Decacene: On-Surface Generation

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In memory of Erich Clar

Abstract: *Acenes are intriguing molecules with unique electronic properties. The difficulties in their preparation owing to low stability under ambient conditions are apparent because successful syntheses of long unsubstituted acenes are still scarce, in spite of the great attention they have attracted. Only unsubstituted acenes up to heptacene have been isolated in bulk, with nonacene being the largest acene detected to date. Herein we use on-surface assisted reduction of tetraepoxy decacene precursors on Au(111) as the key step to generate unprecedented decacene which is visualized and its electronic resonances studied by scanning tunneling microscopy (STM) and spectroscopy (STS).*

Acenes are linear *cata*-condensed polycyclic aromatic hydrocarbons (PAHs) which have fascinated chemists for decades.[1] Small acenes, such as naphthalene or anthracene, are isolated by distillation from coal tar or heavy petroleum fractions. However, larger acenes are not found in natural sources and therefore they are obtained from multistep syntheses, which become more challenging as the length of the molecule increases as a result of their high chemical reactivity under ambient conditions. The instability of large acenes can be predicted bearing in mind that they are PAHs with a single Clar π-electron sextet, regardless of the length of the molecule.[2] This unique π-electron distribution is also responsible of their outstanding semiconducting properties which have promoted the extensive use of acenes in organic electronics.[1e] Recently, acenes have also attracted a lot of attention as they constitute the narrowest zigzag graphene nanoribbons with potential application in spintronics.[3]

A frequently used alternative to circumvent the difficulties associated with the low solubility and high reactivity of large acenes is based on the introduction of substituents in the aromatic core.[1b–i] Following this approach, several nonacene derivatives have been obtained so far.[4] In contrast, the generation of unsubstituted large acenes remains a "formidable challenge".[1k] Notably, crystals of hexacene were obtained from a monoketone precursor and used to fabricate field-effect transistors.[5] The next larger benzologue, heptacene (**1**), was generated photochemically in polymer[6a,b] or noble gas matrices[6c] from bridged α-diketones and characterized by its optical absorption spectrum. Very recently, heptacene (**1**) was obtained in the solid state by thermal cleavage of diheptacenes.[6d] Remarkably, octacene (**2**) and nonacene (**3**) were also generated from bridged α-diketones in cryogenic noble gas matrices.[7] Here we report the on-surface generation of decacene (**4**), the largest unsubstituted acene which has been obtained to date.

In recent years, on-surface chemistry has emerged as a powerful alternative to access highly reactive molecules from soluble and stable precursors.[8] For example, reaction intermediates such as arynes[9a] or elusive PAHs such as triangulene[9b] were generated on surface at cryogenic temperatures under ultra-high vacuum (UHV) conditions, and characterized with submolecular resolution by combining scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with functionalized tips. This approach was used to obtain pentacene on Ni(111) from a thienoacene precursor.[10] Recently, we have employed on-surface chemistry for the preparation of tetracene on Cu(111) from diepoxy precursors[11a] and hexacene on Au(111) by deoxygenation of triepoxyhexacenes.[11b] As a result, it was possible to study the step-wise formation of single tetracene and the electronic structure of hexacene molecules by scanning probe methods.[12]

Based on these precedents, we decided to attempt the generation and characterization of unexplored decacene (**4**) on Au(111). Tetraepoxy derivatives **5** (Figure 1) were selected as stable decacene precursors with five Clar π-electron sextets, and synthesized following a three-steps iterative sequence of aryne cycloadditions (Scheme 1).[13] Starting from commercially available formal naphthodiyne precursor **6**, the treatment with 1 equivalent of CsF presumably led to the formation of mono-aryne **7** which was trapped by means of a first Diels–Alder cycloaddition with highly reactive substituted isobenzofuran **8** to isolate a mixture of regioisomers **9a,b** in 42% yield.[11b] Further reaction of this mixture with another equivalent of CsF generated aryne **10**, which, in the

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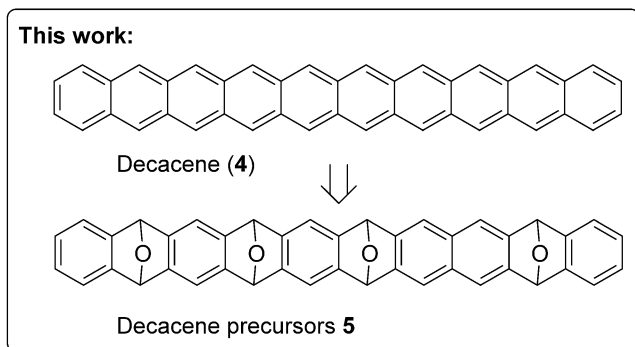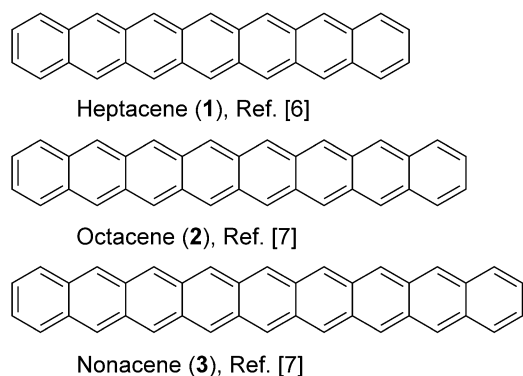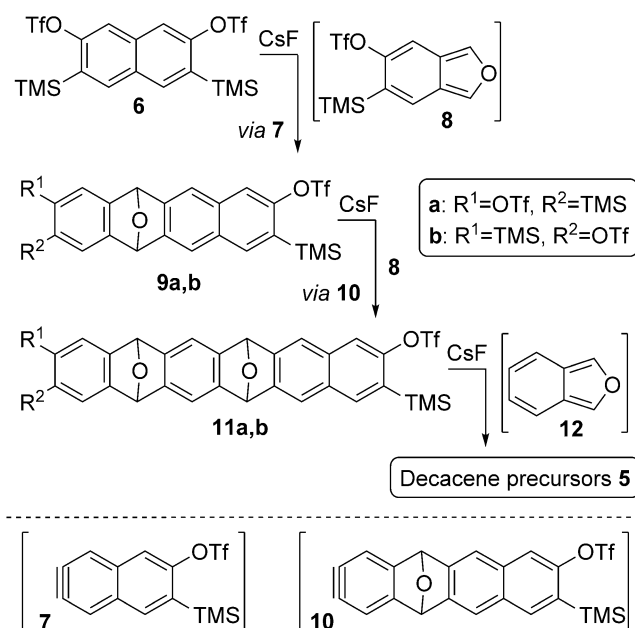https://doi.org/10.1002/anie.201706156.

Heptacene (1), Ref. [6]

Octacene (2), Ref. [7]

Nonacene (3), Ref. [7]

This work:

Decacene (4)

Decacene precursors 5

Figure 1. Largest acenes generated to date and the goal of the present work.

Scheme 1. Iterative synthetic sequence to obtain decacene precursors **5**.

presence of isobenzofuran **8**, afforded regioisomers **11a–b** in 34% yield by means of a second [4+2] cycloaddition.[14] Finally, the mixture **11a,b** was treated with an excess of CsF and in situ formed isobenzofuran **12** to obtain decacene precursors **5** in 33% yield by two consecutive aryne Diels–Alder cycloadditions.[15]

For on-surface investigations, the decacene precursors **5** were sublimated in ultrahigh vacuum conditions onto a clean Au(111) sample kept at room temperature. STM and STS measurements at $T = 5$ K were employed to characterize the isolated molecules on the surface. We assigned the majority of the observed molecules to partially deoxygenated decacene precursors, mostly with two epoxy groups still attached.[13] Presumably, the provided sublimation temperature is large enough to reduce the precursors to some degree when they adsorb on the metal surface. Further deoxygenation steps were induced either by annealing the surface at 220°C for 5 minutes or by scanning single intermediates at constant-current increasing the applied sample voltage V beyond around $+1.6$ V and up to $+2.6$ V.[13] In both cases it was possible to generate decacene (**4**) which was stabilized in this environment for further studies. Constant-current STM images (Figure 2a,b) recorded after tip-assisted synthesis revealed not only the planar topography but also tended to carry submolecular corrugations even if the applied bias was small. These observed modulations indicate that frontier electronic resonances are within a narrow bias window and strongly contribute to the respective image formation[16] of the adsorbed decacene.

Differential conductance measurements allowed us to directly map the electronic density distribution of the two molecular resonances close to the Fermi level for decacene (**4**). For convenience we refer to those resonances as the
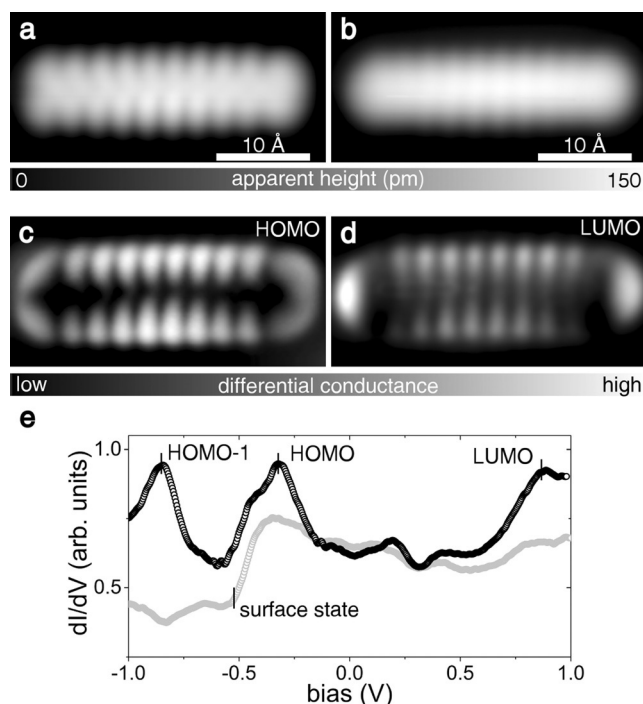

Figure 2. a),b) Constant-current STM images (tunnel current $I = 60$ pA) of decacene (**4**) obtained after tip-assisted synthesis. Measurements were acquired at a sample voltage of $V = -0.4$ V (a), and 0.8 V (b), respectively. c),d) Differential conductance maps acquired simultaneously and close to the resonant sample bias values for HOMO (c), and LUMO (d). e) The dI/dV spectrum (black curve) of a decacene molecule on Au(111) measured with a metal-terminated tip. The gray curve corresponds to a spectrum of the bare metal.

highest occupied molecular orbital (HOMO) resonance (Figure 2c) with a clear central nodal plane, and to the lowest occupied molecular orbital (LUMO) resonance (Figure 2d). Both maps illustrate the extended electronic eigenstates of such a large conjugated molecular system. Similar to what has been observed for shorter acenes before,[11b,16] the constant-current dI/dV images appear laterally enlarged compared to the topography acquired at the same conditions. We confirmed the resonant bias values by performing tunneling spectroscopy of adsorbed decacene in the range from -1 V to $+1$ V. Figure 2e indicates that differential conductance peaks can be found with a metal-terminated tip at -0.32 V and $+0.85$ V for HOMO and LUMO, respectively. This corresponds to an energy gap between the frontier electronic resonances of 1.17 eV on Au(111). As expected, by comparing to the STS spectra of hexacene,[11b] an energy gap reduction of 0.68 eV is observed for decacene with respect to hexacene.

After annealing the adsorbed decacene precursors **5** at 220°C for 5 minutes, we could as well find evidences of isolated decacene molecules (**4**) on the surface by using STM measurements at a resonant bias. A detailed inspection was carried out using a functionalized tip with high *p*-wave character.[17] Constant-height measurements at very small bias of $V = 20$ mV were employed to obtain an image (Figure 3) of a single decacene molecule as well as its orientation along one densely packed direction of the underlying gold substrate. In contrast to Figure 2, the main contribution for the STM image formation is not an orbital resonance but the atomic structure of decacene. Thus, ten linearly fused benzene rings with the extended zigzag edge can be clearly visualized.

In summary, elusive decacene has been generated for the first time, and characterized on gold by high-resolution STM.
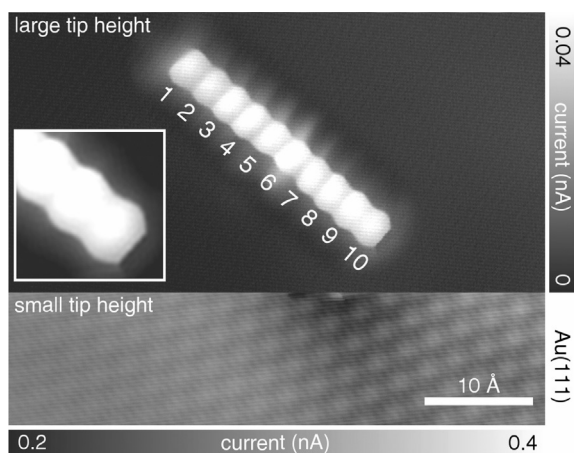
The decacene formation was achieved by on-surface reduction of stable tetraepoxy derivatives which were obtained by solution chemistry following an iterative sequence of four aryne [4+2] cycloadditions within three synthetic steps. This work demonstrates that the collaboration between synthetic chemists and surface scientists can lead to the achievement of long-standing chemical challenges.

Conflict of interest

The authors declare no conflict of interest.

Figure 3. Constant-height STM measurement of decacene (**4**) on Au-(111) using a CO-functionalized tip (sample voltage $V = 20$ mV). Two different tip height domains were employed to resolve the Au(111) lattice as well as the adsorbed molecule with atomic resolution. Six-membered rings can be identified as shown by the inset. The tip-sample gap was increased by 2.5 Å for the upper part of the image to avoid a tip-induced lateral manipulation of the molecule. Since the center of the molecule was bound to a herringbone kink of the Au(111) surface reconstruction, the sixth ring appears slightly brighter compared to the other rings.

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[14] Adducts resulting from the generation of the aryne in the naphthalene moiety of **9a,b** were detected in very small amount.

[15] Compounds **5** were isolated after column chromatography in two fractions, each one as a mixture of two diastereomers out of eight possible ones.

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