

Enhanced Stability of Large Molecules Vacuum-Sublimated onto Au(111) Achieved by Incorporation of Coordinated Au-Atoms

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Engineering of functional molecular structures on surfaces by bottom-up self-assembly is among the key goals of the rapidly developing field of nanotechnology.^{1,2} Adsorption and organization of molecules at the vacuum-solid interface³ have received particular attention for fundamental studies, motivated by the high degree of cleanliness achievable, the large suite of vacuum-based surface science analysis techniques that can be employed, and the superior control of substrate temperature and coverage. Difficulties in this bottom-up self-assembly route arise, however, as larger and more complex molecular building blocks are being studied. In particular thermal fragmentation during vacuum sublimation or induced breaking due to molecule–substrate interactions during/after landing onto surfaces may occur and prevent formation of desired nanostructures.^{4,5} Although advanced deposition strategies have successfully been employed to alleviate these problems, such as pulse-valve⁶ or electrospray⁷ injection of dissolved molecules as well as molecular soft-landing⁸ by mass-spectrometry methods, it is nevertheless of general interest to explore comparatively simple routes toward stabilization of large organic compounds on surfaces.

In this Communication, we show by means of scanning tunneling microscopy (STM) that the stability against fragmentation of a large organic compound sublimated onto a Au(111) surface under ultrahigh vacuum (UHV) conditions can be significantly enhanced by coordinating it to gold atoms prior to deposition. Vacuum-deposition of metal-containing organic compounds has been achieved in several instances previously,^{4–6,9} but this is to our knowledge the first case where the incorporation of coordinated metal atoms is shown explicitly to have a stabilizing effect. The compounds used in this study (calix[4]arene dimelamine derivatives, see Figure 1a and Figure 2a) have previously been investigated as building blocks in liquid-phase self-assembly of multiple hydrogen-bonded “rosette” complexes,¹⁰ and the work presented here forms part of a larger project to explore the transferability of these large supramolecular complexes to the vacuum-solid interface.

The experiments were performed in a UHV chamber equipped with a variable-temperature Aarhus STM.¹¹ The single-crystal Au(111) sample was prepared using standard procedures.¹² Synthesis and characterization of the compounds were performed as described previously.¹⁰ Both compounds were thoroughly degassed and thermally sublimated at 360 K onto a clean Au(111) sample held at room temperature. STM measurements were carried out in

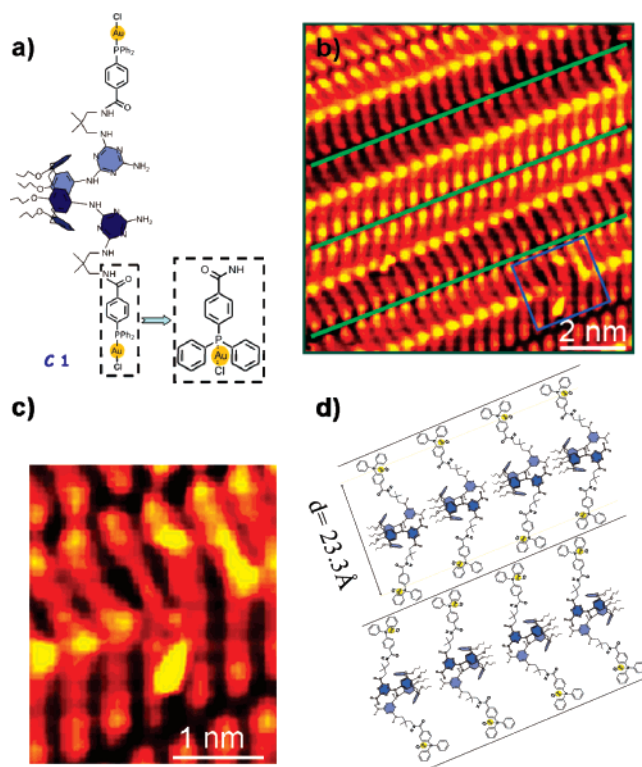


Figure 1. (a) Gold-functionalized compound (**C1**) consisting of a central head formed from a calix[4]arene moiety connected to two identical arms, each starting at a melamine unit and terminating in a triphenylphosphine group that coordinatively binds a Au(I) atom. (b) STM image showing the well-ordered lamella structure formed by **C1** (green lines indicate lamellae boundaries). The two molecular arms are imaged with slightly different apparent heights (by 0.3 Å), which is attributed to the 3D conformation of **C1** as indicated by light/dark blue colors in panel a. $I_t = 0.4$ nA, $V_t = 1250$ mV. (c) Zoom-in on the region indicated in panel b showing tip-induced fragmentation. (d) Proposed molecular model for the lamellae. The distance between gold atoms at the terminal of the molecule is 23.3 Å. The experimentally observed periodicity along the lamellae (4.8 ± 0.5 Å) is less than that of the adsorption model, suggesting that the calix[4]arene head unit adopts a more upright-standing orientation than shown in the model.

a temperature range of 100–160 K to thermally stabilize the formed structures.

Deposition of the gold-containing complex **C1** dominantly leads to regular domains as shown in Figure 1b, coexisting with a smaller fraction of disordered phase (see Supporting Information). The regular domains consist of v-shaped entities stacked to form densely packed lamellae. The individual entities are imaged as one central protrusion with two arms extending from it, each terminating in a

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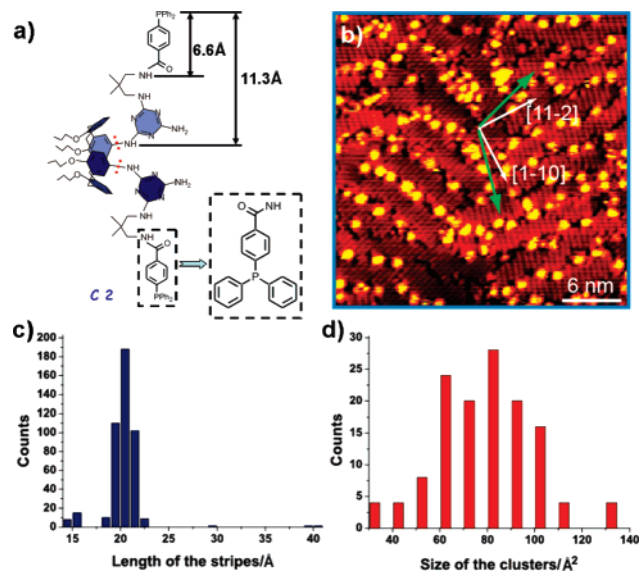


Figure 2. (a) Triphenylphosphine calix[4]arene derivative (**C2**) deviating from **C1** by the lack of coordinated gold atoms. Approximate molecular dimensions are indicated. (b) STM image of the surface morphology after deposition of **C2**. $I_t = 0.4$ nA, $V_t = 1250$ mV; (c) histogram over the length of the observed stripes; (d) histogram over the lateral size of the observed clusters.

region of enhanced contrast in the STM images. This STM signature fits well with the structure of intact **C1**, and a schematic adsorption model for the lamellae is displayed in Figure 1d. The distance between the bright features at the end of the two arms is 22 ± 1.5 Å, which, by comparison to the molecular model of Figure 1d, suggests that these features can be attributed to the coordinated gold atoms.

Considering that **C2** only deviates from **C1** by removal of the coordinated gold atoms, we anticipated to find a similar structure after deposition of this compound. Instead, however, we observed a considerably less-ordered surface morphology as displayed in Figure 2b. The dominating features are (i) bright clusters which appear to be pinned at the ridges of the Au(111) herringbone reconstruction and (ii) domains of regularly spaced stripes occupying both fcc and hcp regions of the Au(111) substrate and oriented along two main directions (indicated by green arrows in Figure 2b). The stripes have a narrow size distribution (Figure 2c) with a mean length of 21.5 ± 1.5 Å. The cluster sizes predominantly lie in the range from 60 to 100 Å² (Figure 2d). The ratio between the number of stripes and clusters is approximately 3:1 (445:132 as determined from Figure 2b). We interpret these features as the result of fragmentation of **C2**. Tentatively, we suggest that fragmentation occurs at the two equivalent amine bonds (marked with red dashed lines in Figure 2a) and that the two resulting arm fragments, each of ~ 11.3 Å extent, dimerize to form the observed stripe features of roughly double this length, for example, through hydrogen bonding of the melamine groups of **C2**.¹³ The observed clusters are accordingly ascribed to several nucleated calix[4]arene head-units.

The stability of the compound **C1** was probed directly by molecular-scale manipulation with the STM tip. By performing a line scan over an intact **C1** molecule at tunneling parameters that bring the tip close to the surface ($I_t = 1.5$ nA, $V_t = 200$ mV), the bright head can be pushed to the side while the two arms remain

relatively unperturbed on the surface (see Figure 1c). This indicates that also **C1** is particularly labile to fragmentation at the position where the head and arms are connected and supports the conclusion that the structure observed for **C2** is due to fragmentation at the amine bonds. Overall more than 20 distinct sample positions (each corresponding to ~ 500 deposited molecules) were examined without finding any evidence for intact **C2** molecules, while for **C1** $\sim 90\%$ of the deposited compounds were found in the ordered regions ascribed to intact molecules. We therefore conclude that the stability of the gold-coordinated compound **C1** is significantly enhanced compared to the compound **C2** without gold atoms.

The stabilization of **C1** may occur either during thermal sublimation or during/after adsorption to the surface as observed previously.⁵ We find it most likely that the stabilizing effect occurs on the surface since (i) the coordinated gold atoms are peripheral to the compound and thus have no obvious stabilizing effect and (ii) the sublimation temperature of 360 K is not particularly high compared to the anticipated stability against pyrolytic dissociation for these compounds. We speculate that the dissociation is induced by charge transfer between molecule and substrate which may be affected by the presence of the coordinated Au(I) atoms, leading to a larger stability of **C1**.

In conclusion, the described results suggest a new route toward self-assembly of molecular nanoscale structures from large organic building blocks and warrants further experimental or theoretical studies into the origin and generality of this unanticipated stabilizing effect.

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Supporting Information Available: STM image for the disordered region of **C1**; histograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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