set of unit cell parameter results appears in Table 1

Table 1: Various measured and calculated unit cell parameters under various stated conditions for NaT2 and, with respect to a three layer repeat, NaT3. The 2D map values are from experimental data while all other values are obtained from structure refinements. The $8 \times 1 \times 1$ and $4 \times 4 \times 4$ model R-factors include reflections comprising the 36 most intense resolved peaks. The $8 \times 1 \times 1$ model includes no flipped NaT2 molecules while the $4 \times 4 \times 4$ model includes 12 flipped NaT2 molecules (see text).

Model	a(Å)	b(Å)	c(Å)	β (°)	V(Å ³)	R-fac.	Temp
NaT2							
644331.cif	20.552(8)	5.964(2)	8.120(3)	96.854(6)	988.2(7)	0.052	293 K
2D map	20.436	5.943	8.120	96.92	979.		Room
2D map	20.491	5.947	8.131	96.38	985.		343 K
2D map	20.486	5.961	8.148	96.12	992.		393 K
8x1x1	20.49	6.006	8.183	96.86	1000.	0.114	Room
8x1x1	20.62	6.054	8.292	96.46	1028.	0.106	343 K
8x1x1	20.62	6.027	8.262	96.12	1021.	0.098	393 K
4x4x4	-	-	-	-	-	0.092	Room
NaT3							
644332.cif	73.996(7)	5.917(1)	7.866(1)	92.564(7)	3440.4(5)	0.145	187 K
6x2x2	76.44	5.843	7.942	101.0	3482.		Room

The composite NaT3 GIXRD 2D map, at top in Fig. 4 is distinctly different. A major difference, *vida infra*, is that the observed peak positions and intensities differ noticeably from those of the reported bulk crystal. Moreover, in comparison to NaT2, there is considerably more arcing of the reflections along with broadening and more diffuse scattering along q_z for the specific individual k - ℓ data sets (each of which forms a 1D line of scattering intensity

perpendicular to the film surface in the 2D image). In addition there are weak but discernible localized scattering features along the $(h\ 0\ 1)$ layer-line. These are symmetry forbidden in the conventional herringbone packing of NaT2 and NaT3 chains. As such this provides strong evidence that NaT3 thin films manifest a surface induced phase (or phases) with appreciable disorder.

Another feature that often appears in the NaT3 2D maps are the peaks at the $(h00)$ positions. Technically these $(h00)$ reflections should not be observed because of the intersection of the detector plane with the Ewald sphere. The aforementioned arcing cause weak vestiges of these peaks to appear in some 2D maps (not shown). We note that the nominal three layer repeat reported allows for measurable intensities in all $(h00)$ reflections although the layer structure implies that $h = 3n$ peaks with $n = 1, 2, 3, \dots$ dominate. These NaT3 thin films only exhibit $h = 3n$ reflections along q_z and, as compared to (kl) layer-lines, have sharper peaks widths along q_z . Thus the cited three layer repeat of the bulk single crystals⁹ is absent in this SIP. Interestingly there is also an $h00$ scan from a thin film sample in Ref. 9 that also shows analogous characteristics.

GIXRD data from the NaT3 sample at the same two elevated temperatures, 343 K and 393 K, are shown in a head-to-head comparisons of individual 1D $(k\ \ell)$ layer-line scans with those at room temperature in the supporting materials (series H). Because this phase is more disordered the changes are less distinct than those in the NaT2 sample. Close inspection identifies variations in the peak positions comparable to those seen in NaT2.

DFT and Preliminary MM Modeling

As one might expect, the DFT calculations reproduce the intramolecular geometry relatively well thus validating the observed internal bond lengths and angles within both NaT2 and NaT3 molecules (see Supporting Materials). In NaT2 the largest deviations in the bond lengths reach approximately 0.03 Å (in comparison with those obtained in the single crystal refinements) but most are less than 0.02 Å. For the MM calculations these bond length

variations are generally within 0.03 Å as well but some well known structural attributes cannot be reproduced. For example, the MM3 parameters cannot be configured to mimic the bond length variations within the naphthyl rings without significant revisions. All told these small deviations are not expected to have a meaningful impact in the structural refinements that follow.¹⁶

The optimized DFT energies and unit cell dimensions are shown in Table 2 for the cases when the unit cell coordinates were locked and also when they were allowed to relax. Slightly different minimization algorithms were used in these two cases and so their respective energies cannot be directly compared. However comparisons of the conventional packing, Model A, and that corresponding to the situation where one oligomer is flipped, Model B, provide insight.

In NaT2 both models yield comparable ground-state energies and, as seen Fig. 5, only modest differences in their respective optimized unit cell geometries when the unit cell coordinates were free to move. The largest deviation, 0.26 eV (per unit cell) larger in the case of Model B, corresponds to a difference of about 3 kcal/mol (on a per molecule basis) which is well in the range of acceptable values for justifying polymorphism.¹⁷

Figure 5: (a) Starting NaT2 configuration. (b) DFT optimized Model A NaT2 configuration.

Model A and B optimized unit cell parameters differ noticeably from that of the reported room temperature crystal structure. For example β shifts by about 5°. Some of this is

Table 2: Energy and lattice parameters of the optimized units cells. Fixed implies that the unit cell parameters were locked to those of the single crystal refinements of Ref. 9. In the case of NaT3 a is one-third that of the real crystal.

	Energy [eV]	$a[\text{\AA}]$	$b[\text{\AA}]$	$c[\text{\AA}]$	$\alpha[^\circ]$	$\beta[^\circ]$	$\gamma[^\circ]$	Volume[$\text{\AA}^3$]
NaT2 Fixed								
Model A	-1234.68	20.552	5.964	8.120	90.00	96.85	90.00	988.2
Model B	-1234.50	20.552	5.964	8.120	90.00	96.85	90.00	988.2
NaT2 Free								
Model A	-1234.42	21.198	6.264	7.618	90.00	101.7	90.00	990.5
Model B	-1234.16	21.670	6.464	7.303	89.19	103.4	90.64	995.0
NaT3 Fixed								
Model A	-1455.46	24.665	5.917	7.850	90.00	92.56	90.00	1144
Model B	-1455.40	24.665	5.917	7.850	90.00	92.56	90.00	1144
NaT3 Free								
Model A	-1454.61	25.823	7.133	6.605	90.17	79.24	89.98	1195
Model B	-1453.91	27.780	7.553	6.054	89.90	76.02	90.12	1233

expected because the DFT is a ground state calculation and not at room temperature. However the unit cell volumes clearly reflect the fact that the intermolecular aspects of these DFT calculations are strictly qualitative in any absolute sense. Both ground state structures exhibit unit cell volumes *larger* than that of an NaT2 crystal at room temperature (and vdW bonded solids typically include rather sizable thermal expansion coefficients). There are limitations in the current DFT treatments of dispersion forces in organic compounds and so absolute accuracy is not expected.

The NaT3 DFT calculations are analogous. In the case of fixed unit cell coordinates the energies are essentially degenerate. However, when the unit cell parameters are freed, the variations become more extreme. Once again the DFT unit cell volumes are larger than those of the crystal. The β angle shifts are over twice as large as those in the NaT2 calculations and the lattice constants, a , b , and c vary considerably from that of reported in the single crystal study¹¹ and from each other. The energy difference also is increased. If flipped molecules become incorporated within NaT3 crystals we theorize that these sites will manifest larger local strains and, as such, may be underlying driving force for the peculiar three layer repeat reported for bulk crystals and the disordered SIP we observe in thin films.

We expect that these calculations are qualitative with respect to the actual unit cell parameters but have sufficient relative merit for comparing and justifying structural polymorphs. One point that should be reemphasized is that these are ground-state model calculations whereas all experimental studies are done at temperatures in excess of 295 K.

Structural Modeling and Refinement

The first model calculation discussed, that of NaT2, employed an $8 \times 1 \times 1$ SC containing zero flipped molecules. To first order this is analogous to using a primitive unit cell but now the individual molecular positions and tilts within each layer become allowable free parameters. In this way the SC refinement can potentially identify attributes arising from local distortions. In general any increase in static disorder within the enlarged cell will be compensated by a decrease in the conventional crystallographic Debye scattering factors. Fig. 3 at bottom displays the simulated 2D GIXRD pattern and all key NaT2 features in the experimental data, to the right of the dashed yellow arc, are reproduced.

Figure 6 exhibits head-to-head comparisons of the individual experimental and refined model k, ℓ layers-lines. There are marked deviations, approaching factors of nearly three, in some of the relative peak intensities. Changing the intensity scale from linear (on left) to the square root (on right) better visualizes weaker features. Particularly troublesome are the peak intensities in the $(h\ 1\ 0)$ and $(h\ 2\ 1)$ layer-lines. Exact fits to the lineshapes are also challenging. There is a very noticeable asymmetry with a larger wing appearing on the low q_z side. This may be attributed to anisotropy in the crystal domain sizes and lattice spacings in the direction perpendicular to q_z . Still the final calculated R -factors, 0.072 (with 20 peaks) and 0.114 (with 36 peaks, Table 3 on page S3 in the supporting materials, SM), are quite good but somewhat larger than that reported in the single crystal study⁹ (with an $R=0.05$). Direct comparisons can be misleading because significantly more reflections are accessed in conventional single crystal refinements.

Once local 180° flips, about the long molecular axis, are introduced any subsequent SRs

Figure 6: Comparisons, at left linear and at right square root, of calculated (black) and experimental (color) intensities along various kl "layer-lines" of the NaT2 $8 \times 1 \times 1$ "no flip" model at room temperature.

necessarily become more complicated because of the local relaxation needed to accommodate these defects. Although MM calculations have clear limitations, a preliminary MM minimum energy calculation enables the system to relax locally to more energetically favorable starting configurations.

In Fig. 7 (and series A, pages S4-S6, of the SM) we present the results of a SR using a model in which eight monomer flips have been chosen at random within each $4 \times 4 \times 4$ supercell (and initially relaxed via MM). This refinement once again assumes rigid molecules which, within individual 4×4 layers, are permitted to reorient and translate. We find that the overall displacements are generally small and do not yield significant increases in the MM energies. The R -factor for this and related models including local disorder are slightly less than that in the "no flip" model above. In this case $R=0.058$ (using 20 peaks) or 0.088 (with 36 peaks). The improvement is modest but does not appreciably address the problems with the $(h\ 1\ 0)$ and $(h\ 2\ 1)$ intensities. Increasing the number of random flips to twelve (series B, pages S7-S9, of the SM) yields comparable fits with $R=0.057$ (using 20 peaks)

or 0.091 (with 36 peaks). In both these cases the changes are rather subtle to discern and highlight how difficult it may be to assess local disorder in these and related compounds.

Although the aforementioned systematic failings are not satisfactorily resolved, this analysis clearly demonstrates that a high degree of structural disorder can be accommodated within the crystal interior in addition to the extensive disorder that occurs at the periphery of crystalites at grain boundaries. To our knowledge this issue has not been assessed by rigorous modeling methods in prior publications. This finding has broad significance because of the implications this attribute may have in limiting OE device performance characteristics.

Figure 7: Comparison of calculated (black) and experimental (color) intensities along various kl “layer-lines” of the NaT2 $4 \times 4 \times 4$ model (incorporating eight monomer flips) at room temperature.

Substrate interactions in combination with an increased proportion of surface interfaces may cause thin film lattices to deviate from those of the bulk. The room temperature lattice constants of the NaT2 thin film, as determined from a position analysis of the most intense peaks in the 2D maps, are close to those of the single crystal¹⁰ with the largest deviation that of the a -axis at about 0.5%. The lattice constants deduced from refinement of an $8 \times 1 \times 1$ supercell model are not identical those values derived directly from the 2D maps but the

largest deviation, for the value of b -axis repeat, is only about 0.7%.

Both the NaT2 and NaT3 thin films are fabricated in a non-equilibrium process and so even mild thermal treatment may lead to more ordered structures if the local energy barriers are small. Although increasing temperature generally results in a small increase in the volume of the unit cell, as one may expect in a vdW bonded solid, any other changes were minimal. The most significant observed difference is a monotonic decrease in the β angle of approximately 0.7° with the 120 K increase in the film temperature.

As far as 2D GIXRD patterns are concerned there are small scale systematic intensity changes and peak position shifts consistent with variations in the lattice constants and slightly increased thermal motions. The calculated R-factors from analogous fits to the data at 343 K and 393 K do not vary appreciably (sets C and D, pages S10-S15, in the SM) from those at room temperature.

We now turn to the NaT3 structural analysis. Modeling the NaT3 thin film structure is necessarily more complicated for at least two reasons. Firstly, the molecule itself is slightly larger with an additional seven atoms from the third thiophene ring. Thus there is a greater likelihood of closely related local energy minima in the molecular packing. Secondly, the reported single crystal unit cell has a nominal repeat consisting of three molecular layers. Using the reported crystallographic .cif file¹¹ as a starting point we address the existence of two symmetry related molecular orientations within the middle layer by constructing a six layer (i.e., 12 molecules) facsimile and then optimizing this structure by an MM energy minimization. The structure function for this model yields peak intensities and positions in reasonably good agreement with those obtained in the reported single crystal NaT3 structure.

The simulated 2D image (E1 on page S16 of the SM) does not well match that of the experimental thin film data. This misfit is better seen in a direct comparison of the various resolved layer lines as shown in E2, page S16, of the SM. Neither the peak positions nor the general scattering intensities are in reasonable agreement. As such this unambiguously supports the assertion that NaT3 thin films manifest a SIP. There are at least two reason-

able starting points for addressing the structure within the disordered SIP of NaT3. One possibility is that the nominal single crystal structure still persists in the thin films but it has a distorted unit cell lattice which includes increased appreciable disorder. Alternately one could look at the motif as observed in NaT2 thin films and then incorporate additional disorder. Of these two possibilities the modeling indicates that the latter structural ordering is more likely. Starting with the NaT3 single crystal model just discussed, then setting $\beta = 94.76^\circ$ and increasing the a -axis repeat by 0.3% and thereafter employing a MM optimization yields a scattering pattern shown in Fig. 8 at left. There is exceptionally good agreement with respect to the features in the $(h\ 1\ 1)$ layer line but, unfortunately, this model fails badly just about everywhere else. We also reiterate that there are no $(h00)$ reflections consistent with anything but a nominal single layer repeat.

Figure 8: Left: Comparison of calculated (black, for a model approximating the single crystal structure with $\beta = 94.76^\circ$) and experimental (color) intensities along various kl “layer-lines” for an NaT3 thin film. Right: Comparison of calculated (black, for the NaT3 model discussed in the text (with $\beta = 100.96^\circ$) and experimental (color) intensities along various kl “layer-lines” for an NaT3 thin film

The alternate approach, based on the single layer repeat seen in NaT2 and then introducing a large number of flipped molecules, does much better but still has shortcomings.

The simulated 2D scattering pattern, shown at bottom in Fig. 3, strongly resembles that of the experimental data with respect to the strongest scattering features. However direct comparison of the individual layer lines as seen in Fig. 8 at right shows clear disagreement in places. For example there is relative poor agreement for peaks forming the $(h\ 2\ 0)$ layer line. A large number of related models were tested without notable improvement. It is likely that a SC containing just 48 individual molecules may be just too limited in scope to adequately mimic this SIP. Subsequent molecular dynamics studies at finite temperatures may provide better insight.

Conclusions

The presence of structural disorder and its effects on electron transport within organic hosts are issues which have seen much effort especially in recent theoretical studies.^{18,19} Computational methods have advanced so that sufficiently small molecules or clusters can be assessed with ab initio methods whereas larger systems necessarily rely on calculations based on various empirical force fields.²⁰ This disorder can be both static, as considered here, or dynamic, from finite temperature effects. Depending the specific nature of the material this disorder can be responsible for either increasing or decreasing charge carrier mobilities.²¹ From the perspective of electronic or optical properties, which typically transpire at nanosecond or shorter time scales, dynamic disorder has almost a static appearance because of this temporal disparity.

As far as NaT2 thin films go, we infer that its charge mobility will almost certainly be impacted by the presence of the flipped molecules. Without follow up calculations of the transport we can only speculate. If these molecules leads to poorer transport then increasing crystallite size, which is often suggested as a method for enhancing charge transport, may not be an especially useful strategy.¹⁴ It is interesting to note that NaT3 thin-film OFETs, which clearly incorporate greater structural disorder than NaT2, typically exhibit higher

mobilities⁹ but are still approximately a factor of ten less than that of NaT4.²²

On the other hand it would be of great utility if, in the molecular design of small molecule OFETs, to develop materials which could be rendered insensitive to this type of disorder. Recent efforts, e.g. pentacene,²³ seek to more fully relate thermal and transport properties by both experimental and computational methods. Of course pentacene, which has bilateral symmetry along its long molecular axis, will be insensitive to these 180° flips.

Deciphering the molecular level structure and its relationship to electronic or optical properties within organic thin-films remains a challenging research topic^{24,25} and, despite intense efforts over many decades, important questions remain. From a structural perspective one desires a full quantitative agreement between the experimental results and model structures.^{26,27} This study of NaT2 thin-films supports the assertion that appreciable structural disorder is present within the interior of crystalline regions. The SIP that typifies thin-film NaT3 samples exemplifies the strong sensitivity of structural phase behavior to the material and environment. While both models achieve reasonably good fits to the experimental data there are systemic shortcomings whose exact origin remains a mystery. Quantitative agreement is an enviable goal but, as is often true in complicated systems, questions of uniqueness will arise.

Experimental

The experimental OFET devices used in this work and film characteristics have been reported previously.^{13–15} NaT2 and NaT3 have many similarities. Phenomenologically, these films exhibit a plate like crystal habit when grown on SiO₂. The top surface of the films exhibits a surface roughness ranging from 6 to 8 nm in the thinner films and from 2 to 4 nm in thicker films. On occasion fibrous crystals have been obtained. Ref. 14 reports that the film morphology differs near the substrate interface and, after some two to four molecular layers, it then adopts the NaTx end-on layering for the remainder of the films thickness

which ranges from 20 to 40 nm.

The basic OFET structure employs an *n*-doped Si substrate with a 200 nm thick SiO₂ gate dielectric and thin interdigitated Ti/Au *e*-beam fabricated electrodes. Oligomer synthesis used a Stille cross-coupling method outlined in Ref. 28. All NaTx thin films were deposited at room temperature using vacuum sublimation (typically 10⁻⁸ mbar with a deposition rate of ca. 0.1 Å/s) to film thicknesses that varied from 50 to 200 nm. In these multilayer stacks the GIXRD is dominated by scattering from NaTx molecules standing on end with the molecular axes nearly perpendicular to the substrate surface.

Detailed investigation

GIXRD measurements were performed at the UK CRG beamline XMaS (BM28) at the European Synchrotron Radiation Facility (ESRF) inside a enclosed chamber filled with helium gas in order to reduce beam absorption and air scattering. Ten keV X-rays were used to form a nominal footprint of 50 μm × 350 μm (height × width). The specific angle of incidence was optimized for maximum sample scattering intensity (and kept between the critical angles of NaTx and SiO₂ of 0.141° and 0.173° respectively). The 2D intensity images were recorded with an MAR165 CCD detector. Two different detector arrangements were employed: 1. A forward direction scan with a sample-to-detector distance of 338 mm (covering a horizontal *q*-vector range (parallel to the surface) of $q_{xy} < 1.95 \text{ Å}^{-1}$ and vertically (perpendicular to the surface) up to $q_z < 1.5 \text{ Å}^{-1}$ and 2. A second forward scan with $q_{xy} < 3.5 \text{ Å}^{-1}$. These two scans were then scaled and merged to give a single GIXRD 2D image. All 2D maps contained two radially sharp and intermittent rings at relatively high angles corresponding to the scattering from the (111) and (200) reflections of the gold electrodes. Using these reflections as calibration measurements sample-to-detector distances were derived for the angle setup. The raw pixel data were transformed into reciprocal *q* space as described in Ref. 29.

DFT ground-state calculations were used for assessing the relative energies of unit cell structures containing two NaT2 or NaT3 molecules. All DFT computations reported here

employ the Atomic Simulation Environment³⁰ and the GPAW package^{31,32} (PAW for projector-augmented wave method) in combination with meta Generalized Gradient Approximation xc-functionals and periodic boundary conditions. These functionals can be used to model intramolecular covalent bonds.

To account for the weaker long-range interactions a number of functionals were tested. Ultimately the system was modeled with the mBEEF-vdW (meta Bayesian Error Estimation-van der Waals) exchange functional. The mBEEF-vdW xc-functional has been shown to have reasonably good accuracy³³ when estimating lattice constants.

All DFT calculations used a plane wave cut-off energy of 700 eV and Monkhorst-Pack ($1 \times 6 \times 4$) k -point grid. Two different scenarios were examined, one with the lattice locked to the unit cell parameters from Ref. 9 (for NaT3 that implies $a/3$) and the other allowing the unit cells to relax. System relaxation allowed for simultaneous movement of the atoms and the unit cell. The system was considered relaxed when the total force on each atom was less than 0.05 eV/Å. The k -point grid was chosen to satisfy $k_{1,2,3}\mathbf{r}_{1,2,3} > 30$ except for the a lattice repeat (due to its large size). Because of computational time constraints a k -point convergence test was only carried out with locked unit cell parameters.

The MM calculations employed the Tinker package³⁴ using well known³⁵ but here slightly modified MM3 force fields (i.e., MM3*). The suitability and transferability³⁶ of empirical force fields, specifically MM3,³⁷ is important. In our case there were two primary justifications for these *ad hoc* alterations. First, we wished to obtain specific carbon-carbon and carbon-sulfur bond lengths and angles that more closely match those ascertained in the converged DFT calculations and from single crystal refinements.⁹ We presumed that this would reduce overt systematic errors in the calculated intensities of the subsequent SF calculations. The various bond lengths are reported in Tables 1 and 2 of the supplementary materials (SM, on S1 and S2). A second modification was small ad-hoc changes in the intermolecular pair potential Lennard-Jones (LJ) coefficients. Empirical force field expressions are straightforward to use but they, in reality, reflect rather simplistic approximations of the true pair

interactions. Preliminary NaT2 MM (and molecular dynamics calculations as well which are not discussed in this work) yielded equilibrium structures somewhat different than those of the single crystal refinement. Particularly troublesome was the appearance of two distinct energy minima with different unit cell lattice constants and oligomer tilts. With standard MM3 parameters the one lowest in energy had unit cell parameters in poorer agreement with those observed in the single crystal study.⁹ Small changes in the LJ carbon and sulfur potential well depth coefficients (typically as ϵ) lowered the relative energy of the minima which most closely matched the unit cell parameters obtained in the NaT2 single crystal refinement.

The utility of the MM methodology becomes evident in models which include disorder (i.e., flipped NaTx molecules). The two closely related polymorphic structures of interest are shown for NaT2 in Fig. 2. Here the letters U and D (for “up” and “down” respectively) with associated red pointing arrows are used to distinguish the pair. The only difference is that one of the two oligomers comprising the unit cell is flipped 180° about its long axis and reflects a type of orientational disorder. Not surprisingly MM and DFT calculations find that the unit cells of the two cited polymorphs have slightly different equilibrium structures (*vide infra*). Thus when incorporating flipped oligomers into any SC necessitates structural relaxation locally to accommodate this defect and thereby obtain a more reasonable starting structure for use in subsequent SF refinements. SC models containing upwards of 25% of units cells with defects were examined.

Once an optimized MM model was formed the resulting base structure was exported for use in a custom SF refinement. Adjustable parameters includes those of the unit cell plus oligomer orientation and translation (uniformly for the herringbone pairs within each layer). In general the geometry within an individual oligomer was keep rigid so as to limit the number of free parameters. SF intensities for the full grid of reciprocal lattice points were calculated and then projected onto the Ewald surface intersected by the 2D detector following methods well described in Ref. 38. Standard geometrical corrections (i.e., Lorentz and polarization),

multiplicity, Debye thermal factors were all incorporated in the SF calculations. In addition the carbon-hydrogen bond length was shortened approximately 0.25 Å when transferring the MM generated coordinates for use in the SF calculations (an artifact of X-ray scattering which only probes the electron wavefunction). We did not observe scattering signatures indicative of multiple scattering.³⁹ The a^* reciprocal lattice (RL) vector is perpendicular to the substrate but there is cylindrical powder averaging of the RL points about this axis to give a uniplanar⁴⁰ type texture. Additionally there can be arcing and broadening of the RL points due to crystallite finite size distribution and paracrystallinity. These effects were mimicked through a limited set of Gaussian and/or composite Gaussian/Lorentzian functions that were convoluted with the original intensities at each Miller index. These also could be chosen as fixed or constrained free parameters in the SRs. The grid point spacing in the simulation scattering patterns was typically 0.01 Å⁻¹ in both the q_{xy} and q_z directions.

To facilitate direct quantitative comparisons of the simulated 2D GIXRD maps with the experimental data both images were transformed into a series of 1D profiles for every observed $k, \ell \neq 0, 0$ “layer line”⁴¹ by integrating data in appropriate q_{xy} ranges (typically between $q_{xy} - 0.03$ Å⁻¹ and $q_{xy} + 0.05$ Å⁻¹). These 1D profiles represent scattering intensity along the a^* direction (i.e., perpendicular to the film surface). Up to twelve individual sets of 1D data were used in the SRs. The SRs function minimized was a weighted χ^2 of the difference between experimental and calculated layer-lines. The weighting scheme eliminated positions with scattering artifacts and decreased the weighting when the relative scattering intensities were lower. An advantage of this approach was that it allowed for a straightforward consideration of the q_z lineshapes and closely spaced reflections. To enable comparisons by more conventional methods (i.e., an R -factor) the specific position of individual reflections were determined then a conventional unweighted R -factor was calculated using

$$R = \left[\sum ||F_{expt}| - |F_{calc}|| \right] / \sum |F_{expt}| \quad (1)$$

and tabulated. If there are overlapping peaks only the most intense reflection has been identified in the tables. As a starting point the structure of the published NaT2 unit cell was used and our calculated intensities were consistent with those generated with those obtained using standard crystallographic software.

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Supporting Information Available

Included in the supporting information are comparisons of the intramolecular bond lengths and the thiophene C-S-C bond angles. In addition there are numerous simulated NaT2 GIXRD patterns, their comparisons with the experimental data and the explicit Miller indices used for assessing the various quoted R-factors. Finally there are head-to-head comparison of the kl "layer lines" at room temperature and two elevated temperatures for both NaT2 and NaT3.

Tables 1 (NaT2 on S1) and 2 (NaT3 on S2): Comparisons of selected bond lengths and angles.

Table 3 (on page S3): Comparisons of calculated and experimental structure factors for various kl layer-lines for NaT2 room temperature data and the $8 \times 1 \times 1$ supercell model (no NaT2 molecule flips).

A1 to F1: Simulated 2D grazing incidence patterns.

A2 to F2: Comparisons of calculated and experimental intensities for various kl layer-lines.

A3 to D3: As above but using the square root of the intensities.

A4 to D4: Tables comparing the calculated and measured structure factors of selected crystal reflections

Series	Monomer	Temperature	Supercell	Monomer Flips	Pages	Note
A	NaT2	Room	$4 \times 4 \times 4$	8	S4-S6	
B	NaT2	Room	$4 \times 4 \times 4$	12	S7-S9	
C	NaT2	70 °C	$8 \times 1 \times 1$	None	S10-S12	
D	NaT2	120 °C	$8 \times 1 \times 1$	None	S13-S15	
E	NaT3	Room	$6 \times 1 \times 1$	None	S16	Approximates single crystal structure
F	NaT3	Room	$6 \times 2 \times 2$	Included	S17	Best fit

Figures G1-G3 on pages S18-S20: Layer-line intensities ($\sqrt{I}$) for the NaT2 sample at room temperature, 343K, and 393K.

Figures H1-H3 on pages S21-S23: Layer-line intensities ($\sqrt{I}$) for the NaT3 sample at room temperature, 343K, and 393K.

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Grapical TOC Entry, For Table of Contents Use Only

Modelling of Grazing-Incidence X-ray Diffraction from Naphthyl End-capped Oligothiophenes in Organic Field-Effect Transistors

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Depicted is a grazing incidence X-ray diffraction 2D image of scattering from a naphthylene-capped oligothiophene, 5,5'-bis(naphth-2-yl)-2,2'-bithiophene, thin-film field-effect transistor assembly in comparison with an analogous scattering pattern as obtained by molecular modelling in conjunction with structure factor refinement methods.

Depicted is a grazing incidence X-ray diffraction 2D image of scattering from a naphthylene-capped oligothiophene, 5,5'-bis(naphth-2-yl)-2,2'-bithiophene, thin-film field-effect transistor assembly in comparison with an analogous scattering pattern as obtained by molecular modelling in conjunction with structure factor refinement methods.

269x105mm (80 x 80 DPI)