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Imaging the Electronic Structure of On-Surface Generated Hexacene

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Justus Krüger,^a Frank Eisenhut,^a José M. Alonso,^b Thomas Lehmann,^a Enrique Guitián,^b Dolores Pérez,^b Dmitry Skidin,^a Florian Gamaleja,^a Dmitry A. Ryndyk,^a Christian Joachim,^c Diego Peña,^{*,b} Francesca Moresco^{*,a} and Gianauelio Cuniberti^a

Surface-assisted reduction of specially designed air-stable precursors allows us to study single hexacene molecules on Au(111) by scanning tunneling microscopy and spectroscopy, mapping with intramolecular resolution their extended electronic eigenstates.

Acenes are polycyclic aromatic hydrocarbons formed by the linear fusion of several benzene rings. These molecules are among the most promising compounds in organic electronics,¹ since their extended aromatic backbone is key for the development of molecule-based devices. For example, pentacene with a reduced HOMO-LUMO gap and an elevated charge carrier mobility is widely considered, in the crystalline form, as an archetypal organic semiconductor. Additionally, pentacene can be considered as molecular model system for high-resolution scanning probe microscopy investigations at the single molecule level, as recently reported by imaging the chemical structure and the molecular orbital resonances, as well as by manipulation experiments.²

Aside from the fundamental interest of accessibility, large acenes are predicted to present superior electronic properties with a further reduction of the HOMO-LUMO gap and a radical character of the ground state increasing with the size.³ In this regard, oligoacenes can be seen as the narrowest graphene nanoribbons with zigzag edge topology and are promising candidates for molecular electronics and spintronics.⁴ However, their low solubility and high reactivity has hampered fundamental studies and application of larger acenes so far.

The isolation and characterization of hexacene (Hn,

Figure 1a) has been a long-standing chemical challenge since 1939.⁵ While Chow and coworkers reported the properties of hexacene crystals obtained from a monoketone precursor in 2012,⁶ no vacuum-processable strategy towards hexacene on surfaces has to our knowledge been presented so far. Spurred by the recent approaches of the synthesis and stabilization of atomically precise nanographenes by surface-assisted reactions,^{4a, 7} we investigate a novel way to access hexacene by deoxygenation.

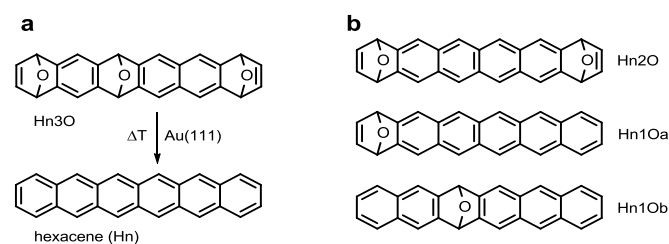


Figure 1. On-surface chemistry. (a) Generation of hexacene from triepoxyhexacenes (Hn3O). (b) Selected epoxy intermediates observed on Au(111).

While we have recently described the reduction of diepoxytetracenes to form tetracene on Cu(111) as verified by atomic force microscopy with atomic resolution,⁸ the true challenge remained to prove the applicability of this method for the preparation of unstable large acenes. Here, we report on the solution-based synthesis of air-stable precursors Hn3O (Figure 1a) and our scanning tunneling microscopy (STM) based investigations on their reduction. We describe the thermally induced deoxygenation of Hn3O on Au(111) in ultrahigh vacuum (UHV) conditions via the detailed characterization of selected intermediates as indicated in Figure 1b. In addition, sub-molecular STM imaging of the final product of the reaction shows the stabilization of hexacene and local spectroscopy measurements reveal its detailed electronic structure.

^aInstitute for Materials Science, Max Bergmann Center of Biomaterials, and Center for Advancing Electronics Dresden, TU Dresden, 01069 Dresden, Germany.
E-mail: francesca.moresco@tu-dresden.de

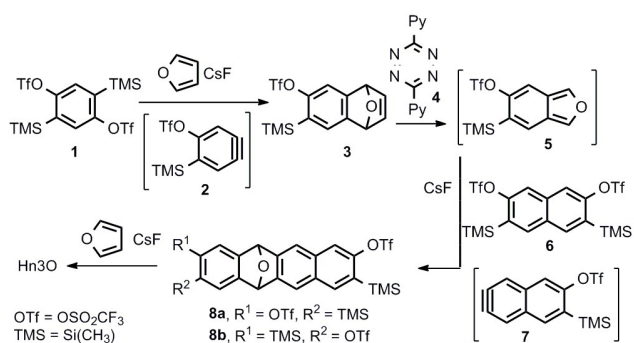
^bCentro de Investigación en Química Biológica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain.
E-mail: diego.pena@usc.es

^cGNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France.

† Footnotes relating to the title and/or authors should appear here.

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The synthetic route to obtain hexacene precursors Hn3O by solution chemistry (Scheme 1) was inspired by the procedure developed by Hamura and coworkers to prepare substituted pentacene derivatives,⁹ and it was based on a sequence of aryne cycloadditions.¹⁰ The reaction of commercially available bistriflate **1** with one equivalent of CsF was supposed to generate highly reactive aryne **2** in the reaction mixture, which was trapped by means of a first Diels-Alder cycloaddition with furan to afford epoxynaphthalene **3**. This compound is an extremely useful building block which presents both a masked diene and a masked dienophile in the same molecular structure. In fact, the heating of compound **3** with tetrazine **4** promoted the formal acetylene extrusion to generate isobenzofuran **5**, which reacted in situ with aryne **7**, generated by reaction of bistriflate **6** with CsF, to afford the mixture of regioisomers **8a-b**. Finally, this mixture was treated with an excess of CsF to sequentially generate the corresponding arynes which reacted with furan to form Hn3O as a mixture of the four possible diastereomers in 40% yield. In global, we obtained the hexacene precursors Hn3O by four consecutive Diels-Alder aryne cycloadditions, taking advantage of selective aryne generation from formal benzodiyne and naphthodiyne precursors **1** and **6**, respectively. Further details on the synthesis and characterization of the precursors are presented in the Supporting Information.



Scheme 1. Preparation of triepoxyhexacenes (Hn3O) by solution chemistry.

On-surface experiments were performed by STM operating at low temperature ($T = 5$ K). We deposited Hn3O molecules as a mixture of the four possible diastereomers on a clean Au(111) surface kept at room temperature and then directly annealed the sample at 120 °C to induce surface-assisted deoxygenation.¹¹ Figure 2a presents a constant-current STM image of the resulting preparation with sub-monolayer coverage recorded at a bias voltage close to the Fermi level. We observed single molecules as elongated protrusions and recognized various different species with respect to distinct peaks in their topography. For instance, the isolated molecule at the top right of Figure 2a features a marked dumbbell-shaped topography. Ab initio density functional theory (DFT) calculations were performed to model the adsorption of all relevant molecules on Au(111) and proved that this particular

topography is connected to the adsorption geometry of the *syn*-diastereomer of Hn2O with both remaining oxygen atoms facing the surface as illustrated in Figure 2b. A detailed comparison with isolated *anti*-Hn2O as well as Hn1Oa is given in the Supporting Information, Figure S2 and S3, respectively. Molecules without a pronounced peak in their topography are of particular interest, since this species indicates the successful formation of hexacene and can be clearly seen for the isolated molecule at the top left of Figure 2a. Thus, the final product of the deoxygenation and various intermediates (see self-assembled cluster of molecules in Figure 2a) were present on the surface after annealing at this particular temperature.

To further explore the on-surface reaction mechanism of the hexacene generation, we investigated the sample after annealing at a higher temperature of 150 °C. The complexity of different observed molecular species was drastically reduced, since large-scale scans as well as high-resolution images (Supporting Information, Figure S4) showed hexacene and intermediate Hn1Ob as the only molecules on the surface. This finding suggests that the activation barrier to cleave the middle oxygen is crucial and must be considerably higher than the barrier involved in the deoxygenation of a terminal ring. Notably, the on-surface generation of hexacene from intermediates Hn2O via Hn1Oa is obtained in a very efficient manner.

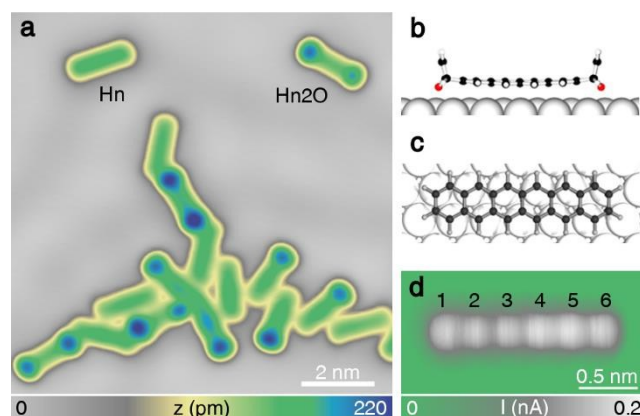


Figure 2. Surface-assisted deoxygenation on Au(111). (a) STM image of the annealed sample showed hexacene molecules as well as partially deoxygenated intermediates. STM scan ($V = +0.1$ V, $I = 45$ pA) features isolated hexacene (Hn) adsorbed at a kink site of the surface reconstruction, while a dumbbell-shaped protrusion close-by indicates presence of the *syn*-diastereomer of diepoxyhexacene (Hn2O). In addition, self-assembled molecules with different topographies are present (b) Ball-and-stick model of the fully relaxed *syn*-Hn2O molecule obtained by DFT. (c) Minimum energy adsorption configuration of physisorbed hexacene with its two middle benzene rings centered above fcc sites of the Au(111) surface. (d) Hexacene imaged with a CO-tip at constant height and $V = -5$ mV.

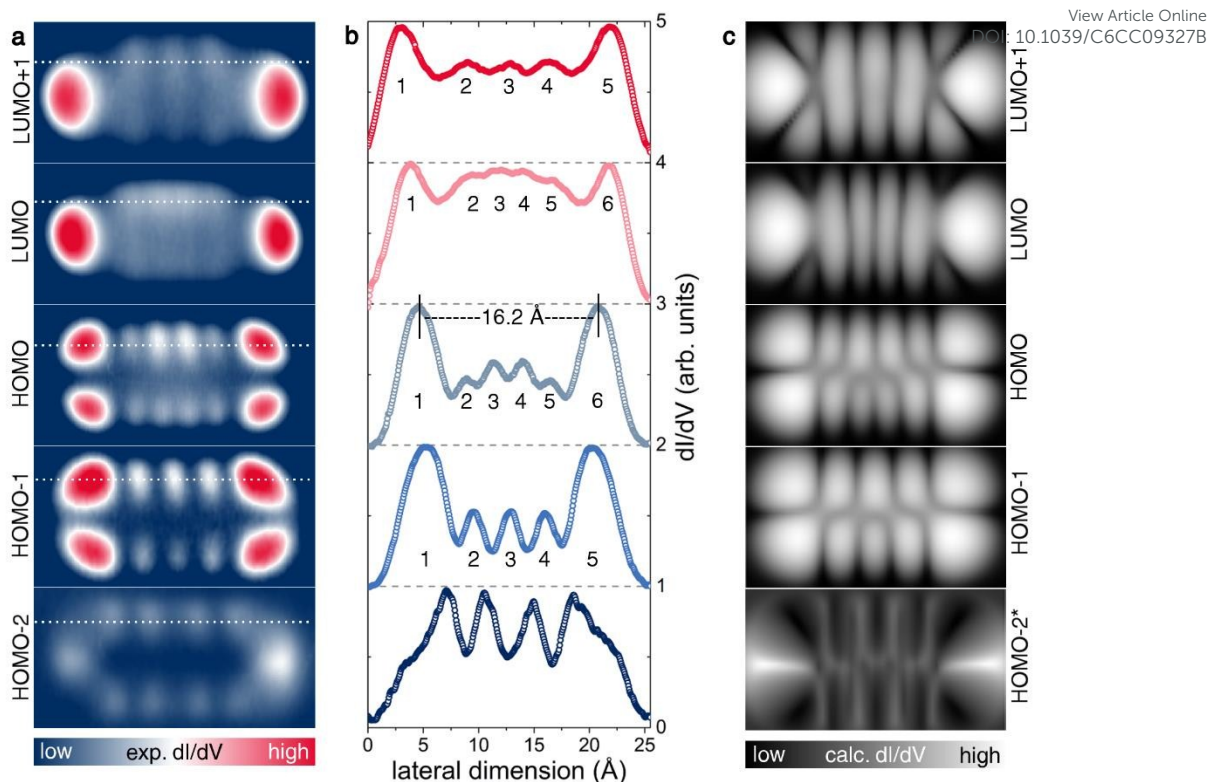


Figure 3. Imaging of molecular orbital resonances of hexacene. (a) Constant-current maps of the differential conductance at respective resonant bias values. Image sizes are 1.3 nm x 2.6 nm. Current values are, from the top, 0.3 nA, 0.5 nA, 0.2 nA, 0.2 nA, and 0.4 nA. (b) Extracted line scans along the dI/dV maps as indicated by white dashed lines in the images in a. The curves are normalized and shifted for clarity. (c) Calculated differential conductance maps at the corresponding mono-electronic energy resonances using ESQC. HOMO-2* was obtained with contributions from HOMO-2 to LUMO+1.

Surface-assisted cleavage of all three oxygen atoms from a hexacene precursor is accompanied by a full planarization of the molecule. Hence, the aromatic system is extended to six linearly fused benzene rings. The adopted planar geometry is shown as a DFT-based model in Figure 2c and is beneficial for detailed investigations by STM. After functionalizing the tip with a single CO molecule, the resolution in STM images of molecules can be enhanced as has been demonstrated by other groups before.^{2a, 2e, 12} We used this technique to image a single hexacene molecule at constant height with sub-molecular resolution. The recorded tunneling current data in Figure 2d shows that six linearly fused benzene rings can be clearly resolved, thus confirming the formation of hexacene.

We also performed scanning tunneling spectroscopy (STS) on single hexacene molecules to investigate the electronic structure in more detail. Differential conductance spectra with a metallic tip presented strong conductance peaks at +1.20 V and +2.55 V (Supporting Information, Figure S5). For convenience, we refer to these electronic molecule resonances as the lowest (LUMO) and second lowest unoccupied molecular orbital (LUMO+1) of the hexacene molecule, respectively. Probing the occupied states showed well-defined resonances at -0.65 V and -1.65 V and a weaker peak at around -2.25 V, which we assign for simplicity to the energy values of the highest (HOMO), second highest (HOMO-1) and third highest (HOMO-2) occupied molecular orbitals, respectively. In contrast, spectroscopy measurements of single pentacene on Au(111)

showed the LUMO level at 1.3 V and HOMO at -0.9 V.^{2c} Therefore, we come to the conclusion that the HOMO-LUMO gap probed with STS on Au(111) decreases from 2.2 eV to 1.85 eV. These values are in agreement with the respective optical gaps determined in argon matrix.^{5f}

Mapping the spatial distribution of the dI/dV signal allowed us to image in detail the electronic structure of hexacene, confirming that the observed resonances are coming from tunneling channels built up from the molecular states of hexacene (Figure 3). The HOMO signature in particular illustrates conclusively the aromatic backbone of six linearly fused benzene rings as it shows twelve lobes of the single electron wave function separated by a nodal plane along the molecular long axis. In our experimental image, four pronounced lobes are spaced over the whole molecule along the molecular long axis. Additionally, eight faint inner lobes can be identified. This symmetry resembles the electronic structure of the free molecule, which is in line with previous experiments on pentacene weakly coupled to ultrathin NaCl films^{2b} or physisorbed on Au(111).^{2c}

Our spectroscopic measurements show that the first four observed electronic resonances of hexacene (from HOMO-1 to LUMO+1) are well separated in energy and appear as non-degenerated states based on the comparison with calculated differential conductance maps. We adopted the mono-electronic elastic scattering quantum chemistry (ESQC) approach¹³ to simulate constant-current dI/dV maps for

hexacene physisorbed on Au(111) at the corresponding electronic resonance energies. Panels a, b and c of Figure 3 show the striking agreement between experiment and theory as the structure, symmetry and corrugation of nodes and lobes match very well. The only major difference is the two second outermost lobes of the LUMO+1 are not visible in the experiment, most likely due to the limited resolution of the tip. Furthermore, it is worth mentioning that the measured dI/dV map at the resonance named HOMO-2 largely deviates from what is expected for the STM image of a pure HOMO-2 calculated in a mono-electronic approximation (Supporting Information, Figure S6). We conclude that an intermixing of molecular orbitals is building up this HOMO-2 electronic resonance, similar to the case of pentacene.^{2c}

In summary, we report the surface-assisted preparation of hexacene and its first detailed characterization by STM and STS. Notably, our results prove that the recently introduced acene formation by on-surface reduction of epoxyacenes is not limited to Cu(111)⁸ but also works for larger acenes on a low reactivity Au(111) substrate. This is beneficial for the subsequent investigations of their intrinsic properties since the coupling between fabricated nanographenes and gold can be considered weak.¹⁴ In particular, the electronic resonances of single π -conjugated molecules, even if broadened and energetically shifted due to interaction with the continuous states of the metal,¹⁵ still correspond to the gas phase ionization and affinity levels. Therefore, the frontier orbital resonances as well as HOMO 1/LUMO+1 levels of hexacene could be visualized in the experiment and showed a conclusive agreement with calculated dI/dV maps.

By designing scaled precursors, this synthetic method might also be applicable for the generation of oligoacenes longer than hexacene. Bearing in mind the predicted increasingly stronger radical ground state for longer oligoacenes,³ this method could provide access to their anticipated unique ground state and pave the way for the unraveling of their electronic structure.

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