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Self-Assembly

Protecting-Group-Controlled Surface Chemistry—Organization and Heat-Induced Coupling of 4,4′-Di(*tert*-butoxycarbonylamino)biphenyl on Metal Surfaces**

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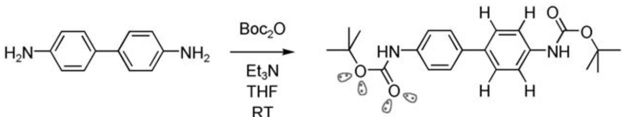
The combination of their almost infinite structural diversity and unique self-assembly properties makes molecules ideal building blocks for tailor-made materials. By utilizing the concepts of supramolecular chemistry[1] impressive results have been achieved for molecular self-assembly on surfaces.[2,3] Noncovalent interactions such as metal coordination,[4,5] hydrogen bonding,[6] and dipolar coupling[7] are usually exploited to create extended supramolecular patterns in various dimensions. However, the formation of such thermodynamically controlled structures is reversible in most cases and the interaction between the molecular components is usually rather weak. A very appealing concept to obtain structures with higher stability (and in the ideal case, improved conductive properties) is to profit from the order of preorganized structures and to interlink the individual molecular building blocks to generate macromolecules. So far, there are only a very limited number of reports on the subsequent linking of (preorganized) molecules adsorbed on surfaces to provide new functional structures or materials.[8–17]

Herein we present a new concept to control both the two-dimensional molecular self-assembly and the subsequent intermolecular coupling through the use of protecting groups. This concept may pave the way towards two-dimensional functional structures which at present are only attainable on a larger scale by lithographic methods. Protecting groups are widely used to distinguish the reactivity of functional groups in synthetic chemistry.[18,19] However, their potential as intermolecular "organizers" for the formation of well-ordered molecular patterns has not yet been explored to the best of our knowledge. Our investigations focus on *tert*-butoxycarbonyl (Boc) protected 4,4′-diaminobiphenyl (**1**) groups (Scheme 1). The use of a Boc-protected aryl amine was particularly appealing for numerous reasons: 1) deprotection generates intermediates that can undergo numerous reactions, 2) the Boc-protected amine should be able to act as both a hydrogen-bond donor and acceptor, and its self-assembly is expected to lead to the formation of intermolecular hydrogen bonds, and 3) Boc-protected amines can potentially be cleaved by a large range of stimuli, such as heat or pressure, which is particular appealing for our studies. The extent to which these solution-based properties can be expanded to immobilized molecules in an ultrahigh vacuum (UHV) experiment is one of the focuses of this study.



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Scheme 1. One-step synthesis of the Boc-protected 4,4′-diaminobiphenyl **1**. In the right half of molecule **1** the hydrogen atoms acting as potential hydrogen-bond donors are shown while in the left half the lone pairs of electrons of the oxygen atoms that act as potential hydrogen-bond acceptors are labeled in gray.

The deposition of Boc-protected diamine **1** at a coverage of less than a monolayer onto a Cu(111) surface resulted in its self-assembly into two different, but similarly ordered, structures. This was revealed by room-temperature as well as low-temperature scanning tunneling microscopy (STM) studies. The bright lobes in the STM images can be assigned to the *tert*-butyl groups of **1**.[20,21] The molecular backbone can be distinguished in high-resolution STM images, thus enabling the identification of the arrangement of individual molecules within the network. Furthermore, atomically resolved STM images (Figure SI7 in the Supporting Information) allowed the orientation of the molecules with respect to the principal directions of the underlying Cu(111) substrate to be determined. It was found that the aromatic backbone is oriented along the [11$\bar{2}$] direction. STM images of samples with a very low coverage of **1** led to the deduction that evolution of the assembly starts in both cases with the formation of individual

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molecular rows which are aligned along the $[01\bar{1}]$ direction (highlighted in yellow in Figure 1 c, see also Figures SI3–SI5 in the Supporting Information). This arrangement allows the molecules to always be located in the same position with respect to the underlying Cu substrate. The molecules within these rows interact with each other through hydrogen bonds between the carbonyl oxygen atom of one molecule and a phenyl hydrogen atom of another molecule (O···H distance ca. 2.3 Å).

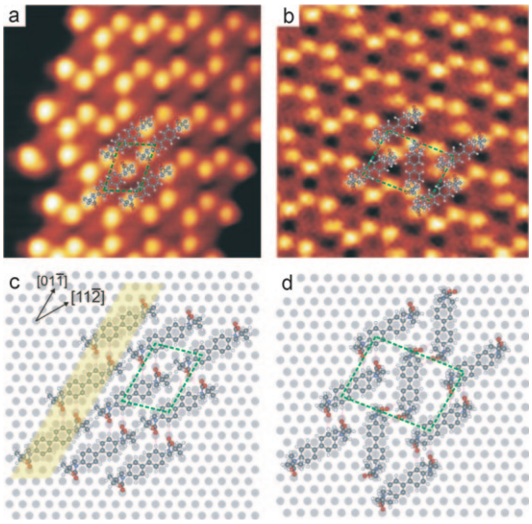


Figure 1. The STM images of **1** on Cu(111): a) the parallel arrangement (7×7 nm^2, 10 pA, 1.6 V, 77 K) and b) the herringbone arrangement (7×7 nm^2, 20 pA, 1.6 V, RT). A few molecules and the unit cell have been drawn in each STM image to illustrate their arrangement. c,d) Schematic representation of the two arrangements. The molecular row highlighted in yellow is the parent stripe motif which is stabilized by hydrogen bonding (red lines) and which leads to both observed arrangements.

The two different densely packed surface patterns are formed at higher molecular coverage by either keeping the same orientation of the one-dimensional molecular rows during their assembly or by mirroring every second row in the $[01\bar{1}]$ direction of the Cu substrate. In the first arrangement (Figure 1 a,c), which we call the parallel arrangement, the molecules are arranged with an oblique symmetry described by a rhomboid with sides of length (12.75 ± 0.4) Å and (9.8 ± 0.3) Å, and an angle of (75.5 ± 1)°. In the second arrangement (Figure 1 b,d), which we call the herringbone arrangement, the rhombic unit cell has sides of length (12.75 ± 0.4) Å and (17.85 ± 0.5) Å, and an internal angle of (82.5 ± 1)°. The parallel arrangement has a slightly lower surface density (0.83 molecules nm^{-2}) than the herringbone arrangement (0.89 molecules nm^{-2}).

Our first attempts to induce intermolecular reactions within the self-assembled monolayers of **1** utilized temperature as a trigger for deprotection. We hoped to be able to profit from the rich chemistry of potential reactive intermediates forming during the cleavage of the Boc group to interlink the preorganized molecular building blocks.

For this purpose, the samples were heated and subsequently investigated after recooling to room temperature. A considerably different and periodic molecular pattern emerged after heating the sample to 196 °C. This new pattern (which we call a double-row arrangement) can be seen in the upper part of Figure 2 a; the lower part shows the herringbone pattern. The unit cell for the double-row pattern is rhombic with sides of length (25.6 ± 0.2) Å and (18.3 ± 0.2) Å, and an internal angle of (73 ± 1)°. Obviously, the number of bright spots arising from the bulky *tert*-butyl groups of the Boc protecting groups is reduced considerably. The pattern seems to consist mainly of molecular rods that still feature terminal Boc groups but which are about twice the length of the initial biphenyl rod **1**. Apparently, each monomer **1** loses one Boc group upon annealing, and two of these modified biphenyl units become interlinked to form a dimer (Figure SI6 in the Supporting Information). Since desorption-reaction-readsorption mechanisms are very unlikely, or even impossible, under UHV conditions, this dimerization reaction must have taken place when the molecules were immobilized on the surface. This hypothesis is further supported by the fact that the number of biphenyl units per surface area remains the same in both surface patterns.

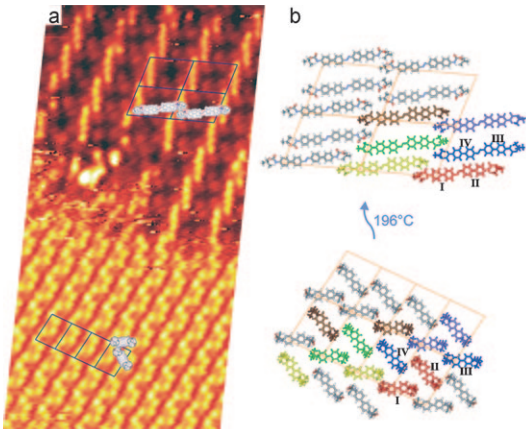


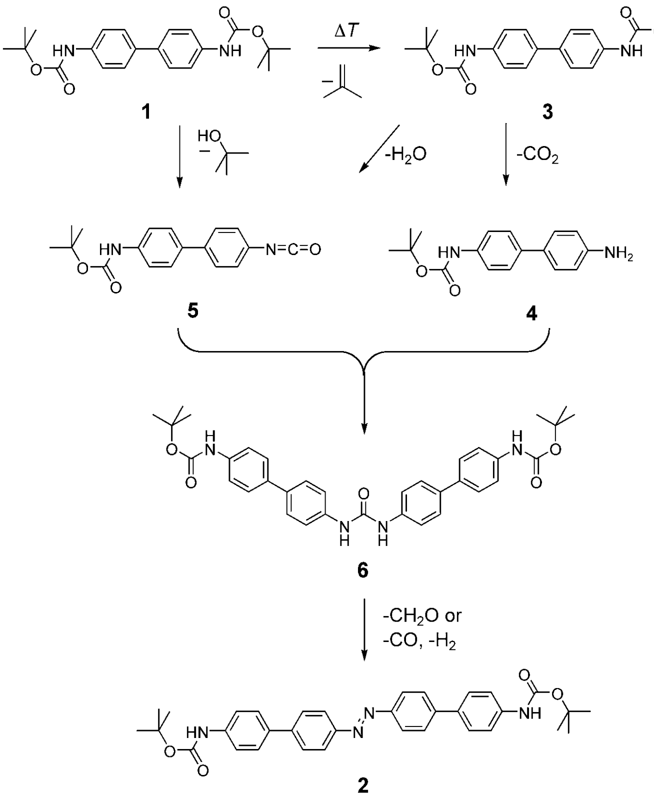
Figure 2. a) Drift-corrected STM image (24×12 nm^2, 22 pA, 1.2 V) of **1** on Cu(111) annealed at 196 °C. The upper half shows the double-row pattern, which is only observed after the annealing procedure. The lower half shows the herringbone surface packing of the doubly Boc-protected biphenyl **1**. The drawn molecules illustrate their arrangement in each of the two patterns. b) Schematic representation of the transition from the herringbone arrangement of **1** to the double-row arrangement of **2**.

The linking group between the two biphenyl subunits seems to be quite rigid and aligns both biphenyl units parallel to each other and also parallel to the $[11\bar{2}]$ direction, as already observed for both monomer phases. The interaction with the underlying Cu substrate appears to play an important role in the arrangement of both the dimers and the monomers. However, the most interesting feature is the selective cleavage of only one of the two Boc groups of **1** to form perfectly organized rows of dimers. While electronic effects may be responsible for the cleavage of a single protecting group, a selection rule that is communicated between individual molecules is required to enable the surprising perfect transformation from the ordered monomer pattern to the double-row pattern of the dimers. A potential mechanism could be a cleavage of individual Boc groups induced by the spatial rearrangement of the neighboring molecules upon formation of the dimer. Both the azo structure R−N=N−R and the hydrazine structure R−NH−NH−R are considered as possible linking structures that would allow the two biphenyl subunits to be aligned at a distance of about 2.5 Å. However, we favor the azo structure R−N=N−R as the linker because of the stiff parallel arrangement of both biphenyl subunits in the dimers. Furthermore, the weak signal in the STM images for the linking unit is in line with previous reports on molecules with azo linkers.[22,23]

Assuming that a covalent coupling reaction between pairs of neighboring molecules is the origin of the dimers, the rearrangement sequence shown in Figure 2b may explain qualitatively both the formation of the dimers and their assembly in to the double-row pattern. While the position of one of the two molecules remains almost unchanged (molecules **I** and **III** in the lower part of Figure 2b), the second rotates by about 60° and moves slightly on the surface to react with the first one (molecules **II** and **IV**), thereby forming the pairs of dimers. Assuming a conformational rearrangement of individual dimers comparable to the one reported by Besenbacher and co-workers,[24] these pairs of dimers may even be stabilized by two hydrogen bonds between the carbonyl oxygen and hydrogen atoms of the biphenyl core of neighboring dimer molecules. The resulting pairs of dimers are separated from each other by terminal *tert*-butyl groups.

A potential reaction mechanism that not only explains the products formed but also the observed monodeprotection of the parent building block **1** is shown in Scheme 2. Upon heating, **1** is expected to lose an isopropene moiety to give the hydroxycarbamate **3**, which decomposes either by decarboxylation to the amine **4** or by condensation to the isocyanate **5**. The isocyanate **5** may even be formed directly through coordination of the lone pair of electrons on the nitrogen atom of **1** to the metal surface and elimination of *tert*-butanol. Subsequent reaction of the free amine **4** with the isocyanate **5** provides the urea derivative **6**. Either formaldehyde or carbon monoxide and hydrogen have to be expelled to obtain the azo derivative **2** from urea derivative **6**. Although urea derivatives are rather stable in solution and comparable reactions have not yet been reported, the coordination of CO to the metal surface might assist this reaction step. Strong indications supporting the proposed reaction step have been obtained by simulating the reaction with suitable model compounds. Furthermore, the decreasing electron-withdrawing character of the terminal substituents of **1**, **3**, **4**, and **5** and also reduced electron-withdrawing ability of the central linker of **2** and **6** compared with **1** increase the stability of the second Boc protecting group, thus providing a chemical argument for the observed monodeprotection during the transformation from **1** to **2**.

In analogy to **1**, the obtained dimer **2** also has two terminal Boc groups which are in proximity in the double-row arrangement, and thus might react further to give even longer structures upon annealing at higher temperatures. In fact, as displayed in Figure 3, the formation of more complex linked structures surrounded by a mobile phase[25] is observed after annealing the sample at ≥ 198 °C. Mainly longer chains and cross-type structures—both consisting of the same prolate building blocks—are observed. We assign these prolate building blocks to the biphenyl subunits, which are interlinked to form these larger structures.[26]



Scheme 2. Possible reaction sequence for the thermal transformation of monomer **1** to dimer **2** on the metal surface.

Of particular interest is the structure of the dimer **2** and the structure of the resulting covalently linked molecules after heating at ≥ 198 °C under UHV conditions. However, the very low yield and the polymeric nature of the reaction products did not allow their analysis by traditional surface-

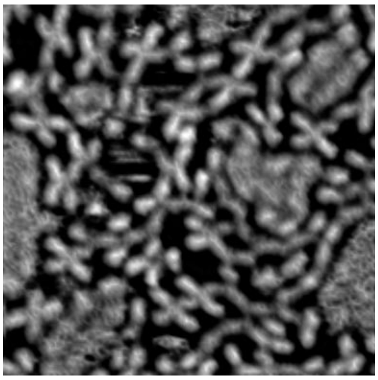
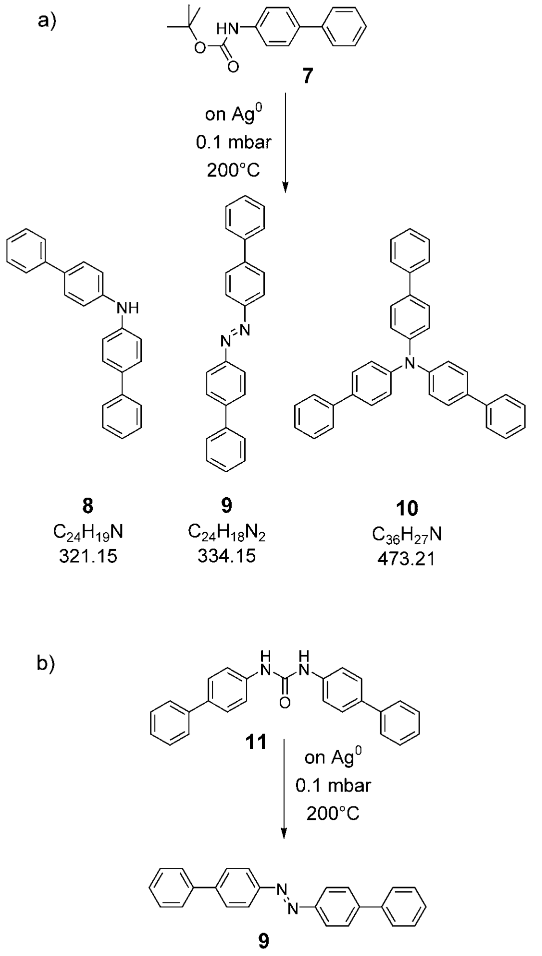


Figure 3. STM image (15×15 nm^2, 1.2 V, 20 pA) of **1** on Cu(111) annealed at > 198 °C. Chains and cross-type structures consisting of interlinked biphenyl subunits were formed.

science techniques. In spite of the successful synthesis of **2**, its sublimation under UHV failed because of its rather low decomposition temperature.

To investigate the chemical processes leading to coupling, model compounds **6** and **7** adsorbed on silver nanoparticles were heated under reduced pressure (0.1 mbar) at 200 °C for 6 h. Silver nanoparticles were used instead of copper nanoparticles as the surface purity of the latter was complicated by oxidation processes.[27] To decrease both the number of potential reaction products and their molecular weights the bifunctional biphenyl **1** was replaced by its monofunctionalized derivative **7** (Scheme 3). Three main reaction products were isolated by preparative thin-layer chromatography (TLC) of the CH_2Cl_2 extract of the nanoparticles. The MALDI-TOF mass spectra of the products showed signals corresponding to structures **8–10**, thus supporting the formation of new N−N and N−C bonds under the reaction conditions. In particular, the isolation of the azobiphenyl **9** corroborates the hypothesized formation of an azo compound on the metal surface. In the proposed reaction sequence shown in Scheme 2, the so far unprecedented step from urea derivative **6** to azo derivative **2** was of particular interest. Indeed, a model reaction of urea **11** on silver nanoparticles under the reaction conditions described above led to the azo derivative **9** being identified by reversed-phase HPLC as a reaction product in the DMF extract.



Scheme 3. Simulation of surface reactions: a) Reaction products **8–10** obtained by thermal decomposition of **7** on silver nanoparticles at reduced pressure. b) Thermal degradation of the urea derivative **11** to the azo derivative **9** on silver nanoparticles at reduced pressure.

In conclusion, a new strategy for the creation of surface-confined polymeric structures starting from preorganized monomers has been presented which profits from concepts from supramolecular and protecting-group chemistry. The validity of the strategy has been demonstrated with the doubly Boc-protected diaminobiphenyl **1**, which was found to self-assemble in two different arrangements on a Cu(111) surface. Annealing these arrangements at 196 °C provided a well-ordered pattern consisting of dimers, also with terminal Boc groups. Further annealing of the samples at ≥ 198 °C led to the formation of cross-type and chainlike structures surrounded by a mobile phase. Experiments were carried out with silver nanoparticles to elucidate the underlying reaction steps and the reaction products. The formation of new N−N and N−C bonds was identified. This observation in turn supports the proposed covalent interlinking of the monomers upon annealing under UHV conditions, a process that is facilitated by the release of the protecting groups. The results demonstrate the potential of using suitably designed protecting groups to arrange monomers on surfaces as well as their cleavage by an external trigger to allow the interlinking of the preorganized monomers. This concept offers various perspectives for the future formation of polymeric structures, since both the molecular core and the protecting group can be modified easily to tune the properties of the obtained surface-immobilized polymers.

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[27] **1** self-assembles in a herringbone structure on Ag(111) and the formation of polymers has been observed upon annealing at 200°C. These experiments are described in detail in the Supporting Information.