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Unusual two-dimensional multicomponent self-assembly probed by scanning tunneling microscopy

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Unusual Two-Dimensional Multicomponent Self-Assembly Probed by Scanning Tunneling Microscopy

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Forming controlled two-dimensional (2D) patterns is an important goal. A very simple but efficient way of preparing ordered films of monolayer thickness is via physisorption at the liquid–solid interface. The formation of 2D crystals leads to a high degree of immobilization, which at the same time allows their study with high resolution imaging techniques such as scanning tunneling microscopy (STM).^[1] In order to control the ordering of molecules in the 2D monolayer structure, directional noncovalent modes of interaction, such as hydrogen bonding, are of great help and importance.^[2] In addition to their directional properties, they may control intermolecular distances and as a result dictate the molecular conformation and properties.

Several oligothiophene derivatives have been extensively studied by STM.^[3] However, hydrogen bonding has been exploited only for a few compounds,^[4] which are related to the compound studied in this report, an oligo(3,4-ethylenedioxythiophene) (oEDOT) derivative (**1**, Scheme 1). **1** is a model compound for poly(EDOT), one of the most successful materials among the numerous electrically conductive polymers that have been developed and studied over the past three decades.^[5]

In contrast to the formation of single component 2D hydrogen-bonded networks,^[2] it remains a challenge to make

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Scheme 1. Structures of the oEDOT derivative **1** and the mono-urea derivative **2**.

stoichiometric assemblies with two or more components^[2a, 6] or to form molecular clusters of limited size.^[7] In this contribution, we have used STM at the liquid–solid interface to investigate the hydrogen-bond directed supramolecular ordering of **1**, which contains two urea functionalities. Unexpectedly, **1** does not form ordered monolayers by itself. Adding another component, a mono-urea derivative, turned out to be successful in coadsorbing **1**, forming two unique types of binary self-assembled monolayers, one of which forms molecular clusters of limited size.

As mentioned, when applying a droplet of a concentrated solution of **1** on the basal plane of highly oriented pyrolytic graphite, to our surprise no 2D ordering of **1** was observed by STM regardless of the solvent (1-octanol, 1-phenyloctane, 1,2,4-trichlorobenzene) used. This lack in ordering is attributed to the bulky nature of the oEDOT group, which prohibits an optimal shape and functionality complementarity. Other urea derivatives studied so far tend to stack in rows, and the intermolecular distance (0.46 nm) reflects the hydrogen-bonding interaction between the urea groups.^[4, 8]

As an alternative approach to promote adsorption and stable monolayer formation, mixed solutions of **1** and mono-urea derivative **2** (Scheme 1) in 1-octanol were investigated. Co-adsorption experiments were previously successfully explored.^[2a, 6, 9, 10] Compound **2** forms monolayers by itself and Figure 1 A shows some typical features. Domains consist of parallel lamellae. The urea groups show up in the images as the brighter features and are aligned in rows. The alkyl chains are oriented perpendicularly to the row of urea groups and run parallel with a major symmetry axis of graphite (Figure 1 B), illustrating the adsorbate–substrate interaction. The lamella width (ΔL_2), as indicated in Figure 1 B, measures 3.5 ± 0.1 nm, which is in agreement with an extended and flattened conformation of the molecules. The intermolecular distance measures 0.46 ± 0.01 nm. Sometimes, the contrast of the urea groups differs within an image, which indicates different orientations of the urea groups (Figure 1 C).^[8]

After characterization of the monolayer features of **2**, a mixture of **1** and **2** in 1-octanol was applied onto the

graphite substrate, which resulted in monolayer formation (Figure 2), which we name Type I. In addition to the characteristic features of the mono-urea adsorbates, individual bright structures are observed, of which the width corresponds to the size of

Figure 1. A) STM images of monolayers of **2** adsorbed at the 1-octanol/graphite liquid–solid interface. The scale bar represents 2 nm. The arrows indicate rows of urea groups. B) The bias voltage was suddenly decreased during scanning, revealing the graphite substrate underneath the monolayer. ΔL_2 is the lamella width. The inset represents the hydrogen bonding motive between urea groups. C) The contrast difference for the urea groups (left versus right) is attributed to differences in orientation.

Figure 2. STM images of monolayers of a **1/2** mixture adsorbed at the 1-octanol/graphite liquid–solid interface, illustrating Type I co-adsorption. Solid arrows point to urea groups of **2**. A) The white arrow points to a single **1** molecule trapped at the boundary between two **2** lamellae (Type II co-adsorption). B) Dashed arrows point to the expected location of urea groups of **1**. ΔL_1 is the lamella width of **1**; ΔL_2 is the lamella width of **2**. The red boxes correspond to oEDOT cores; the yellow lines are alkyl chains. The scale bar measures 2 nm. C) Simplified model illustrating the Type I co-deposition pattern of **1** and **2**. For clarity, the dodecyl groups of **2** pointing to the center of the lamella are only shown in part. Due to space limitations, those dodecyl groups are not fully extended and part of the alkyl chain is expected to point to the supernatant solution. Note that in reality, the EDOT groups do not lie flat on the graphite substrate.

the oEDOT core (~ 1.6 nm for the core and ~ 2.3 nm if the urea groups contribute to the bright contrast). The streaky lines parallel to the scan direction suggest that the oEDOT moieties are not lying flat on the surface. The lamella width ΔL_1 measures 5.6 ± 0.2 nm, which suggests that the molecule adapts an extended conformation similar to other bis-urea derivatives studied.^[4, 8] Some lamellae of **2** are also indicated, ΔL_2 . In the mixed monolayer, **1** appears to form stacks (the preferred way of ordering of other bis-urea derivatives),^[4, 8] which is a surprising observation given the fact that **1** does not form stable monolayers itself. However, the average intermolecular distance between two adjacent oEDOT cores equals 0.84 ± 0.05 nm, which is much larger than expected based upon the "normal" intermolecular distance of urea derivatives (0.46 nm). In addition, close inspection reveals that for each oEDOT core (Figure 2 B, red brick), at each side two alkyl chains are visible instead of one (yellow lines). These observations strongly suggest that within a lamella an alternating sequence of **1** and **2** is formed, which releases the strain otherwise imposed by adjacent molecules of **1** (Figure 2 C). Both compounds contain terminal dodecylurea groups and hydrogen bonds can be formed by the urea groups stabilizing the co-deposited structures.

For mixtures of **1** and **2**, we also found another kind of co-deposition (Figure 3), which we name Type II. At domain boundaries between two domains composed of **2**, which are shifted with respect to each other by about half a molecule length, bright structures reflecting the presence of oEDOT cores were observed. Such bright spots correspond only to a few **1** molecules at most and during imaging the size of these nano-assemblies was not observed to change. The formation of these kinds of isolated clusters with a very small size distribution is a unique phenomenon in two dimensions. To the best of our knowledge, a co-deposition pattern as shown in Figure 3 has not yet been reported. What is the origin of the limited size of these nano-assemblies? First, we will consider their location with respect to the adjacent lamellae of **2**. The distance between the clusters is smaller than the length of **1**. Actually, this distance is determined by the packing of **2** in the adjacent domains and the distance between the bright spots is identical to the length of **2**. For the sake of simplicity, we will discuss the case where only one **1** is trapped between domains of **2**, as shown in Figures 2 A and 3 C (white arrow). Based upon the STM images, we can conclude that at one side of the oEDOT core the urea group of **1** is in line with the urea moieties of a **2** lamella in the upper domain, whereas at the other side of the oEDOT core the urea group is in line with the urea moieties of a **2** lamella in the lower domain. This makes hydrogen bonding feasible (see model in Scheme 2 A). The **2** lamellae in both domains are indeed shifted in such a way to allow

Figure 3. STM images of monolayers of a 1/2 mixture adsorbed at the 1-octanol/graphite interface illustrating Type II co-adsorption. The scale bar represents 2 nm. A) The "shadows" at the right of the bright structures are a scanning artifact. C) The white arrow points to a single **1** molecule trapped at the domain boundary of two **2** domains. The black and white small arrows indicate rows of urea groups. ΔL_2 is the lamella width of **2**. B and D are higher resolution images of A and C.

Scheme 2. Simplified model for the Type II co-adsorption of a monolayer of **1** and **2**. A) A **1** molecule is trapped at the domain boundary of two domains of **2**, which are shifted relatively with respect to each other. Hydrogen bonding leads to the stabilization of **1**. B) Tentative model illustrating the interactions leading to the formation of the clusters of **1** at the domain boundary. Due to interdigitation of the alkyl chains, adjacent **1** molecules most likely do not interact through hydrogen bonding.

this interaction. The small intercluster distance indicates that the alkyl chains of molecules in adjacent clusters are interdigitated. Therefore, hydrogen bonding between molecules of type **1** is not likely, which leads to a decrease in the overall stability (Scheme 2B). This balance between stabilizing (hydrogen bonding) and destabilizing ("steric" hindrance) interactions is believed to be responsible for the limited size of the clusters.

In conclusion, we have illustrated an approach to "immobilize" bulky compounds, which do not form stable monolayers by themselves at the liquid–solid interface, resulting in unique co-deposition patterns. The knowledge gained paves the way for designing molecules for the formation of complex 2D patterns.

Experimental Section

Synthetic methods: See Supporting Information.

STM: Prior to imaging, all compounds under investigation were dissolved in 1-octanol and a drop of the hot solution was applied on a freshly cleaved surface of highly oriented pyrolytic graphite. For the mixtures, the molar ratio of **1:2** was larger than 2. The STM images were obtained in the variable current mode (quasi-constant height) under ambient conditions with the tip immersed in the liquid phase. In this mode, the tip scans at a quasi-constant height over the surface and variations in tunneling current, related to changes in the electronic properties (such as different functional groups) and topography, are recorded and converted into an image. From the contrast, no direct information is available on the sample topography due to convolution of the signal with the local electronic properties. "Mechanical" contact between the tip and parts of the monolayer can be identified due to streaky features parallel to the scan direction. In the acquired STM images, white corresponds to the highest and black to the lowest measured tunneling current. The setpoint current was of the order of 0.8 nA and the bias voltage (sample negative) ranged from -0.2 to -0.7 V.

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Two-Photon Absorption Spectra of Perylene Derivatives

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INDO/CI • perylene • sum-over-states • two-photon absorption

Organic dyes with increased two-photon absorption (TPA) cross sections and large upconversion fluorescence yields,^[1–3] have generated considerable interest in the development of highly efficient two-photon materials.^[4] New applications include two-photon upconversion lasing,^[5–6] two-photon optical power limiting,^[7–8] three-dimensional optical data storage^[9–10] and two-photon photodynamic therapy.^[11] TPA in organic materials involves a direct absorption of two photons through a virtual state to reach an excited state. The transition probability is

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