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*Published in:*  
Advanced materials

*DOI:*  
[10.1002/\(SICI\)1521-4095\(200004\)12:8<563::AID-ADMA563>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1521-4095(200004)12:8<563::AID-ADMA563>3.0.CO;2-7)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2000

[Link to publication in University of Groningen/UMCG research database](#)

### *Citation for published version (APA):*

Rep, D. B. A., Roelfsema, R., van Esch, J. H., Schoonbeek, F. S., Kellogg, R. M., Feringa, B. L., Palstra, T. T. M., & Klapwijk, T. M. (2000). Self-Assembly of low-dimensional arrays of thiophene oligomers from solution on solid substrates. *Advanced materials*, *12*(8), 563 - 566. [https://doi.org/10.1002/\(SICI\)1521-4095\(200004\)12:8<563::AID-ADMA563>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1521-4095(200004)12:8<563::AID-ADMA563>3.0.CO;2-7)

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## Self-Assembly of Low-Dimensional Arrays of Thiophene Oligomers from Solution on Solid Substrates\*\*

By Diederik B. A. Rep,\* Ronald Roelfsema,  
Jan H. van Esch,\* Franck S. Schoonbeek, Richard M. Kellogg,  
Ben L. Feringa, Thomas T. M. Palstra, and Teun M. Klapwijk

Semiconducting organic compounds have been the subject of numerous studies, mostly aimed at understanding the process of charge transport through such systems. For purposes of transport studies, organic oligomers are generally chosen as a model system for organic semiconductors because highly crystalline structures of such molecules can be easily prepared by methods such as vacuum evaporation.<sup>[1,2]</sup> Alternatively, hydrogen-bonded frameworks have been exploited extensively to obtain a variety of supramolecular structures, ranging from finite-sized bowl-shaped aggregates to extended three-dimensional (3D) networks, and most markedly, also low-dimensional assemblies.<sup>[3,4]</sup> In our group, one-dimensional (1D) hydrogen-bonding properties of urea moieties have been exploited for the design of novel gelling agents, which in solution self-assemble into elongated fibers and form 1D ribbons on solid substrates.<sup>[5]</sup> It appears that the bis-urea molecules provide a structurally persistent hydrogen bonding framework that offers unique possibilities for the spatial organization of functional moieties. Recently oligothiophenes with pendant urea groups have been prepared and in solution these compounds self-assemble into elongated fibers that consist of 1D ribbons stabilized by intermolecular hydrogen bonds (Fig. 1).<sup>[6]</sup> It was shown by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) experiments that the

electronic  $\pi$ - $\pi$  overlap between adjacent oligomers results in charge-carrier mobilities of at least  $0.001 \text{ cm}^2/\text{Vs}$  for a single thiophene ring and  $0.005 \text{ cm}^2/\text{Vs}$  for a bis-thiophene.<sup>[5]</sup> When compared to simple thiophene oligomers investigated by PR-TRMC,<sup>[7]</sup> these values are relatively high.

The bis-urea-oligothiophene molecules are of great interest for the construction of electronic devices containing an organic-based 1D semiconducting channel, because of their strong tendency to form conductive, elongated aggregates consisting of 1D arrays of semiconducting molecules. In turn, devices in which charge transport is 1D, are pivotal for detailed studies of the molecule-to-molecule charge transport through organic semiconducting assemblies.<sup>[8,9]</sup> Here we report on the self-assembly of highly ordered, low-dimensional aggregates of bis-urea-*n*-thiophene (U2T<sub>*n*</sub>) molecules onto several substrates, i.e. SiO<sub>2</sub>, mica, and graphite. We will show that the deposition from solution of U2T<sub>*n*</sub> (*n* = 1, 2) results in various macroscopic morphologies which are built up from 1D arrays. We have found that the orientation of supramolecular 1D arrays on the solid substrates is similar to that of known thiophene-based molecules (i.e., upright on oxidic substrates and flat on graphite) despite the fact that we are dealing with large supramolecular 1D arrays instead of single molecules interacting only through van der Waals forces. Also, we will show that we are able to prepare directed and macroscopic structures from solution consisting of 1D arrays. These structures are of such sizes that they should be easily probed for their electrical characteristics.

In solution, U2T<sub>*n*</sub> aggregates into fibers of different lengths and morphology, depending on concentration, temperature, and solvent. From optical microscopy studies we found that at low concentrations fibers grow to several tens of micrometers in length and about 1  $\mu\text{m}$  in width. The extremely elongated shape of these fibers must arise from an anisotropic growth process. In other words, the intermolecular interactions controlling growth along the fiber axis apparently greatly exceed in strength those at the other interfaces. Most likely, the urea groups are exposed at the growing tip of the fibers and as a consequence, the U2T<sub>*n*</sub> molecules are oriented with their molecular axis perpendicular to the long axis of the fibers. At high concentrations (> 1 mg/mL), dendritic growth is found to dominate in solution, resulting in star-like aggregates. Combined X-ray diffraction, electron microscopy, molecular modeling, and scanning-tunneling microscopy results have shown that the fibers are built up from 1D arrays such as the one shown in Figure 1b.<sup>[5,6]</sup> We found that on SiO<sub>2</sub> substrates similar but much longer fibers grow when letting the solvent evaporate from sessile droplets of U2T<sub>*n*</sub> solutions. This will be discussed in the following sections.

In our experiments, solution and substrate are kept at an equal and constant temperature. Figure 2 shows a typical aggregation pattern obtained by evaporating 1-octanol from an U2T<sub>2</sub>/1-octanol<sup>[10]</sup> droplet at 70 °C. The droplet

[\*] D. B. A. Rep  
Department of Applied Physics, Nanotechnology Section  
Delft University of Technology  
Lorentzweg 1, NL-2628 CJ Delft (The Netherlands)  
E-mail: drep@dimes.tudelft.nl

R. Roelfsema  
Department of Applied Physics, Materials Science Center  
University of Groningen  
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)  
Dr. J. H. van Esch, F. S. Schoonbeek, Prof. R. M. Kellogg,  
Prof. B. L. Feringa  
Laboratory for Organic Chemistry, Stratingh Institute  
University of Groningen  
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)  
Prof. T. T. M. Palstra  
Department of Inorganic Solid State Chemistry  
Materials Science Center, University of Groningen  
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)  
Prof. T. M. Klapwijk  
Department of Applied Physics, Delft University of Technology  
Lorentzweg 1, NL-2628 CJ Delft (The Netherlands)

[\*\*] This work was performed at the Materials Science Center of the University of Groningen. Support was received from the Netherlands Foundation for Chemical Research (SON/STW) with financial aid from the Netherlands Organization for Scientific Research (NWO) and the Stichting voor Fundamenteel Onderzoek der Materie (FOM). The research of Dr. J. van Esch has been made possible by a fellowship of the Royal Netherlands Academy of Science (KNAW).

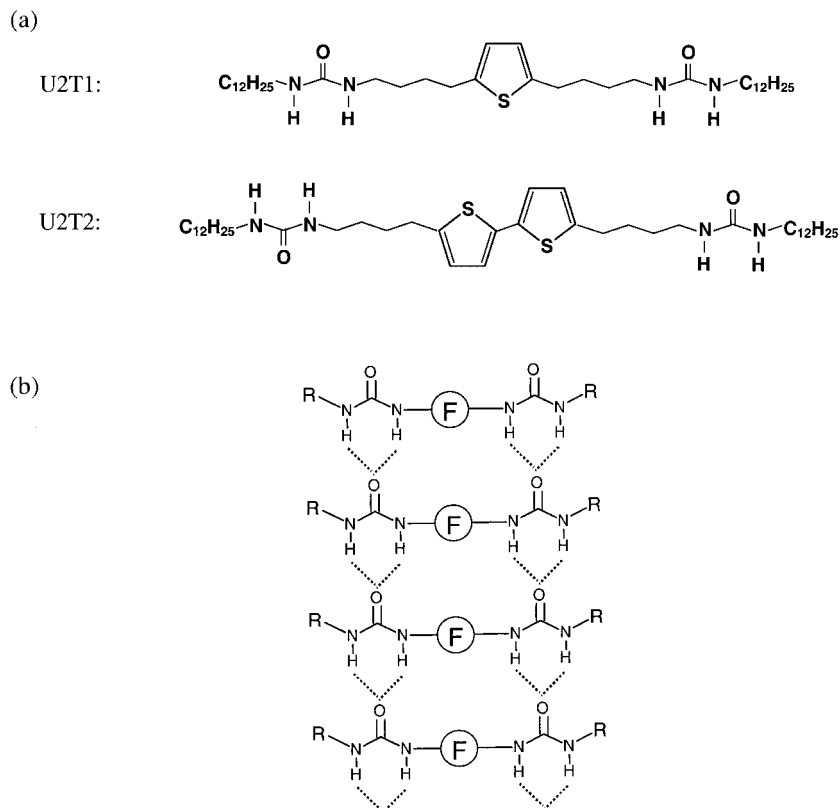


Fig. 1. a) Chemical formulae and abbreviations of the compounds under study; b) through hydrogen-bonds (dotted lines), a framework is created in which the functional units (F) are embedded.

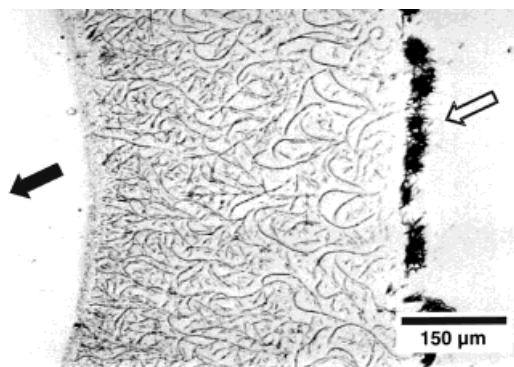


Fig. 2. Typical aggregation pattern of a U2T1/1-octanol droplet evaporated at 70 °C on SiO<sub>2</sub>. The open arrow points at the outer edge of the original droplet, the solid arrow to the optically empty center.

center is optically empty. Near the droplet edge, most of the material is aggregated. Furthermore we found that in a saturated vapor environment no fiber aggregation takes place in the droplet. Apparently, the droplet evaporation triggers the driving force for aggregation. This observation, combined with the remarkable distribution of aggregates of Figure 2 is in excellent correspondence with the effects of a pinned contact line during droplet evaporation. As described recently by Deegan,<sup>[11]</sup> this process involves initial aggregation of material from the solution onto the substrate because of which the contact line of the droplet is prohibited to move towards the center, although evaporation of

the solvent continues. To compensate for evaporation losses near the pinned contact-line, the solution is driven outwards. The outward flow is responsible for the growth of solid aggregates near the outer edge of the solvent. Finally, the contact-line will start to move in stick-slip fashion, leaving a trail of aggregates.

Earlier studies on the formation of ring stains from dried drops of CdS<sup>[12]</sup> or polystyrene<sup>[11,13]</sup> particles in solution yielded uniform circular stains. The U2T<sub>n</sub> solutions yield markedly different stains, consisting of separated fibers. The longest fibers are found mostly along the radial direction (Fig. 2). We suggest this is due to the combined effect of the radial flow of solution and the strong and highly anisotropic interactions between the U2T<sub>n</sub> molecules. The strong intermolecular interactions will lead to the formation of nucleation centers at specific temperatures and concentrations, and further fiber growth will most probably occur at these centers. Moreover, due to the anisotropic nature of the interactions, fiber tips directed along the flow of solvent (i.e., radially) will grow at a faster rate than tips directed perpendicular to

the flow. This can explain the aggregation of fibers that are predominantly directed along the radii of the droplet. We note that for these reasons the quantitative analysis, as proposed by Deegan and coworkers<sup>[11]</sup> or by Maenosono and coworkers,<sup>[12]</sup> cannot be applied to the U2T<sub>n</sub> system. A model quantifying the growth of U2T<sub>n</sub> fibers in drying droplets should include the presence and directionality of intermolecular interactions. The observation that the center of the droplet is optically empty indicates that the outward flow of particles has been sustained sufficiently long to have all the U2T<sub>n</sub> material aggregate from solution. This can mean that either the droplet contour has been pinned during the entire process of aggregation or that droplet shrinkage is by stick-slip motion<sup>[13]</sup> of the contact-line.

Although the process of fiber-growth through droplet evaporation is very sensitive to surface morphology, temperature gradients and so forth, we observe a trend in maximum fiber length as a function of growth parameters (Table 1). Of the three temperatures investigated (20 °C, 70 °C, and 120 °C), the longest fibers are found at 70 °C; of the three concentrations (1 mg/mL, 63 μg/mL, and 16 μg/mL) 63 μg/mL yields the longest fibers. At 70 °C and 63 μg/mL, fibers of up to 500 μm in length are observed. Qualitatively, the trend can be well understood. At the lowest temperature, evaporation is slowest, so mass transport towards the droplet edge is smallest, resulting in a near-equilibrium type of growth. This is also the regime of the highest super-

Table 1. Indication of the maximum fiber lengths on SiO<sub>2</sub> as concluded from optical microscopy. Substrate and U2T2/1-octanol mixtures (of different concentrations) were kept at a constant temperature. All substrates originate from the same piece of thermally oxidized Si. Fibers can be curled so that the effective gap-spanning length can be lower by about a factor of two.

	20 °C	70 °C	120 °C
1 mg/mL	< 10 μm	~ 500 μm	< 10 μm
63 μg/mL	< 10 μm	~ 500 μm	~ 100 μm
16 μg/mL	< 10 μm	< 1 μm	~ 50 μm

saturation and hence a large number of nucleation centers will be formed. This adds up to yield a large number of small fibers. At the other extreme (the highest temperature), mass transport is enhanced but the degree of supersaturation is lower. This can result in diffusion-dominated growth of an unstable nature, yielding dendrites instead of fibers. At intermediate temperatures of about 70 °C, growth is dominated neither by diffusion nor by nucleation, and fibers with the largest aspect ratios are formed.

To gain insight in the molecular packing within the fibers grown by this method, X-ray diffraction (XRD) and tapping-mode atomic force microscopy (TM-AFM) experiments were conducted.

Firstly,  $\theta$ -2 $\theta$  XRD experiments on SiO<sub>2</sub> substrates covered with U2T1 fibers yielded a dominant reflection at  $2\theta = 2.3^\circ$  and several higher-order peaks, all corresponding to a periodicity of 38.6 Å. This value is in excellent agreement with the dominant XRD signal corresponding to 38.9 Å for U2T1 powders and periodicities observed by electron microscopy for U2T1 fibers in solution.<sup>[6]</sup> Earlier we interpreted this periodicity (and the corresponding periodicities observed for other bis-urea compounds) as being due to the stacking of 2D lamellae consisting of tilted 1D arrays of bis-urea molecules.<sup>[5,6]</sup> Consequently, we argue that the U2T1 fibers grown on SiO<sub>2</sub> substrates from solution consist of similar lamellae that are built up from 1D arrays.

As was shown above, the micrometer-sized fibers are not equilibrium morphologies but rather originate from a diffusion-limited growth process. By annealing these fibers on SiO<sub>2</sub> substrates at temperatures slightly below the U2T $n$  melting point, we have tried to allow the aggregates to attain their equilibrium morphologies on the substrates. As shown in Figure 3, this results in the bulk of the material gathering in large droplets, revealing extended mono- and multilayer regions of the same elongated nature as the fibers observed before annealing. In the case of U2T1 and U2T2, the individual layers have heights of about 4 and 4.5 nm, respectively (shown for U2T1 in Fig. 3b). These values agree with the XRD results discussed above for as-grown fibers, and corroborate that the energetically favored 1D array orientation on SiO<sub>2</sub> is upright.

These two sets of experiments show that apparently the molecules behave in very much the same way as do other compounds containing hydrocarbon tails and/or thiophene moieties, in that they take on a perpendicular orientation when deposited on SiO<sub>2</sub>.<sup>[14]</sup> Additional experiments with U2T $n$  on mica<sup>[15]</sup> reproduce this orientation, indicating that

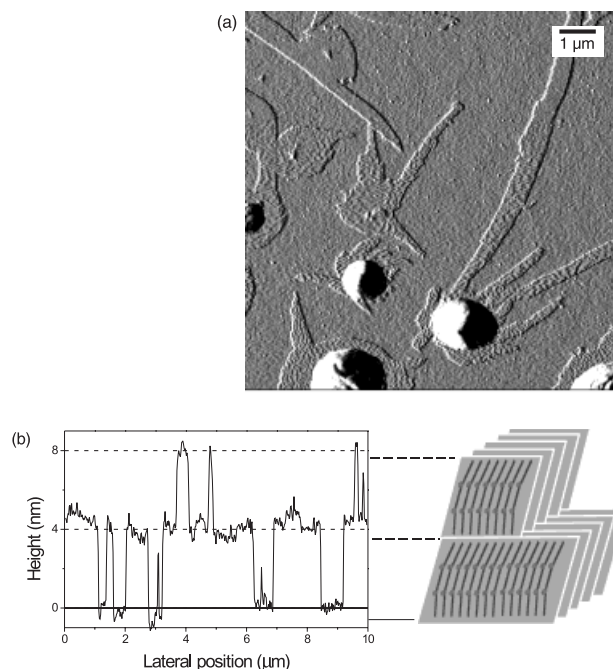


Fig. 3. a) TM-AFM height-scan of U2T1 fibers after annealing at temperatures close to the melting point on hydrophilic SiO<sub>2</sub>. b) TM-AFM line-scan of a region containing mono- and bilayers of about 4 and 8 nm in height, corresponding to U2T1 molecules standing nearly upright. The upright orientation is schematically shown next to the line-scan. In this picture, several upright 1D arrays are depicted, with the round dots representing the urea groups (see also Fig. 1).

it is a property not just of the SiO<sub>2</sub> substrate, but most probably of oxidic substrates in general. The upright orientation can be attributed to the fact that the stacking interaction between the 1D arrays of molecules is energetically favored over the substrate-array interactions.

For many hydrocarbon- or thiophene-based molecules, the latter interactions are enhanced drastically by choosing molecularly-flat highly oriented pyrolytic graphite (HOPG) as the substrate. Consequently, molecules such as  $\alpha$ -alkylated quaterthiophenes<sup>[16]</sup> or long-chain alkanes are known to lie down on HOPG as opposed to standing up on glass or SiO<sub>2</sub>. To see whether the analogy between such compounds and U2T $n$ s can be maintained for the case of HOPG substrates, we have investigated the aggregation of U2T2 on HOPG by adsorbing thin layers from solution. The substrate was dipped (surface down) into a heated solution for several seconds at the most and the solvent was then immediately removed. Figure 4 shows a TM-AFM scan of a U2T2 layer on graphite after solvent evaporation. Parallel arrays can be discerned in three distinct directions, extending over the entire HOPG terrace width. No indication of monolayer regions such as the ones seen in Figure 3 can be found. Thus, we conclude that indeed on HOPG U2T2 does not take on an upright configuration. Interestingly, the array width extracted from Figure 4 (~ 12 nm) corresponds to roughly twice the U2T2 molecule width. This is remarkable since TM-AFM scans of U2C9 (a bis-urea compound with nine hydrocarbon units in place of the

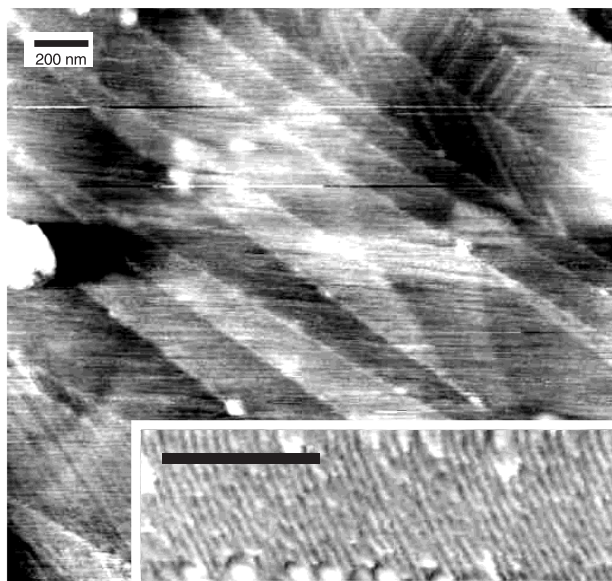


Fig. 4. TM-AFM scans of U2T2 adsorbates on HOPG (adsorption time and temperature: 1 s and 65 °C; annealing time and temperature: 1200 s and 140 °C). Parallel arrays can be discerned, limited by steps in the HOPG. Arrays are along three distinct directions, indicating commensurate growth. Inset shows a series of arrays on a larger scale. Bars are 200 nm long.

thiophene core)<sup>[5]</sup> reveal parallel 1D arrays that are one U2C9 molecule wide, consistent with STM results on the same material reported earlier.<sup>[5a]</sup> Furthermore, STM scans of U2T2 monolayer-aggregation at the liquid/graphite interface<sup>[17]</sup> also unambiguously show parallel 1D arrays with a width of about 6 nm. The origin of the factor of two difference between TM-AFM and STM scans is unclear, but it might suggest that the layer that was imaged by TM-AFM is the top of some thin multilayer structure as opposed to the first monolayer. In STM images only the first monolayer is imaged. The pattern formation of U2T2 on U2T2 might be distinctly different from that of U2T2 on HOPG.

In summary, we have investigated aggregations of U2Tn ( $n = 1, 2$ ) compounds from solution on solid substrates. The compounds have a strong tendency to form highly elongated aggregates. We have related this observation to the presence of 1D arrays of U2Tn molecules in the aggregates. The 1D arrays are due to the ability of the two urea groups incorporated in the U2Tn compounds to form H-bonds. Despite the macromolecular nature of the 1D arrays, their orientation on solid substrates follows the trend observed in the past for a variety of thiophene-based as well as hydrocarbon-based single molecules: the arrays adopt an upright orientation on oxidic substrates such as SiO<sub>2</sub> whereas they tend to lie down flat on HOPG. Using simple means, we have succeeded in growing directed micrometer-sized fibers from solution on SiO<sub>2</sub>. After annealing such fibers, extended monolayer features are obtained that consist of upright 1D arrays standing side by side. We have argued that the various macroscopic aggregates obtained after deposition of U2Tn from solution are all made up from 1D arrays. Therefore these materials appear to be highly prom-

ising candidates for studying 1D molecule-to-molecule charge-transport in organic semiconductors. We are currently preparing devices in which fibers or, alternatively, monolayer features are grown across predefined electrodes.

## Experimental

U2T2 and U2T1 were synthesized as described elsewhere [5]. Substrates were Si(100) covered with thermally grown oxide and cleaned by washing with polar and non-polar solvents. Additionally, freshly cleaved HOPG and mica were used. For droplet evaporation experiments, typically 5  $\mu$ L droplets were deposited onto substrates. Substrates and solutions were kept within an oven to ensure thermal equilibrium. During adsorption experiments, substrate and solution were also kept at the same temperature. To remove solvent from the substrate after adsorption, either the sample was heated on a hotplate or introduced into a (low) vacuum for several min. The surface morphology was investigated by tapping-mode atomic force microscope (TM-AFM, Nanoscope IIIa, Digital Instruments) in order to minimize tip-induced damage to the sample during scanning.

Received: June 16, 1999  
Final version: January 28, 2000

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