



Nanomorphology in thin films of acetamide end-functionalised quaterthiophene

Nina Zeilmann^a, Benedikt Rösner^a, Andreas Späth^a, Ute Schmidt^b, Rainer H. Fink^{a,*}

^a Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) Department Chemie und Pharmazie, Physikalische Chemie 2 and ICMM, Egerlandstraße 3, 91058 Erlangen, Germany

^b WITec GmbH, Lise-Meitner-Straße 6, 89081 Ulm, Germany



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ABSTRACT

α,ω -Functionalised oligothiophenes are promising materials for organic field effect transistors due to their high degree of molecular ordering, crystallinity and π - π stacking. We employ several complementary microspectroscopic probes to investigate the formation of thermally evaporated films of 5,5''-bis(*N*-acetamido-2-ethyl)-2,2':5',2'':5'',2''':5'''-quaterthiophene on inert substrates. These films were found to grow in a mixed fashion, featuring layer-by-layer domains with thicknesses of several monolayers and needle-shaped three-dimensional crystals. Detailed analysis of atomic force microscopy (AFM) and photoluminescence microscopy reveals the micro- and nanomorphology of the films. Linear dichroism in the near edge x-ray absorption fine structure and polarisation-dependent laser excitation corroborate the findings of AFM, *i.e.*, upright standing molecules in the multilayer regime. The shape of the 3-dimensional crystallites and multilayer domains indicates strongly anisotropic growth favoured by the herringbone-arrangement of the thiophene moieties and additional stabilisation by hydrogen bonding of the acetamide end groups.

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1. Introduction

The study of organic electronic devices is one of the fastest evolving fields in modern material science [1]. Organic electronic devices, such as organic field-effect transistors (OFETs), organic solar cells, or organic light-emitting diodes are expected to compete with or even replace silicon in the near future [2]. The advantages of these materials over their inorganic counterparts are multifarious and range from low cost, high mechanical flexibility and solution processability to the ability to tailor properties by variation of functional groups, thus rendering them a very promising and economically worthwhile alternative to the present silicon based electronics [3]. As organic semiconductors are more and more utilised as active components in emerging electronic applications and molecular electronics [4], this class of molecules has been intensively studied and significant progress has been made in the characterisation of both the material-based properties and factors influencing device performance depending on the chemical and physical environment of the semiconductors [5–8].

One auspicious class of organic semiconductors are functionalised oligothiophenes [9,10] with appealing optical, optoelectronic and charge transport properties [11]. They are widely considered as “a third-generation of advanced conjugated materials” [4]. After the first report of an organic field-effect transistor using α -sexithiophene as active material in 1989 [12,13], oligothiophenes and their derivatives

have been the most intensely studied organic semiconducting materials [14]. The reasons for this intense research lie within their high (electro)-chemical stability, outstanding physical and chemical characteristics, straightforward synthesis and wide range of structural modifications [4, 15,16]. Moreover, this class of oligomers provides excellent charge transport properties due to the high polarisability of the sulphur atoms in the thiophene rings and the resulting stabilisation of the π -conjugated system. Systematic functionalization and modification gives access to materials with additional properties compared to unsubstituted oligothiophenes [4]. Especially functionalizing the α - and ω -positions of the π -conjugated system allows tailoring the solubility of the oligothiophene as well as its redox properties [1]. The molecular ordering can also be influenced and increased by directed chemical modification of the molecules. In this respect, the addition of terminal alkyl residues at the α - and ω -positions induces vertical orientation of the thiophene rings on the substrate, providing good molecular arrangement [17].

As the performance of organic electronic devices strongly depends on the degree of molecular ordering, crystallinity and on the extent of π - π stacking in the organic semiconductor [1,18,19], the optimisation of the chemical structure of the semiconductor for good molecular arrangement and maximised orbital overlap is a crucial issue in terms of pushing the performance of organic electronics to state-of-the-art levels [15]. A detailed understanding of the correlation between structural properties and device performance still remains one of the key challenges [5–8,20]. The charge carrier mobility in organic semiconducting films is strongly affected by the density and inherent nature of

* Corresponding author.

E-mail address: rainer.fink@fau.de (R.H. Fink).

grain boundaries [21]. It is limited by defect trapping in disordered regions of the interface of the organic electronic device [3,22] since hopping of charge carriers between distinct molecules is critically influenced by the molecular ordering and arrangement [17,19].

In this work, we conducted a detailed microspectroscopic study on films of the α - and ω -substituted oligothiophene 5,5''-bis(*N*-acetamido-2-ethyl)-2,2':5',2'':5'',2''-quaterthiophene, in the following denoted as Ac4T (Scheme 1). Besides the π -interactions of the thiophene rings, Ac4T exhibits a stronger interaction due to the formation of hydrogen bonds [23] between the acetamide end groups, thus enhancing the intermolecular coupling. Organic field effect transistors based on these quaterthiophene films yielded mobilities up to $0.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratios up to 10^3 [23]. These values reach mobilities and the on/off ratios of OFETs based on alkyl-substituted oligothiophenes [15].

In order to get detailed insight into the morphology and electronic structure of these films, a set of complementary nanoprobe was utilised. As obligatory requirement for real-life applications of organic electronic devices, we investigated the formation of Ac4T films on inert substrates, *i.e.*, silicon oxide and silicon nitride. While atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to study the film morphology on the short and longer length scales, the chemical fingerprints and the linear dichroism of scanning transmission x-ray microscopy (STXM) and photoluminescence microscopy offered insight into the molecular orientation within ordered domains. In addition, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy provided access to the local electronic structure of the condensed Ac4T molecules. It is found that the morphology is governed by the formation of elongated crystals in coexistence with multilayer domains. Since the OFET geometry is far from ideal, the charge carrier mobilities of $1.1 \times 10^{-2} \text{ cm}^2/\text{Vs}$ are reduced compared to maximum values reported so far.

2. Experimental details

The chemical synthesis of Ac4T was carried out according to the synthetic route described by Gebers [23]. Thin films of Ac4T were prepared by vapour deposition under ultrahigh vacuum conditions (base pressure $< 10^{-5}$ Pa). Silicon wafers covered with about 200 nm thermal SiO_2 (CIME at EPFL) and amorphous Si_3N_4 membranes with a thickness of 100 nm (Silson Ltd., UK) were used as substrates. Thin films with a nominal thickness of 55–70 nm were grown at a rate of 0.05 \AA s^{-1} monitored by a quartz microbalance (kept at room temperature) while the substrate temperature was kept at $393(\pm 2) \text{ K}$. Such elevated temperatures yielded the best transport performance and were therefore used for all further studies on the thin film morphology [23].

Organic thin film transistors were fabricated by deposition of nominally 25 nm Ac4T layers onto silicon oxide wafers at a base pressure of 2×10^{-5} Pa. Subsequently, 35 nm thick gold electrodes were deposited on top of the organic film through a shadow mask using the same conditions. The OFET devices have a channel width $W = 300 \mu\text{m}$ and length $L = 20 \mu\text{m}$. Their transport characteristics were determined using a Keithley SCS 4200 parameter analyser.

All samples were investigated by scanning electron microscopy using a Zeiss Leo Gemini 1530 SEM. The energy of the primary electrons

was set to 5 keV. The backscattered electrons were detected by an in-lens detector.

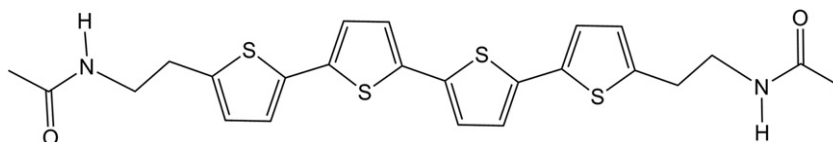
AFM, Raman, and photoluminescence (PL) micrographs of the evaporated Ac4T films were recorded with a WITec alpha 300 RA combined Raman and atomic force microscope. Raman imaging was performed at 785 nm excitation (see ESI), whereas the PL spectra and images were acquired with a 488 nm excitation laser. The AFM and PL micrographs were recorded from a square area of $15 \times 15 \mu\text{m}^2$ with 512×512 and 150×150 pixels respectively. The analysis of the AFM and PL raw data was conducted with WITec Project Plus (version 2.10). A Sobel filter was used on the AFM topography to show the first derivative in x-direction for better visualisation of domain borders and the shape of 3D crystals. SEM micrographs were acquired with a Zeiss Leo Gemini 1530 scanning electron microscope at an acceleration voltage of 15 kV. An in-lens detector was used to record secondary and backscattered electrons.

Soft x-ray microspectroscopy experiments were conducted at the PolLux-STXM at the Swiss Light Source [24]. For STXM, a Fresnel zone plate is used to focus the x-ray beam. For real-space imaging, a resolution of 10 nm has been demonstrated [25]. However, in the present analysis a spatial resolution of about 30 nm was realised. The transmitted x-ray intensity was recorded by a photomultiplier tube detector. STXM micrographs were recorded with a dwell-time of 1–5 ms per pixel with the specimen kept at room temperature. In the present study, we focused on the carbon K-edge absorption to investigate the morphology of the films as the C1s to π^* -transitions represent a very sensitive probe. We have to note that the available photon energy range of PolLux does not allow spectroscopy of the S K- or L-edge absorption. Besides pure imaging, STXM can be utilised to derive the soft x-ray near-edge absorption fine structure (NEXAFS), serving as a spectroscopic fingerprint to monitor the local electronic structure [26]. In addition, the linear NEXAFS dichroism offers insight into the molecular orientation [27]. Carbon K-edge NEXAFS spectra were recorded in the energy range of 280–320 eV in imaging mode and were normalised to the pre-edge (280 eV) and post-edge absorption (320 eV). The major resonance of polystyrene (285.2 eV) [26] was used for energy calibration.

3. Results and discussion

3.1. Morphology of thin Ac4T films

Fig. 1 shows a representative AFM topography image of an Ac4T film grown on a silicon oxide substrate. The image shows elongated domains with a lateral expansion of up to ten micrometres along their long axis. In these highly anisotropic domains, up to seven layers can be identified (see left hand side and upper part of Fig. 1a). In the lower right of Fig. 1a, few crystallites with a height of up to 200 nm are present. Their overall appearance might indicate the existence of several individual crystallites whereas the elongated shape again supports anisotropic crystal growth. The AFM morphology is well in accordance with results from SEM (see ESI). For the chosen preparation parameters, *i.e.*, elevated substrate temperatures during deposition, 3D crystals grow on top of larger domains in the thickness regime of few monolayers. Comparable film morphologies are observed when depositing Ac4T films onto Si_3N_4 membranes (see STXM micrographs below).



Scheme 1. Structural formula of the α - and ω -substituted oligothiophene 5,5''-bis(*N*-acetamido-2-ethyl)-2,2':5',2'':5'',2''-quaterthiophene (Ac4T).

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