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Bicomponent hydrogen-bonded nanostructures formed by two complementary molecular Landers on Au(111)

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The co-adsorption of two molecular Landers equipped with functional groups capable of forming a complementary triple hydrogen-bonding motif is investigated with scanning tunneling microscopy and molecular mechanics calculations. Surprisingly, the anticipated complementary motif is not realised in 2-D terrace structures, but is observed in 1-D structures at step edges where molecular conformational flexibility is confined.

Molecular Landers are a class of molecules designed for surface-adsorption studies in which a poly-aromatic board is separated from the surface by bulky spacer groups which act as legs.[1] The adsorption of molecular Landers on metal surfaces under ultra high vacuum conditions has been studied by scanning tunneling microscopy (STM), providing information regarding the organisation on terraces,[2] step edges and templated surfaces[3] as well as the diffusional[4,5] and electronic[6,7] properties for these relatively large and complex molecules. A unique feature of molecular Landers is their ability to trap metal atoms and act as molecular moulds,[8,9] potentially allowing for bottom-up organisation of metallic nanostructures through pre-assembly of molecular Landers. With the aim to steer the assembly of molecular Landers through hydrogen-bonding interactions, two linear and bi-dentate molecular Landers were recently synthesized[10] each bearing either two diamino-triazine (DAT) or two di-carboxylic imide (DCI) functionalities (Fig. 1a). The DAT and DCI functionalities are complementary and can form a triple hydrogen bonding motif consisting of one N–H···N and two N–H···O bonds. This classical[11,12] supra-molecular motif has on surfaces been observed to drive the organisation of both 2-D networks[13,14] (involving molecules with 3-fold symmetry) and 1-D chains[15,16] (for linear molecules), but in all cases for planar molecules where the functional groups are adsorbed close to and parallel to the surface. For Lander DAT and Lander DCI, however, the three-dimensional molecular structure allows for more conformational flexibility which can affect *e.g.* the subtle interplay between van der Waals interactions and hydrogen bonding.

Here we investigate the co-adsorption of Lander DAT and Lander DCI on Au(111). Surprisingly, our STM experiments reveal that on terraces of the Au(111) surface, the anticipated DAT-DCI motif is not borne out, but the linear Lander DCI and Lander DAT molecules instead form a 2-D network driven by a complex interaction node involving four molecules. The anticipated 1-D arrangement driven by complementary DCI-DAT interaction is instead realised when the molecules adsorb at step edges. The energetic and mechanistic reasons for these observations are identified from molecular mechanics calculations. Our results provide important insights into how the DAT-DCI motif may drive self-assembly on surfaces for three-dimensional molecules with large degrees of conformational flexibility.

The adsorption of Lander DCI and Lander DAT separately on Au(111) surfaces was investigated by us previously.[17,18] Lander DCI forms 1-D chains driven by double hydrogen bonding between the DCI groups.[17] Lander DAT forms various 2-D networks in which the interaction between the DAT groups is optimised through conformational flexibility.[18] In the co-deposition experiments reported upon here, Lander DAT and Lander DCI were evaporated from separate crucibles onto a Au(111) surface followed by annealing to 400 K. Details on experimental and theoretical methods are provided in the supplementary information section.

On terraces of the Au(111) surface, co-deposition of Lander DAT and DCI at sub-monolayer coverage results in the formation of 2D molecular islands with grid-like structure as shown in Fig. 1b. The STM contrast of Lander DAT and Lander DCI is dominated by the four peripheral leg groups which appear as bright protrusions (see Fig. SI1). The two molecules can therefore be distinguished by analysis of the separation between the leg groups (Fig. SI2). In the 2D molecular island the Lander DCI molecules are arranged in chains via head-to-tail interaction while interspersed Lander DAT molecules separate the chains. The periodicity along the Lander DCI chains is ~31.5 Å similar to that determined for isolated 1D chains of Lander DCI molecules[17] suggesting that the interaction between two neighbouring Lander DCI molecules in the 2D network involves the same double N–H···O hydrogen bonding (dashed lines in Fig. 1c) as in the isolated 1D chains. From the STM images and superimposed molecular models we estimate that the two C=O groups of Lander DCI molecules belonging to adjacent chains are separated by d(12) = d(1′2′) = 26.0 ± 0.9 Å (Fig. 1c). This separation accommodates well to the size of the Lander DAT molecules interspersed between the Lander DCI chains. Furthermore, the separation between the C=O groups on adjacent Lander DCI molecules within the chains is d(11') = d(22´) = 5.1 ± 0.5 Å which corresponds well to the distance between two N–H hydrogens in the DAT group of the Lander DAT molecule. As a consequence each DAT Lander may thus interact with four Lander DCI molecules via N–H···O hydrogen bonding (solid lines in Fig. 1c).

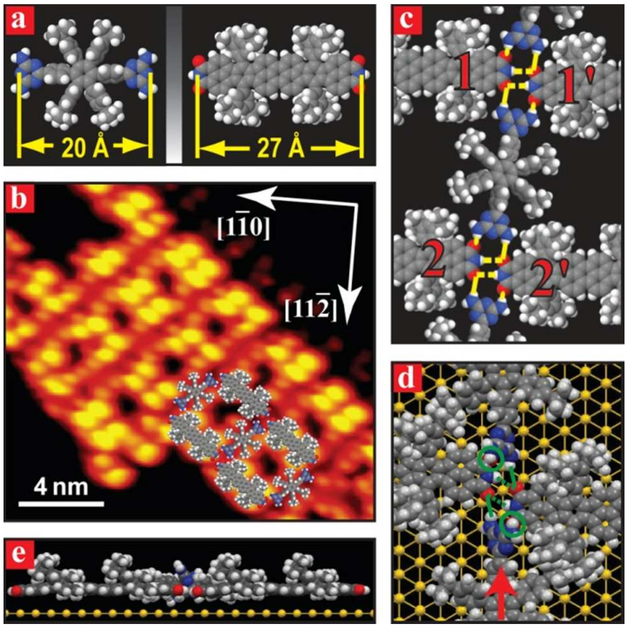

Fig. 1 Two-dimensional island formed from Lander DAT and Lander DCI on the Au(111) surface. (a) Model structures of Lander DAT (left) and Lander DCI (right). (b) STM image of 2D grid-like pattern and (c) a tentative model of this structure. (d) Top- and (e) side-views of the calculated model showing the H-bonds involved in formation of the 2D network. The arrow in (d) indicates the viewing direction for the side view (e). For clarity the DAT molecule under the arrow is removed in the side-view

Molecular mechanics calculations of the 2D structure were performed focusing on a single interaction node composed of two Lander DCI molecules interconnected with two Lander DAT molecules (see SI for details). The fully relaxed structure is shown in Fig. 1d. The calculated distance $d_{NHO(1)}$ = 2.51 Å (dashed lines in Fig. 1d) corresponds well to the N–H···O double hydrogen bonding between consecutive Lander DCI molecules in the chains, while the distances $d_{NHO(2)}$ = 1.86 Å and $d_{NHO(3)}$ = 3.46 Å (circles and solid lines in Fig. 1d, respectively) are assigned to H-bonding between two N–H sites of the DAT group in Lander DAT and C=O sites of two neighbouring DCI molecules in the chains. The terrace promotes adsorption of Lander DAT with its poly-aromatic core parallel to the plane of the surface. This conformation induces a rearrangement of the DAT groups and the connecting phenyl rings as shown in Fig. 1d. The interaction between Lander DAT and DCI molecules is thus enhanced by the ability of the DAT groups to rotate and form H-bonding optimised in three dimensions as also previously found in structures formed from Lander DAT alone.[18]

The co-deposition of Lander DAT and Lander DCI at very low coverage results in preferential anchoring of the molecules at step edges (Fig. 2a). Each molecule adsorbed at the step edge appears as two bright and two dim protrusions ascribed to spacer legs standing on the upper and lower terraces, respectively, as also observed in previous STM studies on related Landers.[19] The small and large four-lobe features have dimensions similar to those of Lander DAT and Lander DCI, respectively. Therefore, the short chains with periodicity ~51.5 Å are attributed to alternating Lander DAT and Lander DCI molecules. Figure 2b shows a calculated model for the 1D hetero-molecular chain at the step edge. The calculated N–H···O and N–H···N distances (dashed and solid lines in Fig. 2b) are 2.30 Å and 2.43 Å, respectively, and correspond well to the anticipated complementary triple H-bonding motif between the DAT and DCI functionalities.

Intriguingly, 1D hetero-molecular chains similar to those found at the step edges were never observed on the Au(111) terraces. To illuminate the reasons for the preferential formation of 2D molecular networks on the terraces, we made calculations for a hypothetical 1D hetero-molecular chain adsorbed on the terrace (Fig. 2c). Table SI1 summarises the total binding energies and contributions from different intermolecular interactions for the 2D network and the 1D chains at terraces/steps. The total energy per DAT-DCI molecular pair is 1.51 eV in the 2D network, while it is 0.44 eV for the 1D terrace chain. The H-bonding energy in the 2D network contributes only 57% (0.86 eV) of this total energy as compared to 73% (0.32 eV) in the 1D terrace chain. Another reason for the higher energy gain in the 2D network is that the van der Waals interaction in this structure (0.65 eV) is five times higher than the value calculated for the 1D terrace chain (0.12 eV). Therefore the van der Waals interaction is comparable to the H-bonding energy in the 2D network and imparts a large fraction of its stability. The calculations thus confirm that the 2D molecular network is energetically more favourable than a 1D hetero-molecular chain on the terraces, in agreement with experimental observations. For the 1D hetero-molecular chain adsorbed at a step edge (Fig. 2b) the total energy is 0.65 eV, arising from van der Waals interaction (0.05 eV) and H-bonding (0.59 eV). The hydrogen bonding between the DCI and DAT groups thus contributes more than 91% of the total energy in this case.

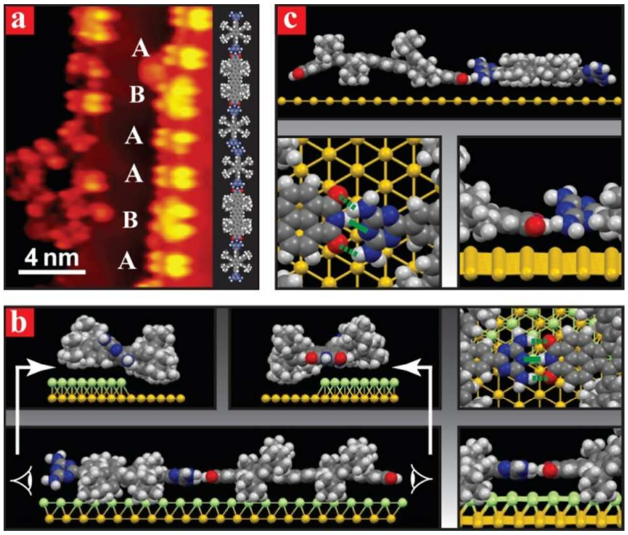

Fig. 2 One-dimensional structures formed from Lander DAT and Lander DCI at step edges of the Au(111) surface. (a) STM image of short molecular chains (left panel) composed of Lander DAT (A) and Lander DCI (B) alongside a qualitative model of this structure. (b) Calculated conformation of the 1D chain at a step edge: side view of this structure along (top-left/middle) and perpendicular (bottom-left panel) to the chain, and zoomed top (top-right) and side

(bottom-right) views of the H-bonding involved in formation of the 1D structure. (c) Calculated model of a hypothetical 1D chain on the terrace: side view (top) and zoomed top (bottom-left) and side views (bottom-right).

In the hypothetical 1D terrace chain (Fig. 2c) the backbone of the Lander DCI molecule is strongly distorted which is not observed for Lander DCI molecules adsorbed alone on Au(111).[17] The distortion results from interaction with the neighbouring DAT group which leads to bending of the Lander DCI molecule facilitated by the flexibility of the hydrocarbon skeleton. The DCI-DAT triple H-bonding motif is adversely affected by the bent DCI conformation on the terrace. In contrast, the Lander DCI molecule adsorbs with relatively straight adsorption geometry in the chain formed at the step edge (Fig. 2b). The straight geometry results from the particular adsorption position with spacer legs at both the upper and the lower terrace. Here, the flexibility of the bond connecting the board and the di-*tert*-butylphenyl spacers allows for optimisation of the van der Waals interaction with the surface as well as the H-bonding between complementary moieties. The H-bonding between the complementary Lander molecules in the hetero-molecular chain is further enhanced at the step edge since the DAT groups are less tilted than on the terrace (Figs. 2b and 2c, respectively). As a result of these differences in adsorption conformation, the DAT-DCI hydrogen bonding in the 1D chain is more directional and stronger at the step edge (0.59 eV) than on the terrace (0.32 eV). This difference is an important reason why 1D hetero-molecular chains are not observed experimentally on the terrace.

In summary we have investigated the co-deposition of Lander DAT and Lander DCI molecules on Au(111). On terraces an extended 2D structure is observed which is composed of head-to-tail hydrogen-bonded Lander DCI chains interconnected by Lander DAT molecules. At step edges short 1D hetero-molecular chains are formed via complementary DAT-DCI triple hydrogen bonds. The scenarios for the formation of the 1D and 2D structures are closely related to the conformational flexibility of the Lander-type molecules, in particular the ability of the DAT groups to rotate with respect to the central core of Lander DAT. The rotation of the DAT group allows for formation of a 3-D optimized H-bonding with Lander DCI in the 2D network. The rotated conformation of the DAT group is, however, not favourable for complementary DAT-DCI interaction in a 1D hetero-molecular chain on the terrace which is further hindered by distortions of the Lander DCI backbone. The consequence is twofold: i) the formation of a 2D network on the terrace consisting of Lander DCI chains interconnected by Lander DAT molecules by interaction nodes optimised in three dimensions and ii) the formation of hetero-molecular chains at the step edge where the adsorption conformation straddling the step edge prevents rotation of the DAT group thereby allowing for DAT-DCI complementary interaction.

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† Electronic Supplementary Information (ESI) available: Experimental and theoretical methods, calculated STM images for Lander DAT and Lander DCI, quantitative analysis of STM images for the 2D terrace structure of Lander DAT and Lander DCI, calculated models in high resolution. See DOI: 10.1039/c000000x/

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