

Competitive Physisorption Among Alkyl-Substituted π -Conjugated Oligomers at the Solid–Liquid Interface: Towards Prediction of Self-Assembly at Surfaces from a Multicomponent Solution**

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The control of molecular adsorption at the solid–liquid interface is relevant both for the tuning of fundamental properties of molecular materials, such as wettability and lubrication, as well as for technological applications, for example, organic electronics. The performance of organic electronic devices, such as field-effect transistors (FETs), relies to a great extent on the optimization of charge injection and transport at interfaces. Therefore, it is crucial to be able to tailor molecular orientations and superstructure at interfaces by achieving full control over the adsorption of molecules on electrically conducting surfaces/electrodes.

Among conjugated molecules, phenylene-thiophene oligomers represent an extremely interesting class of organic semiconductors.^[1,2] They have recently attracted a lot of interest due to their remarkable electronic properties and the reasonably easy synthesis of solution-processible derivatives.^[3]

In particular, [5,5′]-bisphenyl-[2,2′]-bithiophenes (PTTPs) have already been reported to provide very good mobilities and $I_{\text{on}}/I_{\text{off}}$ ratios in FET prototypes.^[4–8]

Although in the past great effort has been devoted to the study of oligothiophenes by means of scanning tunneling microscopy (STM) at the solid–liquid interface,^[9–20] hitherto, PTTP derivatives have not been studied using such an approach.

Scanning probe microscopies are unique tools for the investigation of two-dimensional self-assembled molecular networks. In particular, STM makes it possible to achieve submolecular resolution,^[21] thereby offering direct insight into non-covalent interactions between adsorbates and substrates as well as among co-adsorbed molecules.^[22]

In this Communication, we describe a high-resolution STM study on the self-assembly of different alkyl-substituted PTTPs at the graphite–solution interface. By investigating the competitive adsorption among three similar derivatives simultaneously present in an equimolar mixture in the supernatant solution, we provide direct insight into the thermodynamics of physisorption at the solid–liquid interface. Molecular-modeling simulations provide an atomistic picture of the assembly of molecules on graphite and a quantitative estimation of the energetics of the physisorption process.

We have focused our attention on four PTTP-based alkyl derivatives symmetrically end-substituted with the following groups: di-hexyl, di-(2-methylhexyl), di-octyl, and di-decyl (**1**, **2**, **3**, and **4** in Scheme 1, respectively). Such derivatives were chosen so as to explore the role of subtle changes in the molecular structure on the intermolecular and interfacial forces governing self-assembly on graphite. To avoid even/odd effects that are known to dramatically affect the self-assembly at surfaces,^[23,24] we focused only on alkyl chains possessing an even number of carbon atoms. Highly oriented pyrolytic graphite (HOPG) was chosen as a substrate because it is atomically flat and inert. It was demonstrated to be a suitable support for carbon-based molecules incorporating sp^3 , sp^2 , and sp carbons. For the solvent, we selected 1-phenyloctane since it has a high boiling point and it revealed a poor propensity for co-adsorption on HOPG.

The self-assembly at the graphite–solution interface of all four PTTP derivatives was first explored in monocomponent

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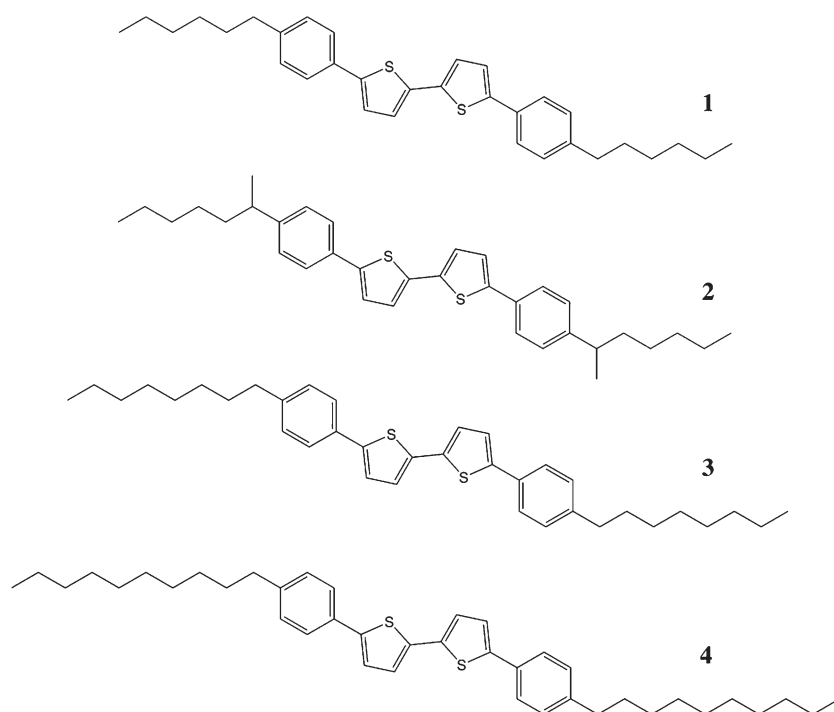
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Supporting Information is available on the WWW under <http://www.small-journal.com> or from the author.



Scheme 1. Molecular structures of the PTP derivatives investigated.

films prepared using different concentrations of the supernatant solution, that is, 0.005, 0.075, 0.01, 0.025, 0.05, 0.075, and 0.1 g L⁻¹. This revealed that densely packed crystalline monolayers are formed for all the derivatives when concentrations of at least 0.025 g L⁻¹ are used.

Figure 1a and b shows two representative images of the monolayer formed by **1** at the HOPG–solution interface. They display large crystalline domains featuring a lamellar structure (a survey STM image is given in the Supporting Information, Figure S1). The high magnification in Figure 1b reveals that the intermolecular distance between adjacent molecules within a given lamella is slightly higher than 1.1 nm.

Due to resonant tunneling between the frontier orbital of the molecules and the Fermi level of graphite, the brighter parts of the images can be ascribed to the conjugated cores of the admolecules, whereas the darker part can be assigned to the alkyl side groups.^[25] This is in accordance with contrasts in STM images of alkyl-substituted oligothiophenes, which are structurally and electronically similar systems.^[9–12]

On the one hand, previous studies on α -alkylated quaterthiophenes physisorbed on a MoS₂ surface showed that the alkyl side chains are interdigitated so as to maximize van der Waals interactions among adjacent molecules belonging to neighboring lamellae, thereby dictating a distance of 1.15 ± 0.05 nm between neighboring molecules belonging to a given lamella.^[12] On the other hand, such an intermolecular distance in neighboring alkyl-substituted oligothiophenes was found to be only 4.62 ± 0.05 Å in systems pre-programmed to self assemble without interdigitation between adjacent molecules belonging to neighboring lamellae.^[14,15]

In light of this, we can conclude that the packing we observed here, featuring a lamellar width over 1.1 nm, is

characterized by interdigitation between alkyl chains belonging to molecules of adjacent lamellae.

Figure 1c and d shows the physisorbed monolayer formed by **2** on the HOPG interface (a survey STM image is displayed in Figure S2). It reveals lamellar domains with sizes comparable to those observed for **1**. A careful analysis of Figure 1c reveals that the two-dimensional assembly consists of rows, each one containing pairs of rows of molecules, as evidenced by the double-stripe motif (highlighted in Figure 1c). The unit cell contains two molecules of **2**, physisorbed in a slightly tilted manner with respect to each other, giving rise to lamellae with intermolecular distances amounting to $\Delta l = 3.2$ nm. Interestingly, the surface areas occupied by one molecule in the crystals of **2** and **1** are extremely different as they are around 2 nm² and 3.8 nm², respectively. This difference can be explained by taking into account the branched structure of the alkyl side chains of **2**. In fact, it is known that the alkyl-branched chains can undergo partial physisorption on graphite to yield a higher packing density.^[26] The size of the unit cell suggests that molecule **2** is physisorbed on HOPG, with the first carbon

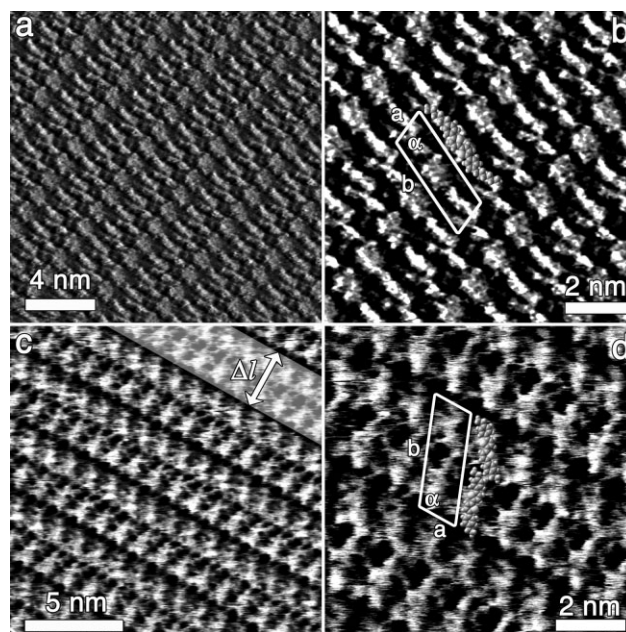


Figure 1. a) STM current images of the physisorbed monolayer formed by **1** at the HOPG–solution interface (average tunneling current $I_t = 5$ pA, sample bias $V_t = -500$ mV). b) The unit cell ($a = 1.13 \pm 0.05$ nm, $b = 3.43 \pm 0.05$ nm, $\alpha = 109 \pm 1^\circ$) and the superimposed CPK molecular model are shown. c) STM current images of the physisorbed monolayer formed by **2** at the HOPG–solution interface ($I_t = 5$ pA, $V_t = -500$ mV). A lamella is highlighted ($\Delta l = 3.20 \pm 0.05$ nm) showing the double stripe motif. d) The unit cell ($a = 1.19 \pm 0.05$ nm, $b = 3.41 \pm 0.05$ nm, $\alpha = 110 \pm 1^\circ$) and the superimposed CPK molecular model are shown.

atom of the alkyl chains, plus the methyl branch, lying on the surface. The remaining fragments of the alkyl chains are backfolded in the supernatant solution, thus interacting with the solvent to minimize the total energy of the system.

Figure 2 shows the STM images of the physisorbed monolayer of molecule **3** at the HOPG–solution interface. In contrast to **1** and **2**, molecule **3** shows the coexistence of two polymorphs,^[27,28] hereafter referred to as phase *3a* and *3b*. To ascertain the thermodynamic stability of the two phases, we investigated a large number of samples (about 20) and followed the packing evolution with time. It revealed that the large majority of the imaged domains exhibits the phase *3a* structure, whereas the *3b* phase was imaged only when highly concentrated solutions (0.1 g L^{-1}) were used. Furthermore, we found that the *3b* domains slowly convert into the *3a* phase (the complete absence of phase *3b* has been observed after about twelve hours). This clearly demonstrates that phase *3a* is thermodynamically favored, whilst *3b* is metastable. The latter forms only when the system is under kinetic control, that is, at high concentration. In this case, nuclei of phase *3b* are formed at the HOPG surface and slowly desorbed and replaced by phase *3a* due to Ostwald ripening.^[11] The role of concentration in polymorphism at the solid–solution interface has been

highlighted recently in the literature, both for monocomponent^[28] and bicomponent self-assembled monolayers.^[29]

Both the *3a* and *3b* phases were studied in detail in order to gain a precise characterization of the two structures. In Figure 2b, a high-magnification STM image of both phases is shown. On the one hand, phase *3b* features a similar packing to molecules **1** and **2**, being characterized by the interdigitation of the side alkyl chains. On the other hand, in phase *3a*, the intermolecular distance is only about 0.65 nm, leading, therefore, to a tightly packed structure where interdigitation is hindered.

The assembly of molecule **3** and the stability of phases *3a* and *3b* were also investigated through molecular-modeling simulations. In order to compare the energetics of the two phases, we modeled a cluster of ten molecules for each phase on a graphite 2D periodic cell by using the STM unit cell parameters as inputs for molecular mechanics (MM) and molecular dynamics (MD) with periodic boundary conditions. Figure 2c and d shows two snapshots (i.e., conformations selected from the MD run at 298 K), chosen among the deepest potential-energy minima. In the *3a* phase (Figure 2c), the molecules are tightly packed and conformational freedom is restrained, that is, the diffusion of the molecules on the basal plane of the graphite is very small. The conjugated segments are partly π -stacked to the first graphitic plane and there are slight torsions between adjacent rings within the molecules. At the supramolecular level, the aliphatic chains phase segregate from the π -cores, leading to the formation of lamellar motifs. The alkyl groups are indeed extended but are also sterically interacting, eventually giving rise to out-of-plane bending. In phase *3b* (Figure 2d), the conjugated segments are quite far apart, while the alkyl groups are fully interdigitated. In this case, the conjugated planes are planar, adsorbed parallel to the graphitic plane. Such a loose structure has also been observed in other alkyl-substituted oligothiophene assemblies.^[20]

The enthalpic contribution to the energy difference between the two phases amounts roughly to 4 kcal mol^{-1} per molecule in favor of phase *3a*, consistent with the experimental observations. This confirms that phase *3a* is thermodynamically favored over phase *3b* (for more details on the energy estimation, see the Supporting Information). It is important to point out that the entropic contribution is not taken into account in this estimation. The price to pay in terms of loss in entropy to form phase *3a* is surely higher than in the case of *3b* because of the higher packing density (number of physisorbed molecules per unit area). Therefore, the difference in free energy of the two phases is even

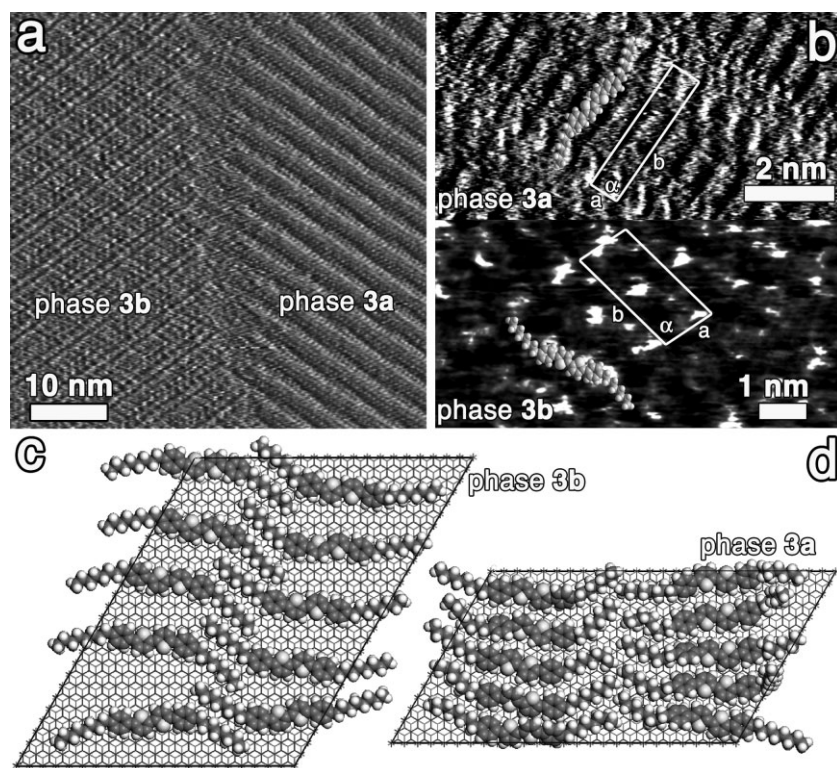


Figure 2. a) STM current image of the physisorbed monolayer formed by **3** at the HOPG–solution interface ($I_t = 7 \text{ pA}$, $V_t = -520 \text{ mV}$). The two polymorphic phases are indicated. b) High-magnification STM current images of the two phases (phase *3a*: $I_t = 5 \text{ pA}$, $V_t = -500 \text{ mV}$; phase *3b*: $I_t = 7 \text{ pA}$, $V_t = -520 \text{ mV}$). Unit cells (phase *3a*: $a = 0.65 \pm 0.05 \text{ nm}$, $b = 3.17 \pm 0.05 \text{ nm}$, $\alpha = 91 \pm 1^\circ$; phase *3b*: $a = 1.14 \pm 0.05 \text{ nm}$, $b = 2.62 \pm 0.05 \text{ nm}$, $\alpha = 102 \pm 1^\circ$) and CPK molecular models are shown for each phase. c) Snapshot of the modeled phase *3a* corresponding to potential-energy minima from the MD runs at 298 K. The PTPP molecules are displayed in CPK models, the graphite planes are shown in dark gray (outermost plane) and light gray (second plane), and the 2D periodic box is shown with the black line. d) As (c) but for phase *3b*.

smaller, explaining their coexistence in our experimental results.

In order to identify which molecule out of **1**, **2**, and **3** is preferentially physisorbed on the HOPG surface at the solid–solution interface in a competitive scenario, we prepared a solution containing an equimolar mixture of the three molecules in 1-phenyloctane, each with a concentration of 0.033 g L^{-1} . The use of STM to unravel competitive physisorption processes at the solid–liquid interface has already been reported for studies using solutions containing only two components.^[15,30] Interestingly, in our experiments, we observed that the HOPG surface is coated by the $3a$ phase, independently of the time after the deposition (a representative STM image of this phase is shown in Figure S3). The same results were also found upon increasing or decreasing the concentration of one molecule by a factor of 25%, while keeping the concentrations of the others constant.^[31]

The greater stability of the assembly of compound **3** (in its $3a$ phase) compared to that of compound **1** is further confirmed by MM calculations of periodic structures. The total adsorption energy per surface unit (here defined as the total energy minus the energy of the graphite minus the energy of the stack, in $\text{kcal mol}^{-1} \text{ nm}^{-2}$) for the dense phase $3a$ is estimated to be around $10 \text{ kcal mol}^{-1} \text{ nm}^{-2}$ (per molecule) more stable than the assembly of **1**, which features a loose packing.

The tendency to form noninterdigitated packings with the increasing length of the lateral alkyl chains (i.e., when going from **1** to **3**) is confirmed by the structures formed by **4**. As in the case of the other PTP derivatives, very stable monolayers were found to form on HOPG (for a large-scale STM image, see Figure S4). High-resolution STM images are shown in Figure 3, showing that the monolayer structure is consistent with the $3a$ phase found for **3**. The unit cell is only slightly larger, because of the longer alkyl chains.

The self-assembled 2D structures obtained using all the molecules under investigation (**1–4**) have also been found to form over atomic steps of graphite (atomic steps are indicated in Figures S1 and S2) providing unambiguous evidence of the high magnitude of intermolecular interactions in the 2D crystal overcoming the loss in physisorption energy due to the mismatch between molecules and HOPG preferential sites.

Taking advantage of the greater affinity of phase $3a$ for HOPG, we also investigated the possibility of selectively desorbing an alkyl derivative by physisorbing another one, which has a greater tendency to form ordered monolayers at the HOPG–solution

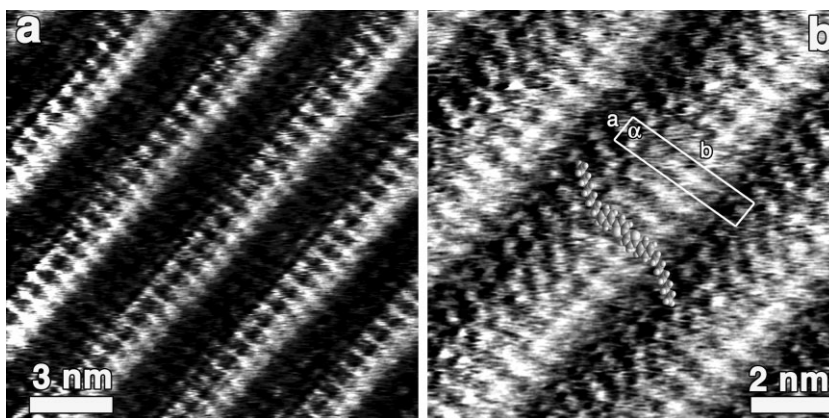


Figure 3. a) STM current images of the physisorbed monolayer formed by **4** at the HOPG–solution interface ($I_t = 5 \text{ pA}$, $V_t = -500 \text{ mV}$). b) The unit cell ($a = 0.68 \pm 0.05 \text{ nm}$, $b = 3.57 \pm 0.05 \text{ nm}$, $\alpha = 94 \pm 1^\circ$) and the superimposed CPK molecular model are shown.

interface. This was accomplished by sequentially i) placing a $5 \mu\text{L}$ droplet of a 0.1 g L^{-1} solution of **1** on graphite, ii) STM imaging the formed monolayer, and iii) adding a $5 \mu\text{L}$ droplet of a 0.1 g L^{-1} solution of **3** on top of the existing droplet in situ (i.e., while scanning). Figure 4 shows the results of this experiment. After the deposition of the second droplet, the monolayer formed by **1** is immediately desorbed. This is shown by Figure 3b exhibiting only noise in the STM image, which can be ascribed to the motions of molecules close to the graphite surface. That is, molecules of **1** are moving away from the surface while, at the same time, molecules of **3** are moving towards the surface and, ultimately, being physisorbed and forming a tightly packed 2D crystalline architecture (phase $3a$). These motions are far too fast to be resolved within our experimentally accessible time scale. In Figure 4c, the early stages of the monolayer formation are observed. During the

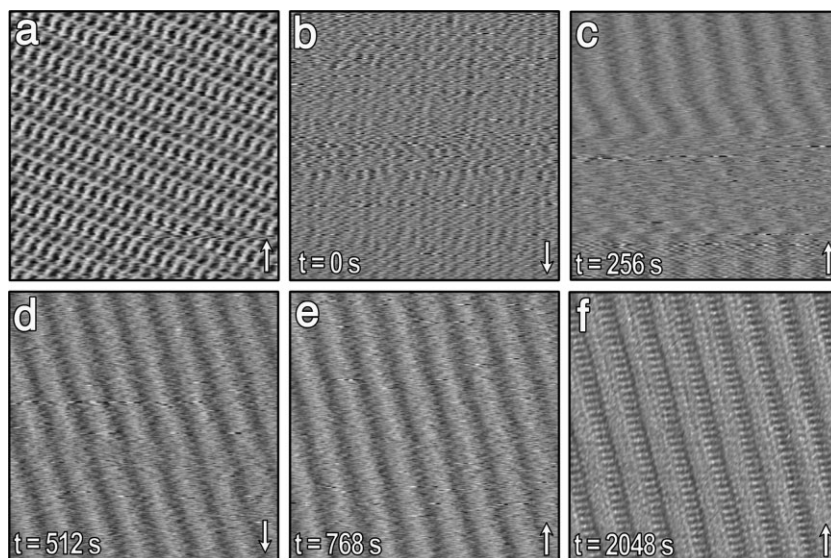


Figure 4. Sequence of STM current images of the physisorbed monolayer formed by **1** at the HOPG–solution interface, to which a solution of **3** was added ($t = 0 \text{ s}$). Image scale: $25 \times 25 \text{ nm}$ ($I_t = 5 \text{ pA}$, $V_t = -550 \text{ mV}$). Arrows indicate the scan direction. The time elapsed is also reported.

first 30 minutes, the resolution of the images improves scan after scan, reflecting the increase in stability of the molecular monolayer, that is, increased immobilization of the molecules on the surface.^[32]

In conclusion, in situ STM studies of the self assembly of PTPP derivatives at the solution–graphite interface revealed that subtle changes in the nature of alkyl side-groups drives the 2D packing towards motifs featuring either interdigitation or noninterdigitation of neighboring alkyl chains. In particular, it was found that, upon increasing the length of the side alkyl group, the interdigitated packing formed by **1** is substituted by the noninterdigitated monolayer formed by **4** and **3** in its *3a* phase. The di-octyl derivative **3** was found to form two polymorphs, which are very close to each other in terms of energetic stability. This made it possible to study both polymorphs in detail and to prove the greater stability of the more densely packed phase, that is, phase *3a*. Molecular-modeling simulations indicate that phase *3a* and *3b* monolayers do not feature π -stacking between adjacent conjugated segments, the main differences between the two phases being the tighter packing in phase *3a*, while phase *3b* is characterized by an interdigitation of alkyl chains and full planarity of the conjugated rings on graphite. Among these two phases, *3a* was found to be more enthalpically stable, with an estimated energy gap of 4 kcal mol⁻¹ (≈ 17 kJ mol⁻¹) per molecule. Finally, we performed a competitive physisorption experiment at the solid–liquid interface with a solution containing three molecules (**1–3**). We found that only the system exposing the longest alkyl side groups (**3**) physisorbs at surfaces into ordered arrangements in its densely packed *3a* two-dimensional phase. Calculations confirm such a result, showing that the monolayer of **1** is less stable by about 10 kcal mol⁻¹ than the phase *3a* monolayer.

These results pave the way towards predictable 2D self-assembly at the solid–liquid interface from a multicomponent solution. Further experiments are now ongoing to semi-quantitatively estimate the contributions to the thermodynamics of physisorption. A precise control over concentration is crucial to extract accurate numbers, and this requires some improvements in terms of the instrumental apparatus. In particular, a liquid cell where the concentration can be precisely controlled is needed to accurately evaluate numbers. The possibility of predicting the selective physisorption can be of interest for controlling the nanopatterning of surfaces and interfaces with functional materials.

Experimental Section

PTTP derivatives have been synthesized following an established procedure.^[2,4,33] ¹H- and ¹³C-NMR are given in the Supporting Information. Solutions were prepared by dissolving PTPP derivatives in 1-phenyloctane (Aldrich) at concentrations ranging from 0.005 to 0.1 g L⁻¹. In order to ensure the full dissolution of the molecules, solutions were heated up to 60 °C for 30 min and then left at room temperature during the next 24 h. All the solutions were still clear after that time, showing no formation of aggregates and ensuring that the concentration was always below saturation at room temperature. For STM measure-

ments at the solid–liquid interface, 10 μ L of solution were placed on top of the freshly cleaved HOPG (Momentive Performance Materials Quartz GmbH) and the sample was immediately scanned.

STM experiments were performed using a Veeco MultiMode microscope running on Nanoscope III D electronics. Images were recorded in constant-current mode at room temperature. The STM tips were mechanically cut from a Pt/Ir (90/10) wire (diameter, 0.25 mm). Bias (defined as sample voltage) and current conditions during each measurement are shown in each figure caption. Tilting was removed by simply fitting the image with a plane. Images were corrected for XY drift by adjusting the experimental HOPG unit cell to its theoretical value. Unit cells were averaged over several images making use of the SPIP software (Scanning Probe Image Processor, version 2.0, Image Metrology ApS, Lyngby, Denmark). No filtering was applied to the presented images.

The methodology for the molecular-modeling simulations is based on that reported for oligothiophene assemblies in periodic boundary conditions on surfaces.^[20] We used the Cerius 2.0 and Materials Studio 4.0 packages from Accelrys for MM and MD calculations. The generic Dreiding^[34] force field was used, and the nonbonded van der Waals interactions were described using the spline method (with cut-on and cut-off parameters set to 11.0 Å and 14.0 Å, respectively), while electrostatic interactions were described using the Ewald summation method for periodic systems (accuracy of 0.01 kcal mol⁻¹). MD simulations were performed at 298 K using the canonical ensemble with the Andersen thermostat. The simulations were carried out on a 1 ns timescale, with a timestep of 1 fs and an output frame every 1 ps. The starting geometries were built by aligning the long axes of the oligothiophenes along the *b* axes of the periodic cells for all phases. For compound **1**, the dimensions of the periodic supercell of graphite (for a cluster of 10 molecules) are: 23 $a_{\text{HOPG}} \times 28 b_{\text{HOPG}}$ (area = 33.75 nm²), where $a_{\text{HOPG}} = b_{\text{HOPG}} = 0.246$ nm. For compound **3** (10 molecule cluster), these dimensions are 15 $a_{\text{HOPG}} \times 26 b_{\text{HOPG}}$ for the *3a* phase (area = 20.43 nm²) and 27 $a_{\text{HOPG}} \times 21 b_{\text{HOPG}}$ for the *3b* phase (area = 29.7 nm²).

Keywords:

oligothiophenes · physisorption · scanning tunneling microscopy · self-assembled monolayers · solid–liquid interfaces

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