Molecular Self-Assembly Driven by On-Surface Reduction: Anthracene and Tetracene on Au(111)

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Supporting Information

ABSTRACT: Epoxyacenes adsorbed on metal surfaces form acenes during thermally induced reduction in ultrahigh vacuum conditions. The incorporation of oxygen bridges into a hydrocarbon backbone leads to an enhanced stability of these molecular precursors under ambient condition; however, it has also a distinct influence on their adsorption and self-assembly on metal surfaces. Here, a low-temperature scanning tunneling microscopy (LT-STM) study of two different epoxyacenes on the Au(111) surface at submonolayer coverage is presented. Both molecules show self-assembly based on hydrogen bonding. While for the molecules with a single epoxy moiety nanostructures of three molecules are formed, extended molecular networks are achieved with two epoxy moieties and a slightly higher surface coverage. Upon annealing at 390 K, the molecules are reduced to the respective acene; however, both systems keep a similar assembled structure. The experimental STM images supported by theoretical calculations show that the self-assembly of the on-surface fabricated acenes is greatly influenced by the on-surface reaction and strongly differs from the adsorption pattern of directly deposited acenes, highlighting the importance of the cleaved oxygen in the self-assembly.

I. INTRODUCTION

On-surface chemistry provides indispensable tools for the formation of extended molecular structures which cannot be prepared by standard solution-based methods due to limited solubility and chemical stability. In particular, the atomically precise and controllable synthesis of nanographene structures has been made possible via on-surface reactions of specifically designed precursors. By reporting on the formation of tetracene, we have added on-surface reduction of epoxyacenes as a novel reaction to the toolbox which allows the generation of polycyclic aromatic hydrocarbons with linearly fused benzene rings. This class of molecules is known as acenes and features compelling properties for applications in molecular electronics and spintronics. However, large acenes are highly reactive under ambient conditions and therefore call for novel preparation methods. Our recent work on the synthesis of hexacene and unprecedented decacene on Au(111) has demonstrated that the surface-assisted deoxygenation of specifically designed epoxyacenes is a synthetic method to access acenes beyond the boundaries set by stability, while the conversion of α-diketone precursors was also shown to be a promising surface strategy.

High-symmetry acenes tend to form densely packed and well-structured films on coinage metal substrates; however, the incorporation of epoxy groups breaks the symmetry and favors directed interaction. In this article, we focus on the role of this moiety at the terminal rings and aim to describe the distinct influence on the molecular self-assembly for two different epoxyacenes. First, we study the epoxyanthracene An1O (see Figure 1a) with an epoxy group at one terminal ring. This allows the detailed understanding of the adsorption geometry and modeling of the observed nanostructures. Notably, the presence of two epoxy groups in either syn or anti-configuration (see Figure 1b) leads to a more complex system. Scanning tunneling microscopy (STM) based studies of the self-assembly and growth mode of molecules on metal surfaces are particularly suited to shed light on the influence of functional groups for intramolecular bonding and the molecule–substrate interactions.

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II. METHODS

STM experiments were performed using a custom-built instrument operating at a low temperature of \( T \approx 5 \, \text{K} \) and ultrahigh vacuum (\( p \approx 1 \times 10^{-10} \, \text{mbar} \)) conditions. All STM measurements were acquired in constant-current mode with the bias voltage applied to the sample. A Au(111) single crystal was used as substrate and prepared by repeated cycles of sputtering (Ne+) and annealing (730 K). After this cleaning procedure, the molecules were evaporated from a Knudsen cell at a crucible temperature of 320 and 410 K for An1O and Tn2O, respectively. In both cases, the molecules were deposited on the clean Au(111) surface kept at room temperature. Temperature-induced experiments were carried out by annealing the sample at the respective temperature for 5 min.

Density functional theory (DFT) was used to study adsorption and self-assembly by obtaining minimum energy configurations of individual molecules and trimers. We applied the Perdew–Burke–Ernzerhof exchange-correlation functionals \( \text{PBE}^{20} \) and valence double-\( \zeta \) basis sets with Goedecker–Teter–Hutter pseudopotentials \( \text{GTH}^{21} \) in the hybrid Gaussian and plane wave approach embedded in the Quickstep code of CP2K. \( \text{DFT-D3} \) method of Grimme \( ^{23} \) accounted for dispersion correction, which adds a sum of pairwise interatomic C6R-6 correction terms to the Kohn–Sham energy. Furthermore, STM images were simulated based on the Tersoff–Hamann approach. The Au(111) surface was modeled by a periodic slab of six layers.

III. RESULTS AND DISCUSSION

An1O Molecules. The An1O molecules (Figure 1a) were deposited with a surface coverage of \( \approx 0.2 \, \text{ML} \) onto the Au(111) surface kept at room temperature. STM images show that molecules on terraces are isolated or form triangular-shaped nanoassemblies (with two different chiral enantiomeric motifs \( \delta \) and \( \lambda \)) as presented in Figure 2a. The former can be recognized by a teardrop-shaped topography which corresponds to a nonplanar adsorption geometry. Density functional theory (DFT) calculations prove that single molecules preferably adsorb with the oxygens facing the surface, and two C–H groups are upright, giving rise to a distinctly enhanced apparent height at one side of the molecule as visible in the close-up image of Figure 2b. The triangular nanostructures are formed by self-assembly of three An1O molecules with nonplanar ends coming close to each other and the 3-fold symmetry of the structure being favored by the underlying Au(111) substrate. DFT calculations have been used to prove that the relaxed structure of the An1O trimmer corresponds to a local minimum in the potential energy surface. The calculated geometry, as presented in Figure 2c, suggests that the trimers are stabilized by three hydrogen bonds formed by intermolecular interactions between electronegative oxygen and hydrogen at the sp\(^3\)-hybridized bridgehead carbon atom as shown in Figure 2d. The structure is confirmed by correctly reproducing intermolecular angles and coinciding simulated and experimental STM images.

After studying the surface subsequent to the room-temperature deposition, we performed thermally induced experiments to investigate changes in the observed structures upon induced deoxygenation. Figure 3 shows the different adsorbed molecular species. Imaging the substrate after heating at 340 K allows the direct comparison between isolated An1O and anthracene molecules as the reduction was not yet achieved at a very high rate. An1O molecules were identified by their characteristic teardrop shape, while on-surface produced anthracenes appeared flat with a clearly reduced apparent height (see color scale in Figure 3a). Similar to the An1O molecules, anthracene molecules were found to be either isolated or in a trimer assembly. Figure 3a shows all prevailing motifs for this preparation in one close-up STM image. However, it is not evident how the structure is stabilized. Since the on-surface interaction between hydrocarbon molecules without any functional groups should not favor directed intermolecular forces, it is generally based on nondirected van der Waals forces which cannot explain the equiangled shape. DFT revealed a metastable trimer configuration of three anthracene molecules.
which is highly unfavorable compared to parallel alignment and unstable in low-temperature molecular dynamics. By considering possible intermolecular interactions which can be pertinent at metal surfaces and bearing in mind the induced surface reaction, it seems likely that this kind of assembly of three anthracene molecules is supported by the byproduct of the on-surface reduction, i.e., cleaved oxygen atoms. Starting from an An1O trimer, the molecules adsorb in such a way that all three oxygen atoms face the surface and are positioned at the center of the trimer. Upon thermally induced deoxygenation, the three cleaved oxygen atoms adsorb on a surface hollow site according to DFT calculation and remain presumably close to the initial adsorption position. Employed simulations clearly show that three oxygen adsorbates stabilize the trimer by providing hydrogen bond anchors on the surface, as depicted in Figure 3c. This effect has been quantified by the change in total potential energy while uniformly approaching three anthracene molecules toward a common center with and without oxygen adatoms (see Figure 3d). Whereas the energy steadily increases for the case without oxygens, a minimum appears at a radius of around $r_{MC} \sim 3 \text{ Å}$ after adding oxygens at three equidistant hollow sites. The obtained radius coincides with the minimum energy periphery of the three oxygens (see Supporting Information for more details). After annealing the An1O-covered sample at 390 K, no precursors were observed anymore but isolated anthracene molecules and An trimers only.

**Tn2O Molecules.** Tn2O molecules were deposited on Au(111) with a slightly higher coverage of $\sim$0.6 ML; however, the principal experimental observations for the as-prepared surface were in line. First, single Tn2O molecules adsorb with a nonplanar geometry and were accordingly imaged as dumbbell-shaped protrusions (see Figure 4). Note that Tn2O is a mixture of syn and anti diastereomers based on the relative configuration of the oxygen atoms on the 1,4-epoxy moieties, and therefore it can appear in a symmetric or antisymmetric configuration on the surface. In contrast to An1O, where isolated nanostructures are formed, the Tn2O molecules build extended networks. This is attributed to the second oxygen atom, favoring directed interaction on both ends of the molecule. Therefore, different bonding motifs are observed. The dimeric features an off-center arrangement, and the trimer motif is equivalent to the triangular nanostructure observed for An1O. Further, we find hexagonal motifs, which are composed of six Tn2O molecules forming trimeric or dimeric patterns, with an inner hexagon of six Tn2O molecules. Figure 4b shows two mirror symmetric examples where individual molecules are marked with white bars. Large-scale scans (Figure 4c) show that one can occasionally find honeycomb domains formed by several adjacent hexagons to establish an open-porous 2D network. This network can be interpreted as a Kagome lattice as will be discussed in more detail later. Hence, a simple, selective, and directed hydrogen bond interaction gives rise to a complex and intriguing self-assembled network which is not limited by the underlying surface reconstruction. The size of...
well-ordered domains of this network is probably limited by the presence of two different diastereomers inducing disorder.

In the field of surface science, there are many examples of supramolecular networks formed by intermolecular bonds between oxygen and hydrogen of neighboring molecules on coinage metal surfaces. Since the diffusion barrier is low on such surfaces, hydrogen bonds strongly dominate the molecular assembly despite the fact that the associated force is considered weak. While there are examples of hydrogen-bonded assemblies which can be moved collectively by STM tip-induced voltage pulses, lateral manipulation with a tunneling resistance in the order of $10^6 \Omega$ could be used to separate the self-assemblies of An1O and Tn2O molecules proving their noncovalent bonded character.

Thermally induced experiments for Tn2O on Au(111) showed that an annealing temperature similar to the experimental conditions obtained by different diastereomers inducing disorder. Following the on-surface produced anthracene occasionally observed for the on-surface produced anthracene, this high surface mobility at cryogenic temperatures was during scanning and hence appear longer or just as fragments. The reaction became apparent by a distinct topography of single molecules. Figure 5a shows that tetracenes appeared as elongated featureless protrusions if imaged at a bias close to the Fermi level. Furthermore, the STM measurements indicated that isolated molecules had the tendency to easily be manipulated by the tip during scanning. One can recognize several imaging artifacts in Figure 5a corresponding to tetracene molecules that suddenly jumped to a different surface position during scanning and hence appear longer or just as fragments.

This high surface mobility at cryogenic temperatures was occasionally observed for the on-surface produced anthracene as well as reported in the literature for tetracene on Ag(111) at 8 K. By contrast, molecules in supramolecular assemblies were found to be less prone to STM tip-induced movement and could always be imaged in a stable manner. Notably, large-scale scans (see Figure S1 in the Supporting Information) showed parts of the surface with well-ordered domains exceeding 100 nm in lateral dimensions. From the detailed image in Figure 5b it is apparent that single molecules within this regular lattice show three different adsorption orientations with the same 3-fold symmetry as the underlying hexagonal gold lattice. If the centers of single molecules are considered, the spatial distribution of molecules can be described by a Kagome lattice, as presented in Figure 6a, where two hexagons (marked in blue) and two triangles join at each vertex. In addition, the fast-Fourier transform of the regular pattern is presented in Figure 6b and shows an average periodicity for the hexagonal tiling of 2.1 nm. This kind of self-assembly of linear molecules has been reported on-surface for simple oligophenylenes functionalized with two nitrile groups, which are however clearly ditopic, meaning that they feature two distinct binding sites at either side. By contrast, no experimental observation of such an assembly for hydrocarbons without any functional group has been presented to our knowledge so far.

Performing the control experiment and depositing tetracene directly onto a clean gold surface led to the observation that no hexagonal tiling of 2.1 nm was present. This kind of self-assembly of linear molecules has been reported on-surface for simple oligophenylenes functionalized with two nitrile groups, which are however clearly ditopic, meaning that they feature two distinct binding sites at either side. By contrast, no experimental observation of such an assembly for hydrocarbons without any functional group has been presented to our knowledge so far.

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minimum annealing temperature to fully reduce the An1O and Tn2O molecules is just 390 K, while previous studies of chemisorbed atomic oxygen on Au(111) have reported that a larger sample temperature of about 500 to 550 K was needed to
detect its desorption as $O_2$.

We note that this regular lattice of tetracenes is connected to
the self-assembly of precursor molecules and persists even after
the thermally induced reduction. Accordingly, the open-porous
networks occasionally observed on the Tn2O-covered surface
(Figure 4c) and first introduced as hexagonal assembly can also
be viewed as Kagome lattice by marking the position of single
molecules instead of trimer centers. The result is shown in
Figure 6c and 6d and illustrates that the ordered self-assembly
of the Tn2O molecules as well as of their reduced form can be
described in an equivalent way. Thus, the ditopic character of
the precursors with two preferred intermolecular hydrogen
binding sites lays the basis for the regular pattern for the
tetracenes after on-surface reduction.

CONCLUSION

In summary, we have studied nanostructures and networks
formed by epoxyacenes on Au(111) after room-temperature
deposition as well as annealing experiments. In the case of
anthracene derivative An1O with a single terminal epoxy group,
trimmer nanostructures are favorable assemblies due to the
presence of intermolecular hydrogen bonds, as confirmed by
DFT calculations. Notably, these trimer structures persist even
after the oxygen is cleaved by means of thermally induced on-
surface reduction due to their stabilization by oxygen
adsorbates. The experimental observations for the tetracene
dervatives Tn2O with two terminal epoxy groups show a clear
equivalence. First, the stabilization of trimeric patterns is
rediscovered and can be identified as a principal building block
for well-ordered hexagonal domains. Second, STM images after
annealing at 390 K showed the reduced form (tetracene) as the
only molecules on the surface. Surprisingly, we occasionally
observed also a Kagome lattice formed by tetracenes which one
would not expect for symmetric hydrocarbons without
functional groups. Bearing in mind the induced on-surface
reaction, it seems likely that this ordered structure is carried
over from the self-organization of the epoxyacenes and is
further stabilized by the cleaved atomic oxygen to form a
bicomponent architecture.55 Our results are an important step
to address the structure of the organic–metal interface correctly
and provide insights on the reaction mechanism of the on-
surface reduction of organic molecules.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.jpcc.7b06131.
Details on the synthesis of epoxyacene An1O and
di epoxyacenes Tn2O, additional STM data, as well as
supplements on the DFT calculations (PDF)

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