Template-directed supramolecular self-assembly of coordination dumbbells at surfaces

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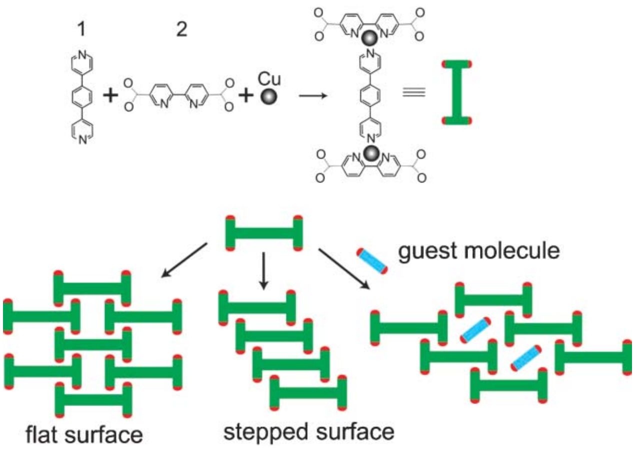
Scanning tunneling microscopy reveals, at single-molecular resolution, how external parameters—substrate morphology and guest addition—re-direct the assembly of dumbbell-shaped coordination supramolecules towards different surface-confined supramolecular organizations.

The assembly of poly-molecular architectures of increasing complexity from molecular building units through non-covalent bonds is the leitmotif of supramolecular synthesis.[1–7] The structures of supramolecular systems rely on the electronic and steric information stored in basic molecular building units as well as on the properties of intermolecular binding (*e.g.*, hydrogen bonds, van der Waals forces and coordination bonds). Generally, the distinct levels of structural complexity encountered in supramolecular systems involve various non-covalent binding modes.[8–11] The fundamental structural level are individual molecular entities, *i.e.* covalent motifs. Specific collection of these entities through non-covalent binding forms finite or extended oligomolecular composites (supramolecules).[12] Inspired by the biological processes, the success of supramolecular synthesis lies in the reversibility of the non-covalent nature of the inter-component binding. This reversibility means that the supramolecular assembly is intrinsically dynamic, which allows self-selection, recognition and self-organization in the extremely complex assembly processes.[13–16] On the other hand, changes of external (solvents, anions, surfaces, *etc.*) or internal (the addition of guest molecules) parameters may alter the energy landscape of the non-covalent inter-component binding. This results finally in distinctive structural configurations for identical systems, a process known as template-directed assembly.[17,18] It has been shown that the template-directed assembly is a powerful strategy to design the outcome of supramolecular structures.[19–22]

In this report we illustrate the importance of template effects in surface-confined supramolecular organizations, which were investigated at the single-molecule level by scanning tunneling microscopy (STM). The essential results are that (i) dumbbell-shaped supramolecules are generated through the heteroleptic coordinative bonding interactions of the nitrogen atoms of 2,2′- and 4,4′-bipyridine-type, ligands **1** and **2**, towards Cu centers on a metallic surface (see Scheme 1), (ii) the dumbbell units self-assemble into supramolecular arrays through multiple hydrogen-bonding and (iii) the organization of the supramolecular arrays can be controlled by the underlying surface structure or by the addition of guest molecules (Scheme 1). This study presents unprecedented single-molecular insight on template-directed self-assembly of supramolecular structures.

Two types of molecular ligands, bis(4-pyridyl)-1,4-benzene (**1**)‡ and (2,2′-bipyridine)-5,5′-dicarboxylic acid (**2**), were co-deposited on a Cu(100) surface by thermal evaporation under ultra-high vacuum conditions. The free copper adatoms present at the surface were coordinated heteroleptically by the nitrogen donor atoms of the pyridine and the bipyridine coordination sites of **1** and **2**.[23] Three-dentate coordination of one molecule of **1** and two molecules of **2** results in a binuclear dumbbell-shaped $Cu_2(\mathbf{1})(\mathbf{2})_2$ complex (Scheme 1). At appropriate molecular ratio almost all of the co-deposited organic molecules form dumbbell-shaped Cu_2-complexes. Under the experimental conditions the carboxylic acid functions of **2** are considered to be deprotonated.[24] The resulting carboxylates, shown as red tips in Scheme 1, can act as effective hydrogen-bonding acceptors. Due to their branched shape and multiple hydrogen bonding sites, the dumbbell $Cu_2(\mathbf{1})(\mathbf{2})_2$ complexes form various supramolecular organizations.

Fig. 1(a) shows an STM topograph of the supramolecular arrays formed on the flat, defect-free terraces of the Cu(100) surface. One can identify two types of rod-shaped objects, long and dim or short and bright. The size of these objects indicates that



Scheme 1

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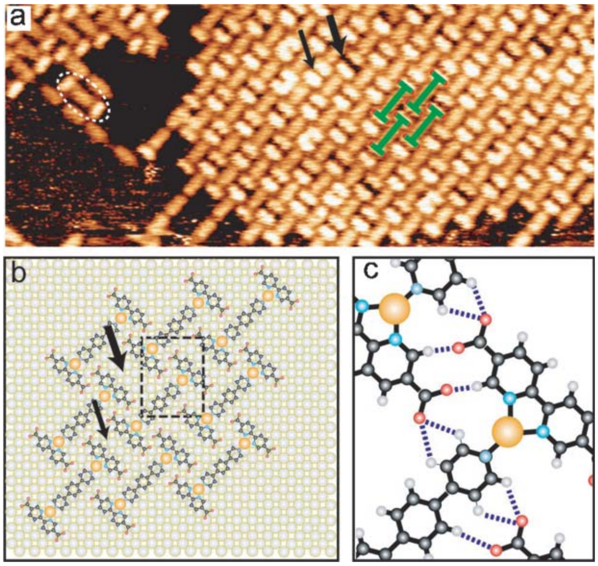

Fig. 1 (a) STM topograph (33 × 14 nm) showing the supramolecular organization of the dumbbells at a flat surface area, where the dotted ellipse highlights an isolated dumbbell, green dumbbells illustrate the brick-wall pattern, the thick (thin) arrow marks the wide (narrow) gap. (b) Molecular structural model of the brick-wall phase with respect to the substrate lattice, where the two arrows point the two gaps of different width. (c) Enlarged view of the rectangular area of (b), the possible hydrogen bonds shown by dotted lines. Carbon in grey, oxygen in red, hydrogen in white, nitrogen in blue and Cu in orange.

they are single molecules **1** and **2**, respectively. Another evidence that the longer, dimmer objects are molecules of **1** is that in Fig. 1(a) one can see occasionally linear chain-like organizations, which are already known from previous studies to consist of Cu-coordinated molecules of **1**.[25] The dotted ellipse in Fig. 1(a) marks a dumbbell-shaped unit consisting of one molecule of **1** and two molecules of **2**—the $Cu_2(\mathbf{1})(\mathbf{2})_2$ complex. Predominantly, the dumbbell complexes assemble in closely-packed arrays resembling a brick-wall pattern (schematic model in Fig. 1(a)). Detailed data analysis reveals that the arrays are not a perfect brick-wall structure since adjacent dumbbells within one row are separated by either a wider or a more narrow gap, as pointed by the thick and thin arrows in Fig. 1(a) and (b), respectively. Fig. 1(b) is a molecular structural model of the brick-wall organization, in which all coordinated Cu centers as well as both aromatic rings of **2** and the central aromatic ring of **1** sit at the four-fold hollow sites of the substrate, *i.e.* an energetically optimized adsorption configuration. This model explains the observation of the two gap widths: there are two possible adsorption sites of identical registration with respect to the substrate for a dumbbell complex, which results in the wide/narrow gap scheme. The dumbbells are interconnected through multiple hydrogen bonds as shown in Fig. 1(c). Structurally possible hydrogen bonds are indicated by dotted lines. All carboxylate oxygen atoms act as strong hydrogen bonding acceptors for aromatic C–H protons, either in a near 180° O···H–C straight single binding or in a bifurcated binding. In total, each dumbbell complex can interact to its neighbors through eight single H-bonds and eight bifurcated H-bonds. The O–H distance of the single H-bonds is 2.1 Å, whereas the bifurcated H-bonds have an O–H distance of 2.5 to 2.8 Å, both falling into the range of typical hydrogen bonds at surfaces.[26]

At a single crystal surface monoatomic high steps are frequently encountered. These step "defects" can have a significant effect on the epitaxial growth of inorganic or organic thin films.[27,28] Fig. 2(a) shows that at the step edges the dumbbells organize in a 1D ladder-like structure. Fig. 2(b) illustrates a structural model of the ladder-like phase, in which one out of four carboxylate oxygen atoms is obviously prevented from hydrogen bonding interactions. Each dumbbell complex connects to its neighbors through eight single H-bonds and four bifurcated H-bonds, as shown in Fig. 2(c). From the energy point of view the ladder-like structure would be less stable than the brick-wall phase if the substrate influence were excluded. Therefore the formation of the ladder structure indicates that the step edges act as a template in the self-assembly process, *i.e.* they re-direct the supramolecular organization. The role of steps is apparent: first, a step forbids the extension of dumbbells towards the down-step side; secondly, as shown in Fig. 2(b), the straight step edge prompts a linear organization of the dumbbells due to preferred adsorption; thirdly, steps offer nucleation sites to initiate the aggregation of the dumbbell complexes. Overall, the steric confinement offered by the steps is significant enough to alter the energy landscape shaped by the hydrogen binding.

Also guest molecules can reorganize the supramolecular structure of the surface-confined monolayer of dumbbell-like $Cu_2(\mathbf{1})(\mathbf{2})_2$ complexes. Fig. 3(a) shows the supramolecular organization obtained after deposition of an excess amount of molecule **2** at the surface. The overlaid schematic model shows the basic structural motif of this new phase: four dumbbell complexes now enclose a non-coordinated molecule of **2**. In addition, cavities which are not occupied by the molecules of **2** can be detected (Fig. 3(a)). Such structure can be also considered as a 2D supramolecular host–guest structure, whereby the dumbbell complexes network comprises a host and the additional molecules

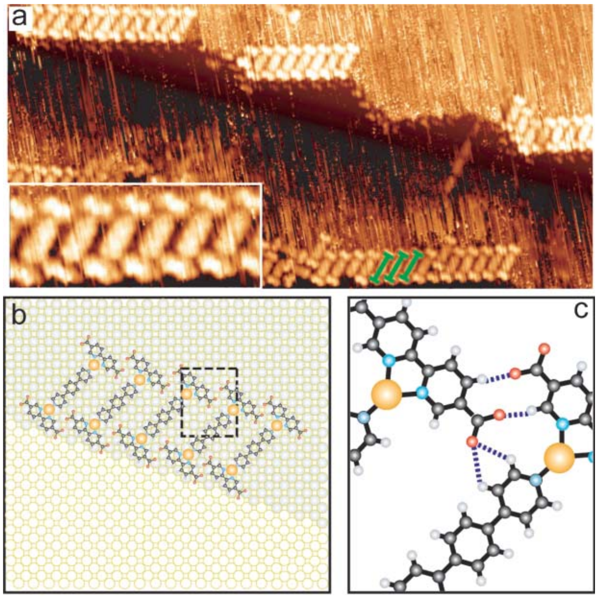

Fig. 2 (a) STM topograph (44 × 22 nm) showing the supramolecular organization of the dumbbells at step edges, green dumbbells illustrate the ladder structure. (b) Molecular structural model of the ladder phase with respect to the substrate lattice, color change of the substrate showing the step. (c) Enlarged view of the rectangular area of (b), the possible hydrogen bonds shown by dotted lines. Color code same as Fig. 1.

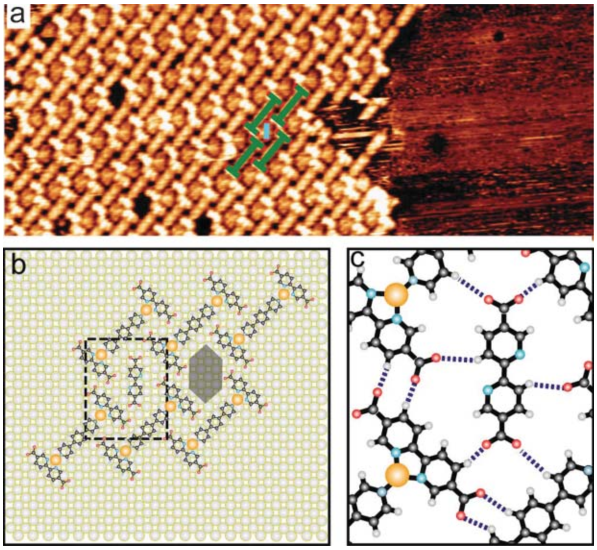

Fig. 3 (a) STM topograph (30 × 12 nm) showing the supramolecular organization of the dumbbells with the additional molecules of **2**, green dumbbells and a blue rod illustrate the host and the guest, respectively. (b) Molecular structural model of the host–guest structure with respect to the substrate lattice, the shaded polygon showing the absence of guest species. (c) Enlarged view of the rectangular area of (b), the possible hydrogen bonds shown by dotted lines. Color code same as Fig. 1.

2 the guests. Fig. 3(b) shows the structural model with respect to the Cu-substrate and Fig. 3(c) the tentative hydrogen bonds. Besides carboxylate oxygen atoms of the dumbbells, the carboxylate oxygen atoms of the enclosed molecule **2** are also involved in hydrogen bonding (an alternative to the bonding model shown in Fig. 3c could consist of a zwitterionic form of **2** interacting *via* two N–H···O to neighboring molecules of **1**), resulting in total in 18 H-bonds for each dumbbell, whereas the number of H-bonds for each dumbbell is reduced to 12 within the empty cavities (shaded area in Fig. 3(b)). Only the inclusion of excess guest molecules gives access to the cavity structure which becomes energetically more favored than the brick-wall structure. Thus, the addition of excess molecules of **2** changes the nature of the supramolecular assembly.

In summary all three structures comprise supramolecular arrays generated by associating dumbbell $Cu_2(\mathbf{1})(\mathbf{2})_2$ complexes through multiple hydrogen bonds. The external parameters—substrate morphology and guest addition—do not alter the formation of the coordination dumbbells but the organization of supramolecular arrays. It is evident that these external parameters are only effective to change the energy landscape of the hydrogen-bond determined assembly of the supramolecular arrays but not the coordination assembly of the dumbbells. Our results exemplify that the subtle change of binding energy induced by the substrate parameters is decisive for surface-confined supramolecular organizations. It is of high interest to study the templated-directed assembly by choosing various guest molecules in future.

Notes and references

‡ Ligand **1** was synthesized following reported procedures.[29,30] Ligand **2** was purchased from Sigma-Aldrich with a purity of 97%. **1** and **2** were sublimed in ultra-high vacuum by Knudsen-cell type evaporators at, 400 and 520 K, respectively, with the substrate at room temperature followed by annealing to 400 K.

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