

# Structural and Charge-Transport Properties of a Liquid-Crystalline $\alpha,\omega$ -Disubstituted Thiophene Derivative: A Joint Experimental and Theoretical Study

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We present a joint experimental and theoretical study of the structural and charge-transport properties of a liquid-crystalline  $\alpha,\omega$ -disubstituted oligothiophene derivative for application in organic field-effect transistors. The structural properties of the crystalline and smectic phases are investigated by atomic force microscopy, X-ray reflectometry, and X-ray diffraction. To complement these data, molecular mechanics calculations together with the simulation of X-ray diffraction spectra were performed to determine the relative positions of the molecules in the unit cell. The electrical characteristics of field-effect transistors based on the oligothiophene derivative were measured and compared in the crystalline and smectic phases. Although the silanation of the SiO<sub>2</sub> gate dielectric promoted a marked improvement in the charge-carrier mobilities in the crystalline phase, the expected suppression of grain boundaries in the liquid-crystalline phase was not unambiguously evidenced. The experimental results were further complemented by a detailed theoretical analysis of the electronic couplings governing the charge-transport properties on the molecular scale.

## 1. Introduction

Interest in organic field-effect transistors (OFETs) has increased tremendously over the past decade owing to the unique properties of organic semiconductors for fabricating flexible, large-area, low-cost integrated circuits.<sup>1</sup> Among organic semiconductors, oligothiophene derivatives were used as the active layer in a plethora of devices because of their intrinsically high hole mobility values<sup>2–4</sup> (i.e., a key feature determining device performance). The mobility of the charges within the active layer is often limited by the presence of structural defects and grain boundaries that introduce traps or scattering centers for the charge carriers.<sup>5,6</sup> Organic discotic liquid-crystalline materials such as triphenylene, hexabenzocoronene, and phthalocyanine derivatives<sup>7–9</sup> were exploited to circumvent these problems because of their unique self-healing properties that yield organized columnar arrays longer than the transistor channel.<sup>10</sup> However, a major drawback of such discotic systems is the 1D character of charge transport that maximizes the detrimental impact of chemical defects or the remaining physical defects; in other words, a single defect along a column is likely to

suppress transport in that column fully.<sup>11</sup> To combine the good transport properties of oligothiophene derivatives with the self-healing properties of liquid-crystalline materials, we developed a one-step procedure to synthesize a liquid-crystalline oligothiophene derivative with the conjugated thiophene core substituted at the extremities with long alkyl chains. Such rod-shaped molecules tend to stack in layered structures in which efficient charge transport is operative, as confirmed by time-of-flight (TOF) measurements.<sup>12,13</sup>

The nature of the dielectric layer used in the field-effect transistors also has to be critically selected; recent studies have indeed shown that variations in the nature of the dielectric layer can modulate the performance of field-effect transistors based on poly(3-hexylthiophene) (P3HT) by up to 3 orders of magnitude.<sup>14</sup> Among the various possible surface treatments, the use of a self-assembled monolayer deposited on top of the dielectrics proved to be successful in increasing the charge mobility by up to 1 order of magnitude for transistors based on pentacene or sexithiophene.<sup>15</sup> This improvement is generally attributed to an increase in grain size in the polycrystalline layer.<sup>15</sup>

In this article, we combined experimental and theoretical tools to study the structural and charge-transport properties of  $\alpha,\omega$ -dioctylterthiophene (DOTT). We report thermal differential scanning calorimetry (DSC) and polarized optical microscopy (POM) characterizations of this compound. We also investigated the structure of the different phases by means of atomic force microscopy (AFM), X-ray reflectometry (XRR), and X-ray diffraction (XRD) techniques; deeper insight into the molecular

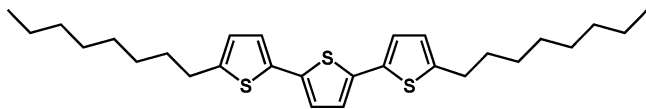
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**Figure 1.** Chemical structure of  $\alpha,\omega$ -diethylterthiophene

packing was inferred from force-field calculations coupled to the simulations of X-ray diffraction patterns. The charge-transport properties were assessed experimentally by fabricating field-effect transistors (with a bottom gate configuration) and by measuring the electrical characteristics in the crystalline phase at room temperature and within the liquid-crystalline smectic phase. The impact of annealing the organic thin films and silanation of the  $\text{SiO}_2$  gate dielectric with different silanes was examined because these two treatments are known to increase the charge-mobility values.<sup>16,17</sup> This study was further complemented by quantum chemical calculations aiming at a molecular-scale description of the electronic coupling (also referred to as transfer integrals) between DOTT molecules, which governs the charge transport. In particular, we analyzed the impact of substrates covered by different silanes on the transfer integrals within the smectic phase.

## 2. Methodology

**Materials.**  $\alpha,\omega$ -Diethylterthiophene (Figure 1) was synthesized and purified according to a previously reported method.<sup>18</sup>

**Differential Scanning Calorimetry.** DSC analyses were performed with a Mettler Toledo DSC821. A typical DOTT amount of 5 mg was scanned under a nitrogen atmosphere at a rate of  $5\text{ }^\circ\text{C min}^{-1}$  between  $-10$  and  $150\text{ }^\circ\text{C}$ .

**Polarized Optical Microscopy.** Temperature-dependent POM analyses were carried out using a Nikon Eclipse 80i polarizing microscope equipped with a Mettler FP82 hot stage at a scanning rate of  $1\text{ }^\circ\text{C min}^{-1}$ . The compounds were placed between two glass plates, and the images were recorded during the cooling of the sample.

**Preparation of Samples for XRR and AFM.** Prior to their functionalization, silicon substrates (covered with native  $\text{SiO}_2$  layers) were cleaned in piranha solution (3:1 v/v 98%  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ) maintained at  $70\text{ }^\circ\text{C}$  for 25 min. After extensive rinsing with ultrapure deionized water (Milli-Q water with a resistivity larger than  $18.2\text{ M}\Omega$  was obtained from a Millipore system), the wafers were dried under flowing dry nitrogen. Before silanation, the silicon substrates were exposed to UV ozone for 10 min. Silanation was realized in the gas phase as follows: the silanation reactor was first cleaned in piranha solution using the same procedure as for the silicon substrates and was then dried for 12 h under vacuum at  $110\text{ }^\circ\text{C}$ . After the introduction of the substrates, the whole system was dried again under vacuum for 4 h at  $80\text{ }^\circ\text{C}$ . The silane mixture (1:2 w/w octyltrichlorosilane/dodecyltrichlorosilane) obtained from Gelest (Germany) was prepared in a glovebox under dry argon. Dry ultrapure argon was introduced into the reactor maintained at  $80\text{ }^\circ\text{C}$  to reach a pressure of 0.4 bar, and 0.3 mL of the silane mixture was injected into the reactor. The silanation reaction was allowed to proceed for 16 h. The substrates were then removed from the reactor and were washed in chloroform Soxhlet for 24 h. The DOTT solution (0.7% w/w in toluene) was prepared and stored at  $4\text{ }^\circ\text{C}$ . The films were deposited by spin coating at a speed of 5000 rpm with an acceleration of 4000 rpm/s for 30 s.

**X-ray Reflectometry.** The XRR measurements were carried out with a modified Siemens D5000 2-circle goniometer fitted to a Rigaku rotating anode operating at 40 kV and 300 mA,

delivering Cu K $\alpha$  radiation of 0.15418 nm wavelength. Monochromatization and collimation were achieved with the help of a collimating curved multilayered mirror (Osmic, Japan) delivering a close-to-parallel beam of about  $0.0085^\circ$  angular divergence. The beam size was defined by a  $40\text{-}\mu\text{m}$ -wide slit. The intensity was scaled to unit incident intensity and corrected for spillover at very low angles of incidence. The reflectograms are reported as a function of the vertical component of the wavevector of the incident photons in vacuum,  $k_{z0} = (2\pi/\lambda)\sin\theta$ , where  $\lambda$  is the X-ray wavelength and  $\theta$  is half the scattering angle. For the DOTT films, XRR analyses were carried out as a function of temperature using a homemade sample holder. The measurements were realized successively at room temperature, at 67, at 77, at 87, and at  $105\text{ }^\circ\text{C}$ . The sample was allowed to stabilize at each temperature for 15 min prior to measurement.

**Atomic Force Microscopy.** AFM analyses were performed with a Pico+ microscope (Agilent Technologies) equipped with a  $100\text{ }\mu\text{m}$  scanner, a heated sample stage, and an environmental chamber. The heated stage and the environmental chamber allow us to perform measurements as a function of temperature under an inert atmosphere (flowing dry nitrogen). The images were taken in amplitude-modulated mode (also known as intermittent-contact mode) using noncontact probes from NanoSensors with a resonance frequency of around 170 kHz, a typical spring constant of  $40\text{ N m}^{-1}$ , and a tip apex radius of curvature smaller than 10 nm. The analyses were done at room temperature,  $67\text{ }^\circ\text{C}$ ,  $77\text{ }^\circ\text{C}$ , and back to room temperature after annealing the sample at  $105\text{ }^\circ\text{C}$  for 15 min.

**Experimental X-ray Powder Diffraction.** XRD experiments were carried out with a Bruker D8 diffractometer using Cu K $\alpha$  radiation in Bragg–Brentano geometry ( $\theta-2\theta$ ). The sample, a powder deposited onto a 1-mm-thick aluminum substrate, was heated in situ using a heating stage; the cooling rate was  $1\text{ }^\circ\text{C min}^{-1}$  with an accuracy of  $0.1\text{ }^\circ\text{C}$ . X-ray measurements were performed for each mesophase observed previously with DSC.

**Simulated X-ray Powder Diffraction.** To simulate the corresponding X-ray diffractograms, a unit cell containing two molecules is first built and is then replicated using periodic boundary conditions to produce an infinite system.<sup>19</sup> The two molecules within the unit cell are placed either in a herringbone arrangement to simulate the crystalline phase, as expected from the X-ray structures of unsubstituted oligothiophenes,<sup>20,21</sup> or in a tilted arrangement for the SmG phase. In both phases, the presence of two molecules within the unit cell is essential to probing the different relative positions of the molecules in the unit cell (Results and Discussion). The unit cell was first optimized from the starting geometries at the molecular mechanics level with the COMPASS force field<sup>22</sup> using the default parameters implemented in the Materials Studio 4.0 package.<sup>23</sup> Ewald summation<sup>24</sup> was used to describe the non-bonded interactions. The optimized unit cell was then used as the starting point for a molecular dynamics (MD) simulation carried out under NPT conditions (constant number of particles, pressure, and temperature). The most stable structure was finally obtained by individually optimizing the 10 most stable frames recorded along the MD run (200-ps-long run with frames saved every 200 fs) and by choosing among them the lowest in energy. X-ray diffractograms were simulated for the most stable structure with the Cerius2 package.<sup>25</sup> The lattice parameters of the unit cell (length of the crystal axes and angles between them) were ultimately refined so that the relative intensities of the X-ray peaks in the simulated pattern best match the experimental results. During this last step, the values assigned to the cell parameters were kept frozen and only the conformations of the

molecules within the unit cell were fully optimized with the COMPASS force field.

**Field-Effect Transistors.** The OTFTs were fabricated on doped Si substrates. First, a SiO<sub>2</sub> layer (30-, 100-, or 130-nm-thick) was grown using a dry process. Source and drain interdigitated electrodes were then fabricated by photolithography and electron-beam deposition of 60 nm of Pd onto a 1 nm Ti adhesion layer. The channel composed of these bottom-gate, bottom-contact devices have a length of  $L = 2 \mu\text{m}$  (or  $L = 4 \mu\text{m}$ ) and a width of  $W = 3 \text{ mm}$ . DOTT solutions were prepared in toluene (HPLC grade, Aldrich) at a concentration of 2% by weight, and the active layer was deposited by drop casting. A mixed self-assembled monolayer (SAM) consisting of octyl- and dodecyl-trichlorosilanes was deposited on the pristine SiO<sub>2</sub> surface to assess the influence of the dielectric layer on the transport properties. Some samples were also treated with decyl-trichlorosilane in the liquid phase for 60 min at room temperature; alternatively, hexamethyldisilazane was chemically grafted in the gas phase for 30 min at 90 °C.

### Quantum Chemical Calculations of the Transfer Integrals.

Whatever the transport mechanism in the organic layer, the transfer integral that reflects the strength of the interactions between the HOMO levels (for hole transport) and between the LUMO levels (for electron transport) of adjacent molecules is a central quantity governing the magnitude of the charge mobility.<sup>26</sup> This parameter is known to be extremely sensitive to the relative positions of the interacting molecules and hence to the nature of the molecular packing. The transfer integrals ( $t$ ) between the HOMO or LUMO levels of the DOTT molecules in the smectic phase were computed here at the INDO (intermediate neglect of differential overlap) level by expanding molecular orbitals  $\phi_1$  and  $\phi_2$  of the two interacting molecules into atomic contributions (eq 1)<sup>27</sup>

$$t = \langle \phi_1 | h | \phi_2 \rangle = \sum_{\mu} \sum_{\nu} C_{1\mu} C_{2\nu} \langle \chi_{\mu} | h | \chi_{\nu} \rangle \quad (1)$$

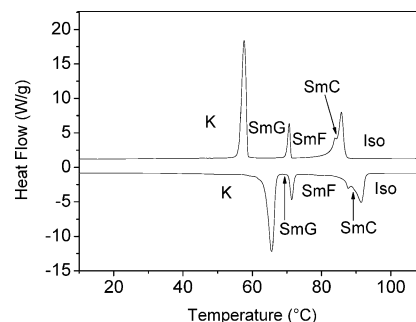
where  $C_{1\mu}$  ( $C_{2\nu}$ ) corresponds to the LCAO (linear combination of atomic orbital) coefficients of the atomic orbital  $\chi_{\mu}$  ( $\chi_{\nu}$ ) in the molecular orbital  $\phi_1$  ( $\phi_2$ ). Matrix element  $\langle \chi_{\mu} | h | \chi_{\nu} \rangle$  is implemented in the INDO method as

$$\langle \chi_{\mu} | h | \chi_{\nu} \rangle = \frac{1}{2}(\beta_A + \beta_B) \bar{S}_{\mu\nu} \quad (2)$$

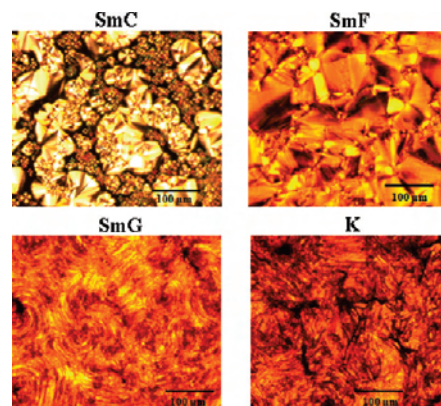
where  $\beta_A$  and  $\beta_B$  are two parameters depending on the chemical nature of atoms A and B and  $\bar{S}_{\mu\nu}$  is the overlap factor between atomic orbitals  $\chi_{\mu}$  and  $\chi_{\nu}$  corrected by empirical factors.<sup>28</sup> The choice of INDO is motivated by the fact that this approach is, in our experience, the best compromise between accuracy and computing time when dealing with the electronic properties of organic conjugated materials.<sup>29,30</sup> INDO generally yields transfer integrals in good agreement with results provided by ab initio Hartree–Fock and DFT calculations.<sup>11,31</sup> First principles approaches are prohibited in our work, aiming at the evaluation of transfer integrals for a large number of different dimers (as a result of the intrinsically disordered nature of the liquid-crystalline phase) in a large number of different snapshots provided by the MD run. Note that in the following text we will exclusively discuss the absolute values of the transfer integrals.

### 3. Results and Discussion

**Differential Scanning Calorimetry.** The thermotropic properties of DOTT were characterized by DSC. At a heating rate



**Figure 2.** DSC curve of DOTT. The transition temperatures are given in °C and the transition enthalpies are in brackets in kJ/mol. Heating: K 64 [−24.4], SmG 71 [−3.3], SmF 85 [−1.6], SmC 90 [−7.3] Iso. Cooling: K 59 [25.6], SmG 72 [3.6], SmF 85 [0.8], SmC 87 [6.8] Iso. K, crystalline phase; SmG, smectic G phase; SmF, smectic F phase; SmC, smectic C phase; and Iso, isotropic liquid.



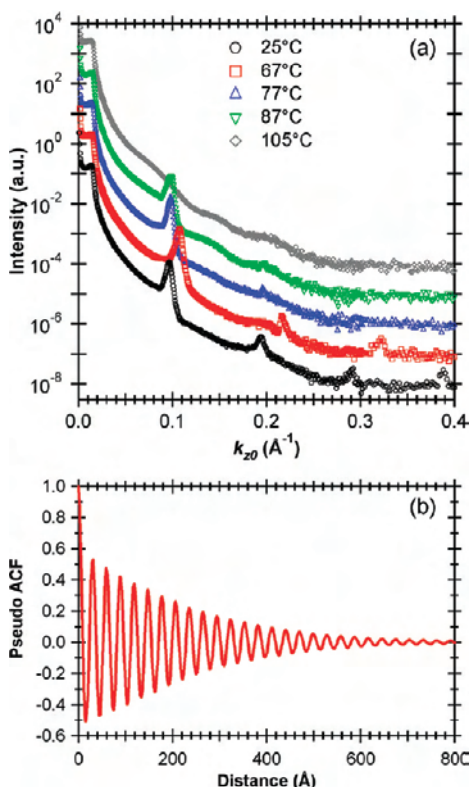
**Figure 3.** POM textures of DOTT for the SmC, SmF, SmG, and K phases.

of 5 °C min<sup>−1</sup>, the DSC curve of DOTT (Figure 2) reveals the presence of three liquid-crystalline phases between 64 and 90 °C that can be attributed to smectic G (SmG), smectic F (SmF), and smectic C (SmC) phases, respectively, as previously reported by Hanna et al.<sup>13</sup> The large transition enthalpy (24.4 kJ/mol) between the crystalline and SmG phases points to significant changes in molecular ordering between the two phases. This relates to the disappearance of the crystal order and to a switch from the herringbone packing characteristic of the crystalline phase of thiophene derivatives<sup>32</sup> to a tilted packing characteristic of smectic phases.<sup>33</sup> In contrast, the transition enthalpies between the smectic phases and between the SmC phase and the isotropic phase are relatively small (3.3, 1.6 and 7.3 kJ/mol for SmG to SmF, SmF to SmC, and SmC to Iso, respectively), thus indicating that no major reorientation of the molecules takes place.

**Polarized Optical Microscopy.** A characteristic of liquid-crystalline phases is the birefringence of the phase that yields a specific texture under the cross-polarized microscope when the sample is put between two plates. The texture observed for the first smectic mesophase (at 87 °C) upon cooling (Figure 3) is the so-called focal conic texture characteristic of the SmC phase organization.<sup>34</sup> Other textures, characteristic of more ordered phases (SmF, SmG, and crystalline), appear at lower temperatures. POM still shows a focal conic texture at 82 °C associated with the SmF phase and typical mosaic textures at 67 and 25 °C, characteristic of highly ordered SmG and crystalline phases.<sup>35</sup>

**X-ray Reflectometry.** The reflectograms measured for a DOTT thin film spin coated onto a C<sub>8</sub>–C<sub>12</sub> mixed silane





**Figure 4.** (a) XRR reflectograms of a DOTT thin film spin coated onto a silanized substrate, as measured at room temperature, 67, 77, 87, and 105 °C. (The curves were vertically shifted for the sake of clarity.) (b) Patterson function derived from the reflectogram measured at 67 °C.

monolayer are presented in Figure 4. They were recorded at different temperatures corresponding to the various structural phases of DOTT (i.e., at room temperature (crystalline phase), at 67 °C (SmG phase), at 77 °C (SmF phase), at 87 °C (SmC phase), and at 105 °C (isotropic phase)). Except for the spectrum measured at 105 °C, all reflectograms present Bragg peaks, thus testifying to the layered organization in the DOTT film. The curve measured at 105 °C does not show peaks because of the complete melting of the film.

The position of the Bragg peaks measured at room temperature (crystalline phase), at 77 °C (SmF phase), and at 87 °C (SmC phase) yields an interlayer repeat unit of 32.5 Å that approximately matches the full extended length of a DOTT molecule (31.7 Å between opposite hydrogen atoms according to the theoretical calculations). This implies that the smectic layer stands parallel to the substrate and that the DOTT molecules lie perpendicular or are only slightly tilted with respect to the substrate in these phases. The Bragg peaks are shifted to larger wavevector values in the curve measured at 67 °C (SmG phase) and thus point to a smaller layer thickness in this phase. It is estimated to be 29.2 Å from the position of the Bragg peaks and from the oscillation of the pseudoautocorrelation function (Figure 4). This smaller value indicates that the DOTT molecules are tilted here with respect to the normal to the substrate.

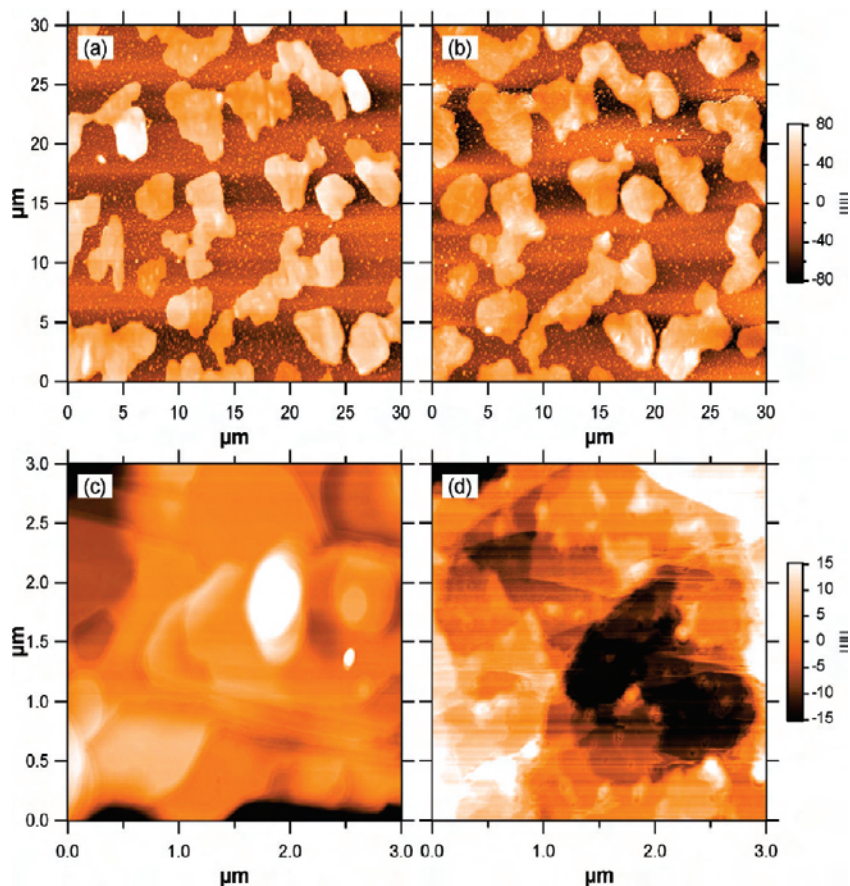
In Figure 4b, the Patterson function corresponding to the reflectogram measured at 67 °C is presented. This function, also referred to as the pseudoautocorrelation function, is obtained from the Fourier transform of the X-ray reflectivity and roughly corresponds to the autocorrelation function of the derivative of the electron density profile perpendicular to the substrate.<sup>36</sup> It gives information in direct space on the roughness and variation

of the electron density in the thin film. The regular oscillations observed on the Patterson function over more than 50 nm demonstrate the regular stacking of the molecular layers from the substrate up to that distance.

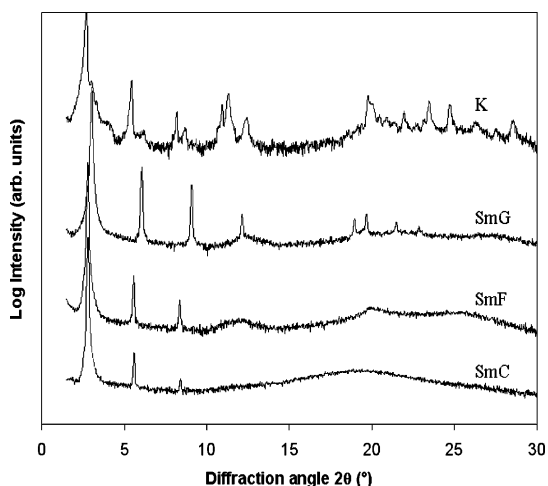
**Atomic Force Microscopy.** To confirm the height of the smectic layer provided by X-ray reflectometry, AFM images were captured for a DOTT film spin coated onto a silanized substrate (C<sub>8</sub>–C<sub>12</sub>) at room temperature (crystalline phase) and at 67 °C (SmG phase) (Figure 5). Both sets of images were acquired at the same spatial location. The large-scale images (30 × 30 μm<sup>2</sup>, Figure 5a,b) suggest that the spin-coated DOTT films are discontinuous with large crystals dispersed either on the SiO<sub>2</sub> substrate or on a very thin continuous DOTT layer. At larger scale, no apparent modification of the film morphology is observed on going from the crystalline phase (room temperature, Figure 5a) to the SmG phase (67 °C, Figure 5b). Enlarged images (3 × 3 μm<sup>2</sup>, Figure 5c,d) taken on top of a large crystal reveal a layered structure with terraces and steps. The values of the step height measured from the AFM images are in good quantitative agreement with the layer thicknesses determined by XRR, both for the crystalline phase (33.0 Å from AFM vs 32.5 Å from XRR Figure 5c) and the SmG phase (27.5 Å from AFM vs 29.2 Å from XRR Figure 5d). Moreover, comparing parts c and d of Figure 5 reveals a modification of the small-scale crystal morphology due to the transition from the crystalline phase to the SmG phase; this is consistent with the expected herringbone packing in the crystalline structure and the tilted packing in the smectic layer.

**X-ray Diffraction.** The experimental X-ray diffractograms measured for DOTT powder upon cooling are presented in Figure 6 at 87 °C (SmC phase), 77 °C (SmF phase), 67 °C (SmG phase), and at room temperature (crystalline phase). For all diffractograms, the first Bragg reflections indexed as (100) correspond to the layer thickness and provide estimates of 31.3, 31.7, 29.1, and 32.4 Å for the SmC, SmF, SmG, and K phases, respectively. These values were confirmed by XRR measurements, which also yield a smaller value for the SmG phase. The presence of higher-order reflection peaks in some mesophases reflects long-range order in the direction perpendicular to the smectic plane. For the SmC phase, no distinct peaks are observed at high 2θ values; only a broad halo centered at 19.80° is observed, thus suggesting a lower degree of organization. In contrast, two halos (at 11.30 and 24.00°) are observed for the SmF phase as well as a broad peak at 19.80° associated with a distance of 4.49 Å corresponding to a typical interplanar distance between DOTT molecules within the smectic layer. The molecules are much more organized within the SmG phase because four distinct peaks are present at large 2θ values (18.94, 19.66, 21.38, and 22.96°). The diffractogram of the crystalline phase displays a more complex pattern characteristic of 3D periodic molecular organization. However, the presence of peaks at small angles (3.07, 3.97°, ...) suggests that different crystalline structures coexist within the powder, thus making the indexation of the different peaks rather difficult. The lack of indexation of the Bragg peaks for the SmG and crystalline phases motivated the simulation of X-ray diffractograms in order to assign the Miller indices of the different experimental peaks.

To simulate the molecular packing in the SmG phase, we introduced two tilted molecules in a unit cell in four different manners (Figure 7). Indeed, different cases should be considered in our conformational search: either the two alkyl chains are pointing to the same side with respect to the terthiophene (structures 2 and 4) or one alkyl chain is pointing to one side and the other is pointing to the opposite side (structures 1 and

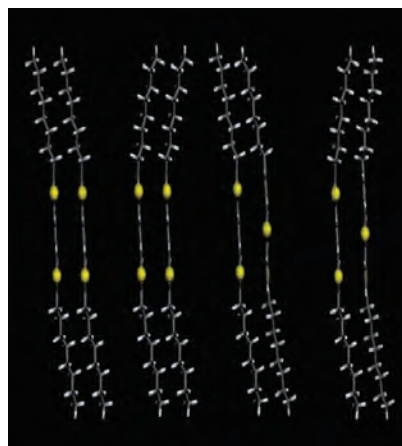


**Figure 5.** AFM images of a DOTT thin film spin coated onto a silanized substrate. (Top) Large-scale images obtained on the same spot at room temperature (a) and at 67 °C (b). (Bottom) Enlarged images captured on the same crystal at room temperature (c) and at 67 °C (d).



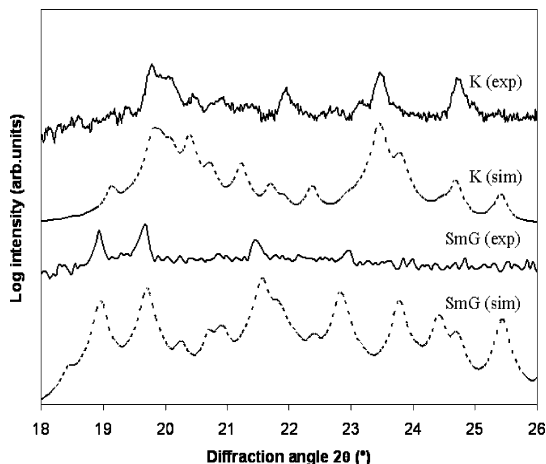
**Figure 6.** Experimental X-ray diffractograms of DOTT in the SmC (at 87 °C), SmF (at 77 °C), SmG (at 67 °C), and K (at 25 °C) phases.

3). However, the two terthiophene can be either parallel (structures 1 and 2) or antiparallel (structures 3 and 4). Note that antiparallel implies that one molecule is rotated by 180° around a horizontal axis passing through the center of mass of the conjugated backbone. After the completion of the search of the equilibrium structure and refinement of the lattice parameters (Methodology), it appears that the simulated X-ray pattern of the third system matches the experimental data in a much better way (Figure 8), where only a part of the X-ray diffractogram has been displayed for the sake of clarity. The simulations indicate that the unit cell is triclinic ( $a = 29.5 \text{ Å}$ ,  $b = 8.78 \text{ Å}$ ,  $c = 4.75 \text{ Å}$ ,  $\alpha = 93^\circ$ ,  $\beta = 89.3^\circ$ ,  $\gamma = 102^\circ$ ) and contains two



**Figure 7.** Schematic representation of the different structures used as a starting point in the conformational search (structures 1–4 from left to right). For the sake of clarity, the sulfur atoms of the terthiophene pointing to the reader are displayed in a ball representation.

antiparallel molecules translated one with respect to the other by 3.1 Å. The tilt angle of the molecules with respect to the normal of the smectic layer is 27°, and the torsion angles between the thiophene units and the alkyl chains lie between 21 and 39°. The calculated height of the smectic layer is 29.05 Å, in full agreement with the height measured by X-ray reflectometry and AFM. We stress that the possibly expected hexagonal packing<sup>33</sup> does not give a good match between the simulated and experimental patterns. These simulations allow us to index the four experimental reflections at high  $2\theta$  values (18.94, 19.66, 21.38, and 22.96°  $\text{Å}^{-1}$ ) to (10-1), (20-1), (120), and (220), respectively.

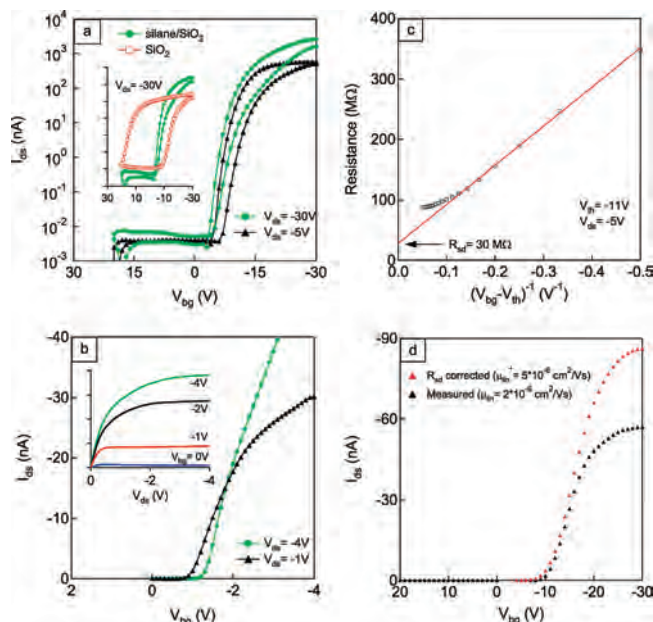


**Figure 8.** Simulated (---) and experimental (—) X-ray diffractograms of DOTT in the crystalline and SmG phases.

The simulation of the molecular packing in the crystalline phase was facilitated by the knowledge of the crystalline structure of a homologue of DOTT, namely, dihexylquaterthiophene (DHQT).<sup>37</sup> The unit cell of DHQT is made of two molecules adopting herringbone packing, with a torsion angle between the quaterthiophene core and the hexyl chains of 6°. On the basis of the assumption that DOTT adopts a packing similar to that of DHQT, we simulated the crystalline phase of DOTT by building a unit cell made of two molecules arranged in a herringbone fashion and by freezing the torsional angle between the terthiophene and the octyl chains at 6°. On that basis, we found a unit cell ( $a = 32.0$  Å,  $b = 5.4$  Å,  $c = 7.6$  Å,  $\alpha = 90^\circ$ ,  $\beta = 93^\circ$ ,  $\gamma = 90^\circ$ ) that nicely reproduces part of the X-ray experimental peaks (Figure 8): the position and relative intensity of the ( $h00$ ) reflections (i.e., the first four peaks in the simulated pattern) are well reproduced whereas all simulated peaks at higher  $2\theta$  values further match experimental reflections. Nevertheless, a lot of experimental reflections are missing in our simulations, most probably because of the coexistence of different crystalline structures.

**Field-Effect Transistor Characteristics.** The drain current  $I_{ds}$  versus drain bias  $V_{ds}$  (output) characteristics and  $I_{ds}$  versus gate bias  $V_{bg}$  (transfer) curves were collected under ambient conditions. Electrical measurements were carried out with an HP4156C semiconductor parameter analyzer equipped with a hot stage allowing for precise temperature control (0.1 °C). The hole mobility  $\mu$  is inferred from the transfer curves in the saturation regime using  $I_{ds} = (W/2L)C_i\mu_{sat}(V_{bg} - V_{th,sat})^2$  or in the linear regime using  $I_{ds} = (W/L)C_i\mu_{lin}(V_{bg} - V_{th})V_{ds}$ . Here,  $C_i$  is the measured capacitance of SiO<sub>2</sub> (constant over the investigated temperature range),  $g_m = \partial I_{ds}/\partial V_{bg}$  is the transconductance,  $V_{th,sat}$  and  $V_{th}$  represent the threshold voltage extracted from  $I_{ds}^{1/2}$  versus  $V_{bg}$  and  $I_{ds}/g_m^{1/2}$  versus  $V_{bg}$  in the saturated and linear regimes, respectively. Other relevant figures of merit are the on-to-off current ratio  $I_{on/off}$  and source-drain resistance  $R_{sd}$ . The latter has been extracted from transfer plots at low source-drain voltages.<sup>38</sup>

We present in Figure 9 the performance at room temperature of typical devices employing SiO<sub>2</sub> dielectrics modified with SAMs, as previously described. No peculiar differences have been found when different treatments of the gate insulator were applied (Methodology). The surface functionalization leads to a significant increase in mobility and in the on-to-off current ratio (typically by 1 order of magnitude). Moreover, lower  $R_{sd}$  values were systematically found upon coating the gate insulator; this is most probably related to the presence of the SAM on



**Figure 9.** Typical transfer curves for DOTT transistors with 130 (a) and 30 nm (b) SiO<sub>2</sub> dielectrics covered with C<sub>8</sub>–C<sub>12</sub> and C<sub>10</sub>, respectively. (a, inset) Comparison between pristine (red, open symbols) and silanized (green, filled symbols) devices. The reduction of the hysteretic trend of the transfer curves upon silanization can be easily noticed. (b, inset) Corresponding output curves at various gate voltages. (c, d) Typical  $R_{sd}$  extraction methodology, exemplified for the device shown in panel a (i.e., the device in the second row in Table 1).

the Pd electrodes. A detailed comparison of the electrical performance of various FETs considered in this work is presented in Table 1. The output curves present clean saturation behavior with a strong field dependence, which is also observed in the transfer response. The slight deviation from the  $I_{ds} - V_{bg}^2$  dependence at large gate bias is a manifestation of the presence of a charge injection barrier, as discussed below.

The overall mobility values are smaller than those measured in TOF experiments ( $2 \times 10^{-2}$  cm<sup>2</sup>/(V s))<sup>12,13</sup> for similar liquid-crystalline compounds. Although they are in agreement with the field-effect value of  $1.9 \times 10^{-7}$  cm<sup>2</sup>/(V s) reported by Akimichi et al.<sup>39</sup> for  $\alpha,\omega$ -dimethylterthiophene derivatives, they are apparently at odds with recent results obtained for longer oligothiophenes (nT, where  $n > 3$  is the number of thiophene units).<sup>32</sup> The observed behavior is consistent with (i) observations that the field-effect mobility is usually much smaller than that determined by TOF<sup>40</sup> because the latter approach determines the upper limit of the microscopic mobility in highly ordered semiconducting layers<sup>41</sup> and (ii) low charge carrier mobilities displayed by odd-numbered nT films due to the coexistence of polymorphs.<sup>42</sup> We attribute the low field-effect mobility of our DOTT layers to (i) the small and odd number of thiophene units; (ii) the fabrication protocol—bottom contact, bottom gate device architecture, and liquid-phase coating; and (iii) characterization procedures under ambient conditions. Generally, thin films of low-mass compounds processed from solutions display a different structural–electrical property relationship with respect to bulk materials analyzed by TOF and a poorer electrical behavior compared to that of thin films processed by sublimation.<sup>43</sup> In particular, the low mobility values measured in the crystalline phase are attributed to the presence of grain boundaries in organic layers<sup>44</sup> and to the presence of polymorphs. Larger grain size and improved structural order can be obtained by organic vapor deposition,<sup>45</sup> organic molecular beam epitaxy,<sup>46</sup> or engineered multilayer growth.<sup>47</sup>



**TABLE 1: Structural and Electrical Properties of Various DOTT-Based FETs Discussed in This Work<sup>a</sup>**

device	channel dimensions	$I_{\text{on/off}}$	$V_{\text{th,sat}}$ (V)	$\mu_{\text{sat}}$ (cm <sup>2</sup> /(V s))	$R_{\text{sd}}*W$ (M $\Omega$ .cm)	$\mu_{\text{lin}}$ (cm <sup>2</sup> /(V s))	$\mu_{\text{lin}}^*$ (cm <sup>2</sup> /(V s))
130 nm pristine SiO <sub>2</sub>	$L = 4 \mu\text{m}$ , $W = 3 \text{ mm}$	$5 \times 10^3$	16	$4 \times 10^{-8}$	47	$1.5 \times 10^{-7}$	$3 \times 10^{-7}$
130 nm SiO <sub>2</sub> /SAM	$L = 4 \mu\text{m}$ , $W = 3 \text{ mm}$	$5 \times 10^4$	-7	$2 \times 10^{-6}$	9	$2 \times 10^{-6}$	$5 \times 10^{-6}$
30 nm pristine SiO <sub>2</sub>	$L = 2 \mu\text{m}$ , $W = 3 \text{ mm}$	200	-1	$2 \times 10^{-6}$	58	$1 \times 10^{-6}$	$4 \times 10^{-6}$
30 nm SiO <sub>2</sub> /SAM	$L = 4 \mu\text{m}$ , $W = 1.5 \text{ mm}$	$10^3$	-1	$2 \times 10^{-5}$	3	$2 \times 10^{-5}$	$5 \times 10^{-5}$

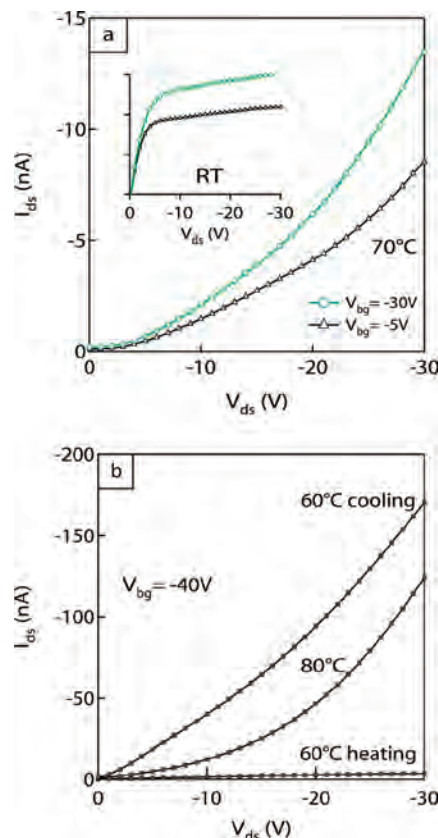
<sup>a</sup> The respective dielectric thickness and coating are specified in the first column. The channel dimensions are reported in the second column, and the on-to-off current ratio is given in the third column. Parameters extracted from the saturation regime ( $V_{\text{th,sat}}$  and  $\mu_{\text{sat}}$ ) are included for typical devices measured at room temperature, with the corresponding source-drain resistance  $R_{\text{sd}}$ . The last two columns present the linear mobilities of the devices  $\mu_{\text{lin}}$  and  $\mu_{\text{lin}}^*$  (the contact-free linear mobility).

The reduction of the hysteresis trend of the transfer curves upon silanization can be clearly noticed in the inset of Figure 9a for DOTT FETs with a 130-nm-thick SiO<sub>2</sub> dielectric layer. Because the hysteresis can be further diminished by thinning the gate dielectric, we have fabricated FETs with 30-nm-thick SiO<sub>2</sub> layers. Their larger capacitance (122 nF/cm<sup>2</sup> with respect to 25 nF/cm<sup>2</sup> for the 130-nm-thick SiO<sub>2</sub>) enables better gate control over the charge carriers, which translates into higher mobilities and electrical stability<sup>48</sup> (Table 1).

We extract  $R_{\text{sd}}$  using the linear transfer curves (i.e., collected at low  $V_{\text{ds}}$ ). The technique consists of plotting the total resistance ( $V_{\text{ds}}/I_{\text{ds}}$ ) versus the inverse of ( $V_{\text{bg}} - V_{\text{th}}$ ), as exemplified in Figure 9c for the device characterized in panel a. The straight portion of the resistance curve (corresponding to  $V_{\text{bg}}$  between -12 and -17 V) has been linearly fitted to obtain the  $R_{\text{sd}}$  value (here, 30 M $\Omega$ ) by extrapolation. The same methodology has been applied to all devices in Table 1.

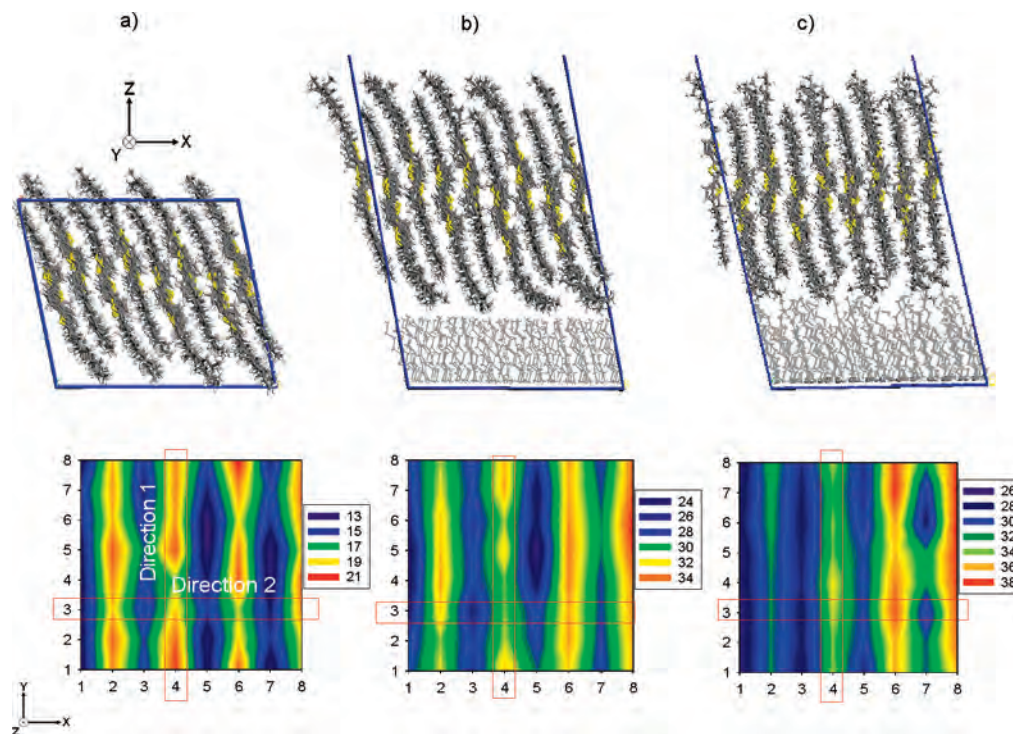
Once this value is determined, we can calculate the magnitude of the corrected source-drain current depicted in red in panel d of Figure 9 by using the equation  $I_{\text{ds}}[R_{\text{sd}} \text{ corrected}] = I_{\text{ds}}/(1 - I_{\text{ds}}*R_{\text{sd}}/V_{\text{ds}})$ . The fact that the current maintains the exact shape of the as-measured signal ensures the correctness of the extraction procedure. The values of the parasitic resistance in series with the active channel extracted for the DOTT FETs with a Pd source and drain electrodes are not far from other reports on oligothiophene-based FETs.<sup>48,49</sup> Moreover, the modest enhancement (by a factor of 2 to 4) implies that our devices do not suffer from an abnormal injection barrier but rather from limited transport abilities at room temperature.

The liquid-crystalline phases in which the grain boundaries are likely to be suppressed exist only at elevated temperature. However, for device applications, high mobility is required at room temperature and over a wide temperature range. To this end, the strategy is to process the organic materials at elevated temperature to reach an optimum self-assembled structure that can be preserved or even improved when cooling to room temperature.<sup>50,51</sup> Accordingly, we have tested whether a controlled recrystallization process can improve the transistor characteristics of DOTT in the absence of a SAM deposited on the dielectric layer. To do so, we performed a series of experiments in which the temperature was slowly changed from room temperature to 87 °C, passing through intermediate steps at 60 and 77 °C. We observe that the electrical performance weakens upon temperature cycling. An example is given in the upper panel of Figure 10, where the superlinearities and lack of saturation appearing upon heating allow for an estimate of only the linear mobility. Here, a 10-fold reduction in  $\mu_{\text{lin}}$  was observed when going from room temperature ( $2 \times 10^{-7}$  cm<sup>2</sup>/V s, consistent with the absence of the SAM on the gate dielectric) to 70 °C ( $2 \times 10^{-8}$  cm<sup>2</sup>/V s). The temperature cycling is found to induce (i) a significant degradation of charge injection at high temperature (Figure 10a); (ii) the disappearance of the field effect and saturation at temperatures corresponding to the



**Figure 10.** (a) Output curves at 77 °C for different gate biases. The inset shows the behavior at room temperature (RT) upon cooling. The transistor ( $L = 2 \mu\text{m}$ ,  $W = 3 \text{ mm}$ ) has a pristine 100-nm-thick SiO<sub>2</sub> dielectric layer. (b) Output characteristics revealing that the recrystallization of DOTT can promote an increased mobility.

smectic mesophases; and (iii) erratic behavior for the output curves measured upon cooling the devices back to room temperature. Unfortunately, these phenomena are also observed in the presence of a dielectric coating. It is worth stressing that the transformation of the DOTT layer from a smectic phase (87 °C) to a crystalline phase (60 °C) is occasionally accompanied by a strong increase in the drain current, suggesting that an improved molecular arrangement has been attained (Figure 10b). The difficulty of probing the electrical response of the liquid-crystalline mesophases might be related to spinodal dewetting on our silane-textured dielectrics. This has been encountered in other oligomer-based devices, with dramatic effects on the charge-transport properties.<sup>52</sup> In the case of liquid-crystalline films, the distortion energy can dominate the van der Waals energy so that spinodal dewetting can occur in rather thick films. Moreover, the misalignment of molecules between electrodes can seriously limit the charge transport in the smectic phases.<sup>53</sup> The quest for better reproducibility and stability thus requires the controlled deposition of the molecules under



**Figure 11.** (Top) Supercells of the three systems under study: (a) a smectic layer in the bulk; (b) a smectic layer deposited on top of a layer of octyl chains ( $C_8$ ); and (c) a smectic layer deposited on top of a layer made of 50% octyl chains ( $C_8$ ) and 50% dodecyl chains ( $C_{12}$ ). For systems b and c, the length of the cell parameter  $c$  has been set to 200 Å to avoid interactions between the replicas. (Bottom) Average value of the  $Z$  coordinate ( $Z$ ) (in Å) of the centers of mass of the 64 molecules of the supercells for systems a–c (from left to right). Directions 1 and 2 are aligned along the  $Y$  and  $X$  axes, respectively.

vacuum,<sup>50</sup> the tailored alignment of molecules with respect to the electrodes on the nanoscale,<sup>53</sup> and the use of elaborate encapsulation procedures. We speculate that for short-channel transistors accommodating perfectly aligned films of DOTT, the mobilities could reach those obtained by the TOF technique.

**Theoretical Characterization of Charge Transport.** We complemented the electrical measurements with theoretical calculations aimed at the description of (i) the charge-transfer processes in DOTT at the molecular level in the SmG phase and (ii) the influence of the silanized substrate on the transport properties. We considered three different systems related to the SmG phase: (a) a smectic layer in the bulk; (b) a smectic layer deposited on top of a layer of octyl chains ( $C_8$ ); and (c) a smectic layer deposited on top of a layer made of 50% of octyl chains ( $C_8$ ) and 50% of dodecyl chains ( $C_{12}$ ). In the third system, the octyl and dodecyl chains are randomly distributed. This corresponds to the most disordered situation and allows us to probe the impact of disorder in the SAM on the charge-transport properties by comparing systems b and c. Note that we did not model transport in the crystalline phase because of the polymorphism suggested by the X-ray diffraction experiments.

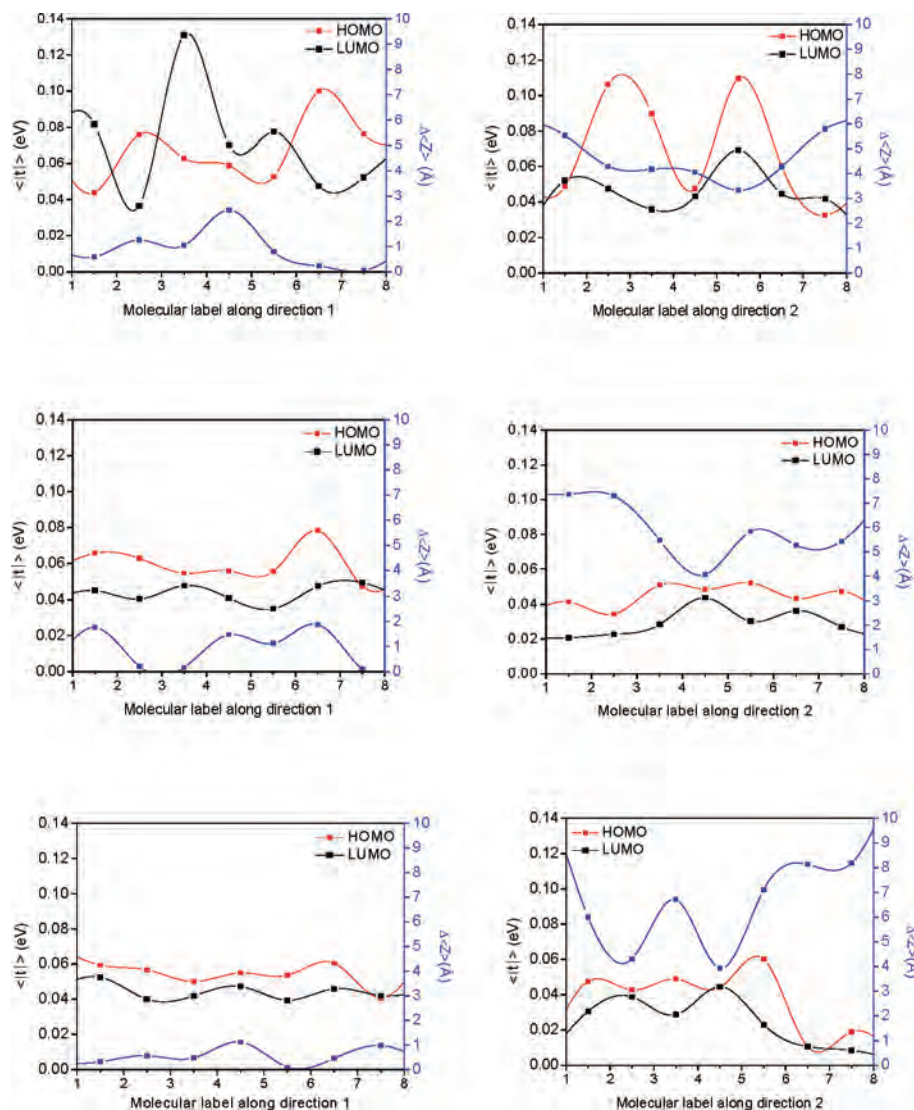
The presence of alkyl chains with different lengths introduces some degree of local roughness on the substrate because the length of a dodecyl chain exceeds that of an octyl chain by about 5 Å. We did not explicitly consider the  $SiO_2$  substrate because the molecular dynamics simulations show that no DOTT molecule penetrates into the silanized layer to interact with the  $SiO_2$  layer. The following procedure was adopted: we first optimized the system using molecular mechanics with the COMPASS force field. On that basis, we ran a molecular dynamics simulation (NVT, 67 °C, 100 ps) to equilibrate the system. Finally, we performed another MD simulation (NVT, 67 °C, 90 ps) for data acquisition by recording the geometry of the system every 30 fs. In each of these 3000 frames, the transfer

integrals associated with the HOMO and LUMO levels of neighboring molecules were computed at the INDO level.

Figure 11 illustrates the supercells used to describe the three systems under study. The  $Z$  axis was chosen to be perpendicular to the smectic layer so that variations in the  $Z$  coordinate measure the amplitude of the vertical displacements of the molecules. The analysis of the MD trajectory indicates that there is no interpenetration of molecules between adjacent layers and that the system is well ordered. The variation of the  $Z$  coordinate for a given molecule does not exceed 2 Å in the bulk, 3 Å when the smectic layer is deposited on top of a layer of octyl chains, and 5 Å when deposited on the mixed layer. The average values of the  $Z$  coordinate ( $\langle Z \rangle$ ) of the centers of mass of the 64 (i.e.,  $8 \times 8$ ) molecules of the supercells, as calculated from the 3000 snapshots extracted from the MD trajectory, are shown in Figure 11. These 2D maps show a striped layout reflecting an alternation in the height of the 1D arrays of DOTT molecules (i.e., corresponding to the 3.1 Å longitudinal shift between adjacent molecules mentioned above). For the third system, the shape of the 2D map is quite different: the periodicity of the stripes is altered because of the random distribution of dodecyl chains within the SAM.

We characterized the charge-transport properties in the smectic layer by calculating the transfer integrals for holes and electrons between adjacent molecules aligned along two orthogonal directions, as highlighted in Figure 11. Figure 12 collects the average values of the transfer integrals in the two directions (in order to account for the impact of lattice dynamics), together with the average relative displacements along  $Z$  ( $\Delta\langle Z \rangle$ ). Note that this parameter is not exactly the amplitude of the translation along the long axis of the oligothiophene backbone (because the molecules are tilted by 27°), but it is nevertheless a valid measure of this displacement.  $\Delta\langle Z \rangle$  is smaller in direction 1 because the latter reflects the relative





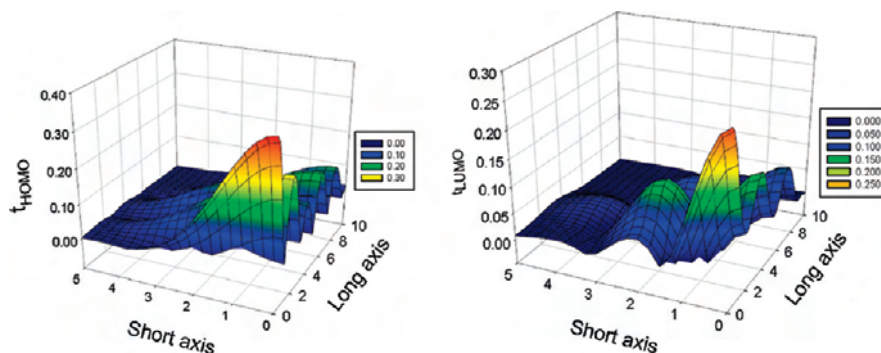
**Figure 12.** Average values of the relative displacement  $\Delta \langle Z \rangle$  and of the absolute value of the transfer integrals for holes and electrons  $\langle |t| \rangle$  along directions 1 and 2 (as defined in Figure 11) for the smectic layer (top panels), the smectic layer deposited on octyl chains (center panels), and the smectic layer deposited on a layer made of 50% octyl chains and 50% dodecyl chains (bottom panels).

displacement between two equivalent molecules, as provided by our X-ray simulations. The data do not show any clear correlation between  $\langle Z \rangle$  and  $\langle |t| \rangle$  not only because of the fact that the molecules move along the long axis direction during the dynamics but also because of fluctuations of the intermolecular distances or displacements along the short molecular axis that occur. Significant values are found for the transfer integrals both for electrons and holes, thus pointing to the potential ambipolar character of the smectic layer, provided that charges can be easily injected from the electrodes in the devices. Indeed, the transfer integrals computed in the smectic layer are almost as large as those computed in the single crystal of pentacene<sup>54</sup> (i.e., one of the best organic semiconductors). In most cases,  $\langle |t| \rangle_{\text{HOMO}}$  is larger than  $\langle |t| \rangle_{\text{LUMO}}$  along direction 2 whereas a reversal in the relative amplitudes is observed along direction 1; all together, the transfer integral values are indicative of a larger mobility for holes than for electrons.

To illustrate better the sensitivity of the transfer integrals to the relative positions of the molecules, we further calculated their values for a simple system consisting of two cofacial molecules of  $\alpha, \omega$ -dimethylterthiophene separated by 3.5 Å and displaced along the long and/or short axis, as illustrated in Figure

13. The theoretical results indicate that (i) the variation of the  $|t|$  values is more pronounced for displacements along the short axis; (ii) when averaging over all geometries,  $|t|_{\text{HOMO}}$  is larger than  $|t|_{\text{LUMO}}$ , even though the reverse can occur for specific geometric configurations. In all cases, an increase in the intermolecular distance leads to an exponential decrease in the transfer integrals because of the reduction of the overlap between the  $p_z$  orbitals of the interacting molecules.<sup>30</sup>

In the case of the smectic layer deposited on the octyl chains,  $\langle |t| \rangle_{\text{HOMO}}$  is always larger than  $\langle |t| \rangle_{\text{LUMO}}$  along the two directions (Figure 12). The larger values found along direction 1 originate from the fact that the molecules are in a more cofacial geometry in the presence of the octyl chains. We note that the calculated transfer integrals for systems b and c are in most cases smaller than those in system a. This originates from the fact that the smectic layer is less organized when deposited on top of the silanized layer. The disorder induced by the silanation layer promotes larger geometric fluctuations within the smectic layer, which are generally detrimental to charge transport. This reduction does not solely arise from displacements along  $Z$  because significant transfer integrals are preserved for translations along this direction (Figure 13). These geometrical



**Figure 13.** INDO-calculated  $|t|_{\text{HOMO}}$  and  $|t|_{\text{LUMO}}$  in a cofacial dimer made of two  $\alpha,\omega$ -dimethylterthiophene molecules as a function of displacement (in Å) along the short and long axes. The intermolecular distance is set here at 3.5 Å.

fluctuations also explain the smoother evolution of the transfer integrals in both directions because the average values are calculated on the basis of many different conformations that exhibit very different transfer integral amplitudes. When the smectic layer is deposited on a rough interface simulated here by a random mixture of 50% octyl and 50% dodecyl chains (Figure 12), we observe that the transfer integrals (and hence the transport properties) in the smectic layer are not drastically modified in comparison to those of the smectic layer deposited on an octyl layer. Thus, the disorder induced by the roughness of the silanized substrate does not appear to have a strong influence on the charge-transport properties on the molecular level; this is partially due to the fact that large transfer-integral values can be preserved despite large displacements along  $Z$  (Figure 13).

#### 4. Conclusions

We have studied the structure of the crystalline and smectic phases of DOTT by means of atomic force microscopy, X-ray reflectometry, and experimental and simulated X-ray diffraction spectra. The combination of these techniques allows us to infer the cell parameters and the relative positions of the molecules within the unit cell. In particular, we find that the molecules adopt herringbone packing in the crystalline phase and tilted packing in the SmG phase. The assignment of the experimental X-ray reflections in the SmG phase is accessed only via the simulation of the X-ray diffraction patterns. In contrast to the SmG phase, polymorphism is expected in the crystalline phase.

For conventional bottom-gate transistors with untreated  $\text{SiO}_2$  dielectrics, the charge mobility in DOTT at room temperature is quite low ( $<10^{-6} \text{ cm}^2/\text{Vs}$ ); a 10-fold or larger increase is observed upon silanation. The theoretical calculations show the high potential of DOTT for charge transport in the SmG phase because the transfer integrals between adjacent molecules are large in the bulk and only slightly smaller when deposited on a silanized substrate. This is supported by the electrical OFET characteristics, showing in selected cases an improvement in the current when heating from the crystalline to the SmG phase or when cooling from the SmG phase to the crystalline phase, most probably because of the suppression of grain boundaries. However, these trends are not yet fully reproducible at this stage, thus requiring better processing and encapsulation conditions. Another challenge currently being pursued is tailoring the nature of the alkyl substituents of the conjugated core in order to shift the liquid-crystalline phase down to room temperature.

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