

# STM Manipulation of Molecular Moulds on Metal Surfaces

Miao Yu<sup>1,†</sup>, Wei Xu<sup>1,†</sup>, Youness Benjalal<sup>2,3</sup>, Regis Barattin<sup>2</sup>, Erik Lægsgaard<sup>1</sup>, Ivan Stensgaard<sup>1</sup>, Mohamed Hliwa<sup>2,3</sup>, Xavier Bouju<sup>2</sup>, André Gourdon<sup>2</sup>, Christian Joachim<sup>2</sup>, Trolle R. Linderoth<sup>1</sup> (✉), and Flemming Besenbacher<sup>1</sup> (✉)

<sup>1</sup> Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Ny Munkegade, 8000 Aarhus C, Denmark

<sup>2</sup> Nanoscience group, CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France

<sup>3</sup> Faculté des Sciences Ben M'Sik, Université Hassan II-Mohammédia, BP 7955, Sidi Othman, Casablanca, Morocco

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## ABSTRACT

Molecular Landers are a class of compounds containing an aromatic board as well as bulky side groups which upon adsorption of the molecule on a surface may lift the molecular board away from the substrate. Different molecular Landers have extensively been studied as model systems for nanomachines and the formation of molecular wires, as well as for their function as “molecular moulds”, i.e., acting as templates by accommodating metal atoms underneath their aromatic board. Here, we investigate the adsorption of a novel Lander molecule 1,4-bis(4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (DAT, C<sub>64</sub>H<sub>68</sub>N<sub>10</sub>) on Cu(110) and Au(111) surfaces under ultrahigh vacuum (UHV) conditions. By means of scanning tunneling microscopy (STM) imaging and manipulation, we characterize the morphology and binding geometries of DAT molecules at terraces and step edges. On the Cu(110) surface, various contact configurations of individual DAT Landers were formed at the step edges in a controlled manner, steered by STM manipulation, including lateral translation, rotation, and pushing molecules to an upper terrace. The diffusion barrier of single DAT molecules on Au(111) is considerably smaller than on Cu(110). The DAT Lander is specially designed with diamino-triazine side groups making it suitable for future studies of molecular self-assembly by hydrogen-bonding interactions. The results presented here are an important guide to the choice of substrate for future studies using this compound.

## KEYWORDS

Scanning tunneling microscopy (STM), molecular Landers, adsorption, STM manipulation, molecular moulding

## Introduction

Functional organic molecules adsorbed individually or organised on surfaces play a vital role in the

rapidly growing area of nanotechnology, especially within areas such as molecular electronics, nanodevices, and molecular recognition [1, 2]. Molecular Landers are a class of compounds in which

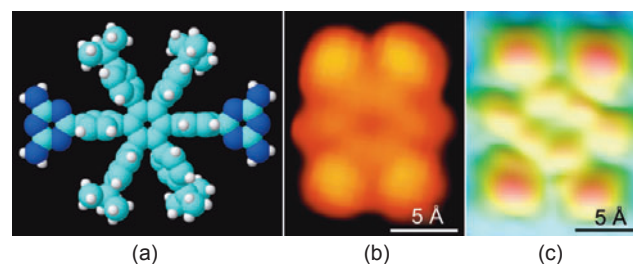
Address correspondence to Flemming Besenbacher, fbe@inano.dk; Trolle R. Linderoth, trolle@inano.dk

† These authors contributed equally to this work.

an aromatic backboard (the  $\pi$  system) is decoupled from the underlying substrate via bulky spacer groups (e.g., *tert*-butyl moieties,  $-\text{C}_4\text{H}_9$ ). Synthesis and deposition of molecular Landers on surfaces have attracted considerable attention recently, both because these compounds may serve as model systems for the formation of “molecular wires” [3, 4] and because of their ability to function as “molecular moulds” by trapping metal atoms in the cavity under the aromatic board [5–7]. Molecular Landers have extensively been studied by several groups including our own [5–21]. Combining the high-resolution imaging capabilities of the scanning tunneling microscope (STM) with its ability to manipulate individual molecules in a controlled manner at the atomic scale, it has proven possible to position the molecules precisely at terraces and step edges [12–14], to steer the switching between different molecular conformations [15], and to drive single-molecule nanomachines [8]. In addition Lander compounds have been organized into wires utilizing substrate templating effects [16], and used as moulds to trap metallic adatoms into clusters at terraces and step edges [6, 13, 14, 17, 18].

Here we augment these previous studies by investigating a novel Lander-type molecule, 1,4-bis(4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (DAT,  $\text{C}_{64}\text{H}_{68}\text{N}_{10}$ ), which consists of a hexaphenyl benzene core with four *tert*-butyl groups as spacer legs and two diamino-triazine functional groups positioned at opposite sides of the molecular board (Fig.1(a)). The compound is specifically designed for studies into organisation of Lander compounds by intermolecular hydrogen bonding interactions, which are enabled by the peripheral diamino-triazine groups. A particularly interesting potential application is to create heteromolecular, one-dimensional chains by co-adsorption of DAT with other Lander-type compounds equipped with functional moieties that are complementary to the diamino-triazine groups. This concept has previously been demonstrated in different bimolecular systems where the compounds are not equipped with elevating legs [22–25].

We have characterized individual DAT molecules adsorbed at terraces and atomic steps on Cu(110)



**Figure 1** (a) Space-filling model of 1,4-bis(4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene molecule (DAT,  $\text{C}_{64}\text{H}_{68}\text{N}_{10}$ ) consisting of a central benzene core connected through phenyl groups to four *tert*-butyl and two diamino-triazine groups. Carbon, hydrogen, and nitrogen atoms are represented in pale blue, white and blue, respectively. (b) A typical high-resolution STM image of a DAT molecule on Cu(110), revealing four bright lobes in a rectangular shape and some delicate sub-protrusions in the center. (Sample voltage,  $-1.73$  V; tunneling current,  $-0.66$  nA). (c) EHMOSQC simulated STM image of DAT on Cu(110) under the same tunneling conditions as in (b)

and Au(111) surfaces by means of high-resolution STM imaging and lateral manipulation UHV conditions. On Cu(110), the contact configurations of the individual DAT molecules at step edges can be modified in a controlled manner by STM manipulation, including lateral translation, rotation, and pushing of molecules to an upper terrace. On Au(111), the Lander DAT molecules are highly mobile and cannot be manipulated in a controlled manner at the same temperature as on Cu(110). The experiments confirm qualitatively that the diffusion barrier for Lander DAT adsorbed on the Au(111) surface is lower than that found on Cu(110). This suggests that substrate alignment effects may be less pronounced on the Au(111) surface, making it better suited for self-assembly of Lander DAT architectures driven by intermolecular interactions.

## 1. Experimental

The experiments were conducted using a variable-temperature Aarhus STM [26] which is mounted in a UHV chamber with a typical base pressure  $p \sim 10^{-10}$  mbar. Electrochemically etched polycrystalline tungsten tips were used to record the STM images. The Au(111) and Cu(110) single-crystal samples were cleaned by repeated cycles of 1.5 keV  $\text{Ar}^+$  ion bombardment and annealing to 800 K for 15 min. The DAT molecules were synthesized by Rosenmund-



von Braun cyanation of 1,4-bis(4-bromophenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene, followed by reaction with dicyandiamide under microwave irradiation. The molecules were deposited from a thermal evaporator held at 510 K onto Au(111) or Cu(110) substrates kept at room temperature. All STM images were recorded in the constant current mode at a temperature of approximately 110 K to stabilize the molecules on the surfaces. The lateral manipulation was performed by reducing the tunnel resistance during scanning by increasing the tunneling current (up to  $\sim 1.5$  nA) while reducing the tunneling voltage (down to  $\sim 200$  mV) [11]. Theoretical simulations of the STM images were performed using extended Hückel molecular orbital-elastic scattering quantum chemistry (EHMO-ESQC) [27] after having relaxed the molecule on the surface using the molecular mechanics MM4(2003) code [28]. The STM image simulations were carried out on Cu(110) under the same tunneling conditions as those for the result in Fig. 1(b).

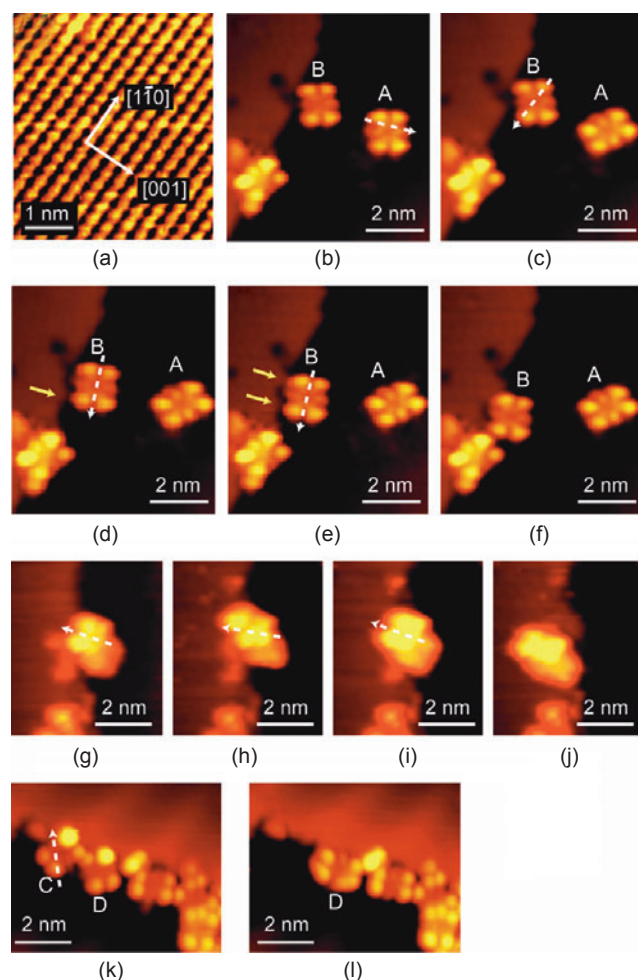
## 2. Results and discussion

A high-resolution STM image of a DAT molecule adsorbed on Cu(110) is depicted in Fig. 1(b). Four characteristic bright lobes are resolved in a rectangular shape ( $11.0 \text{ \AA} \times 6.5 \text{ \AA}$ ) as well as some sub-structure in the center. A similar morphology is observed for DAT molecules adsorbed on the Au(111) surface. For comparison, a simulated STM image obtained using the theoretical EHMO-ESQC approach is shown in Fig. 1(c). In both cases, the four bright lobes in the rectangular arrangement correspond to tunneling through the four *tert*-butyl groups [29], while the sub-protrusions are attributed to the six phenyl rings, which are connected to the central benzene core by  $\sigma$  bonds. Interestingly, there are no features that can be attributed to the diamino-triazine groups in either the experimental or simulated STM images, suggesting that these groups make only a minor contribution to the tunneling current. This is explained by the theoretical modeling studies, which show that molecular orbitals with a preponderant weight on the terminal amino groups lie outside the range of bias voltages used in our experiments. This

will be discussed in detail elsewhere. The optimum adsorption position identified in the molecular mechanics calculations has the central benzene ring of the molecule adsorbed on top of a Cu(110) surface atom. The *tert*-butyl groups induce a lift of the central board to a height of  $4.5 \text{ \AA}$  above the surface. Experimentally, three adsorption orientations of the DAT molecule on Cu(110) are revealed, with the long axis of the molecule oriented at  $-30^\circ$ ,  $0^\circ$ , and  $30^\circ$  relative to the  $[1\bar{1}0]$  direction of the substrate.

STM manipulation experiments were performed on individual DAT molecules on Cu(110) and Au(111) substrates at a temperature of  $\sim 110$  K as illustrated in the sequences of high-resolution STM images displayed in Fig. 2. We used the STM tip as a tool to push the molecules in a gentle manner. The manipulation is performed by reducing the resistance in the STM tunneling junction from  $\sim 3 \text{ G}\Omega$  to  $\sim 0.1 \text{ G}\Omega$  (by either increasing the tunneling current or reducing the tunneling voltage, or both). By controlling the precise tip position, we are thus able to manipulate individual molecules one at a time along a predefined path, leaving the rest of the scan area unperturbed. By such STM lateral manipulations, the molecular orientation for isolated molecules on the Cu(110) terrace can be changed from  $-30^\circ$  to  $30^\circ$  with respect to the  $[1\bar{1}0]$  direction of the substrate, as shown for the molecule marked "A" in Figs. 2(b) and (c). Gradual displacement of a molecule along a Cu(110) step edge is shown in the sequence of STM images depicted in Figs. 2(c)–(f) where the molecule marked "B" is steered by the STM tip. During this lateral translation, the orientation of molecule "B" is simultaneously changed. The molecular manipulation induces changes to the step morphology in the form of protrusions as indicated by the yellow arrows in Figs. 2(d) and 2(e) which may be compared to the smooth step edge along the  $[1\bar{1}0]$  direction in Fig. 2(c).

Manipulation of a molecule over a Cu(110) step edge from a lower to an upper terrace is shown in the sequence of consecutive images depicted in Figs. 2 (g)–(j). In the initial image, the different intensity of the four lobes suggests that the molecule is tilted at the step edge, with some legs of the molecule on the upper terrace and the remainder on the lower



**Figure 2** High-resolution STM images showing adsorption and STM manipulation of individual DAT Lander molecules on the Cu(110) (a)–(j) and Au(111) (k), (l) substrates. White arrows indicate the direction of operations applied between consecutive images. (a) High-resolution STM image of the Cu(110) substrate with principal lattice directions indicated. (b), (c) Rotation on the terrace of the molecule marked A. (c)–(f) Translation of the molecule marked B along the step edge. Yellow arrows indicate protrusions at the step induced by the molecular manipulation. (g)–(j) Manipulation of a molecule over a Cu(110) step edge from a lower to an upper terrace. (k), (l) Manipulation of DAT molecules adsorbed at a step edge of Au(111). The molecule marked C is removed from the step edge and diffuses out of the scanned region. The neighboring molecule marked D undergoes a concomitant rotation

terrace. Manipulated by the STM tip, the molecule is subsequently gradually pushed over the step edge until finally all four legs are moved onto the upper terrace. Various contact configurations are created along the manipulation path.

On the Au(111) surface at  $\sim 110$  K, individual molecules are observed at step edges as shown in Figs. 2(k) and 2(l). Similar STM manipulation as described

above was attempted on Au(111) for comparison. In Fig. 2(k), where two legs of the molecule “C” are in contact with the step edge, an STM manipulation operation was applied to the DAT molecule in an attempt to rotate and push it towards the upper terrace as was successfully performed on Cu(110). Surprisingly, this led to removal of molecule “C” from the step edge and it subsequently diffused out of the scanned region. Furthermore, as seen from Fig. 2(l), the manipulation of molecule “C” induced a rotation of the neighboring molecule “D” from a configuration with the axis of its board approximately parallel to the step edge into a perpendicular orientation. These findings indicate that the DAT molecule is more weakly bound to the Au(111) substrate than to Cu(110) and that, in particular, the molecular mobility is higher on Au(111), since individual molecules cannot be stabilized at the terraces at the investigated temperatures.

These experimental findings are consistent with previous theoretical and experimental results for the adsorption of organic molecules on metal substrates. Gold is a noble inert metal and it is expected that the molecule–substrate interaction on a Au(111) surface is weaker than on Cu(110). Furthermore, the corrugation of the molecule–substrate potential energy surface for the close-packed Au(111) surface is smaller than that of the more open, anisotropic Cu(110) surface, which implies that the diffusion barrier for molecules is lower on Au(111) as compared to Cu(110). These findings may be relevant for selecting suitable substrates for eventual assembly into 1-D molecular chains. The specific close-packed orientation of the anisotropic Cu(110) substrate might provide a templating effect, but the fairly strong local molecule–substrate interaction may hinder the formation of hydrogen bonded patterns which are determined mainly by molecule–molecule interactions. In this respect the weak molecule–substrate interaction may make the close-packed Au(111) surface a more suitable substrate for self-assembled molecular structures.

Generally, when a large complex molecule is adsorbed on a metal surface an energetically-preferred geometry is adopted rather than the one desired for an electronic contact. To achieve an



efficient charge transfer between the molecule and a connected electrode, it is required that the elevated molecular board of a Lander molecular wire is anchored to the electrode, for example, at a protrusion of the step edges. To assemble an appropriate electronic contact, STM manipulation may be used to change the adsorption site and/or orientation of Lander molecules relative to the step edges as shown above. The ability of Lander molecules to mould nanostructures at the step edge of Cu(110) has previously been reported [11, 19]. In these cases, the reshaping occurred at room temperature, where the diffusivity of Cu adatoms is relatively high, such that diffusing Cu adatoms can be trapped under the molecular  $\pi$  board to form specific metallic nanostructures. Subsequent STM manipulation of the molecular moulds was performed at low temperature in order to thermally stabilize the underlying metallic nanostructures. The case presented in Figs. 2(c)–(f) is different, revealing that even at low temperature ( $\sim 110$  K), the attractive interaction between the DAT molecule and the Cu(110) step edge is sufficient to induce a rearrangement of the step edges. The restructuring is temporary and reversible, since once the molecule is moved away, the atoms of the protrusions reassemble into the step edges. For molecules straddling the step edges, Grill et al. have previously reported that Lander molecules with a non-planar configuration have a shorter perpendicular spacing between the central molecular  $\pi$  board and metal electrodes than that of the planar case [13]. Since a shorter spacing may lead to a stronger molecule–substrate interaction, the manipulation over a step edge shown in Figs. 2 (g)–(j) is also a way to modify the electronic interaction of the DAT molecule with the Cu(110) surface.

### 3. Conclusions

Using STM imaging and lateral manipulation, we have studied the morphology and anchoring of a specially designed Lander molecule, DAT, on Cu(110) and Au(111). On Cu(110), various contact configurations of individual DAT molecules were formed at step edges in a controlled manner, steered by the STM tip, including rotation, lateral translation,

and pushing of the molecules over the step edge. The manipulation experiments show that the diffusion barrier for Lander DAT is higher on Cu(110) than on Au(111). Based on these experimental results, we conclude that Au(111) may be the more suitable substrate for the self-assembly of Lander DAT molecules since the weaker molecule–substrate interaction will be beneficial for the formation of ordered molecular architectures mainly driven by intermolecular interactions.

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### References

- [1] Joachim, C.; Gimzewski, J. K.; Aviram, A. Electronics using hybrid-molecular and mono-molecular devices. *Nature* **2000**, *408*, 541–548.
- [2] Browne, W. R.; Feringa, B. L. Making molecular machines work. *Nat. Nanotechnol.* **2006**, *1*, 25–35.
- [3] Gourdon, A. Synthesis of “Molecular Landers”. *Eur. J. Org. Chem.* **1998**, *1998*, 2797–2801.
- [4] Magoga, M.; Joachim, C. Conductance and transparency of long molecular wires. *Phys. Rev. B* **1997**, *56*, 4722–4729.
- [5] Gross, L.; Rieder, K. -H.; Moresco, F.; Stojkovic, S. M.; Gourdon, A.; Joachim, C. Trapping and moving metal atoms with a six-leg molecule. *Nat. Mater.* **2005**, *4*, 892–895.
- [6] Schunack, M.; Rosei, F.; Naitoh, Y.; Jiang, P.; Gourdon, A.; Lægsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. Adsorption behavior of Lander molecules on Cu(110) studied by scanning tunneling microscopy. *J. Chem. Phys.* **2002**, *117*, 6259–6265.
- [7] Savio, L.; Gross, L.; Rieder, K. -H.; Gourdon, A.; Joachim, C.; Moresco, F. Interaction of a long molecular wire with a nanostructured surface: Violet Landers on Cu(211). *Chem. Phys. Lett.* **2006**, *428*, 331–337.
- [8] Grill, L.; Rieder, K. -H.; Moresco, F.; Rapenne, G.;

- Stojkovic, S.; Bouju, X.; Joachim, C. Rolling a single molecular wheel at the atomic scale. *Nat. Nanotechnol.* **2007**, *2*, 95–98.
- [9] Shirai, Y.; Osgood, A. J.; Zhao, Y. M.; Yao, Y. X.; Saudan, L.; Yang, H. B.; Chiu, Y. -H.; Alemany, L. B.; Sasaki, T.; Morin, J. -F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. Surface-rolling molecules. *J. Am. Chem. Soc.* **2006**, *128*, 4854–4864.
- [10] Sasaki, T.; Guerrero, J. M.; Leonard, A. D.; Tour, J. M. Nanotrains and self-assembled two-dimensional arrays built from carboranes linked by hydrogen bonding of dipyrindones. *Nano Res.* **2008**, *1*, 412–419.
- [11] Rosei, F.; Schunack, M.; Jiang, P.; Gourdon, A.; Lægsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. Organic molecules acting as templates on metal surfaces. *Science* **2002**, *296*, 328–331.
- [12] Otero, R.; Rosei, F.; Besenbacher, F. Scanning tunneling microscopy manipulation of complex organic molecules on solid surfaces. *Annu. Rev. Phys. Chem.* **2006**, *57*, 497–525.
- [13] Grill, L.; Moresco, F. Contacting single molecules to metallic electrodes by scanning tunneling microscope manipulation: Model systems for molecular electronics. *J. Phys.: Condens. Matter* **2006**, *18*, S1887–1908.
- [14] Grill, L.; Moresco, F.; Jiang, P.; Joachim, C.; Gourdon, A.; Rieder, K. -H. Controlled manipulation of a single molecular wire along a copper atomic nanostructure. *Phys. Rev. B* **2004**, *69*, 035416.
- [15] Moresco, F.; Meyer, G.; Rieder, K. -H.; Tang, H.; Gourdon, A.; Joachim, C. Conformational changes of single molecules induced by scanning tunneling microscopy manipulation: A route to molecular switching. *Phys. Rev. Lett.* **2001**, *86*, 672–675.
- [16] Otero, R.; Naitoh, Y.; Rosei, F.; Jiang, P.; Thostrup, P.; Gourdon, A.; Lægsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. One-dimensional assembly and selective orientation of Lander molecules on a O–Cu template. *Angew. Chem. Int. Ed.* **2004**, *43*, 2092–2095.
- [17] Grill, L.; Rieder, K. -H.; Moresco, F.; Stojkovic, S.; Gourdon, A.; Joachim, C. Controlling the electronic interaction between a molecular wire and its atomic scale contacting pad. *Nano Lett.* **2005**, *5*, 859–863.
- [18] Alemani, M.; Gross, L.; Moresco, F.; Rieder, K. -H.; Wang, C.; Bouju, X.; Gourdon, A.; Joachim, C. Recording the intramolecular deformation of a 4-legs molecule during its STM manipulation on a Cu(211) surface. *Chem. Phys. Lett.* **2005**, *402*, 180–185.
- [19] Otero, R.; Rosei, F.; Naitoh, Y.; Jiang, P.; Thostrup, P.; Gourdon, A.; Lægsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. Nanostructuring Cu surfaces using custom-designed molecular molds. *Nano Lett.* **2004**, *4*, 75–78.
- [20] Otero, R.; Hümmelink, F.; Sato, F.; Legoas, S. B.; Thostrup, P.; Lægsgaard, E.; Stensgaard, I.; Galvão, D. S.; Besenbacher, F. Lock-and-key effect in the surface diffusion of large organic molecules probed by STM. *Nat. Mater.* **2004**, *3*, 779–782.
- [21] Kuntze, J.; Ge, X.; Berndt, R. Chiral structures of Lander molecules on Cu(100). *Nanotechnology* **2004**, *15*, S337–340.
- [22] Xu, W.; Dong, M.; Gersen, H.; Rauls, E.; Vazquez-Campos, S.; Crego-Calama, M.; Reinhoudt, D. N.; Stensgaard, I.; Lægsgaard, E.; Stensgaard, I.; Linderoth, T. R.; Besenbacher, F. Cyanuric acid and melamine on Au(111): Structure and energetics of hydrogen-bonded networks. *Small* **2007**, *3*, 854–858.
- [23] Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. Controlling molecular deposition and layer structure with supramolecular surface assemblies. *Nature* **2003**, *424*, 1029–1031.
- [24] De Feyter, S.; Miura, A.; Yao, S.; Chen, Z.; Wurthner, F.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W.; De Schryver, F. C. Two-dimensional self-assembly into multicomponent hydrogen-bonded nanostructures. *Nano Lett.* **2005**, *5*, 77–81.
- [25] Ruiz-Oses, M.; Gonzalez-Lakunza, N.; Silanes, I.; Gourdon, A.; Arnau, A.; Ortega, J. E. Self-assembly of heterogeneous supramolecular structures with uniaxial anisotropy. *J. Phys. Chem. B* **2006**, *110*, 25573–25577.
- [26] Lægsgaard, E.; Osterlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A high-pressure scanning tunneling microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.
- [27] Sautet, P.; Joachim, C. Calculation of the benzene on rhodium STM images. *Chem. Phys. Lett.* **1991**, *185*, 23–30.
- [28] Allinger, N. L.; Chen, K.; Lii, J. -H. An improved force field (MM4) for saturated hydrocarbons. *J. Comput. Chem.* **1996**, *17*, 642–668.
- [29] Zambelli, T.; Goudeau, S.; Lagoute, J.; Gourdon, A.; Bouju, X.; Gauthier, S.; Molecular self-assembly of jointed molecules on a metallic substrate: From single molecule to monolayer. *Chem. Phys. Chem.* **2006**, *7*, 1917–1920.

