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**Controlling Molecular Assembly in Two Dimensions: The Concentration Dependence of Thermally Induced 2D Aggregation of Molecules on a Metal Surface\*\****Meike Stöhr,\* Markus Wahl, Christian H. Galka, Till Riehm, Thomas A. Jung, and Lutz H. Gade\**

The “bottom-up” construction of functional structures relies on the sophisticated interplay between individual structural units.<sup>[1–3]</sup> In most cases, the assembly of these building blocks is based on noncovalent interactions that shape extended supramolecular entities in variable dimensions.<sup>[4–6]</sup> Herein, well-ordered molecular patterns on surfaces are created from highly mobile precursor molecules which are transformed subsequent to their deposition and form autocomplementary species in the process. The end groups of the mobile precursors are activated by a thermally induced surface-assisted reaction to enable intermolecular hydrogen-bonding interactions which then lead to the formation of highly ordered structures. We demonstrate control over the 2D pattern of the assembly and over the dimensionality of the aggregate by variation of the surface concentration of the precursor prior to its transformation. Furthermore, we show that the combination of resonance-assisted hydrogen-bonding<sup>[7]</sup> and the interaction of the rectangular-shaped molecules with the metal surface leads to highly robust supramolecular networks which may serve as templates for the incorporation or trapping of guest molecules.

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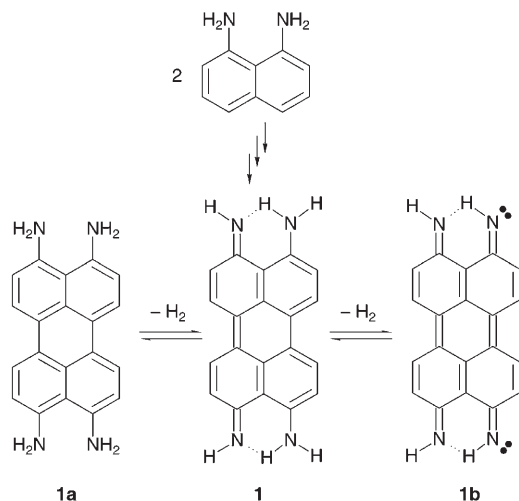
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As the starting material for the surface studies, we chose a perylene derivative, 4,9-diaminoperylene-quinone-3,10-dimine (DPDI; **1**), which is readily obtained by oxidative coupling of two 1,8-diaminonaphthalene molecules<sup>[8]</sup> and displays a particularly rich redox chemistry.<sup>[9]</sup> The most stable form of this compound corresponds to the semiquinoidal structure displayed in Scheme 1, which on the one hand can

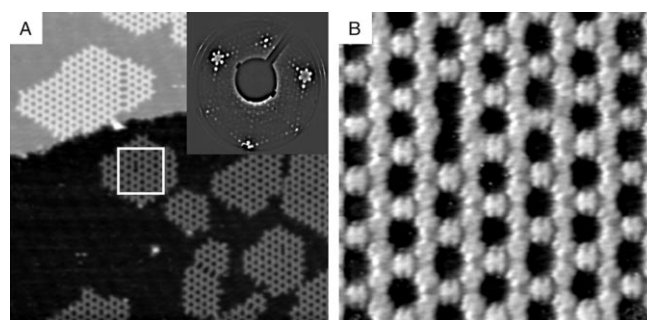


**Scheme 1.** The formation of DPDI (**1**) by oxidative coupling of two 1,8-diaminonaphthalene molecules, and its redox conversion into **1a** and **1b**.

be reversibly converted into the perylene **1a** by a two-electron reduction,<sup>[9]</sup> as previously shown for derivatives bearing bulky *N*-silyl groups, whereas a two-electron oxidation gives rise to the quinoidal redox state **1b**.<sup>[10]</sup> Because of this redox convertibility, **1** lends itself to chemical modification subsequent to its controlled deposition on metal surfaces and, thus, to significant changes in its intermolecular interactions.

Thin layers of **1** that range from submonolayer to monolayer (ML) coverage were prepared by thermal deposition onto a Cu(111) crystal and by subsequent annealing at 300 °C under ultra high vacuum (UHV) conditions (one monolayer of DPDI corresponds to the amount of molecules that is needed to cover the complete Cu surface and corresponds to 0.84 molecules nm<sup>-2</sup>). The structures of the organic layers were characterized in UHV with room-temperature scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) before and after annealing. Before the annealing of submonolayer coverages of **1**, only a mobile phase and no ordered arrangement is found. The full monolayer assembles in an ordered aggregate with the monomers aligned in a rectangular unit cell of the size 0.92 nm × 1.3 nm,<sup>[11]</sup> an arrangement which is controlled by the molecular shape of **1**. The high mobility of **1** on the metal surface is unsurprising as there is no possibility of intermolecular hydrogen-bonding interactions in two dimensions, as the nitrogen functions are exclusively hydrogen-bond donors and there are no appropriate acceptor functionalities. As a result of the annealing process at 300 °C, the deposited molecules of **1** are chemically modified, as is reflected in the

comparison of X-ray photoelectron spectroscopy (XPS) data before and after the thermolysis.<sup>[12]</sup> For surface coverages below 0.7 ML, the mobile monomers aggregate to give a well-ordered 2D honeycomb network (Figure 1 a,b). Based on the

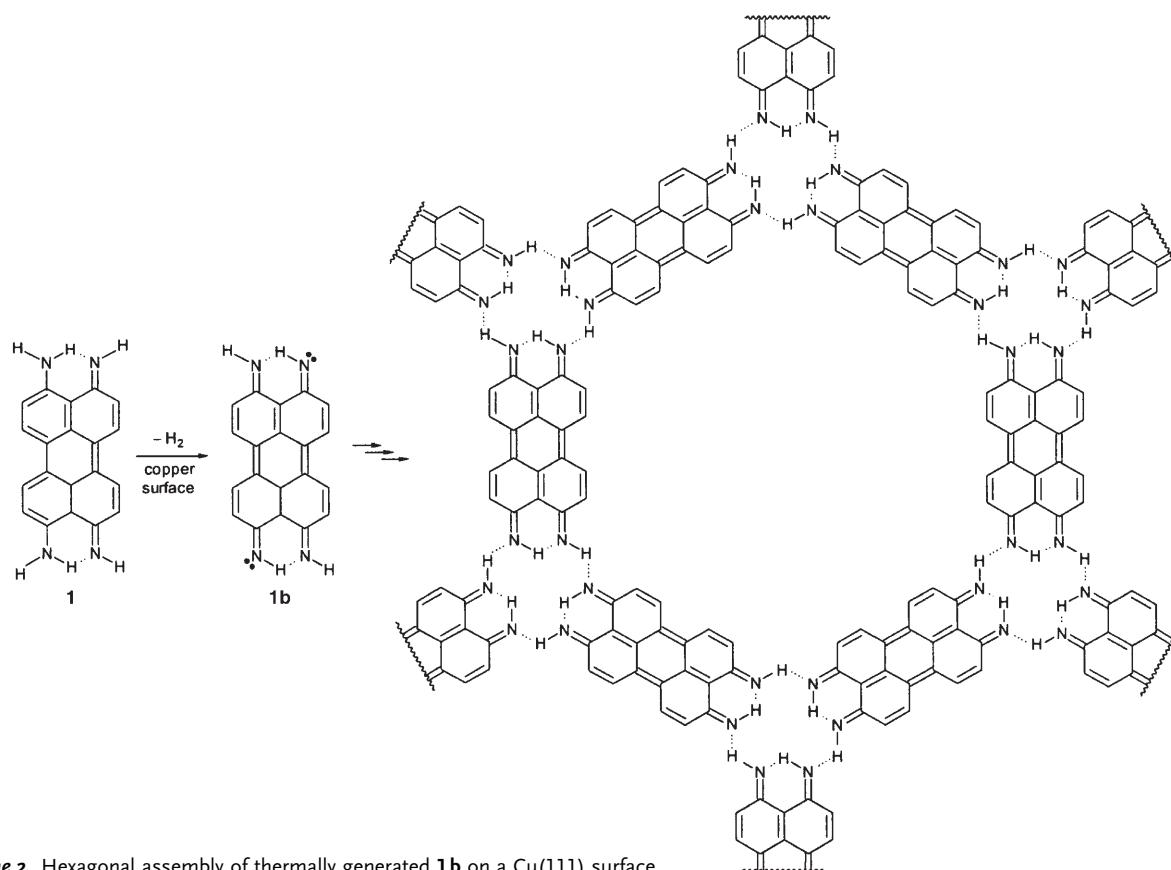


**Figure 1.** Self-assembly of 0.3 ML of DPDI on Cu(111) annealed at 300 °C. a) A large-scale STM image (100 nm × 100 nm, *I* = 25 pA, *U* = −1.5 V) of several DPDI islands that exhibit a honeycomb structure. Inset: LEED pattern that corresponds to this overlayer, as obtained at 52 eV primary energy representing a Cu(111)-p(10 × 10) DPDI lattice registry of the monomeric components. b) A high-resolution STM image (15 nm × 15 nm, *I* = 25 pA, *U* = −2 V) of the marked region, thus exhibiting the honeycomb network in detail and showing a vacancy defect.

STM data and the information obtained from the LEED pattern shown in the inset of Figure 1 a, a commensurate arrangement with regard to the Cu substrate of the DPDI monomers in a p(10 × 10) superlattice with a lattice constant of 2.55 nm is determined.

The assembly of these honeycomb networks can be readily explained by dehydrogenation of the DPDI monomers on the copper surface to provide the autocomplementary compound **1b**, in which the now-modified nitrogen functions may act as both hydrogen-bond acceptors and donors. The molecules, thus, link up through hydrogen-bonding interactions with each DPDI monomer binding to a total of four neighboring monomers to form the honeycomb network (Scheme 2). Hydrogen-bonding interactions between the nitrogen functions is consistent with the structural data from the STM and LEED experiments, from which a N...N distance between adjacent molecules of about 3.1 Å is derived.

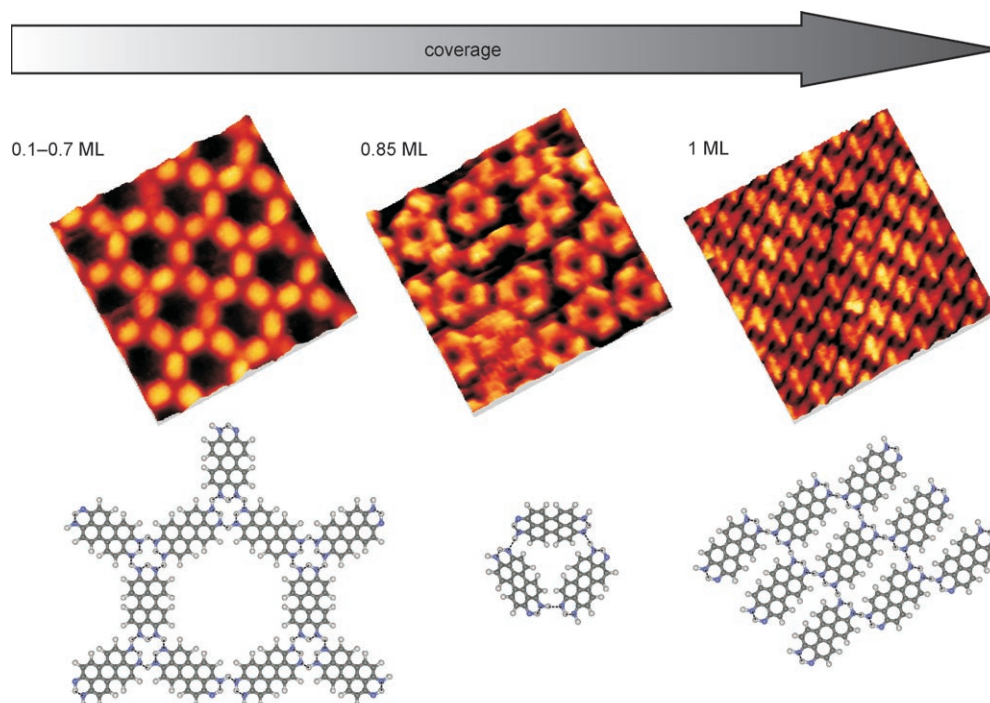
The network itself exhibits an extraordinary stability, as is reflected by its inertness towards manipulation of individual monomers with the STM tip. Moreover, in LEED experiments performed while annealing the sample, the diffraction pattern of the overlayer persisted up to a temperature of 450 °C. Further increase in the temperature resulted in an irreversible destruction of the hexagonal perylene network. The considerable stability of this hexagonal network together with its commensurability with the Cu surface may be attributed to a combination of resonance-assisted hydrogen bonding<sup>[7,13]</sup> and a strong interaction with the Cu support. A similar case for a commensurate overlayer is reported for perylene tetracarboxydianhydride (PTCDA) adsorbed on a Ag(111) surface.<sup>[14]</sup>



**Scheme 2.** Hexagonal assembly of thermally generated **1b** on a Cu(111) surface.

A key requirement for the formation of this highly ordered structure appears to be the free mobility of **1**, and subsequently **1b**, on the Cu(111) surface to attain the appropriate molecular arrangement and also the rather low molecular coverage on the metal support to accommodate the large hexagonal cavities in the 2D network. Thus, for geometrical reasons, the honeycomb structure corresponds to a maximum coverage of 0.7 ML. It was, therefore, of interest to assess if and how the polymer structure changed upon going to higher surface coverage.

Upon annealing a sample with a coverage of approximately 0.85 ML DPDI at 300 °C, trimeric structures in the form of rings are found (Figure 2

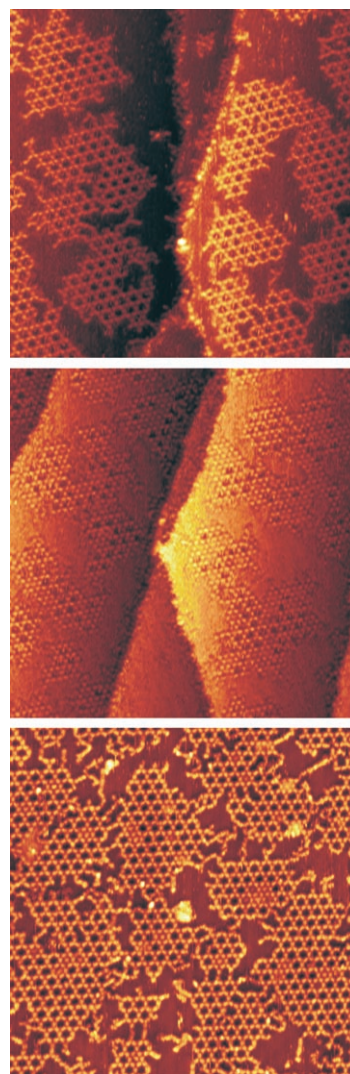


**Figure 2.** STM images (9 nm×9 nm) and the corresponding chemical structures of the surface aggregates at variable coverage of **1**. All the polymeric islands were obtained by annealing the samples at 300 °C. For 0.1–0.7 ML of DPDI, an extended 2D honeycomb network is formed (left). Increasing the coverage to 0.85 ML yields a 0D trimeric structure (center), whereas at monolayer coverage a chain structure (right) is produced.

center), which are packed more densely on the surface than the honeycomb network discussed above. The formation of these trimers may be explained by the same dehydrogenation reaction as proposed for the honeycomb network that yields **1b**. This compound, activated for hydrogen-bond formation, then forms the observed cyclic hydrogen-bonded structure in a self-assembly process which is modified by a characteristic change of the diffusion length at the higher 2D molecular density. For the steric, repulsive interactions between the inwards-pointing hydrogen atoms of the perylene trimer, the overall structure is expected to deviate from a strictly planar arrangement and is expected to adopt an overall bowl-shaped form, a notion which is also supported by the STM images. Because of this steric interaction and because of the fact that each monomer is only hydrogen bonded to two neighboring monomers, a less robust structure of lower binding energy is expected in this case. This is evidenced by the observation of a dynamical equilibrium of “open” and “closed” structures (trimers, chains, and individual molecules) upon subsequent scanning of the same sample area at room temperature.<sup>[15]</sup> Furthermore, it was observed that only two preferred orientations of the trimers relative to the substrate exist, thus indicating that the structure of the Cu surface potentially contributes to the stabilization of the cyclic trimer.

For the final step of probing the concentration dependence of the polymerization pattern, we prepared full monolayers of DPDI on a Cu(111) surface. In contrast to the mobile submonolayer phases of the monomer, there is little room for molecular reorientation upon annealing of such a densely packed and highly ordered molecular array. The result of the thermal annealing of a DPDI monolayer on Cu(111) at 300 °C is displayed in Figure 2 on the right. STM analysis reveals a zigzag chain structure of the polymer with the chains packing one alongside the other. These chains derive from the regular monolayer structure of the monomer by an apparently concerted “shearing” movement, which is accompanied by shortening of the distance between adjacent molecular rows along the long molecular axis by approximately 1 Å. The same dehydrogenation reaction as for submonolayer coverage is thought to take place, thus resulting in each monomer being linked through hydrogen bonds to four adjacent monomers. The Moiré pattern in the STM images, as well as the LEED patterns, indicate that the molecular arrangement obtained in this annealing process is not commensurate to the underlying lattice of the Cu substrate.

Direct evidence for the importance of the conversion of **1** into **1b**, and thus for the formation of a monomer capable of the formation of 2D hydrogen-bonded networks, was obtained by deposition of the equivalent of approximately 0.15 ML of additional DPDI onto the previously prepared honeycomb network (Figure 3). These additional monomers in their initial, non-dehydrogenated form are not assembled into the existing honeycomb network at room temperature.<sup>[17]</sup> Instead, the additional monomer molecules are mobile on the metal surface, as found for submonolayer coverage prior to thermal treatment, and additional DPDI molecules are trapped in the hexagonal cavities of the honeycomb network, in which they are still mobile as can be deduced from their blurred appearance in the STM images. Extension of the



**Figure 3.** STM images (70 nm × 70 nm) of the same sample at different phases of sample preparation. First, the honeycomb network was prepared (top) and subsequently 0.15 ML DPDI were deposited (center). The additional DPDI molecules form a mobile phase on the bare Cu substrate and some are trapped in the pores of the honeycomb network. Annealing this sample at 300 °C converts the mobile phase into a solid phase because of dehydrogenation of DPDI, thus resulting in an enlargement of the honeycomb network (bottom). Individual molecules remain trapped within the network. However, the characteristic confined mobility disappears after annealing.

honeycomb structure only occurs after a second annealing process. These findings indicate that the highly robust honeycomb network can be used as a template to arrange or trap molecules that are even larger than the DPDI monomers.

In conclusion, the deposition of 4,9-diaminoperylenequinone-3,10-diimine (**1**) on a metal surface provides highly mobile submonolayer phases because of the impossibility of significant intermolecular interactions in two dimensions. However, thermally activated dehydrogenation leads to **1b**, which is autocomplementary and serves both as an hydrogen-bond donor and acceptor. This behavior leads to well-defined polymeric structures that can be controlled by the typical diffusion length between the activation of the precursor and



its “polymerization”, which in turn is controlled through different amounts of initial monomer coverage. This reactive self-assembly represents a “surface dilution principle” akin to the dilution principle in chemical synthesis.<sup>[18]</sup> The connectivity and the resulting dimensionality of the aggregates may be varied between 0D for the trimers and 2D for the hexagonal network. Once formed, these molecular surface assemblies are highly robust and, therefore, suitable for the construction of hierarchic structures by self-organization of subsequently deposited material at lower temperatures; such investigations are currently under way.

### Experimental Section

The experiments were conducted in a UHV system composed of different chambers for sample preparation and characterization (base pressure:  $10^{-10}$  mbar). The Cu(111) substrate was prepared by subsequent cycles of sputtering with Ar<sup>+</sup> ions and annealing at 870 K. Thermal evaporation from a homemade crucible at a rate of about 0.5 ML min<sup>-1</sup> was used to prepare thin films of DPDI on the Cu(111) surface while the substrate was kept at RT. Annealing of the DPDI films was performed by radiative heating. The investigation of the samples was carried out with a homebuilt STM operated at room temperature, by LEED and by XPS.

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