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On-Surface Hydrogenation of Buckybowls: From Curved Aromatic Molecules to Planar Non-Kekulé Aromatic Hydrocarbons

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ABSTRACT: Functionalization of surfaces with derivatives of Buckminsterfullerene fragment molecules seems a promising approach towards bottom up fabrication of carbon nanotube modified electrode surfaces. The modification of a Cu(100) surface with molecules of the bucky bowl pentaindenocorannulene has been studied by means of scanning tunneling microscopy, carbon monoxide-modified non-contact atomic force microscopy, time-of-flight secondary mass spectrometry and quantum chemical calculations. Two different adsorbate modes are identified, in which the majority is oriented such that the bowl cavity points away from the surface and the convex side is partially immersed into a four-atom vacancy in the Cu(100) surface. A minority is oriented such that the convex side points away from the surface with the five benzo tabs oriented basically parallel to the surface. Thermal annealing leads to hydrogenation and planarization of the molecules in two steps under specific C–C bond cleavage. The benzo tabs of the convex side up species serve as hydrogen source. The final product has an open shell electron structure that is quenched on the surface.

KEYWORDS buckybowls; scanning probe microscopy; open-shell aromatic hydrocarbons; density functional theory; on-surface chemistry

On-surface chemistry of polyaromatic hydrocarbons (PAHs) has become an important bottom-up approach towards large polymeric structures for functional interfaces that are not available by classical solution chemistry.^{1–3} Graphene nanoribbons and macrocycles, for example, have been synthesized after deposition of polyaromatic precursors followed by thermally-induced C–C coupling reactions.^{4,5} Dehalogenation and cyclodehydrogenation are thereby the most important steps of surface-based C–C coupling chemistry nowadays.^{6–8} Cyclodehydrogenation, in general, is the usual thermally-induced pathway of sterically overcrowded polyaromatic compounds at surfaces.^{9–12} Even carbon nanotubes (CNTs) can be obtained in such process.¹³ On the other hand, hydrogenation of curved carbon sheets, such as Buckminsterfullerene (C₆₀) leads to

unzipping into planar PAHs only at high temperatures and hydrogen pressure.^{14,15}

Buckminsterfullerene fragment molecules, so called buckybowls,^{16,17} are promising interface modifier molecules, because they have outstanding electronic properties. Besides a pronounced blue-light electroluminescence,¹⁸ corannulene (COR, C₂₀H₁₀, Fig. 1a) and its derivatives show a prominent electron acceptance from alkali metals.^{19–21} Confined to metal surfaces, buckybowls show interesting 2D crystallization phenomena, such as pentagonal tiling and symmetry mismatch,^{22–28} non-covalent concave complexation,^{29,30} as well as reversible, entropy-driven phase transitions.^{31,32}

Figure 1. (a) Top and side views onto ball-and-stick models of corannulene (COR). (b) Structure and full-space model of penta-indenocorannulene (PIC).

Adsorption of buckybowl leads to substantial Pauli repulsion on metal surfaces.^{33,34} The high electron density at the convex bowl side causes a push-back of metal electrons into the substrate, which, in turn, leads to a substantial interface dipole moment without any charge transfer. COR engages in a tilted configuration on Cu(111).³¹ Tilted adsorbate modes have also been observed for monoindenoCOR and terphenylCOR on Cu(111).^{35,36} So far, only the isolated C₇₀ fragment bowl C₃₈H₁₄ engaged with the bowl axis aligned normal to the surface, but became tilted upon intermolecular interactions.³⁷ As origin of tilted configuration of isolated buckybowl, special binding configurations to the surface, e.g., C6 rings over hollow sites, maximization of van der Waals contact and minimization of Pauli repulsion has been discussed.³⁸

In order to achieve a defined surface functionalization with CNT caps, the buckybowl penta-indenocorannulene^{39–44} (PIC, Fig. 1b) seems the logical choice. Its cyclodehydrogenation should yield a C₅₀H₁₀ entity that could become upon further dehydrogenation a standing CNT.^{45,46} Motivated by such possibility, the interaction of PIC with a Cu(100) surface has been studied by means of scanning tunneling microscopy (STM), scanning force microscopy (AFM) as well as dispersion-enabled density functional theory (D-DFT) and density matrix renormalization group (DMRG) calculations. A major fraction of isolated PIC molecules stands 'bowl-cavity-up' at low-temperatures. PIC is thereby partly submerged into the surface by creating a four-atom vacancy underneath the pentagonal center ring. A minority fraction stands convex side-up, pointing with the pentagonal centered C5 ring away from the surface.

Scheme 1. PIC and its hydrogenation products PIC/+{2,4}H

Instead of cyclodehydrogenation upon thermal treatment, a vast majority of PIC becomes hydrogenated and C-C bond cleavage occurs at the corannulene core in two steps (Scheme 1). Both reaction products are planar and are clearly identified by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and carbon monoxide-tip-modified AFM (CO-nc-AFM). By theoretical means it is evaluated if the hydrogenated products have open shell character.

RESULTS AND DISCUSSION

Figure 2 shows ST micrographs of PIC on Cu(100) at 5 K. The molecules ($\sim 8 \times 10^{-3}$ molecules/nm²) were deposited at 330 K prior to cooling. Most of the molecules appear with 5 protrusions, suggesting that the 5 benzo tabs are pointing away from the surface (cavity-up configuration). A minority is imaged as one bright protrusion surrounded by 5 shallow features. Such appearance is expected for a configuration in which the PIC cavity is facing the surface (cavity-down configuration). These two configurations are observed for isolated molecules. As previously observed for the C₃₈H₁₄ bowl,³⁷ tilted configurations can occur due to intermolecular interactions when two or more molecules aggregate.

The cavity-up configuration is experimentally the most commonly observed adsorbate mode here. Constant height nc-AFM images with a CO-modified tip of cavity-up and cavity-down PIC (Figure 3), in combination with force spectroscopy (Figure S1 and Table S3), allows determination of the height of parts of the species above the surface. The images are compared with AFM simulations using the particle probe method.^{47,48} For the cavity-up adsorbate, the simulated STM and AFM images reproduce well the experimental contrasts (Figure S2). However, the experimental height of the 5 benzo tabs was only achieved in the simulation when a 2×2 atom vacancy in the topmost Cu(100) surface layer was considered under the molecule (Figure 4a,b). Experimental and theoretical heights of the of the indeno group ends agree with such configuration within a 20 pm error (Table S3).

Figure 2. STM images of PIC recorded at 5 K after deposition on Cu(100) at 330 K (STM imaging parameters are listed in Table S1). (a) Overview image (100 × 100 nm²). (b) STM image (10 × 10 nm²) showing tilted species due to intermolecular interaction. (c) STM image with CO-modified tip (10 × 10 nm²). Most molecules adsorb such that the cavity points away from the surface (cavity-up). A cavity-down configuration is also indicated.

Figure 3. Experimental and simulated CO-nc-AFM images of PIC in cavity pointing up (a,b) and cavity pointing down (c,d) orientation. The Cu(100) substrate orientation as indicated in (d) applies to all images.

Surface Modification with Pentaindenocorannulene

The observation of a cavity-up configuration is not supported by previous DFT calculations, which did not consider vacancies in the surface.³⁸ Relaxation starting from a cavity-up adsorption mode leads to tilted configurations with maximal van der Waals (vdW) contact to the surface and presumably smaller Pauli repulsion (Table S2).^{35,38} Nevertheless, Note that for C_{60} on Cu(100) multiple-atom vacancies, leading to a reconstructed stripe phase, has been observed,⁴⁹ and C_{60} -induced vacancies were also observed on Cu(111) and Pt surfaces.^{50,51} Adsorption on a 4-adatom cluster or the presence of 8 surrounding adatoms also yields a stable cavity-up configuration in DFT (Table S2), but these structures strongly disagree with the AFM height results (Figure S1 and Table S3). In the case of PIC taking the cavity-down configuration, constant height nc-AFM leads to an image in which only the central 5-ring is observed. The corresponding particle probe modelling reproduces well AFM contrast and height (Figure 3, S1 and Table S4).

Buckybowls may reshape a Cu(110) surface at step edges.⁵² But how can a PIC molecule create a four-atom vacancy? In particular on Cu(100) vacancies are known to be originated at step edges and diffuse into the surface with an activation barrier almost as low as for single adatoms diffusion.^{53,54} Being initially pinned to such vacancy, a PIC molecule may then either cause three surface atoms adjacent to the vacancy to become adatoms on the terrace or 3 more diffusing vacancies will get pinned under the PIC once they arrive there. Another scenario is initial formation of an entire four-atom vacancy that become then occupied by PIC. Figure 2a shows that there are much more cavity-up bowls near the step edge on the upper terrace than on the lower terrace or further away from step edges. Such observation agrees well with the proposed mechanism of vacancy formation at a step edge, followed by vacancy diffusion into the upper terrace.^{53,54} Finally, it has been shown that Cu metal islands on Cu(100) display a dynamic system until certain island size is reached.⁵⁵ It is therefore also possible that the step-edges diffuse around the pre-adsorbed PIC molecules, trapping them in 4-atom vacancies.

Figure 4. Top and side views of fully relaxed DFT models of PIC on Cu(100) in the cavity-up (a,b) and cavity-down adsorbate mode (c,d). Four substrate atoms of the top layer are missing under the molecule in the cavity-up mode. For clarity Cu atoms of the two lowest slab layers (a) or of the top layer (b) have in part been omitted.

Figure 5. ToF-SIM spectra acquired from Cu(100) covered with $\sim 3 \times 10^{-2}$ PIC molecules/nm². The expected mass distributions of PIC ($C_{50}H_{20}^-$), PIC/+2H ($C_{50}H_{22}^-$), PIC/+4H ($C_{50}H_{24}^-$) and Cu (Cu_{10}^-) are shown as colored bars. Annealing to 516 K induces the formation of hydrogenated PIC/+2H and PIC/+4H species and the disappearance of the PIC ($C_{50}H_{20}^-$) signal.

Figure 6. STM (a,b) and CO-nc-AFM images (c) of PIC/Cu(100) after annealing to 490 K. The images were recorded at 5 K, imaging parameters are documented in Table S1. (a) Overview STM image (80 × 80 nm²) Most molecules appear to be planar. (b) Classification into two different types based on different opening angles (indicated by blue lines). (c) CO-nc-AFM of an area containing both species. (d) AFM image simulation of both types based on DFT models shown in (e). (e) DFT models of adsorbed PIC/+2H and PIC/+4H, assuming hydrogenation under C–C bond cleavage at one corannulene C6 ring (type **A**), and in a second step hydrogenation under C–C bond cleavage at the C5 center ring (type **B**).

Planarization Chemistry of Pentaindenocorannulene

The temperature-induced surface chemistry of PIC on Cu(100) is well studied by means of ToF-SIMS, a method analyzing the mass of adsorbates after bombardment with primary ions or ion clusters. Figure 5 shows anion ToF-SIMS spectra of about 3 × 10^{−2} molecules/nm² with increasing temperature. After deposition of PIC onto the substrate kept at room temperature, the signal at 620.2 u and its characteristic isotope pattern is identified as the PIC molecular anion C₅₀H₂₀[−]. After annealing to 516 K, fragments such as C₅₀H₂₂[−] (622.2 u) and C₅₀H₂₄[−] (624.2 u) are detected, corresponding to doubly (PIC/+2H) and quadruplicate (PIC/+4H) hydrogenated PIC. Annealing to 570 K still shows PIC/+4H signals (at smaller intensity due to non-specific decomposition), but much more decreased signals for PIC/+2H. After annealing to 623 K all PIC-derived signals disappear.

The corresponding cation ToF-SIMS data (Figure S3) and SIM spectra acquired at lower coverage (~10^{−2} molecules/nm², Figure S4) also show the two hydrogenation steps (PIC/+{2,4}H). The fact that the intensity of carbon (C[−] ions) is not significantly decreased (Table S5) shows that the disappearance of PIC-derived signals after annealing to 624 K is due to non-specific C–C coupling and fragmentation rather than desorption. These processes yield randomly linked carbon aggregates and ultimately (at higher temperatures) graphene.⁵⁶

STM images of PIC/Cu(100) acquired after annealing to 490 K show that the PIC has been transformed into planar entities (Figure 6). As in case of pristine PIC, these species appear with 5-lobes, but with a larger distance between two of them. Based on the angle spanned by these two lobes, two different planar species (types **A** and **B**) are actually identified (Figure 6b). High resolution CO-nc-AFM images of these two types are shown in Figure 6c. Simulation of AFM images has been performed based on DFT modelling of PIC/+2H and PIC/+4H species (Figures 6d,e). Excellent agreement in AFM contrast and height (Figure S1 and Table S6) is achieved by C–C bond cleavage at the corannulene core (Scheme 1). That is, in the first step C–C bond cleavage occurs on a core C6 ring, followed by C–C bond cleavage of the center C5 ring. Consequently, type **A** corresponds to PIC/+2H and type **B** corresponds to PIC/+4H.

AFM images show that the wider opening angle of species **B** is because the central 5-ring has been opened (Figure S5). Thus, the alternative reaction product where C₅₀H₂₄ (i.e. PIC/+4H) is obtained by cutting the first C–C bond but then doubly hydrogenating both carbon atoms (sp² → sp³) must be excluded. Furthermore, it is noteworthy that abundance of type **B** molecules (wider cut) increases with increasing temperature at the expense of type **A** molecules (Table 1), consistent with the increasing relative intensity of PIC/+4H with respect to PIC/+2H (Figure 5).

Table 1. Abundance of planarized molecules*

Annealing temperature	type A PIC/+2H	type B PIC/+4H
490 K	55 ± 3%	34 ± 2%
543 K	19 ± 2%	72 ± 3%

* For counts and STM obtained after annealing to 543 K see Table S7 and Figure S6.

A planar entity is favored in energy due to the larger surface contact area over a curved carbon bowl. As mechanism, however, the C–C bonds either open after hydrogen adatoms are added to the molecule or a Cu adatom acts as catalyst and opens the C–C bond by forming a metalorganic intermediate. Such intermediate is known to play a role in the reverse step, the C–C bond formation in the Ullmann coupling reaction.^{29,30} Although

temperature-dependent reversibility has been concluded for the debromination step of the Ullmann reaction,⁵⁷ to our knowledge is was not observed so far for the demetallization prior to C–C bond formation.

What remains to be discussed is the origin of hydrogen leading to the formation of PIC/{2,4}H. The possible sources are either the residual hydrogen gas in the vacuum chamber or hydrogen transfer from other molecules that have become dehydrogenated. It has been shown in the case of nickel that hydrogenation of adsorbed molecules may occur by subsurface hydrogen,⁵⁸ a mechanism that has not been observed for copper under ultrahigh vacuum conditions. As control experiment, ToF-SIMS measurements have been performed after annealing a PIC/Cu(100) sample in presence of D₂ gas (2×10^{-7} mbar), D₂O vapor and co-adsorbed dekadeuteriumacenaphtene (Figure S6). For the D₂ and D₂O experiments, no signal at the mass of PIC/+4D is detected. Rather, the SIM spectra are consistent with formation of PIC/{2,4}H, which means that deuterium from the gas phase is not involved. This result excludes residual hydrogen in the vacuum chamber, which is present at a partial pressure below 1×10^{-10} mbar, as source of hydrogenation. With coadsorbed dekadeuteriumacenaphtene (C₁₂D₁₀) as deuterium source, however, deuterated PIC is observed. Consequently, the hydrogen originates from other PIC molecules. It was not possible to clearly identify specific mass signals corresponding to dehydrogenation products of PIC. This could be due to an unspecific dehydrogenation mechanism or due to a very low ionization probability of the respective dehydrogenation products. Moreover, the complex fragmentation pattern at lower masses than the mother ion (PIC^(+,-)) could obscure any signal of dehydrogenated species.

After annealing, bright molecules with a centered pentagonal ring structure are observed predominantly at the step edges (Figure 6a, Figure S6). Their relative abundance of 20% corresponds approximately to the abundance of cavity-down PIC before annealing (Figure S7). Hence, these bright entities after annealing are assigned as bowl-shaped dehydrogenation products, similar to previously reported observations.^{59,60} The major source of atomic hydrogen is dehydrogenating cavity-down molecules. Assuming that the two configurations are still present at reaction conditions, it seems likely that only the cavity-up species will become hydrogenated, because only then can the atomic hydrogen, which is located on the surface, reach the reaction sites at the bowl. These conclusions are based on the assumption that dehydrogenation of cavity-down PIC indeed occurs. However, in the unlikely case that cavity-down PIC does not show a PIC mass signal in ToF-SIMS, the absence of such signal after annealing (Figure 5) cannot serve as

evidence that the bright molecules with a centered pentagonal ring structure became dehydrogenated.

PAHs may exist in planar non-Kekulé diradicaloid structures,^{51–66} but also in non-planar species, such as helicenes or buckybowl.^{67–70} That means, a closed-shell structure is being pushed to the limit of dissociation of one π bond to generate an open-shell structure with two weakly coupled unpaired electrons within the molecule. Hence, the hydrogenated products were evaluated for potential planar non-Kekulé diradicaloid structures by theoretical means. Interestingly, both D-DFT and DMRG calculations predict for the free PIC/+2H a closed shell structure, but an open shell character for the PIC/+4H product (Figures S9, S10 & S11). While the PIC/+2H triplet state is 0.3 eV higher than the closed-shell singlet, for PIC/+4H the open-shell structures are favored by 0.5 eV. However, due to interaction with Cu surface states, the open-shell structure becomes quenched (Figure S12). Recently, it has been shown that diradicaloid structures in relatively small, planar PAHs can survive on a metal surface without being quenched by surface states.⁷¹ Therefore, the PIC/+4 product will be tested for Kondo effect in further studies on less reactive metallic substrates such as Au(111).

CONCLUSIONS

The buckybowl pentaindenocorannulene engages in two different adsorbate modes on Cu(100), a cavity pointing up and a cavity pointing down mode, whereby the 'cavity-up' mode represents the major configuration. DFT calculations and AFM height measurements strongly suggest that in this configuration the bowl is immersed into a 4-atom vacancy in the surface.

In contrast to common planarization of PAH by thermally induced dehydrogenation,^{4,11,12} PIC turns planar by hydrogenation and C–C bond cleavage. In a first step, a C6 ring in the corannulene core between two indeno groups opens, and in a second step a C–C bond cleavage in the centered pentagonal ring is observed. Each step is accompanied by adding hydrogen atoms to the respective C-atoms involved in the former C–C bonds. These hydrogenated carbon atoms are part of pentagonal carbon rings, which suggest the possibility of open shell diradical structures. Such scenario is confirmed for the PIC/+4H by theoretical means for the free species. Because no deuterated species were found under backfilling the chamber with deuterium gas residual hydrogen gas as source can be excluded here. Atomic hydrogen most likely originates from dehydrogenation of bowl molecules at step edges. It is anticipated, that hydrocarbon-induced magnetization at metal-organic electrodes becomes an alternative approach towards spintronics interfaces design.

METHODS

The experiments were performed in ultrahigh vacuum on a Cu(100) single crystal surface prepared by cycles of Ar⁺ ion sputtering and annealing. The molecules were sublimed from a crucible kept at 345 to 360°C with typical sublimation times ranging from 5 to 20 min. Negative and positive ion ToF-SIMS (IONTOF, ToF-SIMS 5) spectra were recorded using a 25 keV beam of Bi₃⁺ primary ions. The beam was randomly rastered over an area of 0.25 mm². The extraction voltage was 3 kV. The pressure during preparation and measurements was below 10⁻⁸ mbar. The STM and nc-AFM data were recorded at 5 K using a qPlus sensor. The pressure in the STM/AFM chamber during preparation was around 3 × 10⁻⁹ mbar. The STM images were recorded in constant current mode with the imaging parameters described in Table S1. nc-AFM images were recorded in constant height mode using an amplitude set point of 50 pm and a bias voltage of 5 mV.

The DFT calculations have been performed using the FHI-AIMS code.⁷⁰ For the calculations involving the substrate, the general gradient approximation PBE potential was used.⁷¹ The gas phase calculations were performed using the hybrid potential b3lyp including electron spin.⁷² A light basis set was used in both cases. Van der Waals interactions were considered by employing the Tkatchenko–Scheffler method.⁷³ The Cu(100) substrate was described with a (9 × 9) slab with 3 layers. The bottom layer was kept fixed and the two upper layers were allowed to relax. The Brillouin zone was described at the Γ point. The energy and force tolerances for convergence were set to 10⁻⁵ eV and 0.01 eV/Å, respectively. The character of the singlet state wavefunctions of PIC/+2H and PIC/+4H was evaluated also by means multireference approach employing the DMRG method,^{74,75} in which 34 electrons were correlated in 34 orbitals. The def2-SVP basis set was used in these calculations.⁷⁶ The orbitals around the Fermi level, which were used for the active space construction were obtained using the ORCA program package.⁷⁷ The DMRG calculations with bond dimensions of 6000 were performed by means of the parallel MOLMPS program.⁷⁸

The AFM images were simulated with the particle probe model.^{45,46} The parameters of the probe particle were selected to mimic a CO-tip, using a quadrupolar charge of -0.05 e (s and p_z orbitals) with and a lateral stiffness of 0.24 Nm⁻¹. The electrostatic force was included in the probe particle model calculations using the Hartree potential calculated by DFT.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: [doi].

Experimental parameters, comparison of DFT calculations, AFM height analyses, additional ToF-SIM spectra, product

statistics, additional STM and AFM images, and density of states calculation results (PDF).

Notes

The authors declare no competing financial interest.

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