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Structural basis for a naphthyl end-capped oligothiophene with embedded metallic nanoparticles for organic field-effect transistors

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We report on the apparent structure of 5,5’-bis(naphth-2-yl)-2,2’,5’,2”-terthiophene (NaT3) in organic field-effect transistors (OFETs) with and without embedded silver nanoparticles. Using regular- and microbeam grazing incidence wide- and small-angle X-ray scattering, the device structure is characterized locally in the area with the embedded particles. The NaT3 thin film order is reduced and the found unit cell (a = 25.7 Å, b = 5.87 Å, c = 8.03 Å and β = 98.9) differs significantly from the one reported in bulk, but shows no significant change, when the particles corresponding to the crystal size are incorporated into the device structure. At the same time, the apparent thin film crystal sizes in OFETs are found to be similar with and without the embedded particles. In both cases the carrier mobilities are of the order of 10^{-4} cm^2/Vs.

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Organic field-effect transistors (OFETs) are subject to interest for use in modern electronics due to their inexpensive, low-temperature processing, low materials costs and application potential in e.g. flexible electronics,1 gas sensors,2 pressure sensors,3 and optical sensors (organic phototransistors, OPTs).4 Numerous studies have been carried out on conjugated oligomers and polymers, whose properties can be tuned through design and functionalization.5,6 Of particular interest are thiophene-based oligomers because of their hole transport properties and stable device performance under atmospheric conditions.7-9 By end-capping the thiophene rings with aryl groups, the polymerization potential is hindered and intermolecular packing is promoted.

We have recently shown that the photoresponsivity in naphthyl end-capped oligothiophene based OPTs can be enhanced by utilizing the plasmonic properties of embedded metallic nanoparticles.10 However, while it is well known that the carrier mobility is connected to the orientation and crystal size of the organic molecules,11-13 the literature of structural evaluation of oligothiophenes in OFETs with embedded metallic particles remain less comprehensive.

The molecular structure of organic thin film devices is often evaluated by the use of grazing incidence X-ray scattering.14-16 OFETs with embedded nanoparticle arrays are prepared using electron-beam lithography, which does not allow for a simple preparation of suitably large samples for grazing-incidence studies. Therefore it remains difficult to probe the micrometer scaled areas of interest. Nevertheless, recent advances in synchrotron radiation has made it possible to probe structures locally in devices using micro- and nanobeams.17

In this letter, we use micro-focused X-rays to investigate 5,5’-bis(naphth-2-yl)-2,2’,5’,2”-terthiophene (NaT3) and establish its structural fundamentals in OFETs with and without embedded silver nanoparticles.

Figure 1(a) shows the chemical structure of NaT3. The synthesis of NaT3 follows the Suzuki cross-coupling protocols reported in Ref. 9.

Figure 1(b) shows the structure of the investigated OFETs fabricated by the following procedure, as described in Ref. 10. A highly n-doped Si substrate formed the back electrode with a 200 nm thick thermally grown SiO₂ layer as a gate dielectric. The interdigitated source and drain electrodes were fabricated by E-beam evaporation of 30 nm Au on top of 3 nm of Ti, structured by photolithography and lift-off in acetone. The transistor channel dimensions were 2 mm × 10 μm (width × length) corresponding to a width/length (W/L) ratio of 200:1. Ag nanoparticles with diameters of ~ 40 nm were subsequently patterned in a nominal square lattice (period = 200 nm, corresponding to a surface coverage of ~ 3%) on top of the gate dielectric and electrodes by E-beam lithography in poly(methyl methacrylate) (PMMA) followed by thermal evaporation of 40 nm of Ag on top of 3 nm Ti and lift-off in acetone. Finally, a 55 nm thick NaT3 layer was deposited atop the substrate by vacuum sublimation. The film thickness was
The GIWAXS images were transformed to the reciprocal space by reciprocal space mapping (RSM) using the Figxax python library and the fiber transformation originally described by Stribleck.\textsuperscript{18} This transformation is valid since the film exhibit fiber texture in the $x$-$y$ plane around the surface normal ($z$-axis). The GISAXS images were converted to the $q$ space using FitGISAXS.\textsuperscript{19} The crystal grain-sizes were analyzed using Scherrer grain-size analysis adapted for grazing incidence scattering with an area detector.\textsuperscript{20} In this procedure, the tangential full width half maximum (FWHM) of the RSM peak intensities were fitted with a Lorentzian distribution. Carrying out the resolution analysis, the experimental contribution to the peak broadening (including smearing from the beam divergence, energy bandwidth, and the finite length of the beam footprint) was determined to be less than 10\% of the total peak width and was therefore treated as negligible.

To obtain a qualitative understanding of the molecular packing inside the thin film unit cell, density functional theory (DFT) was employed using the GPAW package.\textsuperscript{21} The A Form packing reported in Ref. 8 was used as a starting point together with the experimentally found unit cell, and the atoms were allowed to relax until the atomic forces were below $1 \times 10^{-2}$ eV/Å. The Bayesian error estimation functional\textsuperscript{22} (BEEF-vdW) and projector-augmented wave potentials were used, with a plane-wave cutoff of 700 eV and a converged $1 \times 6 \times 4$ Monkhorst-Pack grid.

The electric characterization of the OFETs were performed with a custom-built characterization set-up based on a LabVIEW-controlled data acquisition card connected to voltage and current amplifiers providing the input and a probe station measuring the output signal from the OFET. The gate voltage ($V_G$) was swept from 0 to $-15$ V with a constant drain-source voltage $V_{DS} = -15$ V.

Figure 2(a) shows a 2D GIWAXS pattern of the NaT3 thin film from the OFET by a regular beam. The pattern exhibits a series of vertically smeared peaks (Bragg rods) originating from the mosaicity of the NaT3 crystallites, with the molecules standing nearly vertically on the substrate. The smearing of the Bragg peaks along $q_z$ suggests that NaT3 exhibits a higher degree of disorder along the stacking direction perpendicular to the substrate compared with the closely related but symmetrically $5,5'$-bis(naphth-2-yl)-2,2'$'$-bithiophene (NaT2), which shows equally resolved Bragg peaks (rather than rods) in both directions.\textsuperscript{7} Yet the pattern has prominent similarity to what is reported for 5-decyl-$5'$- (naphthalen-2-yl)-2,2'$'$-terthiophene (D3TN) in Ref. 23, which likewise contains three thiophene rings with one end-group replaced by an alkyl-group. The observed Bragg peaks can be consistently indexed assuming a monoclinic unit cell with parameters $a = 25.7$ Å, $b = 5.87$ Å, $c = 8.03$ Å.
and $\beta = 98.9^\circ$ and volume $V = 1.20 \times 10^4 \text{Å}^3$. Our unit cell choice follows the notation described in Ref. 7 with (100)-texture and standing molecules (defined with $a$ as the long axis nearly along the backbone of the molecule). The unit cell observed in our thin film devices differs significantly from the unit cell reported for bulk NaT3 in Ref. 8. The reported bulk unit cell has 6 molecules (and the volume $3.44 \times 10^4 \text{Å}^3$), compared to $Z = 2$ for the thin film case. This suggest that the long range order along the long axis is reduced for films.

Figure 2(b) shows a typical GIWAXS pattern from the area of the OFET with embedded particles measured by a $\mu$-beam. The data are consistently indexed with the same unit cell parameters, indicating that there are no significant changes in the NaT3 unit cell with and without embedded particles. The proposed molecular packing is shown in Fig. 2(c).

Table I compiles the determined crystal sizes for NaT3 in devices with and without embedded particles. There are no significant changes in crystal sizes between these two cases within the given error bounds (calculated as ±1 standard deviation from the least square fitting). Interestingly, the typical crystal sizes of NaT3 in films are on the same order of magnitude as the nominal size of the embedded particles. It is therefore likely that the particles are incorporated into the mosaic crystal structure causing only local hindrance to the molecular growth. The opposite could be the case if the average crystallite size was much larger.

Figure 3 shows the GISAXS images from different areas of the device when the incident X-ray was perpendicular to the interdigitated electrodes, with $q_{x}$ and $q_{xy}$ corresponding to the out-of-plane and in-plane wave vectors, respectively. The image from the bare SiO$_2$ substrate [Fig. 3(a)] features a bright specular rod along $q_z$ with the specular reflected beam covered by the beamstop (indicated with an S). The specular beam is located at an exit angle equal to the incidence angle of $\alpha_i = 0.42^\circ$. At $q_z = 0.65$, the observed horizontal scattering feature is the so-called Yoneda peak (indicated with a Y) from SiO$_2$ that appears at the critical angle of the material ($\alpha_c = 0.146^\circ$ for SiO$_2$). On the image from the area with Au electrodes on top of SiO$_2$ [Fig. 3(b)], multiple bright scattering peaks are found along the specular rod at $q_{xy} = 0$. These peaks correspond to the diffraction pattern from the 1D lateral grating formed by the Au electrodes, aligned perpendicular to the incoming beam. The same feature is present on the image from the area with NaT3 deposited on top of the electrodes [Fig. 3(c)] with small modulations due to reflection/refraction effects in the thin film overlayer. The Yoneda peak for NaT3 ($\alpha_c = 0.115^\circ$) appears at $q_z = 0.61$, just below the Yoneda peak of SiO$_2$. Furthermore, there is an increase in diffuse scattering from the disorder of the thin film structure.

Figure 3(d) shows the image from the area with Ag particles embedded in NaT3 on top of the interdigitated Au electrodes. The scattering intensity in the in-plane $q_{xy}$ direction is dominated by a series of sharp peaks that appear to be correlated with the peaks found along the specular rod and are located on arcs extending from $q_z = 0$. The high scattering order and sharpness of peaks found along $q_{xy}$ may point to a high correlation between particles and due to the large footprint of the beam, it is inferred that the particles are well-aligned across the de-
vice. From the peak spacing, the average interparticle distance can be derived as:

$$d_{\text{particle}} = \frac{2\pi}{|q_x|}$$

where $q_x$ is the in-plane scattering angle, $m$ is the order of diffraction, $\lambda$ is the X-ray wavelength and $d$ the grating period.

The observed scattering patterns correspond to the computed diffraction peaks for a grating with $d = 10 \mu m$ [red dots on Fig. 3(e)]. Here the diffraction patterns are shown for $m = -5$ to 4 for 20 equally spaced values of $2\theta$ in the range $\pm 0.2^\circ$.

Figure 4 shows the transfer curves of the OFET with and without embedded particles. The saturation mobilities are extracted from the slopes of the $I_{DS}^1$ vs $V_G$ curves (not shown) in the high bias regime between $V_G = -10$ and $-15$. The saturation mobilities from 8 devices are compiled in Table II. The mean values for devices with embedded particles is $1.2 \times 10^{-4}$ cm$^2$/Vs compared to $1.1 \times 10^{-4}$ cm$^2$/Vs for devices without the embedded particles. The two results lie within the range of uncertainty, indicating that the particles do not notably affect the field-effect mobility of the device. Since the charge transport in OFETs occur near the interface between the semiconductor and the gate dielectric, where the particles are also positioned, we expect that the particles would influence the FET performance. However, this is not observed. This could be due to the fact that the particles only occupy $\sim 3\%$ of the channel area, and that a noticeable change in performance would only be visible if a larger fraction of the channel area was covered.

In conclusion, we have found that the NaT3 thin film unit cell differs significantly from the one reported for bulk, with decreased long range order and only two molecules per unit cell. When E-beam deposited silver particles are embedded in the OFET device structure, there is no further change in the NaT3 unit cell or apparent crystal sizes. The measured field-effect mobility in the saturated regime averaged as $1.2 \times 10^{-4}$ cm$^2$/Vs for OFETs with the particles compared to $1.1 \times 10^{-4}$ cm$^2$/Vs for devices without particles. These results form a structural base for designing field-effect transistors with aryl...
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(a) 

(b) 

(c) 

GIWAXS

GISAXS
\( V_{DS} = -15 \text{ V} \)

- **without nanoparticles**
- **with nanoparticles**