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Growth of individual hydrogen-bonded nanostructures on gold monolayers†

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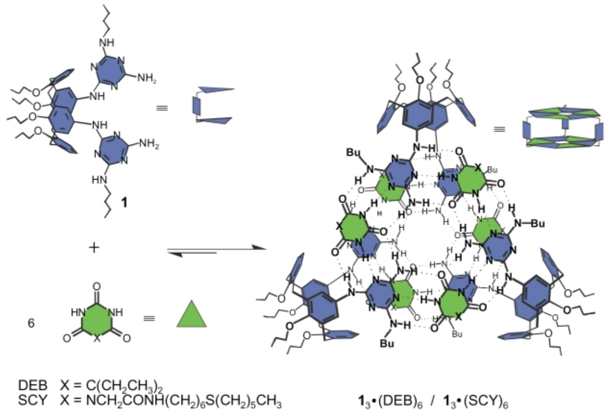
The growth of individual nanometer-sized (3.4 ± 1.4 nm) hydrogen bonded assemblies $\mathbf{1}_2\cdot(\mathrm{DEB})_6$ on gold monolayers was achieved through an exchange reaction between single isolated calix[4]arene dimelamine 2 (1.1 ± 0.2 nm) embedded in hexanethiol monolayers and double rosette hydrogen bonded assembly $\mathbf{1}_3\cdot(\mathrm{DEB})_6$ in solution. The growth process was monitored by tapping mode atomic force microscopy (TM-AFM).

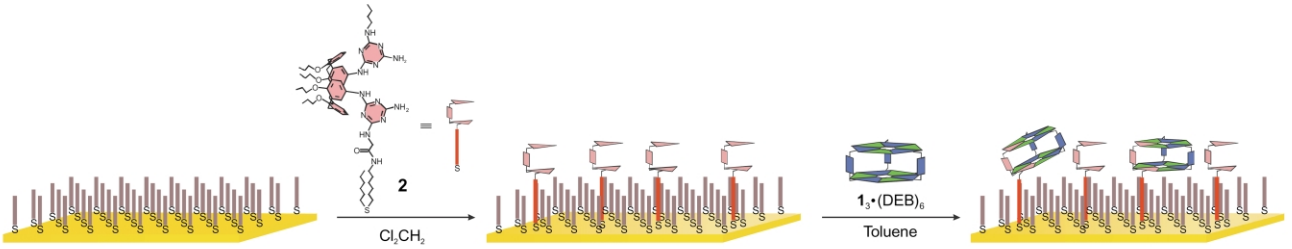
Nanotechnology comprises two different and opposite trends, *i.e.* the *top-down*[1] and the *bottom-up*[2] approaches. *Top-down* involves the use of physical methods to create small structures by means of lithographic and layering techniques, while the *bottom-up* approach involves the use of molecular building blocks for the construction of nanometer scale devices capable of specific functions.[3] It is accepted that noncovalent synthesis and especially self-assembly will play an important role[4] in the future development of large scale nanometer-sized devices. In this respect, new tools and methodologies are needed for the assembly of these individual functional 3D structures on solid support.[5] In this sense, modification of gold surfaces through self-assembly is a promising strategy. Recently, our group showed the controlled growth of surface immobilized isolated molecules by metal coordination on gold surfaces. These studies showed that monolayer protected Au nanoclusters or dendritic molecules interact *via* coordination with Pd$^{\mathrm{II}}$ pincer adsorbate molecules isolated in alkanethiol monolayers.[6] Moreover, we have also shown the noncovalent synthesis of individual molecular containers *via* coordination reactions on surfaces.[7] Due to their cooperative strength, directionality and high selectivity, hydrogen bonds are also very interesting for the self-assembly of complex structures.[8] However, their use on solid supports has been mainly limited to DNA. Specific DNA hybridization has been successfully used for the construction of nanostructured materials,[9] and for the selective positioning of proteins[9c] and metal or semiconductor nanoclusters.[10] More importantly, DNA microarrays are crucial in nucleic acid analyses and genome research.[11] In this communication we report for the first time the noncovalent growth of individual synthetic hydrogen-bonded assemblies on gold monolayers.

Our method is based on calix[4]arene dimelamines and barbituric/cyanuric acid derivatives which in apolar solvents spontaneously form stable hydrogen bonded assemblies $\mathbf{1}_3\cdot(\mathrm{DEB})_6$, where 9 molecules are held together by 36 hydrogen bonds (Scheme 1).[8a,12] The growth of the hydrogen-bonded assemblies was performed starting from isolated calix[4]arene dimelamine **2** embedded into hexanethiol self-assembled monolayers (SAMs)[13] (Scheme 2). Gold [Au (111)] substrates covered with hexanethiol monolayers were exposed to a solution of adsorbate **2** (20 μM) in CH_2Cl_2 for one hour (Scheme 2). After rinsing with CH_2Cl_2, EtOH and water, TM-AFM images in air of these monolayers (Fig. 1a) show single isolated features with an average height of 1.1 ± 0.2 nm, in good agreement with the height obtained from the CPK model (0.9 nm) of the adsorbate **2**.

Subsequently, monolayers containing these embedded calix[4]arene dimelamine **2** were immersed in a solution of assembly $\mathbf{1}_3\cdot(\mathrm{DEB})_6$ (50 μM) in toluene for 1 h. After extensive rinsing with toluene, TM-AFM images in air of these monolayers show two different size features (Fig. 1b). The height of the largest feature (3.51 nm, Fig. 1c) agrees well with the expected size for



Scheme 1 Schematic representation of the double rosette assemblies $\mathbf{1}_3\cdot(\mathrm{DEB})_6$ and $\mathbf{1}_3\cdot(\mathrm{SCY})_6$.



Scheme 2 Schematic representation of the methodology followed for the growth of assemblies $\mathbf{1}_2\cdot\mathbf{2}\cdot(\mathrm{DEB})_6$ on gold monolayers.

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† Electronic supplementary information (ESI) available: Characterization of compound **2**, assemblies $\mathbf{1}_3\cdot(\mathrm{DEB})_6$, $\mathbf{1}_2\cdot\mathbf{2}\cdot(\mathrm{DEB})_6$ and preparation of monolayers. See http://www.rsc.org/suppdata/cc/b2/b210996d/

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the assembly $\mathbf{1}_2\cdot\mathbf{2}\cdot(\text{DEB})_6$ considering the crystal structure of a similar double rosette assembly.[14] Therefore they are attributed to mixed assemblies $\mathbf{1}_2\cdot\mathbf{2}\cdot(\text{DEB})_6$ obtained through reversible exchange of components **1** and **2**, similarly to what occurs in solution[15] (as studied by ^{1}H NMR spectroscopy). The height of the smallest features (0.95 nm, Fig. 1c) corresponds to single isolated molecules of **2** which were not involved in exchange reactions with assemblies $\mathbf{1}_3\cdot(\text{DEB})_6$. In another experiment we investigated the concentration effect of **2** in the growth of the assemblies on the monolayer. In this case, hexanethiol monolayers were subsequently exposed to a solution of adsorbate **2** (50 µM, CH_2Cl_2) and to a solution of assembly $\mathbf{1}_3\cdot(\text{DEB})_6$ (50 µM, toluene), as described before. The increase in the starting concentration was reflected in an increased number of molecules of **2** available for exchange reactions, and therefore in a higher number of individual assemblies $\mathbf{1}_2\cdot\mathbf{2}\cdot(\text{DEB})_6$ in the final monolayer (Fig. 2). The histogram analysis of this monolayer reveals an average height of 3.4 ± 1.4 nm.

Several control experiments were performed to rule out physisorption and nonspecific interactions. Hydrogen bonded assemblies $\mathbf{1}_3\cdot(\text{SCY})_6$ (Scheme 1) bearing sulfide groups on the cyanurate units were directly inserted in hexanethiol SAMs on gold. TM-AFM images in air show the same single isolated nanometer-sized features with an average height profile of 3.23 ± 0.48 nm corresponding with fully assembled double rosettes $\mathbf{1}_3\cdot(\text{SCY})_6$ and are consistent with the above description of assembly $\mathbf{1}_2\cdot\mathbf{2}\cdot(\text{DEB})_6$. Hexanethiol SAMs were treated with a solution of an adsorbate similar to **2**, but lacking the sulfide group, under identical conditions. TM-AFM images in air of these monolayers did not show any individual features. In the second control experiment, hexanethiol monolayers without calix[4]arene dimelamines **2** were exposed to a solution of double rosette assembly $\mathbf{1}_3\cdot(\text{DEB})_6$ under the conditions used for the growth of the assemblies $\mathbf{1}_2\cdot\mathbf{2}\cdot(\text{DEB})_6$ on the monolayer. The absence of features on the TM-AFM images confirms that the insertion of calix[4]arene dimelamine **2** into the monolayer is a necessary first step for the growth of the assemblies and hence, rules out nonspecific interactions and physisorption processes.

In conclusion, the experiments described here show for the first time that it is possible to grow individual finite nanometer-sized assemblies through hydrogen bonds in two-dimensional SAMs on gold when one building block is embedded into the monolayer. Moreover, similar to DNA, the building blocks can be easily chemically manipulated allowing the attachment of functional units at different positions without destabilizing the assemblies.[16] Thus, we envision that these hydrogen-bonded platforms can be used for the design of chemical diversity at the nanometer level. Research following these ideas is currently underway.

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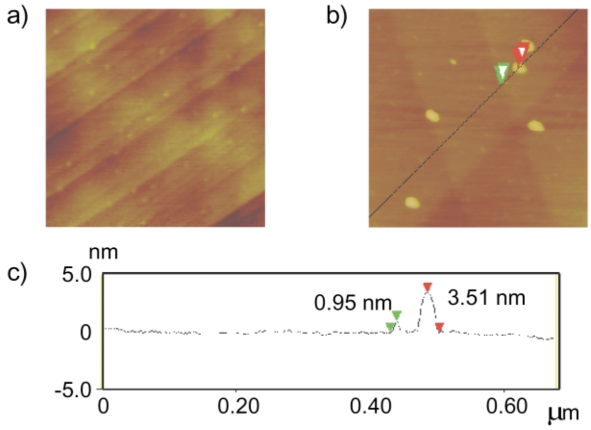

Fig. 1 a) TM-AFM image in air (500 × 500 nm) of hexanethiol monolayers on Au (111) containing calix[4]arene dimelamine **2**. b) TM-AFM image (500 × 500 nm) after treatment with a solution of assembly $\mathbf{1}_3\cdot(\text{DEB})_6$. c) Comparison of heights. The height profile corresponds to the line drawn in the AFM image 2b. Color scale from dark to yellow: Z = 10 nm.

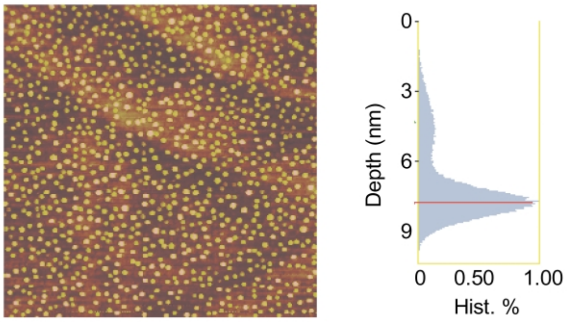

Fig. 2 TM-AFM image in air (1 × 1 µm) and histogram analysis of hexanethiol monolayers on Au (111) after sequential treatment with a solution of calix[4]arene dimelamine **2** (50 µM, CH_2Cl_2) and a solution of assembly $\mathbf{1}_3\cdot(\text{DEB})_6$. Color scale from dark to yellow: Z = 10 nm.

Notes and references

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