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# Formation of Self-Assembled Organosilicon-Functionalized Quinquethiophene Monolayers by Fast Processing Techniques

Elena V. Agina,*,[†] Ivan A. Usov,[†] Oleg V. Borshchev,[†] Jingbo Wang,[‡] Ahmed Mourran,[‡] Maxim A. Shcherbina,[†] Artem V. Bakirov,[†] Souren Grigorian,[§] Martin Möller,[‡] Sergei N. Chvalun,[†] and Sergei A. Ponomarenko[†]

[†]Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences, Profsoyuznaya st. 70, Moscow 117393, Russian Federation

[‡]Interactive Materials Research DWI an der RWTH Aachen e.V. and Chair of Textile and Macromolecular Chemistry, RWTH, Aachen University, Forckenbeckstr. 50, 52056 Aachen, Germany

[§]Institute of Physics, University of Siegen, Walter-Flex-Str., 3 D-57068 Siegen, Germany

ABSTRACT: Different techniques for a relatively fast self-assembled monolayer film formation such as Langmuir–Blodgett (LB), spin-coating, and dip-coating methods have been compared using chloro[11-(5''''-ethyl-2,2':5',2''':5''',2''''-quinquethiophene-5-yl)undecyl]dimethylsilane as a reactive precursor. It was shown that both spin-coating and LB techniques are very promising methods for preparation of highly ordered monolayer films of organosilicon-functionalized quinquethiophene with vertical orientation of oligothiophene fragments, while dip-coating gives only partial coverage. Optimal conditions for complete filling out the substrate surface by the quinquethiophene-containing monolayer by spin-coating and LB methods have been found. Grazing incidence X-ray diffraction measurements confirmed formation of in-plane crystalline order within the monolayer film. Changes in the layer structure were established by X-ray reflectivity and grazing incidence X-ray diffraction methods.
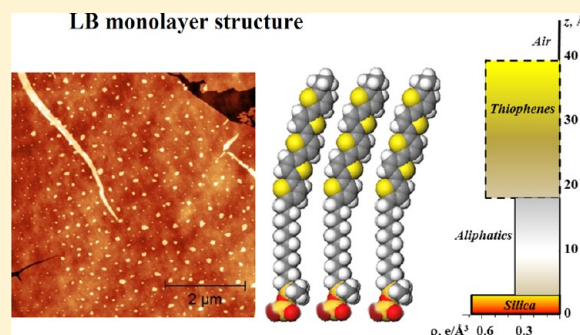
INTRODUCTION

Nowadays π-conjugated semiconducting oligomers and polymers attract significant attention of researchers due to their unique optical and electric properties that give large possibilities for their application as functional materials for a new generation of electronic and optoelectronic devices such as light-emitting and information displays, radiofrequency identification tags, solar cells, lasers, sensors, and others.[1] The basic elements of these devices are organic thin-film transistors (OTFTs),[2] organic light-emitting diodes (OLEDs),[3] or organic photovoltaic cells (OPV cells).[4] It was shown that in the case of OTFTs a major charge transport takes place just in the first layers of the organic semiconductor with the thickness of a few nanometers.[5,6] At the same time, the semiconducting films with the thickness from several tens to hundreds of nanometers are usually used for a fabrication of stable working OTFT due to inhomogeneity of the coatings obtained that leads to additional consumption of the organic semiconducting materials and raise a price of the target devices. Therefore, a reduction of the semiconductor film thickness in OTFTs without losing its electronics performance is a challenge. In order to solve this problem, different functional derivatives of π-conjugated oligomers capable of self-assembling monolayer formation on a dielectric surface have been developed.[7,8] The first so-called self-assembling monolayer field-effect transistors (SAMFETs) have been fabricated,[9,10] but until recently they had working characteristics significantly worse than those of the traditional OTFTs.

Oligothiophenes and their derivatives are prospective materials for organic electronics due to their high charge carrier mobilities in OTFTs.[11] It was shown that the oligothiophenes functionalized with monochlorosilane reactive group and aliphatic spacer can self-assemble on hydrophilized dielectric surfaces to form 2D-crystalline monolayers.[12−15] This approach allows to prepare SAMFETs with mobilities of up to 0.04 cm^2/(V s), which are comparable to the respective values measured in thick oligothiophenes films.

In the literature, one can find other examples of SAM applications for organic electronics,[16] for instance as monolayer dielectrics layers, which reduce driving voltage of organic transistors,[17,18] as SiO$_2$ dielectric layer surface modifiers for reducing content of Si–OH groups acting as traps for electrons,[19] or for creation of highly ordered dielectric OTS layer leading to higher charge carrier mobilities of organic semiconductors.[20,21]

It was shown that thin spin coated OFET devices on silanized SAMs appear to be significantly efficient and more temperature stable compared to their thick counterparts.[22] It was found that
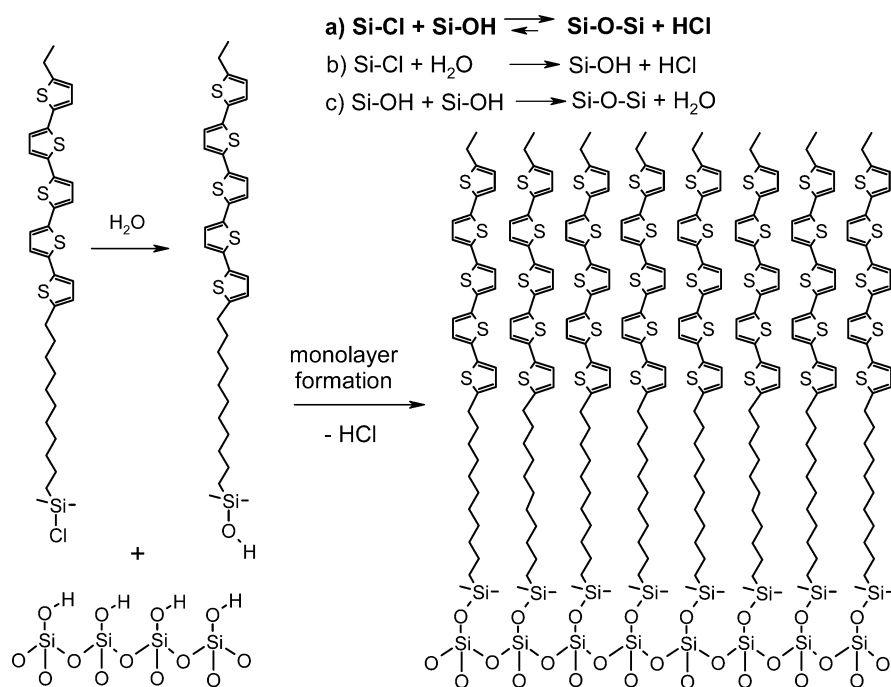
Figure 1. Schematic representation of Si-Und-5T-Et chemisorption on the hydrated silicon dioxide surface.[12]

despite the fact that annealing improves crystallization, the mobility of the film is decreasing. Therefore, independently of degree of crystallinity, charge carrier mobility is mostly caused by overall good planar uniformity and interconnectivity of conducting domains within thin film which might be easily achieved by LB technique.

The aim of this work is to study and compare the structure of self-assembled monolayers (SAMs) prepared by different techniques on the base of the end-reactive quinquethiophene. We have chosen chloro[11-(5′′′′-ethyl-2,2′:5′,2″:5″,2‴:5‴,2″″-quinquethiophene-5-yl)undecyl]dimethylsilane (mentioned below as Si-Und-5T-Et), the synthesis of which was described elsewhere,[12] as the object of investigation keeping in mind two reasons. First, reactivity of the chlorosilane toward hydroxyl groups of the silicon dioxide allowed covalent bonding of 5T to the dielectric surface (see Figure 1). Second, the long flexible undecyl spacer decouples the anchor from the conjugated core enabling formation of highly crystalline monolayer. The same 5T derivative has been used for preparation of SAMs from solution by submerging the activated silicon substrate in a dry toluene solution of the chlorosilane in question. It has been found that fully covered semiconducting monolayer was formed only when the immersion time was 15 h.[15] However, for practical applications, it would be highly desirable to form such a layer within a few minutes rather than several hours. The present investigation seeks alternative processes enabling faster SAM formation without affecting the surface coverage, crystal structure, or electrical properties. For this purpose, we have chosen Langmuir–Blodgett method (vertical deposition), spin-coating, and dip-coating techniques, all of which are quite fast as compared to the classical self-assembly from solution.

■ EXPERIMENTAL SECTION

Materials. Synthesis of chloro[11-(5′′′′-ethyl-2,2′:5′,2″:5″,2‴:5‴,2″″-quinquethiophene-5-yl)undecyl]dimethylsilane (Si-Und-5T-Et) was described elsewhere.[12] Toluene (Acros) was distilled over sodium before use. Isopropanol (Acros) was used as received.

Langmuir and LB Films. The spreading solution was prepared by dissolving Si-Und-5T-Et in toluene at the concentration of 0.33 g/L. The solution was spread on the water surface with a microsyringe, and the film was then left for 5 min to equilibrate before the compression started. Data were collected with a Nima 712BAM system equipped with a Brewster angle microscope (MicroBAM2) using a Teflon trough and barriers at room temperature. Ultrapure water obtained from an Akvilon deionizer D-301 system was used for the subphase. The monolayers were compressed with speeds ranging from 50 to 100 mm/min, with almost no influence of the barrier velocity on the observed behavior. LB films were obtained by transfer on silicon wafers that were previously activated by an oxygen plasma treatment followed by a cleaning in a pure isopropanol under ultrasonic treatment. The vertical dipping method with a dipping speed of 8 mm/min was used to obtain monolayer films. Film transfers were preformed at surface pressures close to the collapse point corresponding to the most condensed phase in the monolayer (30, 40, and 42 mN/m).

Spin-Coating. Silicon wafers were cleaned by sonication in isopropanol for 5 min, dried in an air stream, and activated with UV radiation under flux of O_2 for 12 min. These treatments provided a clean silicon surface with a water contact angle of <5°. All solutions were prepared inside a glovebox in order to minimize traces of water which may be detrimental for the stability of chlorosilane based compounds. A stock solution of 1 g/L of Si-Und-5T-Et in dry toluene was prepared inside a glovebox. The solution was filtered through a 0.2 μm filter PTFE syringe which was then diluted to the desired concentration. The vials were sealed with septum for spin-coating outside the glovebox (Convac 1001S, Germany), and all solutions were kept at 40 °C before use. The coating was done in two steps: first, for a given concentration of the solution (0.9 g/L), the rotation speed was optimized to achieve high surface coverage. In the second stage, the spinning rate was constant (700 rpm), and the concentration was varied from 0.2 to 0.9 g/L.

Dip-Coated Films. Films were prepared under argon atmosphere with variable withdrawal speed (4 or 18 mm/min). The solution concentration was similar to the one used to prepare LB films, that is, 0.33 g/L.

Thin Film Characterization. Morphology of the thin films was investigated by a tapping model SFM (NanoScope V) under ambient conditions. Commercially available standard silicon cantilevers (PPP-SEIH-W from Nanosensors) with a spring constant of 5−37 N/m and an oscillation frequency of ~125 kHz were used. Data analysis was
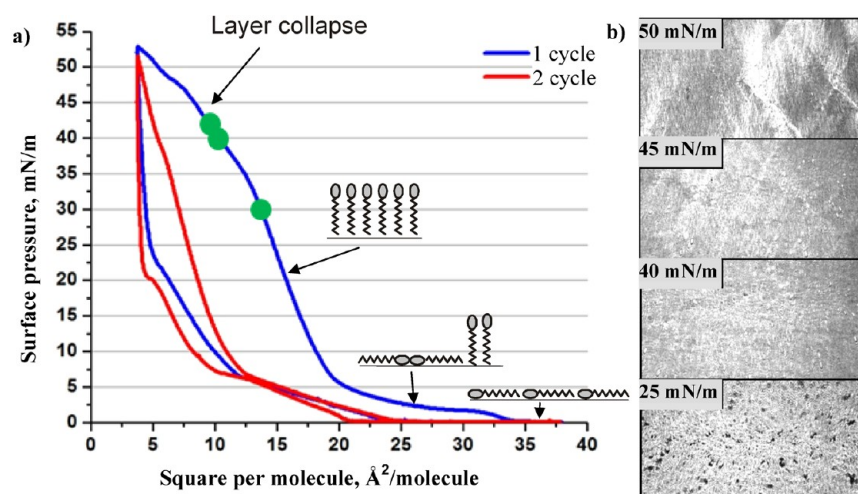
Figure 2. (a) Langmuir isotherms for Si-Und-5T-Et (first and second compression−decompression cycles) and cartoon, showing the most probable molecular structure of the layer at different degrees of compression at the first compression cycle. Green points correspond to the transfer surface pressures: 30, 40, and 42 mN/m. (b) BAM micrographs of Langmuir films at different surface pressures (first compression cycle).

processed by using NanoScope Analysis software, V1.10. Scanning electron microscope (SEM) experiments were performed with a Hitachi S4800 high resolution field emission instrument with an accelerating voltage of 1.5 kV.

X-ray Analysis. Grazing incidence X-ray diffraction (GIXD) and X-ray reflectivity studies were performed at the high-resolution diffraction P08 beamline, PETRA III synchrotron radiation source (Hamburg, Germany). Incident X-ray beam with the energy of 15 keV that probed polymer films had the size of 200 and 50 μm in vertical and horizontal directions, respectively. Diffracted and reflected beams were monitored via a 2D flat panel (PerkinElmer) and a MYTHEN linear position sensitive detectors, respectively. During the experiment, the samples were kept under helium atmosphere to reduce radiation damage. X-ray reflectivity data were analyzed using StochFit program which utilizes stochastic fitting methods to model specular reflectivity curves. The obtained distributions of electron density were afterwards interpolated by two- or three-slab models with subsequent solution of scattering problem and following reconstruction of reflectivity curves. The electron density $\rho = 2\pi\delta/\lambda^2\gamma_e$, where γ_e is the classical electron radius equal to 2.814 × 10^{-5} Å and δ is the dispersion coefficient,[23] as well as thickness d and roughness R of monolayers were calculated.

Molecular Modeling. Accelrys Materials Studio program set was employed for molecular modeling of compounds studied. We used two sets of potentials, which allow taking into account noncovalent interactions of oligothiophene groups inside the monolayer: COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) and UFF (Universal Force Field). The COMPASS set is suitable for modeling of isolated molecules and condensed phases of mainly organic, polymeric and of some inorganic compounds,[24−26] and it also allows one to parametrize partial charges and valencies ab initio with subsequent system optimization. To prove the results of modeling, we applied UFF potentials, used for calculation of geometry of organic molecules, and this does not have any limitation on the chemistry of compounds involved.[27−29]

■ RESULTS AND DISCUSSION

LB Technique. First, the behavior and structure of the Si-Und-5T-Et films at the air−water interface was investigated (Figure 2). Langmuir isotherms under the first and second cycles of the film compression−decompression do not coincide and show significant hysteresis effects (Figure 2a). Such behavior could be explained by spontaneous crystallization of 5T units on the air−water interface, or most likely hydrolysis takes place

as chlorosilyl groups react with water to form silanol, which subsequently reacts with chlorosilane or with silanol, leading finally to a 5T-based siloxane dimer (Figure 3a). It is necessary to note that the increase in surface pressure promotes the formation of dimer by condensation of silanol end groups. We suppose that during the first compression we deal with a monolayer that predominantly consists of silanol molecules (since hydrolysis of chlorosilane is relatively fast and does not depend on the layer compression), while during the second compression the layer predominantly consists of siloxane dimers. Since interactions of the siloxane groups with water are weaker than those of the silanol groups, we suppose that bilayer formation is the more preferred variant for the dimer instead of a monolayer. Due to crystallization, a part of the dimer molecules leaves the water surface and forms a bilayer (Figure 3b). This hypothesis can be traced back to the decrease in the surface area per molecule (5T fragment) in the most condensed state during the first and second compressing cycles (21 and 11 Å^2/mol, respectively).

During the first compression cycle, the onset of the pressure increase occurs at high area values (∼33 Å^2/mol). The most probable structural interpretation of the initial increase of pressure is the change of the molecule's long axis orientation during the layer compression (see cartoon in Figure 2a). At high area values (more than 33 Å/mol), the molecules lie horizontally on the water surface, forming hydrogen bonds both with the oxygen in silanol groups and the sulfur in thiophene rings. Such a layer could be compressed up to the pressure of 2 mN/m and the area per one molecule of 33 Å/mol. Under further film compression, molecules undergo gradual transition from the "lying" to "standing" position during which the thiophene fragments come off from the water surface. This process is continuous, looks like a plateau on the isotherm, and finishes approximately at 4 mN/m and 23 Å/mol. After that, we compress the film that consists of the molecules with vertical orientation.

Brewster angle microscopy (BAM) data show that a collapse of the Si-Und-5T-Et film starts at the surface pressure equal to 45 mN/m (Figure 2b). That is why for further investigations we have transferred the LB films by vertical deposition on silicon substrate at different surface pressure of 30, 40, and 42 mN/m,
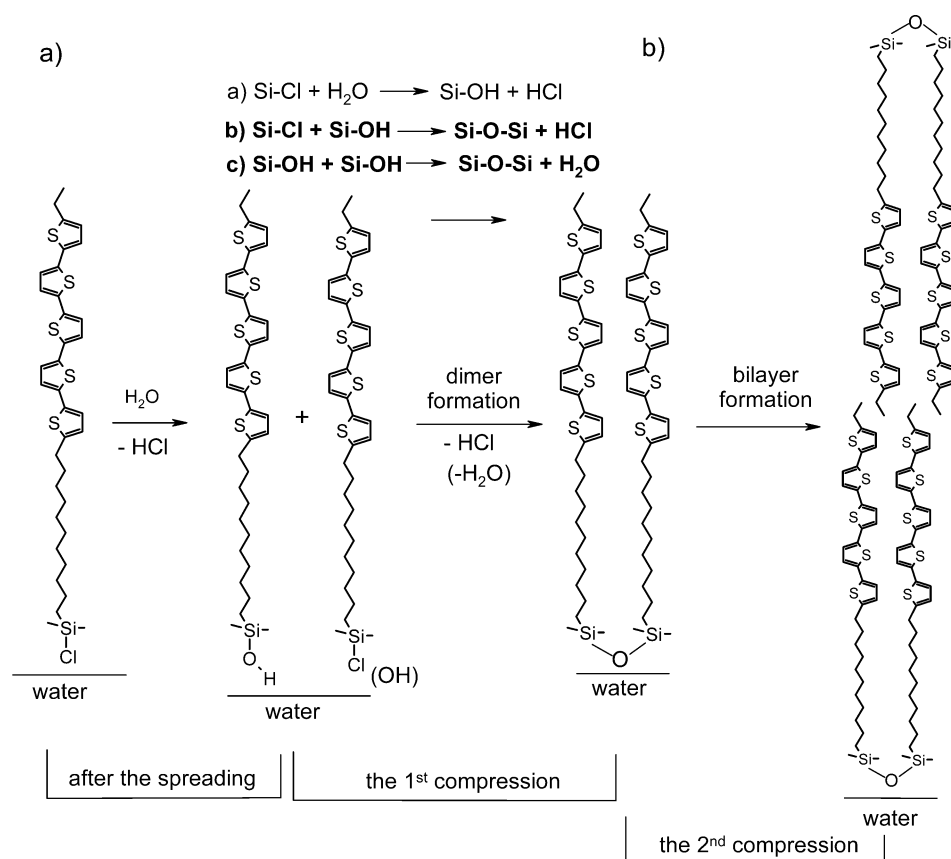
Figure 3. Scheme of chemical and structural transformations of the Si-Und-5T-Et compounds at an air–water interface under the layer compression.

corresponding to a monolayer in the most condensed state just before the collapse. We supposed that in this condensed state the molecules form a two-dimensional crystal where the long molecular axis is oriented nearly perpendicular to the water surface. The argument supporting this suggestion is based on the surface area per molecule which is equal to 21 Å^2 that is very close to a half of the square of a rectangular unit cell determined earlier[30] for a self-assembled monolayer of the same molecule (i.e., 40 Å^2 the cell is centered, has the lattice constants of 5.6 and 7.2 Å and consists of two molecules). This suggestion was confirmed by XRD measurements (see below).

Morphological investigations of the LB films after transfer were performed using scanning electron and force microscopes (Figure 4). FE-SEM micrographs indicate that all films consist of homogeneous roundish domains with an overall dimension of approximately 5−10 μm. Homogeneous substrate coverage could be achieved for film transferred at a surface pressure equal to 40 mN/m (Figure 4d), while at 30 mN/m (Figure 4a) the surface coverage was incomplete and at 42 mN/m (Figure 4g) the domains were collapsed along their boundaries. SFM data shows that the domains have uniform thickness of around 3.5 nm ascribed to a monolayer; in some locations, dotlike features are also observed with a height commensurate with a bilayer (Figure 4b,c,e,f,h,i). It should be noted that the thickness of the monolayer is in good agreement with the estimated molecular length (36 Å),[14] suggesting a vertical orientation of the molecule (Si-Und-5T-Et) relative to the substrate/air interface. The presence of the bilayer is additional evidence of the dimerization process due to spontaneous hydrolysis as described above.

X-ray reflectivity has also revealed the presence of homogeneously thick domains at pressures as low as 30 mN/m.

Reflectivity patterns of LB films, prepared at different conditions are shown in Figure 5. One can observe distinct fringes which are directly related to the layer thickness due to a good contrast of the X-ray scattering. Reconstruction of the electron density in the direction perpendicular to the film plane has shown that monolayers contain two regions of substantially different density (Table 1). Closest to the silicon substrate ($\rho_e = 0.67$ e/Å^3) is the low density aliphatic zone ($\rho_e = 0.342$ e/Å^3), and a distant one having substantially higher density ($\rho_e = 0.566$ e/Å^3) accommodates quinquethiophene parts. Such dense packing of oligothiophene fragments should enable good electronic properties of Langmuir films obtained.[31] Experimental electron densities are in a good agreement with the theoretically estimated ones.[32] Comparison of the structural parameters of the sublayers obtained at different pressures taking into account geometrical considerations and molecular modeling (contour length of 5T fragments is 19.8 Å, the one of undecyl spacers is 13.3 Å, etc.) reveals that an increase of the surface pressure leads to a growth of the thickness of the oligothiophene region due to decrease of the tilt of the oligothiophenes relative to the substrate surface from 22° to 13° with the aliphatic region width being virtually the same. Changes of the monolayer structure with the pressure are illustrated in Figure 6. It is worth to note that the same tilt of 13° was observed after annealing of the monolayer obtained from the same 5T derivative by self-assembly from toluene solutions, while freshly prepared SAM has no tilt of 5T fragments.[30]

To summarize the data of SAM prepared by LB-transfer technique, the increase of the surface pressure resulted in high surface coverage and reduced the tilt angle of the oligothiophene molecules relative to the surface normal.
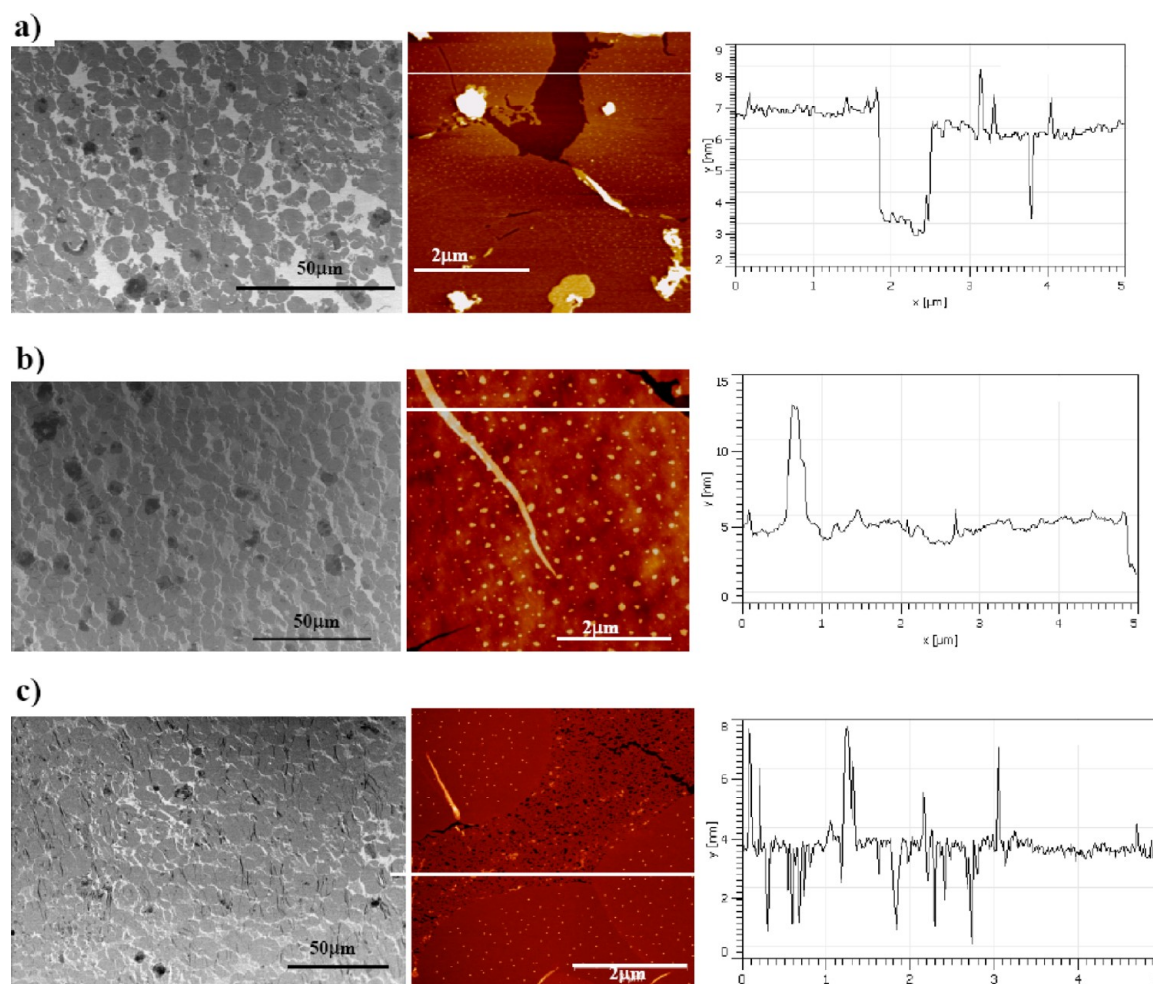
Figure 4. SEM and SFM images of the LB films of Si-Und-5T-Et on the silicon substrate that have been transferred at different surface pressures: 30 mN/m (a), 40 mN/m (b), and 42 mN/m (c).
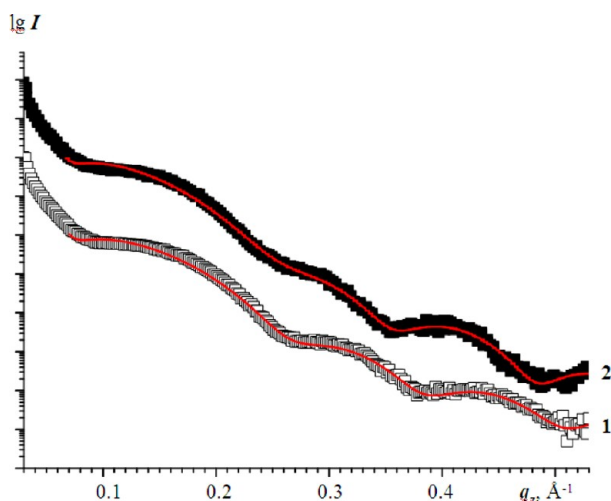

Figure 5. Reflectivity curves for LB films of Si-Und-5T-Et, prepared from 0.33 g/L solutions at pressures of 30 mN/m (1) and 40 mN/m (2). For the sake of representability, the latter is shifted along the I axis in the logarithmic scale. Best stochastic fits are shown by red curves.

Table 1. Monolayer Parameters of LB Films Prepared at Different Pressures $(c = 0.33 \text{ g/L})^a$

π, mN/m	L, Å	d_1, Å (Thio)	R_1	d_2, Å (Alk)	R_2
40	39.6	21.5	6.4	18.1	5.3
30	38.1	20.3	5.1	17.8	4.8

$^a\pi$, surface pressure; L, monolayer thickness; d_1 and d_2, thicknesses of quinquethiophene and alkyl sublayers, respectively; R_1 and R_2, roughness of quinquethiophene and alkyl sublayers, respectively.

systematically varied from 400 to 2500 rpm at given concentration of the solution (0.9 g/L). In the second stage, the spinning rate was constant (700 rpm) and the concentration was varied from 0.2 to 0.9 g/L.

Figures 7 and 8 present morphological data that summarize the results of the preparation conditions. Morphological comparison of the micrographs indicates a considerable reduction in the surface coverage was observed for a rotation speed greater than 1500 rpm (Figure 7). This suggests the use of a low rotation speed to achieve high surface coverage. Apparently, for slow speeds (≤600 rpm), the surface tension becomes higher than that of the centrifugal force which hinders a homogeneous spreading of the droplets. As a result, the optimal rotation speed was found to be of about 700 rpm. In the next step, the spinning rate was constant (700 rpm), and the concentration of the solution was varied from 0.2 to 0.9 g/L (see Figure 8).
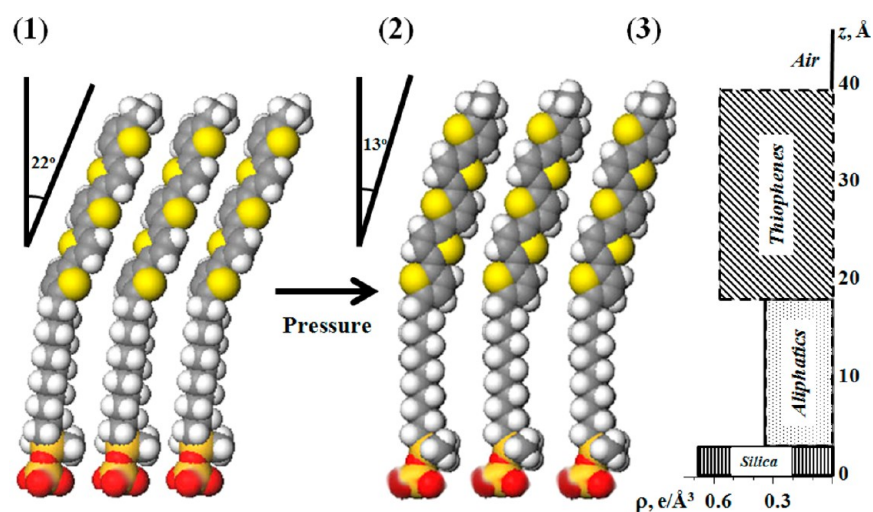
Spin-coating. Structure and morphology investigations of the spin-coated thin films have been made in two stages. To achieve high surface coverage, first the spinning speed was

Figure 6. Molecular models of the LB monolayer structure at 30 mN/m (1) and 40 mN/m (2). Plot (3) shows distribution of the electron density along the z axis perpendicular to the substrate surface.
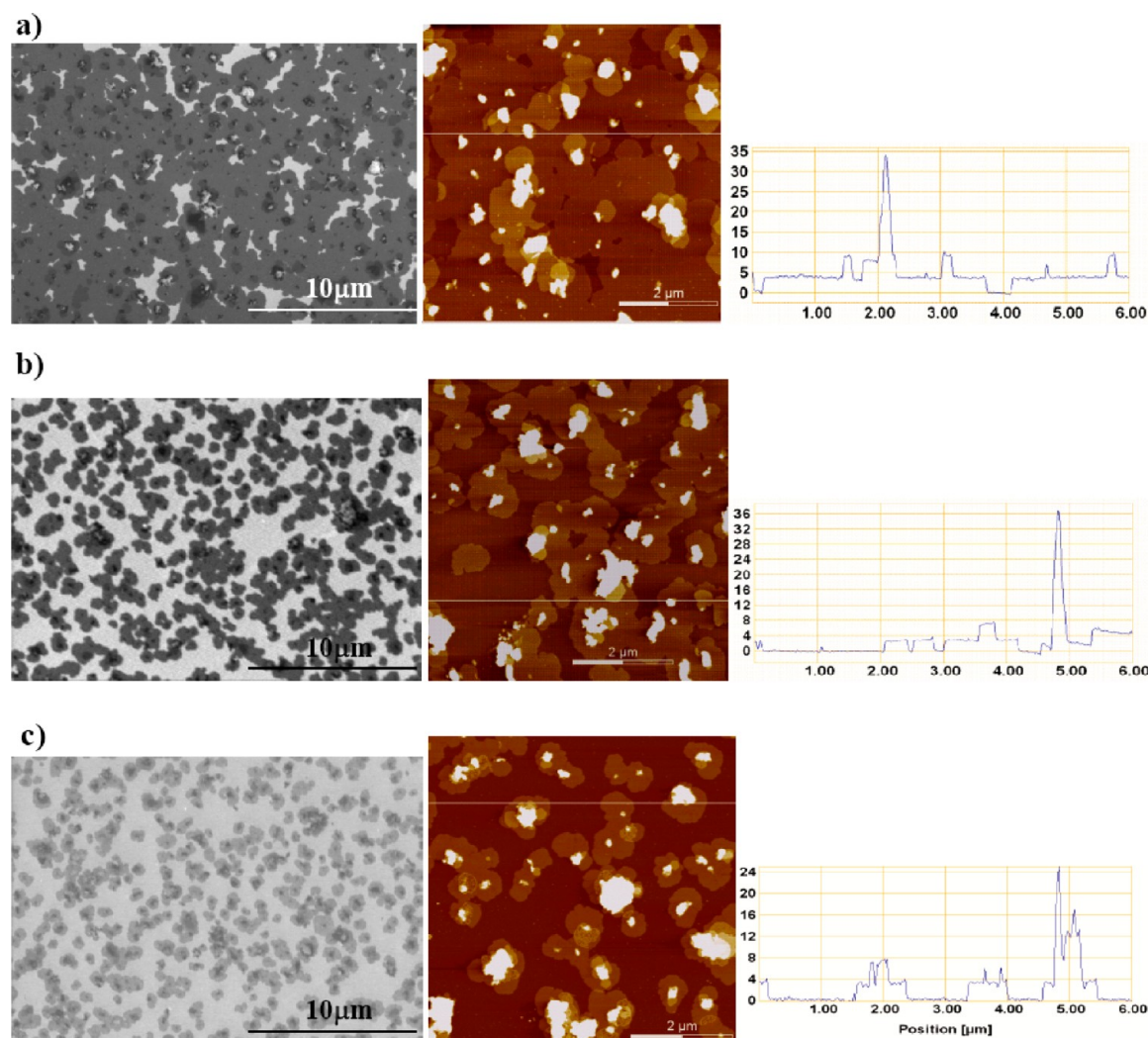

Figure 7. SEM and SFM images of the thin films on the silicon substrate obtained by spin-coating a solution of Si-Und-5T-Et with a concentration of 0.9 g/L. The rotation speeds were 600 rpm (a,b), 1500 rpm (c,d), and 2500 rpm (e,f).

The SFM data show that the substrate is at least covered by a monolayer and the surface coverage increases with the concentration. Full coverage is achieved for a concentration of about 0.6 g/L or higher (Figure 8). The presence of a tiny noncovered substrate area (Figure 8c) confirms this statement. Further increase of the solution concentration promotes formation
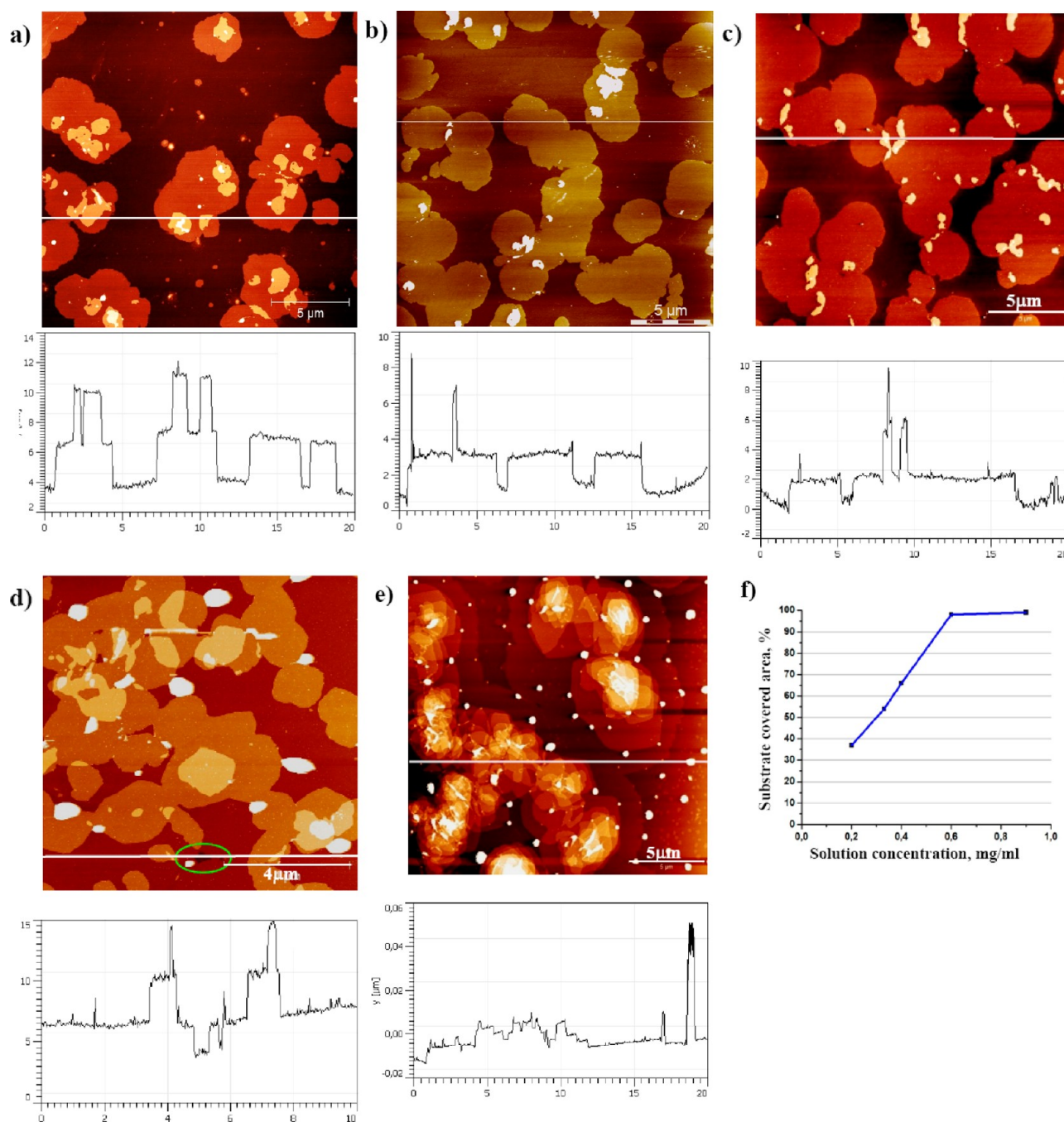
Figure 8. SFM images of the thin films on the silicon substrate obtained by spin-coating at 700 rpm from the toluene solution of the Si-Und-5T-Et with the concentrations: (a) 0.2 g/L, (b) 0.33 g/L, (c) 0.4 g/L, (d) 0.6 g/L, and (e) 0.9 g/L. (f) Dependence of the substrate area covered by the oligothiophene on the concentration of its initial solution.

of multilayered domains. Figure 8f shows the surface coverage increase with the concentration of the solution and full coverage is attained at around 0.6 g/L above the multilayer structure formed. The roundish shape of the structures formed at low solution concentrations (Figure 8a−c) allows one to assume that the domains grow from crystallization centers to the periphery as it was observed for LB films (see Figure 4) and self-assembled from solution films.[15] Analysis of the height profiles shows that Si-Und-5T-Et forms a monolayer with the long axis of the molecule perpendicular to the substrate, similar to LB transferred films, and in good agreement with the estimated molecule length.

The compound under investigation contains a highly reactive chlorosilane functional group, which can either directly react with Si−OH groups of the substrate or hydrolyze easily and fast under water vapor present normally in the air. Since we did the spin-coating under normal conditions (not in the dry or glovebox), we could expect that at least a part of the chlorosilane groups could hydrolyze during the spin-coating and chemisorb to the substrate.

In order to estimate the amount of Si-Und-5T-Et molecules that are chemically bonded to the surface (see Figure 1), the spin-coated substrate was immersed in hot toluene (60 °C) for 6 min. In principle, this treatment allows dissolving physisorbed
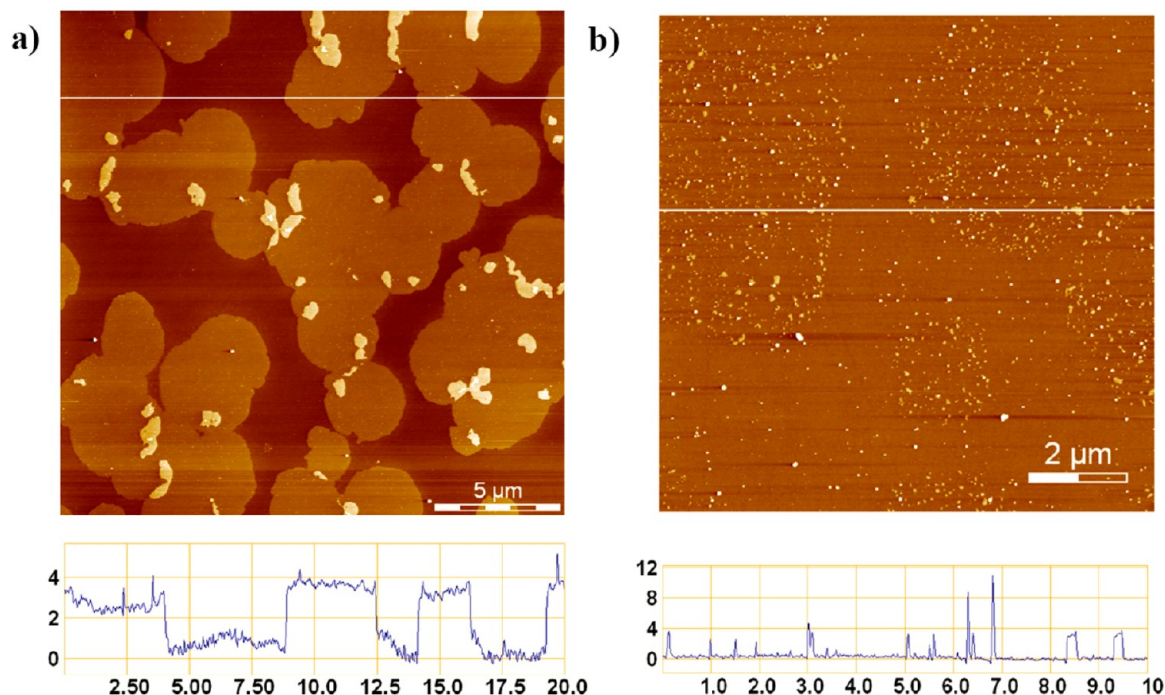
Figure 9. SFM height image and the corresponding cross-sectional profile of the Si-Und-5T-Et monolayer obtained by spin-coating technique before (a) and after (b) rinsing in hot toluene (60 °C) for 6 min.
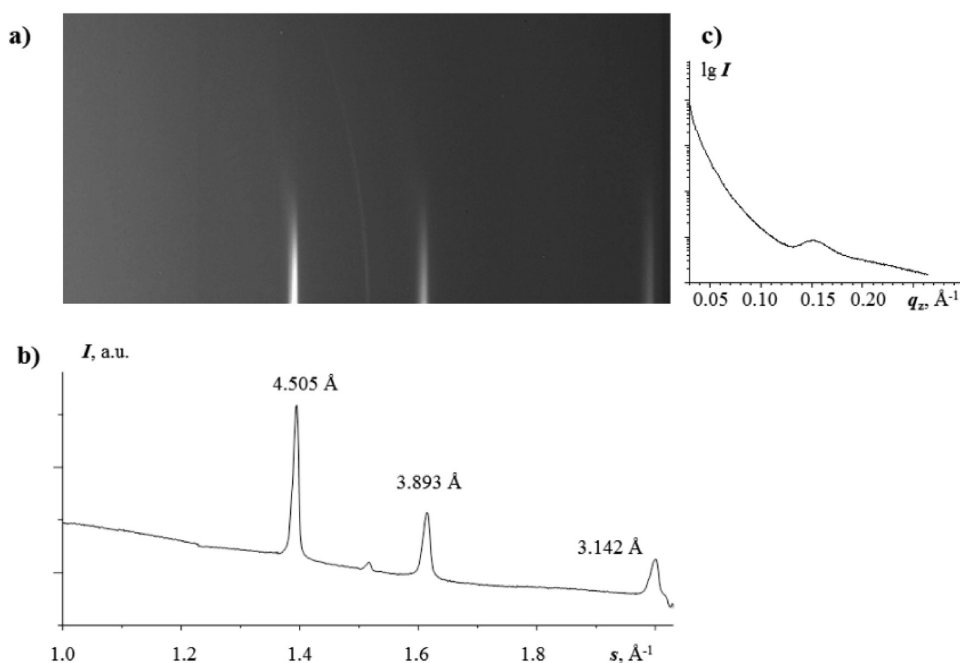

Figure 10. Grazing incidence 2D pattern (a), its radial scan (b), and reflectivity curve (c) for Si-Und-5T-Et films formed in single step spin-coating deposition method.

layers and the remainder of the film was imaged by SFM. Figure 9 shows that nearly 95% of the film was dissolved.

The structure of the spin-coated films was investigated by X-ray reflectivity and GIXD. It was revealed that the most perfect crystals were observed for samples prepared from 0.6 g/L solutions. Grazing incidence patterns (Figure 10) of such samples show three Bragg rods, corresponding to d-spacings of 4.505, 3.893, and 3.142 Å which are very characteristic for the dense herringbone packing of polythiophene.[33] Narrow and weak circular reflection ($d = 4.134$ Å) is caused by a reflection

from uncovered substrate surface. It is important to note that the spin-coating procedure leads to the formation of large islands which do not cover substantial chunks of the substrate surface. Such a conclusion can be drawn not only from the presence of substrate reflection on grazing incidence diffracto-grams, but also from characteristic shape of the reflectivity curve (Figure 10c), providing a well pronounced Bragg peak without thickness oscillations typical for a uniform thin slab. Such a broad peak is formed when several monolayers are stacked on each other, forming large pyramidal islands on the
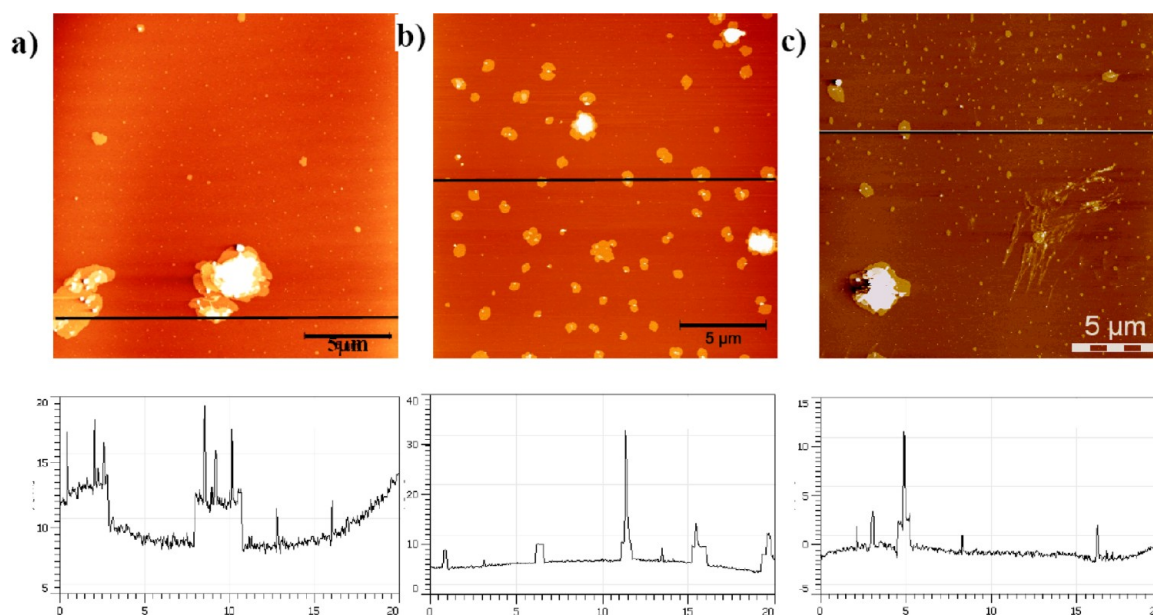
Figure 11. SFM images of the Si-Und-5T-Et films on the silicon substrate formed by dip-coating technique from toluene solution at 0.33 g/L concentration with the speeds: (a) 4 mm/min, (b) 6 mm/min, and (c) 18 mm/min.

substrate surface. Monolayer height calculated from the position of such Bragg reflection is 40.5 Å which is in good agreement with data obtained on studies of Langmuir−Blodgett films.

Therefore, notwithstanding the fact that the film received by spin-coating technique has only a small amount of molecules covalently bonded to the substrate, this method under the optimal conditions allows to obtain the multilayer film with the fully covered sublayer and perpendicular orientation of Si-Und-5T-Et molecules. However, it is important to note that for the preparation of such multilayer film one do not need to use the functionalized chlorosilane molecules; the same results could be obtained for the nonfunctional molecules such as α,α'-dialkyloligothiophenes.[34] Moreover, the active layer of the film prepared from the Si-Und-5T-Et molecules using spin-coating technique could contain nonhydrolyzed chlorosilane groups that can negatively affect the electrical properties of the film.

Dip-Coating. Dip-coated films have been formed by the vertical dipping method of activated silicon wafers in a dry toluene solution of quinquethiophenechlorosilane as described in the Experimental Section. SFM-images of the films obtained are shown in Figure 11. It is clearly seen that regardless of the dipping speed the surface coverage area does not exceed 10%. Since the dip-coating technique did not give satisfactory results in terms of substrate coverage, it could be used only for the submonolayer monolayer formation (partially covered substrate) and was discarded for further investigations.

CONCLUSIONS

To summarize all the data obtained, we can conclude that Langmuir−Blodgett technique employed under the optimal conditions is a very promising method for formation of the self-assembled crystalline monolayer films of the linear organosilicon-functionalized quinquethiophene Si-Und-5T-Et with vertical orientation of oligothiophene fragments that should be appropriate for practical application in OFETs. It should be emphasized that the LB technique allows one to prepare Si-Und-5T-Et monolayers significantly faster than the previously used method of self-assembling from solution.[14,15] We could suppose that the

observations found are more or less universal for similar organosilicon-functionalized molecules. It is necessary to point out that the LB technique does not result in a monolayer formation for nonfunctional linear oligothiophenes (i.e., for α,α'-dialkyloligothiophenes); therefore, the presence of chlorosilane functional group plays a significant role for further development of functional π-conjugated oligomers for SAMFETs. Our results revealed an advantage of the LB technique for organic electronics in comparison to spin-coating and dip-coating techniques. Thin films prepared by coating techniques are less uniform and, typically, without complete substrate coverage. However, under the optimized conditions, highly oriented films with fully covered sublayers can be obtained by the spin-coating technique. Preliminary investigations of electrical properties of the SAMs prepared from Si-Und-5T-Et using LB technique reveal their good semiconducting properties. The details will be published elsewhere.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: werdas@mail.ru.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting pi-conjugated systems in field-effect transistors: a material odyssey of organic electronics. *Chem. Rev.* **2012**, *112*, 2208−2267.

(2) *Organic Electronics. Materials, Manufacturing and Applications*; Klauk, H., Ed.; Wiley-VCH: Weinheim, 2006; 428 pp.

(3) *Organic Light Emitting Devices. Synthesis, Properties and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006; 410 pp.

(4) *Organic Photovoltaics. Materials, Device Physics and Manufacturing Technologies*;Brabec, C., Scherf, U. Dyakonov, V., Eds.; Wiley-VCH: Weinheim, 2008; 597 pp.

(5) Tanase, C.; Meijer, E. J.; Blom, P. W. M.; de Leeuw, D. M. Local charge carrier mobility in disordered organic field-effect transistors. *Org. Electron.* **2003**, *4*, 33−37.

(6) Dinelli, F.; Murgia, M.; Levy, P.; Cavallini, M.; Biscarini, F.; de Leeuw, D. M. Spatially correlated charge transport in organic thin film transistors. *Phys. Rev. Lett.* **2004**, *92*, 116802−1−116802−4.

(7) Chen, J.; Murphy, A. R.; Esteve, J.; Ogletree, D. F.; Salmeron, M.; Frechet, J.M. J. Preparation and nanoscale mechanical properties of self-assembled carboxylic acid functionalized pentathiophene on mica. *Langmuir* **2004**, *20*, 7703−7710.

(8) Chen, J.; Ratera, I.; Ogletree, D. F.; Salmeron, M.; Murphy, A. R.; Frechet, J. M. J. Atsomic force microscopy study of β-substituted-T7 oligothiophene films on mica: mechanical properties and humidity-dependent phases. *Langmuir* **2005**, *21*, 1080−1085.

(9) Tulevski, G. S.; Miao, Q.; Fukuto, M.; Abram, R.; Ocko, B.; Pindak, R.; Steigerwald, M. L.; Kagan, C. R.; Nuckolls, C. Attaching organic semiconductors to gate oxides: in situ assembly of monolayer field effect transistors. *J. Am. Chem. Soc.* **2004**, *126*, 15048−15050.

(10) Mottaghi, M.; Lang, P.; Rodriguez, F.; Rumyantseva, A.; Yassar, A.; Horowitz, G.; Lenfant, S.; Tondelier, D.; Vuillaume, D. Low-operating-voltage organic transistors made of bifunctional self-assembled monolayers. *Adv. Funct. Mater* **2007**, *17*, 597−604.

(11) Roncali, J.; Leriche, P.; Cravino, A. From one- to three-dimensional organic semiconductors: in search of the organic silicon? *Adv. Mater.* **2007**, *19*, 2045−2060.

(12) Ponomarenko, S. A.; Borshchev, O. V.; Setayesh, S.; Smits, E. C. P.; Mathijssen, S. G. J.; Pleshkova, A. P.; Meyer-Friedrichsen, T.; Kirchmeyer, S.; Muzafarov, A. M.; de Leeuw, D. M. Synthesis of monochlorosilyl derivatives of dialkyloligothiophenes for self-assembling monolayer field-effect transistors. *Organometallics* **2010**, *29* (19), 4213−4226.

(13) Gholamrezaie, F.; Mathijssen, S. G. J.; Smits, E. C. P.; Geuns, T. C. T.; van Hal, P. A.; Ponomarenko, S. A.; Cantatore, E.; Blom, P. W. M.; de Leeuw, D. M. Ordered semiconducting self-assembled monolayers on polymeric surfaces utilized in organic integrated circuits. *Nano Lett.* **2010**, *10* (6), 1998−2002.

(14) Smits, E. C. P.; Mathijssen, S. G. J.; van Hal, P. A.; Setayesh, S.; Geuns, T. C. T.; Mutsaers, K. A. H. A.; Cantatore, E.; Wondergem, H. J.; Werzer, O.; Resel, R.; Kemerink, M.; Kirchmeyer, S.; Muzafarov, A. M.; Ponomarenko, S. A.; de Boer, B.; Blom, P. W. M.; de Leeuw, D. M. Bottom up organic integrated circuits. *Nature* **2008**, *455* (7215), 956−959.

(15) Mathijssen, S. G. J.; Smits, E. C. P.; van Hal, P. A.; Wondergem, H. J.; Ponomarenko, S. A.; Moser, A.; Resel, R.; Bobbert, P. A.; Kemerink, M.; Janssen, R. A. J.; de Leeuw, D. M. Monolayer coverage and channel length set the mobility in self-assembled monolayer field-effect transistors. *Nat. Nanotechnol.* **2009**, *4*, 674−680.

(16) Miozzo, L.; Yassar, A.; Horowitz, G. Surface engineering for high performance organic electronic devices: the chemical approach. *J. Mater. Chem.* **2010**, *20*, 2513−2538.

(17) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. Ultralow-power organic complementary circuits. *Nature* **2007**, *445*, 745−748.

(18) Zschieschang, U.; Halik, M.; Klauk, H. Microcontact-Printed Self-Assembled Monolayers as Ultrathin Gate Dielectrics in Organic Thin-Film Transistors and Complementary Circuits. *Langmuir* **2008**, *24*, 1665−1669.

(19) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. General observation of n-type field-effect behaviour in organic semiconductors. *Nature* **2005**, *434*, 194−199.

(20) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. Crystalline ultrasmooth self-assembled monolayers of alkylsilanes for organic field-effect transistors. *J. Am. Chem. Soc.* **2009**, *131*, 9396−9404.

(21) Virkar, A.; Mannsfeld, S.; Hak, J. O.; Toney, M. F.; Tan, Y. H.; Liu, G. Y.; Campbell, J. S.; Miller, R.; Bao, Z. The role of OTS density on pentacene and C60 nucleation, thin film growth, and transistor performance. *Adv. Funct. Mater.* **2009**, *19*, 1962−1970.

(22) Joshi, S.; Pingel, P.; Grigorian, S.; Panzner, T.; Pietsch, U.; Neher, D.; Forster, M.; Scherf, U. Bimodal temperature behavior of structure and mobility in high molecular weight P3HT thin films. *Macromolecules* **2009**, *42*, 4651−4660.

(23) Kotov, N. A.; Meldrum, F. C.; Fendler, J. H.; Tombacz, E.; Dekany, I. Spreading of clay organocomplexes on aqueous solutions: construction of Langmuir−Blodgett clay organocomplex multilayer films. *Langmuir* **1994**, *10*, 3797−3804.

(24) Sun, H. COMPASS: an ab initio force-field optimized for condensed-phase applications. Overview with details on alkane and benzene compounds. *J. Phys. Chem. B* **1998**, *102*, 7338−7364.

(25) Sun, H.; Ren, P.; Fried, J. R. The COMPASS forcefield: parameterization and validation for polyphosphazenes. *Comput. Theor. Polym. Sci.* **1998**, *8*, 229−246.

(26) Rigby, D.; Sun, H.; Eichinger, B. E. Computer simulations of poly(ethylene oxide): forcefield, PVT diagram and cyclization behavior. *Polym. Int.* **1998**, *44*, 311−330.

(27) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024−10035.

(28) Casewit, C. J.; Colwell, K. S.; Rappé, A. K. Application of a universal force field to organic molecules. *J. Am. Chem. Soc.* **1992**, *114*, 10035−10046.

(29) Rappé, A. K.; Colwell, K. S.; Casewit, C. J. Application of a universal force field to metal complexes. *Inorg. Chem.* **1993**, *32*, 3438−3450.

(30) Flesch, H.-G.; Mathijssen, S. G. J.; Gholamrezaie, F.; Moser, A.; Neuhold, A.; Novák, J.; Ponomarenko, S. A.; Shen, Q.; Teichert, C.; Hlawacek, G.; Puschnig, P.; Ambrosch-Draxl, C.; Resel, R.; de Leeuw, D. M. Microstructure and phase behavior of a quinquethiophene-based self-assembled monolayer as a function of temperature. *J. Phys. Chem. C* **2011**, *115*, 22925−22930.

(31) Anokhin, D. V.; Defaux, M.; Mourran, A.; Moeller, M.; Luponosov, Yu.N.; Borshchev, O. V.; Bakirov, A. V.; Shcherbina, M. A.; Chvalun, S. N.; Meyer-Friedrichsen, T.; Elschner, A.; Kirchmeyer, S.; Ponomarenko, S. A.; Ivanov, D. A. Effect of molecular structure of α, α′-dialkylquaterthiophenes and their organosilicon multipods on ordering, phase behavior and charge carrier mobility. *J. Phys. Chem. C* **2012**, *116*, 22727−22736.

(32) Tolan, M. *X-Ray Scattering from Soft-Matter Thin Films*; Springer: Germany, 1999; 197 pp.

(33) Samuelsen, E. J.; Mardalen, J. Structure of Polythiophenes. In *Handbook of Conductive Molecules and Polymers: Vol.3 Conductive Polymers: Spectroscopy and Physical Properties*; Nalwa, H. S., Ed.; John Wiley and Sons, 1997; Chapter 2, pp 5−29.

(34) Zhu, X.; Mourran, A.; Beginn, U.; Möller, M.; Anokhin, D. V.; Ivanov, D. A. Self-assembled structures formed by a wedge-shaped molecule in 2D and 3D: the role of flexible side chains and polar head groups. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1444.