



## Structural Evaluation of 5,5-Bis(naphth-2-yl)-2,2-bithiophene in Organic Field-Effect Transistors with n-Octadecyltrichlorosilane Coated SiO<sub>2</sub> Gate Dielectric

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Interfaces: Adsorption, Reactions, Films, Forces, Measurement Techniques, Charge Transfer, Electrochemistry, Electrocatalysis, Energy Production and Storage

## Structural evaluation of 5,5'-bis(naphth-2-yl)-2,2'-bithiophene in organic field-effect transistors with n-octadecyltrichlorosilane coated SiO<sub>2</sub> gate dielectric

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Luciana Tavares, Jakob Kjelstrup-Hansen, and Matti Knaapila

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11 bithiophene in organic field-effect transistors with n-  
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16 octadecyltrichlorosilane coated SiO<sub>2</sub> gate dielectric  
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4 **ABSTRACT:** We report on the structure and morphology of 5,5'-bis(naphth-2-yl)- 2,2'-bithiophene  
5 (NaT2) films in bottom-contact organic field-effect transistors (OFETs) with octadecyltrichlorosilane  
6 (OTS) coated SiO<sub>2</sub> gate dielectric, characterized by atomic force microscopy (AFM), grazing-incidence  
7 X-ray diffraction (GIXRD) and electrical transport measurements. Three types of devices were  
8 investigated with the NaT2 thin-film deposited either on (1) pristine SiO<sub>2</sub> (corresponding to higher  
9 surface energy, 47 mJ/m<sup>2</sup>) or on OTS deposited on SiO<sub>2</sub> under (2) anhydrous or (3) humid conditions  
10 (corresponding to lower surface energies, 20–25 mJ/m<sup>2</sup>). NaT2 films grown on pristine SiO<sub>2</sub> form  
11 nearly featureless 3-dimensional islands. NaT2 films grown on OTS/SiO<sub>2</sub> deposited under anhydrous  
12 conditions form staggered pyramid islands where the interlayer spacing corresponds to the size of the  
13 NaT2 unit cell. At the same time, the grain size measured by AFM increases from hundreds of  
14 nanometers to micrometers and the crystal size measured by GIXRD from 30 nm to more than  
15 100 nm. NaT2 on OTS/SiO<sub>2</sub> deposited under humid conditions also promotes staggered pyramids but  
16 with smaller crystals 30–80 nm. The NaT2 unit cell parameters in OFETs differ 1–2% from those in  
17 bulk. Carrier mobilities tends to be higher for NaT2 layers on SiO<sub>2</sub> ( $2-3 \cdot 10^{-4}$  cm<sup>2</sup>/Vs) compared to  
18 NaT2 on OTS ( $2 \cdot 10^{-5} - 1 \cdot 10^{-4}$  cm<sup>2</sup>/Vs). An applied voltage does not influence the unit cell  
19 parameters when probed by GIXRD *in operando*.  
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48 **Keywords:** conjugated oligomers; oligothiophenes; OFETs; GIWAXS; GIXRD in operando;  
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50 directional crystallite size  
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## INTRODUCTION

$\pi$ -Conjugated oligomers are often used in organic field-effect transistors (OFETs) and related devices where the interface structure and film morphology including crystal size are closely related to the carrier mobilities.<sup>1-3</sup> Characteristic for these thin-film devices are various crystal growth and interface phenomena including substrate-induced phases (SIPs) driven by the film and device environment and confinement.<sup>4,5</sup> Important factors for the vacuum deposition are the rate of nucleation, the growth mode and the grain size and connectivity.<sup>6-9</sup> In this process, the molecules adsorb and desorb in a dynamic manner. The more tightly the adsorbed molecules are bound to the surface, the less time they have to desorb and the more time they have to diffuse and nucleate into stable clusters with other molecules. Some molecules manifest 2-dimensional growth mode (layer-by-layer or Frank-van der Merwe), whereas others manifest 3-dimensional growth modes (island formation or Volmer-Weber) or their combination (a monolayer-plus islands or Stranski-Krastanov). All this depends on the surface morphology and surface and interface energies.

One commonly employed strategy to modify the interface structure in OFETs is to incorporate a self-assembled monolayer (SAM) atop the OFET gate dielectric.<sup>10-13</sup> The SAM surface smoothens the non-treated surface and typically lowers its surface energy with manifold effects on the morphology and structure of the active layer. While the bulk structure can be significantly influenced by SAMs, every molecule-surface combination has its own specific energetic interactions and must be considered unique.

Bao and co-workers<sup>14,15</sup> compared pentacene deposited on either vapor deposited or spin-coated octadecyltrichlorosilane (OTS) layers on SiO<sub>2</sub>/Si in OFETs and studied these configurations by AFM and grazing-incidence X-ray diffraction (GIXRD). They showed how the spin-coating promotes

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4 crystallinity of OTS and 2D rather than 3D or island growth of pentacene. In another example, the  
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6 same authors used various fluorene-bithiophene-fluorenes as active layers and reported two different  
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8 unit cells, rectangular and monoclinic, depending on the film thickness.<sup>16</sup>  
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11 Elsewhere, Walter et al.<sup>17</sup> prepared similar OFETs with a benzothenodithiophene derivative and  
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13 deposited an OTS layer either under anhydrous or humid conditions. These authors found that both the  
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15 crystal size of the organic semiconductor thin-film and the corresponding charge carrier mobility  
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17 increase with higher relative humidity during OTS deposition.  
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21 In another consideration, Yang et al.<sup>18</sup> studied pentacene OFETs and coated the gate dielectric by  
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23 chemically different poly(imide-siloxane)s with a range of surface energies. The authors found that the  
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25 pentacene growth mode changes from Stranski-Krastanov growth mode to Volmer-Weber mode with  
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27 lowering surface energy. Counterintuitively, the authors observed higher carrier mobilities for the latter  
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29 mode with smaller grains. They interpreted this in terms of better interconnections and improved  
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31 intergrain contacts.  
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35 The possibilities to synthesize  $\pi$ -conjugated oligomers have become exceedingly advanced.<sup>19,20</sup> One  
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37 line of research has been on aryl end-capped oligothiophenes where substitutions are used to avoid  
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39 polymerization, oxidation and degradation and to promote intermolecular packing. The end-caps  
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41 include fluorene,<sup>21</sup> naphthyl and thionaphthyl,<sup>22</sup> *N*-containing aryls,<sup>23</sup> or styrene or 1-pentyl -4-  
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43 vinylbenzene<sup>24</sup> variants to name a few. Common to all these materials are good thermal and chemical  
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45 stability and the carrier mobilities falling within the range of  $10^{-3} - 10^{-2} \text{ cm}^2/\text{Vs}$ . These materials tend  
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47 to form polycrystalline films where the characteristically rigid molecules organize along the surface  
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49 normal in an end-to-end manner.  
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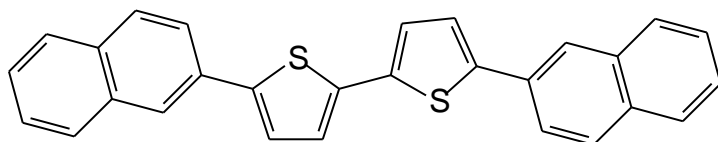
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4 Kjelstrup-Hansen and co-workers have recently placed attention on 5,5'-bis(naphth-2-yl)-2,2-  
5 bithiophene (NaT2) — a naphthyl end-capped oligothiophene synthesized first by Tian et al.<sup>22</sup> This  
6 material is suitable for thin-film devices and maintains its structure in OFETs over long (10 hrs)  
7 periods.<sup>25</sup> It also shows peculiar crystal growth effects forming nanometers thick but micron long  
8 fibrous structures on mica.<sup>26</sup> The nanofibers can be employed further in low voltage phototransistors,<sup>27</sup>  
9 where the molecular alignment in the fibrous structures results in strong optical absorption.<sup>28</sup> This  
10 motivated us to find further ways to control NaT2 structure and morphology.  
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20 In this paper, we investigate structure and morphology of NaT2 in bottom-contact bottom-gate  
21 OFETs with and without an OTS layer prepared under anhydrous or humid conditions. We find that  
22 OTS promotes staggered 3-dimensional structures and increases lateral crystal size from 30 nm to 100  
23 nm. At the same time we observe a slight lowering of the hole mobility. Unlike Walter et al.<sup>17</sup>, we  
24 observe that the OTS layer deposited under anhydrous conditions lead to largest effect on the apparent  
25 grain size and measured crystal size. We also monitor NaT2 structure *in operando* and found it stable  
26 with OTS layer. These results provide new structural insight on interesting NaT2 materials in an OFET  
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## EXPERIMENTAL SECTION

**Materials.** Scheme 1 shows the chemical structure of NaT2. The synthesis of NaT2 followed a Stille cross-coupling approach as described in Ref. <sup>27</sup> OTS (>90%), hexane (95% purity) and toluene (99.8% purity) were purchased from Sigma-Aldrich.

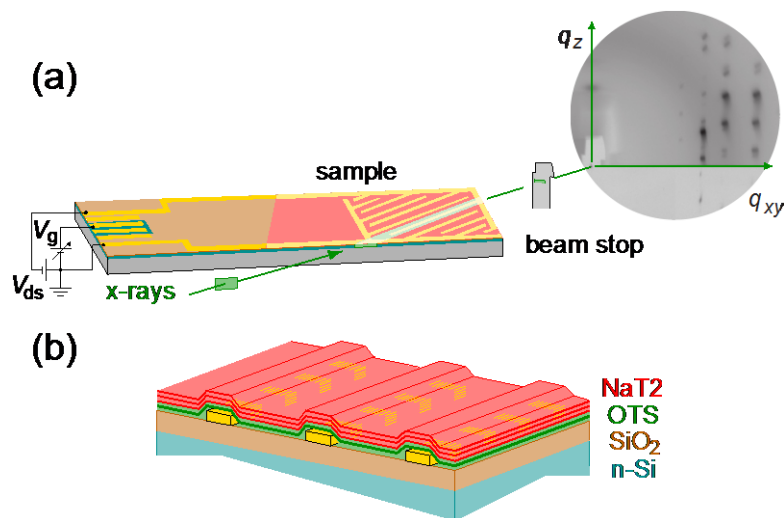
### Scheme 1. Chemical structure of NaT2.



**Substrate fabrication.** Figure 1(a) illustrates the design of employed OFETs. The OFET substrates were fabricated as reported by us.<sup>25</sup> The substrates consisted of n-doped Si that served as both carrier substrate as well as back gate electrode covered by a 200 nm thick thermally grown SiO<sub>2</sub> dielectric layer. Interdigitated source and drain electrodes were prepared by electron beam evaporation of Ti/Au (3 nm/30 nm) and patterned by photolithography and lift-off processes on top of the SiO<sub>2</sub>. Fabricated substrates were cleaned in acetone, isopropanol and lastly deionized water under sonication for 3 min and dried in a nitrogen gas.

The source and drain electrodes were separated by a 500 μm gap and the finger width was 20 μm. The transistor channel had a width-to-length ratio of 269. The area covered by the interdigitated electrode pattern was 10 mm × 10 mm. In this design, only 4% of the active layer was on top of the gold electrodes and most the film was consequently deposited directly on the gate dielectric. The design was made to be compatible with ZIF (zero insertion force) sockets, which allowed easy and consistent sample mounting while performing GIXRD measurements *in operando* (see below).





**Figure 1.** (a) Illustration of employed OFET design allowing GIXRD studies *in operando* and (b) the layer profile of the interdigitated electrode area. Not drawn to scale.

**Table 1. Notation of OFET configurations based on the film thickness and substrate treatment.<sup>a</sup>**

Thickness of NaT2 layer (nm)	No OTS	OTS - anhydrous deposition	OTS - humid deposition
7.9	N8	A8	H8
10.9	N11	A11	H11
25.1	N25	A25	H25

<sup>a</sup> The film thickness is determined by a QCM thickness monitor.

**Organic film deposition.** Figure 1(b) illustrates the deposited layers in the studied OFETs. Table 1 lists the different sample configurations referred to throughout this paper. Three types of devices were investigated. NaT2 film deposited on (1) pristine SiO<sub>2</sub>, (2) OTS deposited on SiO<sub>2</sub> under anhydrous conditions and (3) OTS deposited on SiO<sub>2</sub> under humid conditions. The samples are denoted as “N”, “A” and “H” referring to “none”, “anhydrous” and “humid”, respectively. The subsequent number refers to the nominal thickness of NaT2 layer. This would be the physical film thickness if the all the material was evenly distributed on the substrate. The OTS monolayers were deposited following methods of Walter et al.<sup>17</sup>

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4 For anhydrous OTS depositions, the OTS-toluene solution was mixed in a nitrogen-purged glove box  
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6 and the OFET substrates were immersed in this solution in capped beakers for 15 hours. After  
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8 removing the substrates from the solution, they were cleaned in acetone, isopropanol and lastly  
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10 deionized water under sonication for 3 min and dried in a nitrogen stream. For humid OTS deposition,  
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12 the OTS-hexane solution was mixed in a fume hood with 48% relative humidity. The beaker with this  
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14 solution was left to stabilize for an hour. This ensured equilibrium between the humid air and the  
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16 solution. The substrates were subsequently immersed in this solution for an hour. After removal, they  
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18 were cleaned in the same way as the substrates prepared in anhydrous conditions. Finally, nominally 8  
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20 nm, 11 nm, or 25 nm thick NaT2 layers were deposited on all three types of substrates by vacuum  
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22 sublimation on top of the transistor substrates. The deposition pressure was  $10^{-8}$  mbar and the  
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24 deposition rate  $\approx 0.1 \text{ \AA/s}$ . The film thickness was determined by a quartz crystal microbalance (QCM)  
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26 thickness monitor. All substrates and OFETs were stored under vacuum after preparation and between  
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28 characterizations.  
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34 **Surface energy characterization.** The surface energies of OFET substrates were estimated by  
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36 measuring the contact angles of three test liquids, water, diiodomethane and ethylene glycol. The  
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38 evaluation considers the geometric mean of the dispersive and polar parts of the surface tensions of  
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40 liquids and of the surface energy of solids in terms of Owens-Wendt-Rabel-Kaelbe (OWRK) model  
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42 incorporated in Young's equation. This yields the equation  
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$$\frac{\sigma_l (1 + \cos \theta)}{2\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p} \sqrt{\frac{\sigma_l^p}{\sigma_l^d}} + \sqrt{\sigma_s^d}, \quad (1)$$

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51 where  $\theta$  is the contact angle.  $\sigma_l$  is the surface energy of liquid and  $\sigma_s^p$ ,  $\sigma_s^d$ ,  $\sigma_l^p$ , and  $\sigma_l^d$  the polar  
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53 and dispersive components of the surface energies of liquid and solid. These parameters were evaluated  
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4 by creating a regression line (shown in Figure S1 in the Supporting Information). The total surface  
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6 energy of a solid was subsequently calculated as the sum of the polar and dispersion components

$$\sigma_s = \sigma_s^p + \sigma_s^d. \quad (2)$$

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11 **AFM.** AFM measurements of the thin-film morphology were performed on a Veeco Dimension 3100  
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13 AFM operated in tapping mode using BudgetSensors Tap300Al-G cantilevers. AFM images were  
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15 analyzed using AFM image analysis software Gwyddion.<sup>29</sup>

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18 **GIXRD.** GIXRD experiments were conducted at the UK CRG beamline XMaS (BM28) at the  
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20 European Synchrotron Radiation Facility (ESRF). Samples were mounted onto a custom made circuit  
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22 board allowing electrical connections to a ZIF-socket as illustrated in Fig. 1(a). This circuit board was  
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24 placed inside a nylon/metal-printed sample chamber continuously flushed with helium in order to  
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26 reduce absorption and air scattering. The X-ray energy was 10 keV and the beam size was 50  $\mu\text{m} \times 350$   
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28  $\mu\text{m}$  (height  $\times$  width). The incidence angle was optimized for each sample to maximize the diffraction  
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30 intensity and was kept between the critical angle of NaT2 and SiO<sub>2</sub> (0.141°-0.173°). In this  
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32 configuration, the X-ray footprint spans across the entire board for the employed incidence angles. The  
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34 X-ray intensity images were recorded with an MAR165 CCD detector.

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39 Two different detector arrangements were employed. In the first arrangement, the detector was  
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41 directly in the forward direction and the sample-to-detector distance 338 mm covered the  $q$  vector  
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43 range horizontally up to  $q_{xy} < 1.95 \text{ \AA}^{-1}$  and vertically up to  $q_z < 1.5 \text{ \AA}^{-1}$ , calibrated by a silver behenate  
44  
45 standard. In the second arrangement, the detector was used in two different positions and two datasets  
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47 were merged to extend the horizontal range to  $q_{xy} < 3.3 \text{ \AA}^{-1}$ . In the first position the right-hand edge of  
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49 the detector seen from the beam was tilted 5.6° and the upper edge 7° towards the beam. In the second  
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51 position, the corresponding tilts were 25.1° and 7°. The sample-to-detector distance was also 338 mm.  
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4 The latter data showed two characteristic continuous rings at high angles corresponding to the powder  
5 scattering rings from the (111) and (200) reflections of the gold electrodes (see Figure S6 in the  
6 Supporting Information). Using these reflections as calibration measurements, sample-to-detector  
7 distances were derived for the angle set-up.  
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13 The raw pixel data were transformed into reciprocal  $q$  space as described in Ref. <sup>30</sup>. This allows for  
14 each pixel to be mapped unto the effective detector angles (see Fig. 1 in Ref. <sup>30</sup>). As the samples were  
15 not rotated ( $\phi_h = 0^\circ$ ), the pixels effective angular position corresponded to momentum transfer vectors  
16 in the horizontal geometry as  
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$$\mathbf{H} = \begin{bmatrix} X \\ \cos \omega_h Y + \sin \omega_h Z \\ \cos \omega_h Z + \sin \omega_h Y \end{bmatrix}, \quad (3)$$

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29 where the sample tilt is  $\omega_h = 0^\circ$  for the images in question and where  $(X, Y, Z)$  are momentum  
30 transfers in the laboratory frame. The peak positions were found by fitting cuts along the radial  
31 direction from the direct beam point and the lattice parameters were refined using weighted nonlinear  
32 regression. The refinement used previously reported cell dimensions for NaT2 single crystals as a  
33 starting point.<sup>22</sup> The error estimate of the fitted parameters was found by the diagonal of the variance-  
34 covariance matrix of the fit and is given as  $\pm 1$  standard deviation.  
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43 Figure 2 illustrates the contributing factors to intensity pattern broadening. The observed intensity  
44 pattern is smeared due to experimental imprecision  $G(s)$  as  
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$$I_{obs} = I(s) * G(s), \quad (4)$$

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51 where  $I(s)$  is ideal peak profile that is obtained under an ideal instrumental condition without  
52 instrumental broadening.  
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4 For the vertical profile (crystal thickness), we considered intensity peaks close to the horizontal  
5 direction and one-pixel wide slices across the maxima as depicted in Fig. 2. Under these conditions, the  
6 experimental broadening is given by the beam height as  
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$$10 \quad G_z(s) = b(s), \quad (5)$$

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14 where  $b(s)$  represents the broadening due to the limited beam. However, with the beam height  $50 \mu\text{m}$   
15 of which slightly more than half impinges on the sample, this becomes negligible compared to the  
16 crystal size broadening.  
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21 For the horizontal profile (lateral crystal size), the slices were wider. Considering similar intensity  
22 maxima near the horizontal direction, the experimental broadening becomes a convolution of beam  
23 width ( $b(s) = 350 \mu\text{m}$ ) and a sharply limited function  $p(s)$  representing primary intensity in the  
24 NaT2 film along the finite width of the film as  
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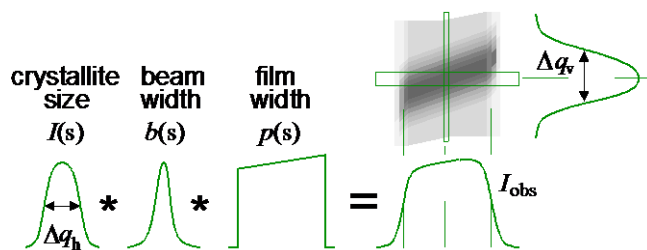
$$31 \quad G_{xy}(s) = b(s) * p(s). \quad (6)$$

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34 Finally, the crystal size was estimated from the peak width analysis using the Scherrer equation  
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$$37 \quad \tau = \frac{5.655}{\Delta q}, \quad (7)$$

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40 where  $\tau$  is the mean crystal size, 5.655 is an approximate shape factor and  $\Delta q$  the FWHM of  $I(s)$ .  
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44 The form of  $p(s)$  depends on the incidence angle and the consistency of estimated crystal sizes was  
45 checked by varying the incidence angle. We estimate that our method is reliable for crystal sizes below  
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**Figure 2.** Schematics of intensity broadening due to the crystal size, beam width and film width.

The terms grains and crystals or crystallites (understood as small single crystals) are usually used interchangeably. In our discussions, however, we denote grains as 3-dimensional domains with vacant grain boundaries as observed by AFM. We denote crystallites as single crystals observed by X-rays (*vide infra*). Thus, grains can be polycrystalline and can contain several crystallites that consist of a single phase.

**Electrical characterization.** Electrical transport measurements were carried out during GIXRD measurements *in operando* by biasing the device with programmable voltage supplies Kepco BOP 100-10 MG and Hewlett Packard E3620A one output for the gate and one for the drain biasing relative to common ground on source and recording the transfer characteristics with a Keithley 486 picoammeter.

A fixed drain-source voltage  $V_{ds}$  was applied starting at  $V_{ds} = 0$  V, to the sample while the gate voltage  $V_g$  was swept from 0 V to -30 V. A 90 s GIXRD measurement was then recorded and the gate voltage swept back to 0 V. This procedure was repeated for  $V_{ds} = 0, -10, -20$  and -30 V. Additional measurements were done using a probe station set-up outside the beamline. The saturation mobility was calculated from<sup>3</sup> as

$$\mu_{sat} = \frac{2L}{C_i W} \left( \frac{\partial \sqrt{I_{ds}}}{\partial V_g} \right)^2, \quad (8)$$

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4 where  $C_i$  is the capacitance per unit area and  $L$  and  $W$  the channel length and width. This assumes  
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7 that the contact resistance is negligible compared to the channel resistance, however, as the HOMO  
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9 level of NaT2 (5.43 eV)<sup>20</sup> is relatively close to the work function of the gold electrodes (5.1 eV), this is  
10  
11 a reasonable assumption. The errors in measured mobilities were estimated from the uncertainties that  
12  
13 result from fitting the measured data to Eq. (8). The threshold voltage  $V_{th}$  was found by the intercept  
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16 between the square of the current  $I_{ds}$  and voltage axis.  
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## RESULTS AND DISCUSSION

**Surface morphology.** We first consider the surface characteristics of the substrates studied by contact angle measurements. Table 2 compiles the surface energies for the employed OFET substrates with pristine SiO<sub>2</sub> and with the OTS layer after anhydrous (A) or humid deposition (H). The data show clearly how OTS layer decreases the surface energy. Pristine SiO<sub>2</sub> was interpreted as hydrophilic and the OTS treated substrates as hydrophobic in nature.

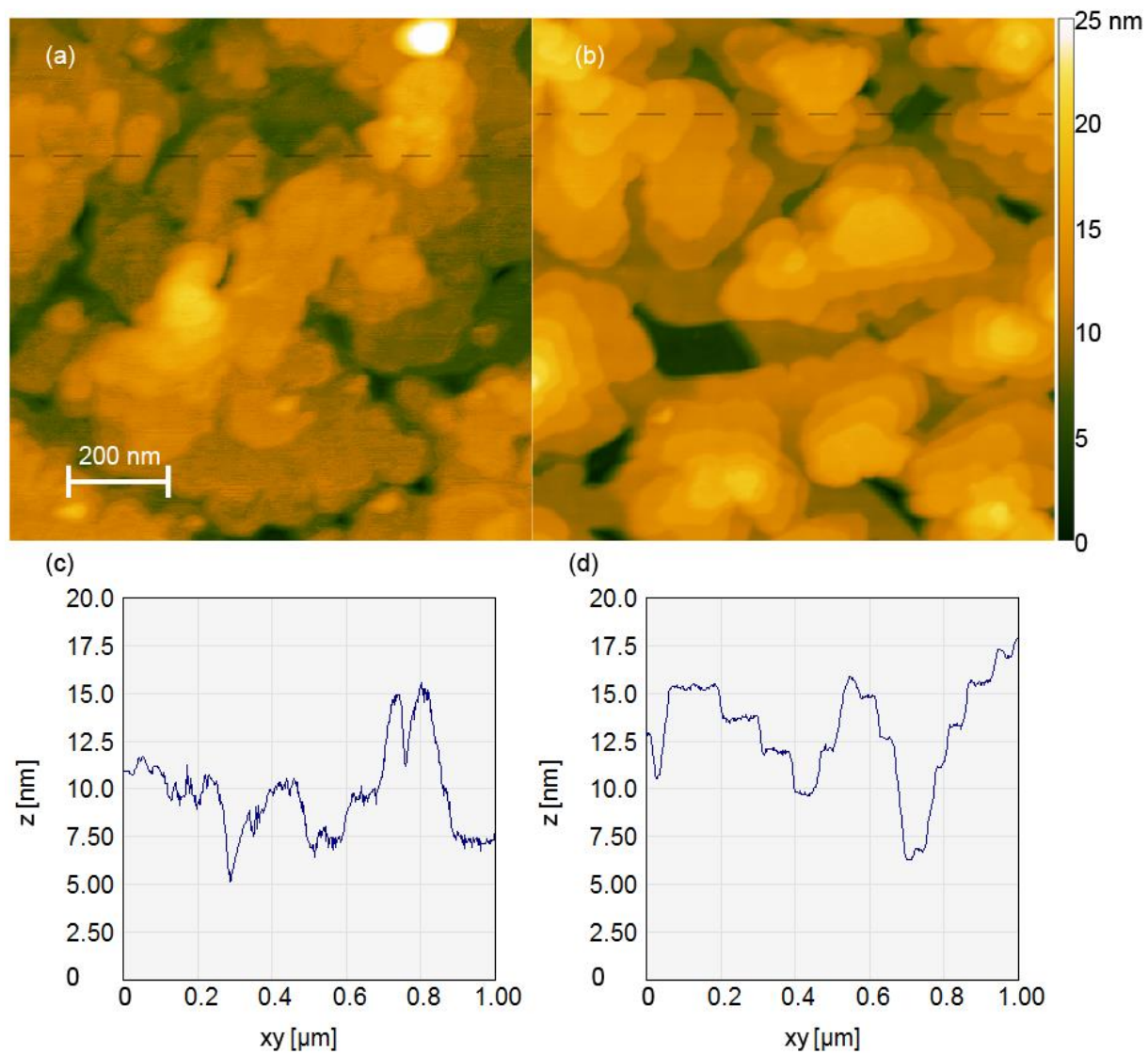
**Table 2. Surface energy of prepared OFET substrates. <sup>a</sup>**

Gate dielectric	Contact angle (°)			$\sigma_s^p$	$\sigma_s^d$	$\sigma_s$
	Water	Diiodo-methane	Ethylene glycol			
SiO <sub>2</sub>	43	70	71	37	10	47
OTS A	102	69	70	1	24	25
OTS H	107	75	84.	1	19	20

<sup>a</sup>  $\sigma_s^p$ ,  $\sigma_s^d$ , and  $\sigma_s$  are the total surface energy and its polar and dispersive components.

We next focus on the surface morphologies of the substrates and NaT2. We observe significant differences between NaT2 layers deposited on pristine SiO<sub>2</sub> or OTS-covered SiO<sub>2</sub>. As the largest differences are between NaT2 layers on SiO<sub>2</sub> and NaT2 layers on anhydrously deposited OTS, we focus on these two cases. We begin our considerations from nominally 11 and 25 nm thick films and continue with 8 nm thick films.

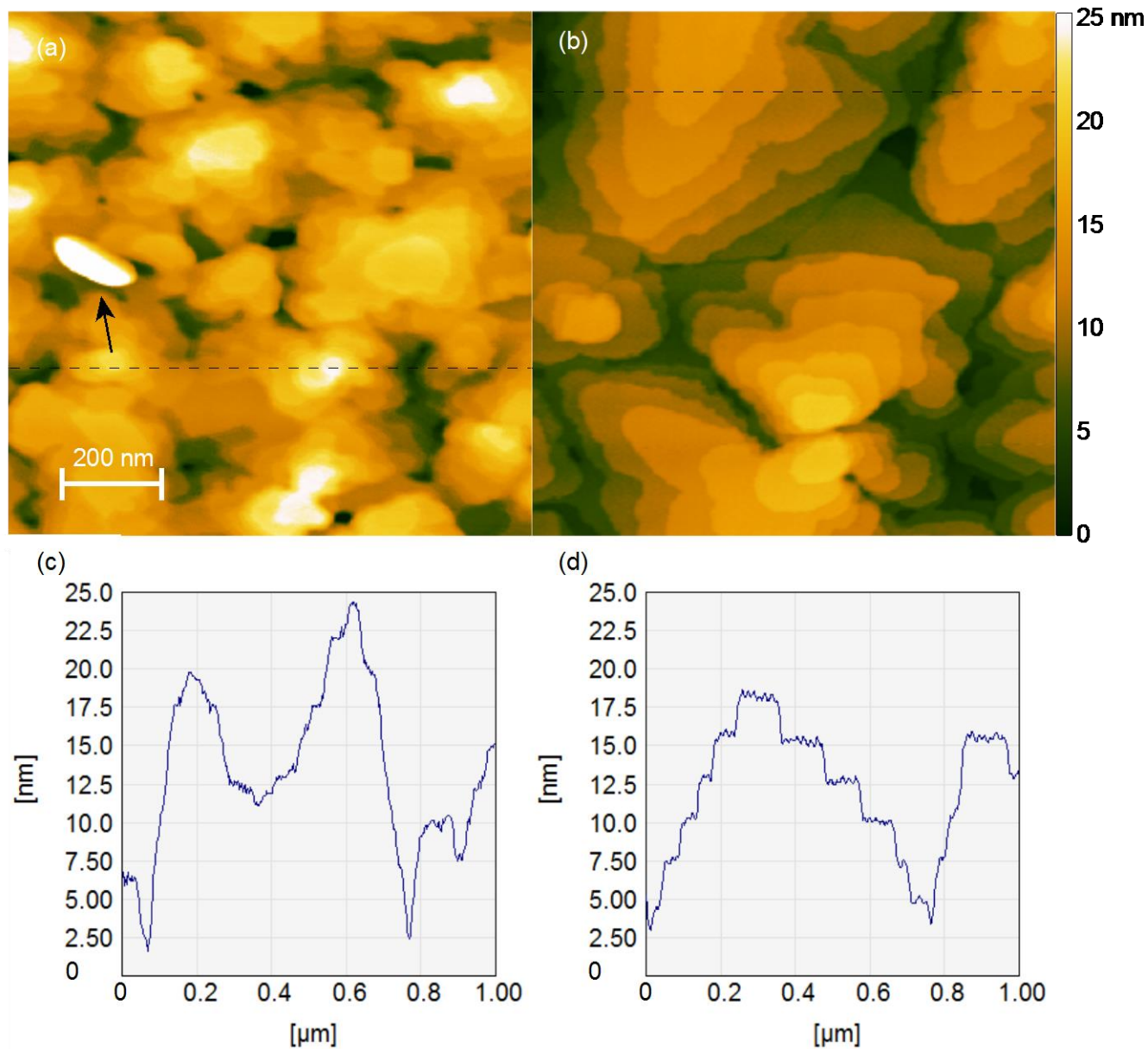




**Figure 3.**  $1\ \mu\text{m} \times 1\ \mu\text{m}$  AFM scans of (a) N11 and (b) A11. Cross sections of (c) N11 and (d) A11 marked by dashed lines in panels (a,b).

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4 Figure 3 shows characteristic AFM scans for nominally 11 nm thick NaT2 films on SiO<sub>2</sub> (panel a)  
5 and on anhydrously deposited OTS (panel b) alongside characteristic cross sections (panels c and d).  
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7 Corresponding 3D presentations are shown in the Supporting Information (Figure S2). All or nearly the  
8 entire surface is covered. In both cases NaT2 begins to form island-like formations, which are 100-300  
9 nm wide and a few nm tall. These islands appear as featureless pyramids on SiO<sub>2</sub>. The situation is  
10 distinctively different on OTS where NaT2 grows as staggered pyramids where each step height  
11 corresponds precisely to one molecular layer (2 nm) or its multiple with the step distance of 50-100 nm.  
12 This is an evidence for well-ordered 3-dimensional islands composed of distinct layers of NaT2  
13 molecules. At the same time, the apparent grain size increases from approximately 100 nm on SiO<sub>2</sub> to  
14 several hundreds of nanometers on OTS. This indicates that the nucleation density is significantly  
15 affected by the presence of the OTS layer leading to fewer and larger grains, which could indicate  
16 higher NaT2 diffusivity.  
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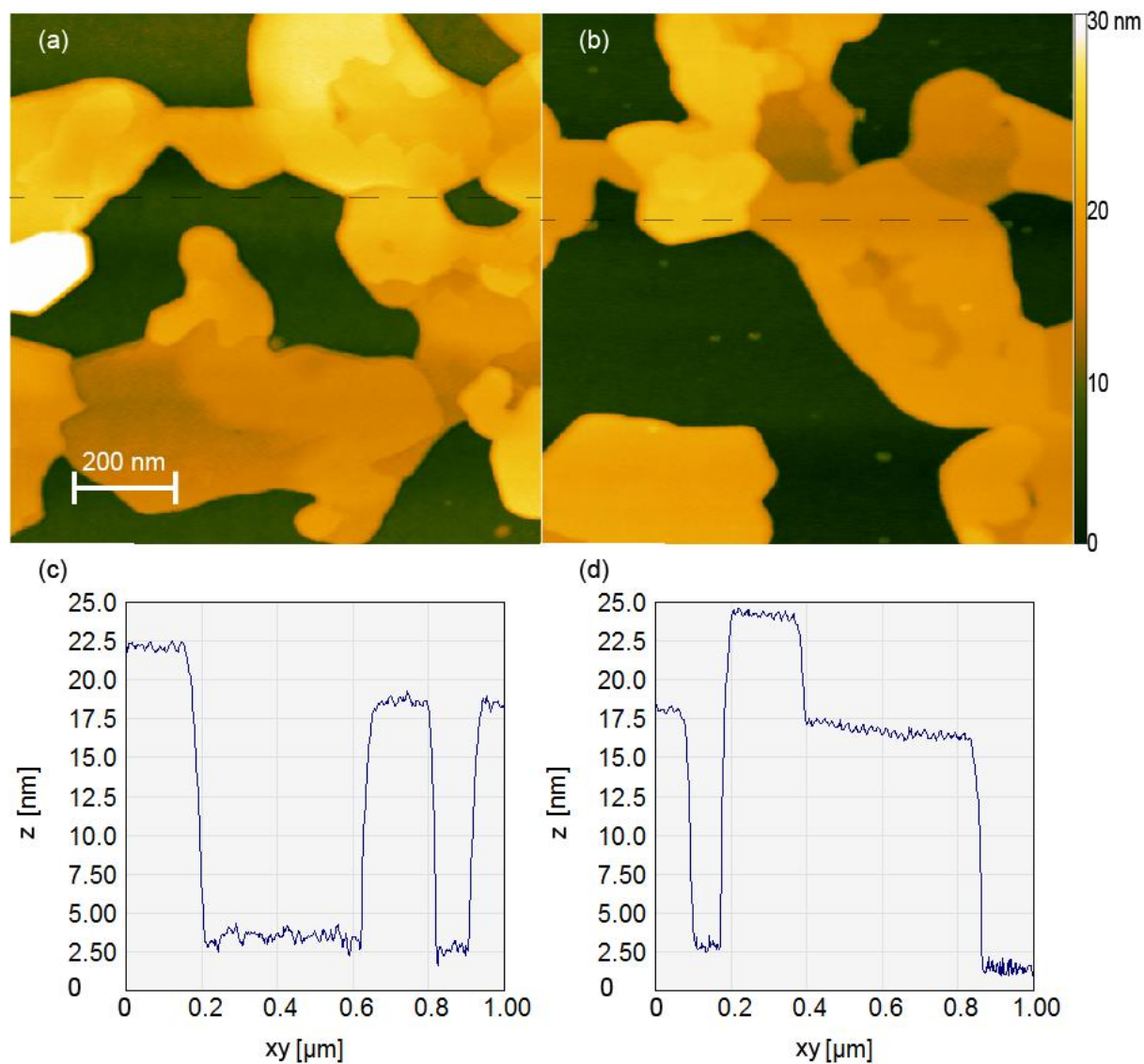
31 Figure 4 shows AFM scans for nominally 25 nm thick NaT2 films on SiO<sub>2</sub> (panel a) and on  
32 anhydrously deposited OTS (panel b) alongside characteristic cross sections (panels c and d).  
33 Corresponding data over 10 μm × 10 μm areas as well as the 3D presentation of Fig. 5(b) are shown in  
34 the Supporting Information (Figures S3 and S4). Again, the oligomer layers assemble as 10-20 nm tall  
35 pyramid grains (counted from the bottommost layer) that appear relatively smooth on SiO<sub>2</sub> and well-  
36 structured and staggered on anhydrously deposited OTS. The step height in the staggered pyramids  
37 corresponds to the individual molecular layer height (2 nm). These grains are clearly larger on OTS,  
38 which is better seen in 10 μm × 10 μm scan (Fig. S3). The characteristic grain size is of the order of  
39 100 nm for N25 and several hundreds of nanometers for A25. The fact that the regular, staggered  
40 pyramid architecture spans over larger macroscopic areas becomes obvious in Fig. S4.  
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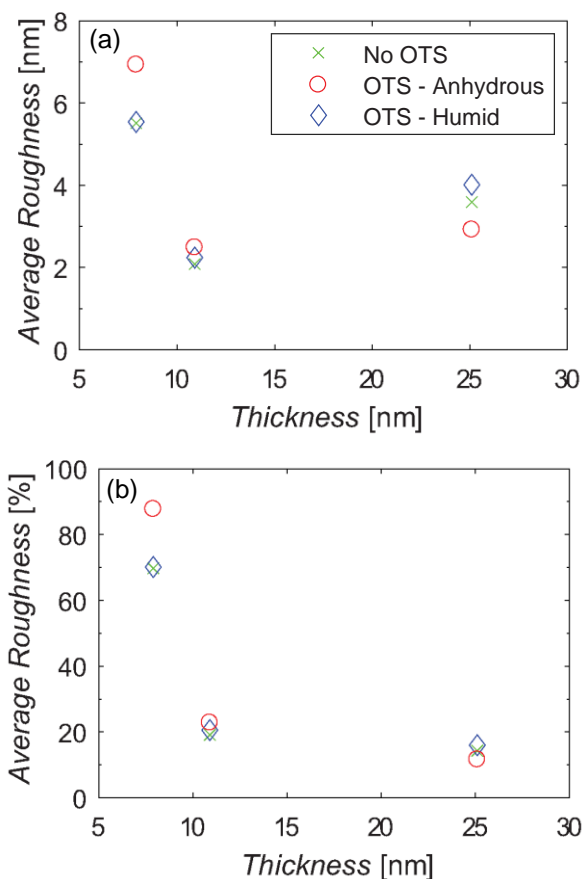
**Figure 4.**  $1\ \mu\text{m} \times 1\ \mu\text{m}$  and AFM scans of (a) N25 and (b) A25. An arrow shows a spike-like “nanofiber”. Cross sections of (c) N25 and (d) A25 marked by dashed lines in panels (a,b).

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4       Regardless of sample preparation, NaT2 layers manifest sporadically distributed 100-500 nm long  
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6 100 nm tall towering structures and these are most frequent for films on the OTS prepared in humid  
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8 conditions. We tentatively identify them as the previously observed NaT2 “nanofibres”,<sup>26</sup> which  
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10 correspond to molecules lying at a small angle to the surface, and which are known to form directly on  
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12 the substrate surface on certain substrates such as muscovite mica under optimized growth conditions .  
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14 One spike-like structure is seen in Fig. 4(a) and several in Fig. S3(b) and Fig. S5(b). Also shown in the  
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16 Supporting Information are the corresponding data for 25 nm thick NaT2 on OTS deposited under  
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18 humid conditions (Figure S5). The observed characteristics of H25 configuration are in between N25  
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20 and A25 containing both terraces and smoother areas.  
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25       Figure 5 shows characteristic AFM scans for nominally 8 nm thick NaT2 films on pristine SiO<sub>2</sub>  
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27 (panel a) and on anhydrously deposited OTS (panel b). Also shown are characteristic cross sections  
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29 deduced from these scans (panels c and d). These thinner films, which represent the early stage growth,  
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31 differ significantly from the above discussed thicker films. Both films contain flat 100-300 nm wide  
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33 domains or grains that form continuous dewetting “percolating” networks over the device surface.  
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35 These domains are approximately 1.5 times thicker (10-14 nm) than the nominal films thickness (8 nm)  
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37 covering approximately two thirds of the surface while the rest of the surface remains seemingly  
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39 empty. The overall thickness corresponds to 5-7 molecular layers each 2 nm thick. The total domain  
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41 volume as estimated from the lowest surface level is close to the amount of substance evaporated for  
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43 the given area. This suggests that the seemingly empty domains are actually empty and there is no  
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45 NaT2 monolayer covering the entire surface. We are not able to say whether the first NaT2 layer could  
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47 be partially embedded in the OTS layer.  
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**Figure 5.** 1  $\mu\text{m} \times 1 \mu\text{m}$  AFM scans of (a) N8 and (b) A8. Cross sections of (c) N8 and (d) A8 marked by dashed lines in panels (a,b).



**Figure 6.** The RMS surface roughness of NaT2 layers on top of pristine SiO<sub>2</sub> (green crosses) and on top of OTS from anhydrous deposition (red circles) or OTS from humid deposition (blue diamonds) in absolute (a) and relative units (observed roughness against the nominal thickness). (b). All data were measured over the area of 10  $\mu\text{m} \times 10 \mu\text{m}$  (Fig. S3 and Figure S5).

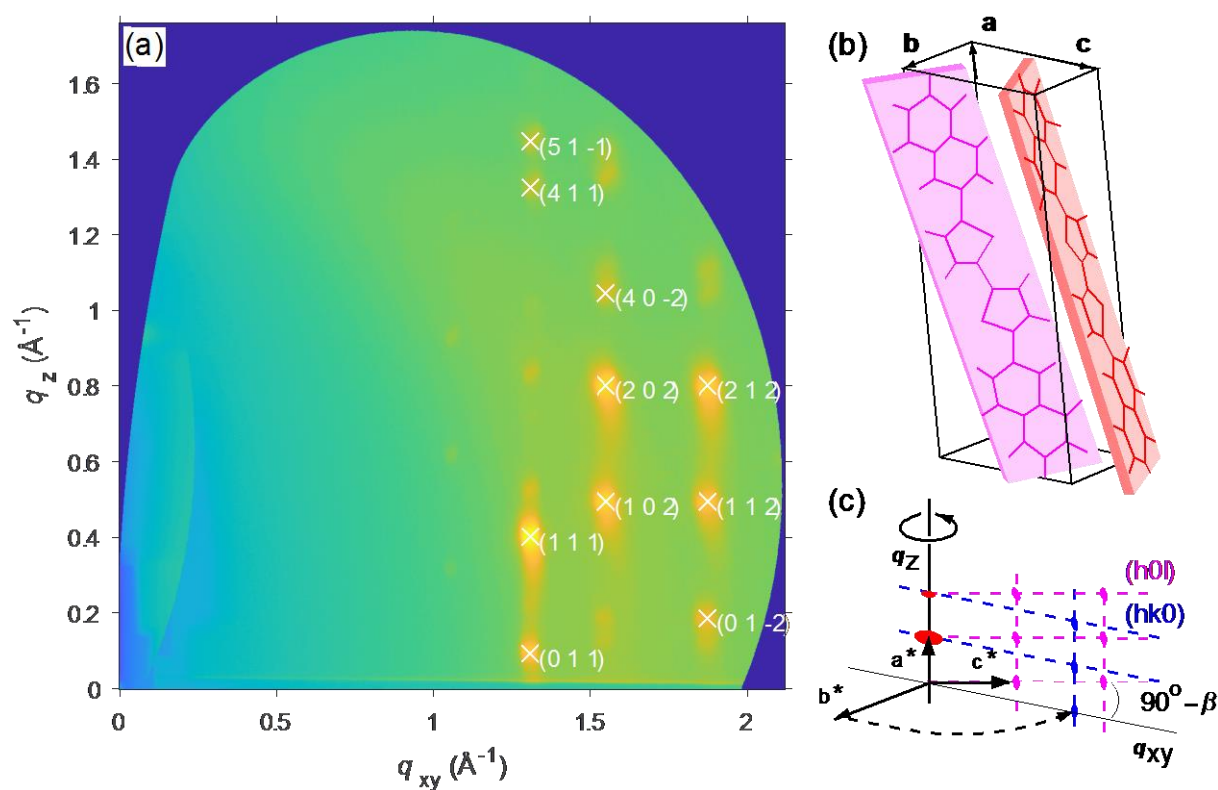
Figure 6 plots the RMS surface roughness of the employed NaT2 films. The surface roughness of nominally 8 nm thick films is about 75-90% of the nominal film thickness. This agrees with the observation of thicker domains covering most but not the entire substrate surface. Thicker films are significantly smoother (11 nm - 20% and 25 nm - 10%).

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4 **Crystalline structure and directional crystal size.** We next focus on the crystalline structure and  
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6 crystal size within the apparent film morphology. For this task we used GIXRD in two settings, which  
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8 provided the overall data for the further analysis.  
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11 Figure 7 shows the GIXRD patterns for N25 at  $q_{xy} < 1.95 \text{ \AA}^{-1}$ . A high and a low angle diffraction  
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13 pattern interlaced of the same sample covering a range of  $q_{xy} < 3.3 \text{ \AA}^{-1}$  are shown in the Supporting  
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15 Information (Figure S6). Corresponding image pairs were taken for all configurations and the lattice  
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17 parameters and crystal sizes were deduced from data like these. Figure S7 plots the so obtained lattice  
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19 parameters for all samples listed in Table 1. The unit cell level structure determined for NaT2 is  
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21 monoclinic for all the employed OFETs with unit cell parameters  
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23  $a = 20.3 \text{ \AA}$ ,  $b = 5.9 \text{ \AA}$ ,  $c = 8.1 \text{ \AA}$  and  $\beta = 96.9^\circ$ . The cells are oriented forming a mosaic of crystallites  
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25 where the  $b$ - and  $c$ -axes on the plane and where the surface normal is defined by  $a \cdot \sin \beta$ .  
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31 Compared to the bulk structure, we do not observe characteristic substrate-induced phases, *i.e.*, other  
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33 polymorphs in OFETs.<sup>5</sup> Interestingly, we do not observe significant differences in the unit cell  
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35 parameters between NaT2 films on SiO<sub>2</sub> and NaT2 films on OTS. The unit cell parameter  $c$   
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37 corresponds to that in bulk while  $a$  and  $b$  are 1-2% smaller in films than in bulk.<sup>22</sup> The unit cell volume  
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39 tends to be smallest for the thinnest films, approaching that of bulk as the film thickness increases up to  
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41 25 nm (Figure 8). This trend is less clear for films on anhydrously deposited OTS which do not show a  
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43 clear trend towards unit cell parameters of bulk. These effects may stem from differences in physical  
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45 bonding between employed substrates and the first NaT2 layer,  
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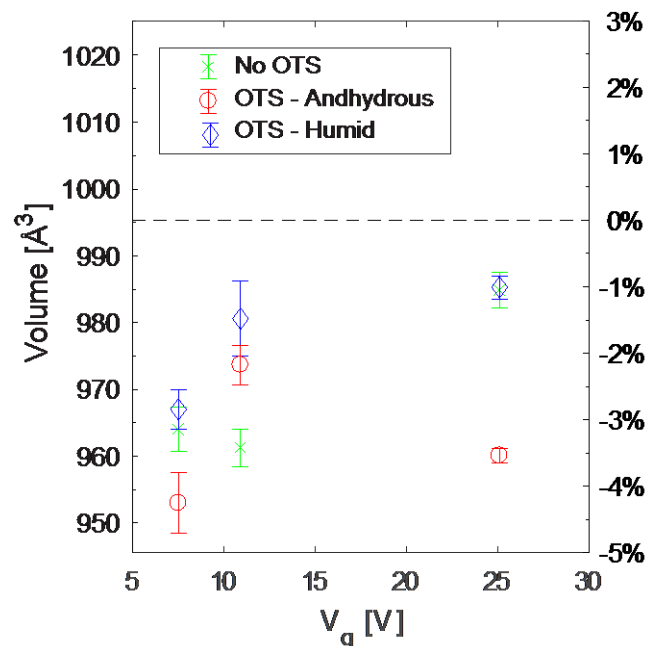




**Figure 7.** (a) GIXRD pattern of N25. White crosses mark the fitted peaks used for structure refinement.

(b) Schematics of NaT2 unit cell and (c) experimental coordinates.





**Figure 8 .** NaT2 unit cell volume for the studied sample configurations. Green crosses refer to pristine SiO<sub>2</sub> and red circles and blue diamonds, respectively, to OTS deposited under anhydrous or humid conditions. A horizontal line marks the unit cell volume in bulk reported by Tian et al.<sup>22</sup>

**Table 3. Crystal sizes corresponding to various crystallographic planes compared to the film thickness estimated from the X-ray data.**

Sample	Crystal size in given directions				Thickness [nm]
	(010) [nm]	(h11) [nm]	(002) [nm]	(012) [nm]	
N8	36	50	28	35	12.3 ± 0.2
A8	> 100	90	45	54	13.4 ± 0.6
H8	37	58	31	35	16.1 ± 0.4
N11	28	25	16	16	9.3 ± 0.4
A11	73	79	33	40	11.5 ± 0.4
H11	47	47	23	28	10.9 ± 0.7
N25	29	39	21	24	19.6 ± 0.2
A25	> 100	> 100	58	65	19.7 ± 0.4
H25	63	79	28	37	20.2 ± 0.3

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4 Table 3 compiles the determined crystal sizes for NaT2 along four crystallographic planes for all here  
5 employed OFETs. Also shown is the corresponding film thicknesses estimated from the X-ray data.  
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7 While the unit cell structures remain similar regardless the sample configuration, OTS promotes larger  
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9 NaT2 crystals, especially when the OTS is deposited under anhydrous conditions.  
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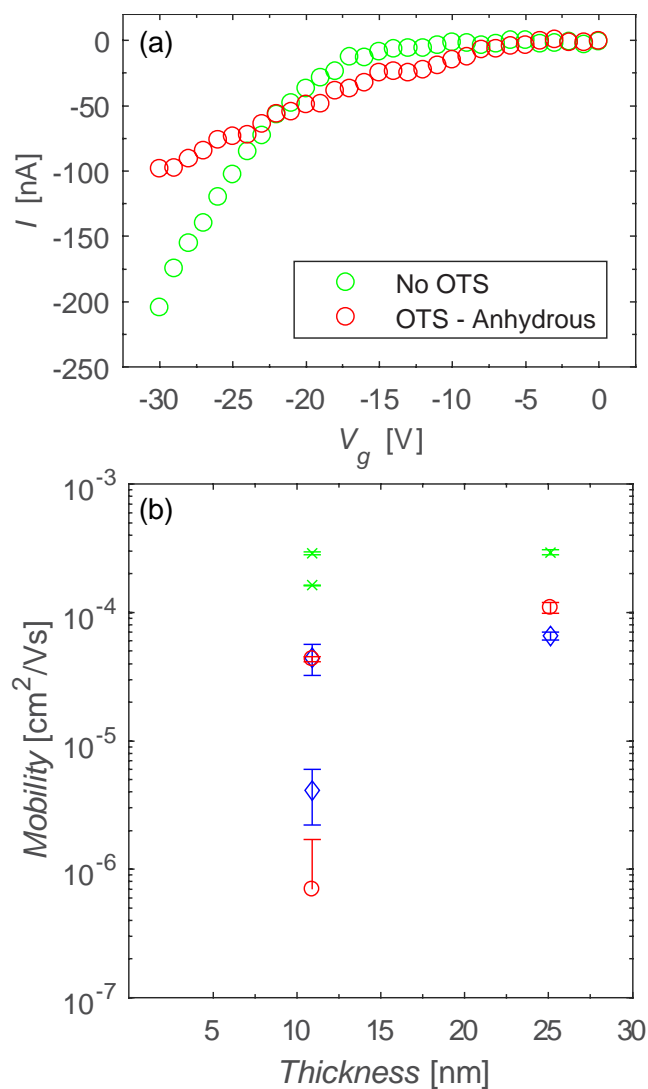
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13 We can identify the following tendencies. First, considering every possible configuration, the crystal  
14 size is smallest for NaT2 films on pristine SiO<sub>2</sub> and largest for NaT2 films on OTS prepared under  
15 anhydrous conditions. The crystal size for the NaT2 films on OTS prepared in humid conditions is in  
16 between these two cases. Second, crystal size is larger along the b-direction than along the c-direction.  
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18 Third, the trends in the lateral crystal size follow those in the grain size. We note that while crystal  
19 sizes of A8 and N8 are very different, this difference is notes reflected in their morphology as shown  
20 by AFM images (Fig. 5). This implies that the morphological domains of N8 consist of several small  
21 crystals observed by X-rays. For the two thickest films the calculated film thicknesses agree with the  
22 nominal thicknesses determined by QCM measurements. Similarly, the crystal size along the surface  
23 normal corresponds to around 80-100% of the average film thickness for the 11 and 25 nm films,  
24 indicating a mosaic of single crystals. For the nominally 8 nm films the measured thickness maximum  
25 exceeds the nominal by around 50-100 %. This is not an artefact but reflects the 10-14 nm tall domains  
26 covering roughly 2/3 of the device surface.  
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4       **Electrical characterization and crystalline structure *in operando*.** We will finally consider the  
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6 electrical characteristics of the prepared OFETs — whether the morphology and crystal size influence  
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8 their performance and whether the crystalline structure is influenced by the transistor operation. The  
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10 IV-curves were measured for all the samples and the GIXRD images were recorded simultaneously.  
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12 The saturation mobilities and the threshold voltages were estimated from the so obtained IV-curves.  
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14 The 11 nm and 25 nm films conduct reliably but not all 8 nm thick samples (among several parallel  
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16 samples) act as working OFETs. The reason for the latter is attributed to the lack of full coverage.  
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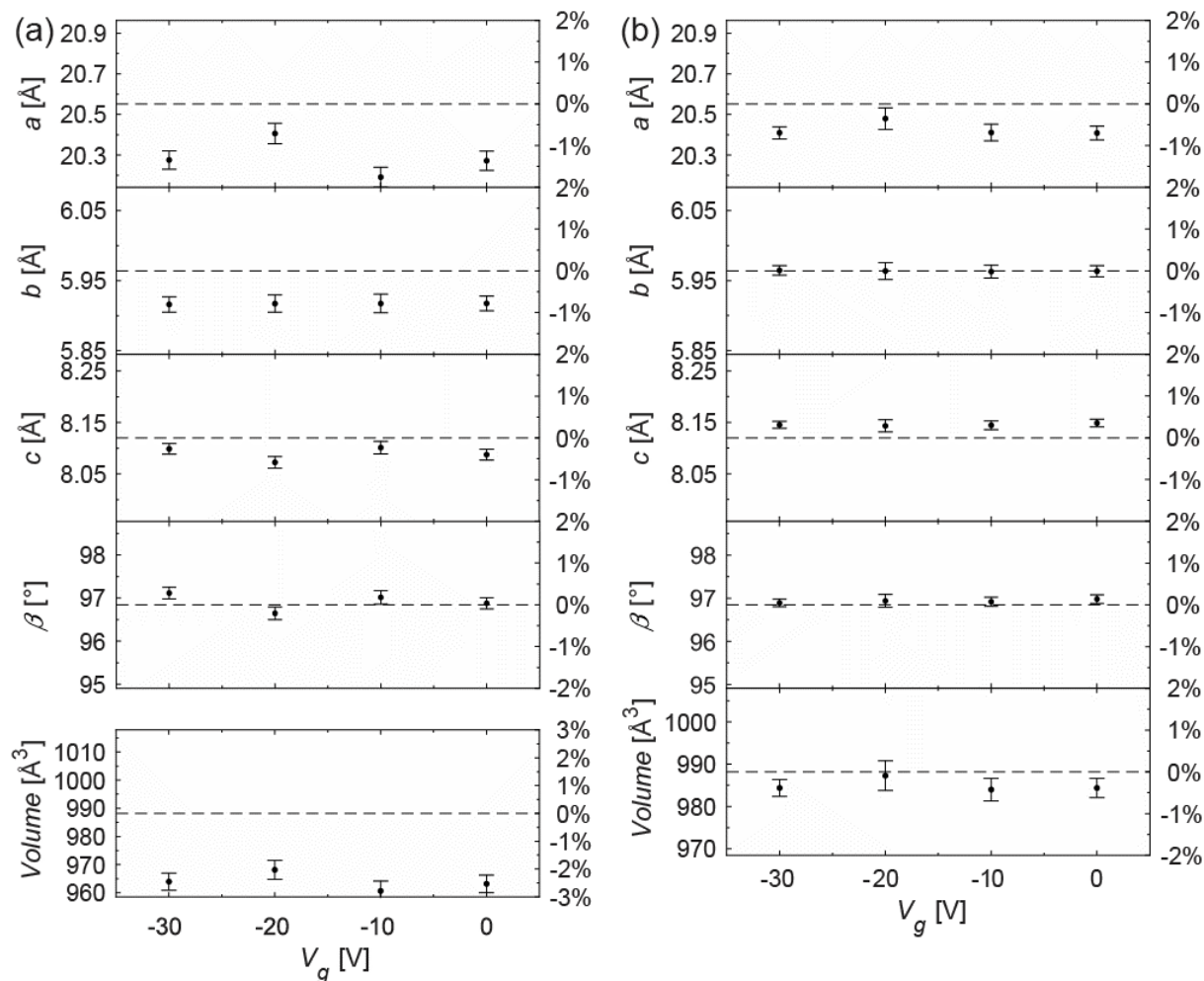
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20       Figures 9 (a) plots the IV-curves of 11 nm NaT2 films on SiO<sub>2</sub> and on anhydrously deposited OTS.  
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22 Figure 9(b) compiles the saturation mobilities for 11 nm and 25 nm OFET configurations. IV-sweeps  
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24 of the 8 nm film configurations shortly after deposition did not show consistent IV-curves and carrier  
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26 transport in 8 nm film configurations were thus deemed unreliable. Considering all the studied samples  
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28 with their parallel samples, mobilities are higher for NaT2 layers on SiO<sub>2</sub> ( $2-3 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ )  
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30 compared to NaT2 on OTS ( $2 \cdot 10^{-5} - 1 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ ).  
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35       While we observe larger grains and at least 3-fold increase in the lateral crystal size driven by OTS  
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37 deposited under anhydrous conditions, the mobility levels are actually lower for OFETs with OTS. This  
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39 is in contrast to the common assumption that larger grains lead to less grain boundary scattering and  
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41 consequently higher mobility. We propose that the growth of larger grains is indicative of a more 3-  
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43 dimensional growth mode that results in voids and poorer intergrain connections in the first few  
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45 molecular layers leading to a low intergrain mobility. In contrast, the thin-films on pristine SiO<sub>2</sub> with  
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47 smaller grains might exhibit a more continuous morphology in the first few layers and consequently  
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49 better intergrain mobility, leading to the observed differences in hole mobility.  
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Indeed, there are several reports that some of the best performing thin-films consisted of small grains (see Ref. <sup>6</sup> and references herein).



**Figure 9.** (a) I-V forward sweeps at  $V_{ds} = -30$  V for N11 and A11. (b)  $\mu_{sat}$  for the nominally 11 nm and 25 nm film configurations. Green symbols refer to pristine SiO<sub>2</sub> and red and blue symbols to OTS deposited under anhydrous or humid conditions.



**Figure 10.** (a) Lattice parameters and unit cell volume as a function of  $V_g$  for (a) N8 and (b) N25.

Figure 10 plots the lattice parameters against the employed gate voltage  $V_g$  for the thinnest and thickest NaT2 OFETs. The NaT2 unit cell remains stable under an applied voltage with and without OTS for at least tens of minutes time. Similar data are observed for other configurations (see Figure S8 in the Supporting Information). This agrees with our previous report<sup>25</sup> where we observed 50 nm thick NaT2 films being stable and unit cell parameters staying constant under the same conditions for 10 hours of cycling. This can be discussed alongside the work of Liscio et al.<sup>31</sup>, who reported that pentacene will tilt towards the applied field in OFETs.

## CONCLUSIONS

This study concerns NaT2 and shows how its structure and morphology can be controlled by an OTS layer on the SiO<sub>2</sub> gate dielectric in bottom-gate OFETs. This effect depends on the deposition conditions of the OTS layer.

NaT2 deposited directly on the pristine SiO<sub>2</sub> dielectric preferentially forms a mosaic of crystals where the film thickness matches the crystal size across the film. The lateral crystal size is approximately 30 nm. NaT2 deposited on OTS/SiO<sub>2</sub> shows distinctive staggered pyramidal islands where the interlayer spacing corresponds to one unit cell with upright standing molecules. At the same time, lateral grain size observed by AFM increases from hundreds of nanometers up to micrometers. The lateral crystal size determined by X-rays is larger (100 nm) if the OTS layer is deposited under anhydrous conditions and smaller (30–70 nm) if the layer is deposited under humid conditions. The unit cell parameters determined for OFET differ 1–2% from those in bulk. The unit cell volume is 1–4% smaller than that of bulk. Regardless of the OTS layer, the overall morphology depends on film thickness. While the 11 and 25 nm thick NaT2 films cover the whole OFET surface, nominally 8 nm thick films consist of submicron sized domains whose thickness exceeds the nominal thickness by 50% and covering two thirds of the FET area. Considering 11 nm and 25 nm thick films, the mobility levels tend to be higher for OFETs without OTS ( $2-3 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ ) compared to those with OTS ( $2 \cdot 10^{-5} - 1 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ ). This is in contrast to the common assumption that larger grains lead to less grain boundary scattering and consequently higher mobility. This implies that the smaller grains in smoother films can be better interconnected and more tightly packed leading to improved

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4 intergrain transport for larger grains. An applied voltage does not influence the unit cell parameters  
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6 when probed *in operando*.  
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8  
9 Forthcoming studies should focus on the effect of deposition temperature, as this is known to  
10 influence the surface diffusion of the molecules, the grain size, and the resulting charge carrier  
11 mobility.<sup>22</sup> They could also concern longer molecules such as NaTn with more thiophene rings and  
12 make a connection between surface morphology and crystallinity at the polymer-oligomer limit.<sup>32</sup>  
13 Other material variations could involve alkane substituted oligothiophenes or similar, but asymmetric  
14 oligothiophenes where one naphthyl end-cap is replaced by aliphatic chains.<sup>33</sup> It would be interesting to  
15 study the samples with complementary techniques such as cross-sectional transmission electron  
16 microscopy to characterize the thin-film morphology near the interface. Another possibility is to use  
17 naphthalenes not as end-caps but as repeat units.<sup>34,35</sup> Expanding studies from OFETs to photodetectors<sup>36</sup>  
18 is yet some of the avenues worth pursuing.  
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## 34 ASSOCIATED CONTENT

### 35 Supporting Information

36  
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38 Regression lines according to Eq. 1 and additional AFM and GIXRD data. This material is available  
39 free of charge via the Internet at <http://pubs.acs.org>.  
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## 20 **Notes**

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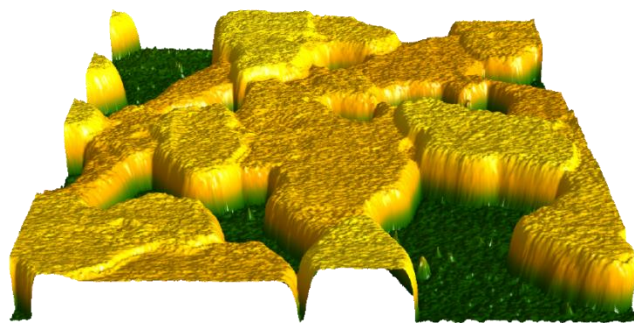
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### For Table of Contents use only

“Structural evaluation of 5,5'-bis(naphth-2-yl)-2,2'-bithiophene in organic field-effect transistors with octadecyltrichlorosilane coated SiO<sub>2</sub> gate dielectric”



by Andreas E. Lauritzen, Mika Torkkeli, Oier Bikondoa, Jes Linnet, Luciana Tavares, Jakob Kjelstrup-Hansen and Matti Knaapila