On-surface synthesis of a nitrogen-embedded buckybowl with inverse Stone-Thrower-Wales topology

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Curved π-conjugated polycyclic aromatic hydrocarbons, buckybowls, constitute an important class of materials with wide applications in materials science. Heteroatom doping of buckybowls is a viable route to tune their intrinsic physicochemical properties. However, synthesis of heteroatom-doped buckybowls is a challenging task. We report on a combined in-solution and on-surface synthetic strategy toward the fabrication of a buckybowl containing two fused nitrogen-doped pentagonal rings. We employ ultra-high-resolution scanning tunneling microscopy and spectroscopy, in combination with density functional theory calculations to characterize the final compound. The buckybowl contains a unique combination of non-hexagonal rings at its core, identified as the inverse Stone-Thrower-Wales topology, resulting in a distinctive bowl-opening-down conformation of the buckybowl on the surface. Our controlled design of non-alternant, heteroatom-doped polycyclic aromatic frameworks with established bottom-up fabrication techniques opens new opportunities in the synthesis of carbon nanostructures with the perspective of engineering properties of graphene-based devices.
P olycyclic aromatic hydrocarbons (PAHs) and their hetero-
cyclic analogs possessing curved π-conjugated architectures
(e.g., saddle- or bowl-shaped) attract substantial attention
of the broad scientific community due to their unparalleled
properties and potential application in the field of organic elec-
tronics1–6. Seminal publications on the synthesis of coronulene
reported by Scott’ and Siegel3,8,9 encouraged chemists all over
the world to pursue the goal of bottom-up synthesis of fullerene
and carbon nanotubes10. Indeed, truly enthralling architectures have
been synthesized over the recent years11–14. Displacement from
planarity in π-extended systems usually requires harsh reaction
conditions, which heterocycles rarely tolerate. Incorporation of
heteroatoms into polycyclic aromatic frameworks, however,
should drastically change their intrinsic optoelectronic proper-

ties15. Several examples of such systems are graphene nanoribbons
30, single-chirality single-walled carbon nanotubes16,17,18,19.

The aim of this study is to present a concise preparation of the
π-extended system by surface-assisted techniques motivated us to apply this
approach to compound 6a. In this case, on-surface cyclodehydro-
genation effectively leads to the formation of half-closed
species with only one heptagonal ring, 7a (Fig. 1, right panel).

Here we report a concise preparation of the first fully con-
jugated buckyball based on the PP scaffold. Our synthetic
pathway encompasses a combination of in-solution and on-
surface chemistry. In particular, on-surface cyclodehydrogenation
of suitably designed precursor molecules on an Au(111) surface
was the crucial step toward formation of the nitrogen-embedded
buckyball. Bond-resolved scanning tunneling microscopy (STM)
equivalently confirms the structure of the final molecule. In
addition, scanning tunneling spectroscopy (STS) in combination
with density functional theory (DFT) calculations further lend
support to the synthesis of the final product. Notably, the core
of the buckyball contains a unique combination of pentagonal and
heptagonal rings: the inverse Stone–Thrower–Wales (ISTW)
topology, a topological defect in graphene that remains challen-
ging to obtain experimentally. As a consequence of this unique
topology, the nitrogen-doped buckyball adopts a dome-shaped
bowl-opening-down conformation on the surface—a property
unprecedented for isolated buckyballs on surface.

Results
Design and synthesis of precursor molecules. Our previous
studies indicated that scrupulous design of TAPPs bearing bro-
mine atoms and aryl rings in ortho position with respect to the
central core facilitates smooth expansion of the π-system by
means of intramolecular direct arylation and oxidative aromatic
coupling, respectively25,27. Highly conjugated molecules based on
the PP core adopt nonplanar architecture due to the close spatial
vicinity of adjacent benzene rings.

Our initial assumption was that the naked analog 6a (lacking
any bulky groups at the peripheries) might serve as a precursor
for the on-surface cyclodehydrogenation. We thus began with the
synthesis of the parent TAPP 4a bearing bromine atoms and
phenyl rings in suitable ortho positions with respect to the central
core (Fig. 1, left panel). One-pot multicomponent condensation
between 2-bromo-6-phenylbenzaldehyde (1a), aniline (2a) and
butane-2,3-dione (3) gives 4a in 36% yield. Subjecting 4a to
palladium-catalyzed intramolecular direct arylation leads
smoothly to the formation of two new carbon–carbon bonds
around the core and hence to the planar derivative 5a obtained
in 80% yield. In the final step we employed oxidative aromatic
coupling utilizing iron(III) chloride. As a result, the central core is
connected with two peripheral benzene rings leading to the
nonplanar compound 6a produced in 90% yield. Subjecting 6a
prepared in this way to subsequent traditional oxidation methods,
such as DDQ/TIOH, MoCl5, etc., however, does not give the
desired compound 8.

Previous success in the formation of highly π-extended species
by surface-assisted techniques motivated us to apply this
approach to compound 6a. In this case, on-surface cyclodehy-
genation effectively leads to the formation of half-closed
species with only one heptagonal ring, 7a (Fig. 1, right panel).

Conversely, the targeted fully conjugated compound containing
two heptagons is not formed.

This partial success prompted us to design an alternative
precursor 6b, which possesses two preformed heptagonal rings. In
this approach, additional benzene rings originate from aniline
derivatives. Indeed, condensation between 2-bromobenzaldehyde
(1b), 2-amino-biphenyl (2b), and butane-2,3-dione (3) gives
TAPP 4b in 33% yield (Fig. 1, left panel). Analogous to the
previous synthesis, subjecting TAPP 4b to palladium-catalyzed
intramolecular direct arylation produces planar π-extended
derivative 5b in 80% yield. Compound 5b undergoes efficient
oxidation with iron(III) chloride in dichloroethane at 80 °C giving
6b in 60% yield. This reaction leads to the formation of two new
C–C bonds and results in a highly distorted π-extended PP
derivative possessing two heptagons in its structure.

Unlike 6a, cyclodehydrogenation of 6b requires the closure of
two hexagonal instead of two heptagonal rings to obtain the fully
conjugated target species 8. Oppurtunately, precursor 6b proves
to be viable for on-surface cyclodehydrogenation. Annealing this
compound to 320 °C under ultra-high vacuum (UHV) conditions
on a Au(111) substrate effectively leads to the formation of the
desired nitrogen-embedded buckyball 8 (Fig. 1, right panel).

On-surface synthesis of nitrogen-embedded buckyballs. After
sublimation of precursor 6a under UHV conditions onto an
atomically clean Au(111) surface held at room temperature, large-
scale STM images (Fig. 2a) acquired at 5 K show the presence of
self-assembled chains that follow the Au(111) herringbone
reconstruction, along with sporadically distributed individual
molecules. Figure 2b shows a representative high-resolution STM
image of the predominant species on the surface (95% of 170
molecules), which presents two bright lobes of 2.5 Å in height
(measured at a sample bias of −1 V). The experimental features
are well reproduced by the DFT-optimized geometry of 6a on an
Au(111) surface (Fig. 2d, e), which shows that 6a adopts a twisted
conformation on the surface. In addition, the corresponding STM
simulation (Fig. 2c) agrees well with the experimental STM
image.

Annealing the surface to 280 °C brings about notable changes
in the surface topography. Large-scale STM images (Fig. 2f)
show an absence of chains, with isolated molecules present on
the surface. Majority of the species have a two-lobed appearance
(38% of 100 molecules) and presumably did not undergo cyclodehydrogenation. Notably, there is appearance of a new species (15% of 100 molecules) that present only one lobe of much lower apparent height compared to \(6a\) (highlighted with a white circle in Fig. 2f). While it could be speculated that appearance of only one lobe hints at partial intramolecular cyclodehydrogenation and concomitant planarization of one lobe, it is rather difficult to conclusively identify the exact chemical structure of this product via STM imaging alone, which fundamentally probes the local density of states (LDOS) near the Fermi energy. To circumvent this limitation, we functionalize our tip by a CO molecule that helps us probe the sample in the regime of the onset of Pauli repulsion, thereby allowing to visualize the chemical structure of the molecule. It has been shown that STM tips functionalized with single atoms or molecules can serve as a nanoscale transducer, converting atomic-scale forces exerted by the sample on the tip functional moiety to conductance variations in the tunneling junction\(^3\). Our choice of CO as the tip functional moiety is governed by its facile manipulation on metal or insulating substrates and its rigid bonding to the metal tip, yielding images of high fidelity\(^3\). Figure 2g shows a high-resolution STM image of the one-lobed species acquired with a CO-functionalized tip. While only weak intramolecular contrast can be discerned, it is nevertheless clear that this species adsorbs flat on the surface except for a sharp ridge around the position of the lobe. Furthermore, at the expected position of the second lobe in \(6a\), we instead find a smooth bay indicating a possible bond closure. Finally, an ultra-high-resolution STM (UHR-STM) image (Fig. 2h) of the bottom part of the molecule (highlighted with a blue rectangle in Fig. 2g) clearly shows formation of a heptagonal ring at the aforementioned bay position (indicated with a red arrow), which leads us to conclude that at this temperature, partial intramolecular cyclodehydrogenation occurs to form the half-closed species \(7a\).

Figure 2i, j show the DFT-optimized structure of \(7a\) on Au(111), which correctly reproduces the experimental features—i.e., the out-of-plane bending of a benzenoid ring corresponding to a

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**Fig. 1** Synthetic route to the nitrogen-embedded buckybowl \(8\). (Left panel) Solution-synthetic routes to precursor molecules \(6a\) and \(6b\). (Right panel) Subsequent on-surface synthetic route to partially closed species \(7a, 7b\) and the fully conjugated nitrogen-embedded buckybowl \(8\). Crucial rings formed in the final steps are marked in colors (via oxidative aromatic coupling—yellow, via on-surface cyclodehydrogenation—blue)
single lobe in the STM images, and the otherwise planar adsorption geometry of the molecule on the surface.

Finally, we anneal the surface upwards of 350 °C in an attempt to induce full ring closure. Unfortunately, it was seen that for higher temperatures, intermolecular covalent coupling and side reactions dominate and full ring closure is not observed (see Supplementary Fig. 21). It is worth to mention that we systematically tried to induce ring closure on more catalytically active coinage metal surfaces—i.e., Ag(111) and Cu(111). On Ag (111) (see Supplementary Fig. 19) half-closure to form 7a does take place, but the molecules start to decompose upwards of 300 °C without full ring closure. On the most active Cu(111) surface (see Supplementary Fig. 20), we observe neither half- nor fully-closed species, with widespread intermolecular coupling and decomposition upwards of 260 °C. Thus, with precursor 6a, while intramolecular cyclodehydrogenation to form one heptagonal ring is feasible (on Au(111) and Ag(111) surfaces), closure of the second heptagonal ring, however, is not favored.

We next investigate the on-surface reaction of an alternative precursor 6b, which requires closure of two hexagonal rings (instead of two heptagonal rings as in 6a), with preformed heptagonal rings. When 6b is sublimed under UHV conditions onto an atomically clean Au(111) surface held at room temperature, large-scale STM images (Fig. 3a) show presence of predominantly discrete quasi-rectangular structures with two centrally located bright lobes of roughly 3.5 Å in height (measured at a sample bias of −1 V), in contrast to the long chains seen in case of 6a (c.f. Fig. 2a). High-resolution STM imaging (Fig. 3b) reveals the intramolecular features in more detail, where it is seen that apart from the two prominent central lobes, additional lobes of weaker contrast are present at the terminus. In addition, we also find the occasional species with only one prominent lobe on one side and two lobes of weaker contrast on the opposite side (indicated with the white arrow in Fig. 3b). Evidently, the quasi-rectangular species are, in fact, non-covalently bonded, self-assembled dimers of the isolated species which we assign to be 6b. The rather nontrivial conformation of 6b presenting only one prominent lobe is elucidated by theoretical calculations, wherein its DFT-optimized structure (Fig. 3d, e) on Au(111) shows that, unlike 6a, 6b adopts neither twisted nor folded conformation, but a peculiar conformation in which two benzenoid rings are bent out-of-plane as in a folded conformation (magenta rings in Fig. 3d, e), giving rise to the two weak lobes in STM images; while one of the terminal benzenoid rings is strongly bent out-of-plane (violet ring in Fig. 3d, e), leading to the appearance of one prominent lobe in STM images. Furthermore, the STM image simulated for this conformation
Fig. 3 On-surface reaction of 6b on Au(111). a Overview STM topography image of the surface after room temperature deposition of 6b, showing the predominant presence of self-assembled dimers (V = −1 V, I = 50 pA, scale bar: 5 nm). b High-resolution STM image of the highlighted area in a, consisting of a dimer, and an isolated molecule indicated with the white arrow (V = −1 V, I = 70 pA, scale bar: 1 nm). c DFT-simulated STM image of 6b corroborating the experimentally observed features (V = −1 V, scale bar: 1 nm). The colored dots serve as a guide to the eye for comparing the intramolecular features in experimental and simulated STM images. d, e Top and side views of the DFT equilibrium geometry of 6b. Rings highlighted in violet and magenta colors show an out-of-plane bending contributing to the distinguishing features in the STM images. f Overview STM topography image of the surface after annealing to 270 °C (V = −1 V, I = 40 pA, scale bar: 5 nm). The white circle highlights the half-closed species 7b. The white arrow indicates a still-present 6b on the surface. g High-resolution STM image of 7b (V = 10 mV, I = 50 pA, scale bar: 0.5 nm). h Corresponding UHR-STM image of 7b (open feedback parameters: V = −5 mV, I = 50 pA; Δz = −40 pm; scale bar: 0.5 nm). The red arrow indicates the hexagonal ring formed after this annealing step. i, j Top and side views of the DFT equilibrium geometry of 7b. The newly formed bond at this annealing step is highlighted in red.

(Fig. 3c) agrees well with the experimental one, concluding the structural assignment of 6b on the Au(111) surface. Having clarified the structure of 6b, we anneal the sample to 270 °C. Figure 3f shows a large-scale STM image of the surface after annealing, where there is a considerable decrease in the number of dimers with a concomitant increase in individual species presenting one prominent lobe (highlighted with a white circle in Fig. 3f). STM images show that these one-lobed species (referred to as 7b), however, are different from 6b, evidenced by a lack of two weaker lobes present at the molecule terminus. Whether isolated or present as dimers, 7b constitutes the predominant species on surface (82% of 141 molecules), while only 7% is present as 6b (the white arrow in Fig. 3f indicates an isolated 6b). Figure 3g, h show a high-resolution STM image and the corresponding UHR-STM image of 7b, respectively. Formation of a hexagonal ring (indicated with a red arrow) is evident in Fig. 3h, allowing us to conclude that 7b results from partial intramolecular cyclodehydrogenation of 6b, where one of the two hexagonal rings have formed. Its DFT-optimized structure on Au (111) (Fig. 3i, j) is in line with experimental observations, where the out-of-plane bent benzenoid ring is responsible for the bright lobe in STM/UHR-STM images, while the rest of the molecule adopts an almost planar geometry on the surface.

After further annealing the surface to 320 °C, large-scale STM images show appearance of a new species (31% of 181 molecules, referred to as 8) with apparent hexagonal shape and no prominent lobes (Fig. 4a, highlighted with the white circles). Furthermore, concomitant with the appearance of 8 is a decrease in the amount of half-closed species 7b on the surface (42% of 181 molecules). Figure 4b shows a high-resolution STM image of 8 acquired with a CO tip, where the presence of six bays at the periphery of molecules clearly hints toward complete ring closure. Finally, the UHR-STM image of 8 (Fig. 4c) unambiguously proves the structure of the intended nitrogen-embedded buckybow. We note that current state-of-the-art scanning probe techniques used for chemical structure visualization, i.e., noncontact atomic force microscopy and UHR-STM, show no appreciable contrast between carbon and nitrogen atoms evident through previous structural studies employing these techniques on nitrogen-doped graphene nanostructure.25,38. This is reflected in the UHR-STM image of 8 where the presence of nitrogen atoms is not apparent. However, any ambiguity regarding the loss of nitrogen atoms...
from the framework of 8 is alleviated by the fact that Au(111) is a relatively mild substrate for catalyzing on-surface reactions, and previous works on synthesis of nitrogen-doped graphene nanostructures on Au(111), with temperatures similar to or higher than those reported in our work, have shown no loss of heteroatoms from the corresponding organic frameworks. DFT calculations suggest that the molecule adopts a dome-shaped conformation after complete dehydrogenation on a Ir(111) surface, or locally due to perturbation with the STM tip. Similar bidirectional conformational switching has also been observed in supramolecular assemblies of surface-supported porphyrin derivatives. Interestingly, coronene molecules were also shown to adopt a dome-shaped conformation after complete dehydrogenation on a Au(111) surface. However, to the best of our knowledge, we show here the unprecedented case of isolated surface-adsorbed buckybowls with a preferential bowl-opening-down conformation (see Supplementary Figs. 25 for a discussion pertaining to the origin of the bowl-opening-down conformation of 8 on the surface). This class of bowl-opening-down buckybows may provide a template to intercalate atomic species underneath such structures, allowing for atomic-scale tuning of their chemical or electronic properties, and potential application in emerging fields, such as spintronics.
buckybowl57. Finally, a short discourse regarding the merits and shortcomings of on-surface synthetic methodology is appropriate. It is evident that on-surface synthesis provides for a powerful synthetic toolbox to fabricate complex nanostructures, which are otherwise difficult or impossible to achieve in solution phase. Furthermore, this approach allows for a detailed structural and electronic characterization at the atomic scale via scanning probe microscopies. However, submonolayer coverage of products obtained on the surface and the difficulty of post-synthetic transfer of products to insulating substrates or organic solvents poses challenges toward device fabrication and employment of bulk characterization techniques. Thus, while on-surface synthesis opens new avenues in the fabrication and characterization of novel materials with great potential, its limited scalability currently stands as a challenge toward device applications. Nevertheless, recent progress in post-synthetic transfer techniques for surface to device translation holds great promise in this regard58.

**Discussion**

We developed a concise synthetic pathway to the first buckybowl containing the PP core. Starting from the parent TAPP, the nitrogen-embedded buckybowl was obtained via successive ring-closing steps through in-solution oxidative aromatic coupling and on-surface cyclodehydrogenation on Au(111). The buckybowl represents the first discrete molecule possessing the ISTW topology, leading to the unprecedented case of isolated surface-adsorbed buckybowl with a preferential bowl-opening-down conformation. The electron-rich fully fused nitrogen-embedded buckybowl assuming curved bowl-like architecture may serve as an ideal candidate for a host-guest study and may play a role as a foundation for further \( \pi \)-extension. This work shows the potential of on-surface synthesis toward the formation of unprecedented \( \pi \)-extended aza-analogs of graphene and atomically precise incorporation of challenging non-hexagonal ring topologies as a route
to tailor the electronic and chemical properties of graphenic structures and provide a ground for new functionalities.

Methods

Synthesis. The synthesis of compounds 4a, 4b, 5a, 5b, 6a, and 6b is described in detail in the Supplementary Information (see Supplementary Methods). For NMR and 2.

Sample preparation and STM measurements. STM experiments were performed with a commercial low-temperature STM (T = 3 K) from Scienta Omicron operating at base pressure below 1 × 10⁻¹⁰ mbar. Au(111), Ag(111), and Cu(111) single crystal surfaces were prepared by iterated cycles of sputtering with Ar⁺ ions (p = 6 × 10⁻⁸ mbar) and annealing to 750 K for 20 min at pressures below 5 × 10⁻¹⁰ mbar. STM was used to check the quality of the surfaces before deposition of molecules. Precursor molecules 6a and 6b were sublimed at 583 and 603 K, respectively, on the single crystal surfaces held at room temperature. Owing to the large distance between the evaporator and the substrate, only ~2% of the sublimated molecules reach the substrate. All STM images were acquired in constant-current mode, unless otherwise noted. Indicated tunneling bias voltages are given with respect to the sample. Unless otherwise mentioned, gold-coated tungsten tips were used for STM imaging and spectroscopy. Differential conductance spectra and associated maps were measured using the lock-in technique to obtain a signal proportional to dI/dV from the first harmonic of the tunneling current. UHR-STM images were acquired with a CO-terminated tip in constant-height mode, at biases close to the Fermi energy, and the current signal was recorded. Open parameter and subsequent approach distances (Δz) are given in respective figure descriptions. CO-terminated tips were obtained by picking up individual CO molecules from NaCl islands deposited after completion of on-surface reactions.

NCI islands facilitate the identification and pickup of individual CO molecules. All STM and dI/dV images were processed and analyzed with WSxM software.[8]

Calculation methods. To obtain the equilibrium geometries of the molecules adsorbed on the Au(111) substrate and to compute corresponding STM images, we used the CP2K code[6,6] implementing DFT within a mixed Gaussian plane wave approach[8]. The surface/adsortate systems were modeled within the repeated slab approach[6,6]. The surface/adsorbate systems were modeled within the repeated slab replicas.

To obtain simulated STM images[8], within the Tersoff–Hamann approximation[8], we extrapolated the electronic orbitals to the vacuum region in order to correct the wrong decay of the charge density in vacuum due to the localized basis set. The inversion energy barrier for the molecule in the gas-phase was obtained by means of the nudged elastic band method[70], employing nine replicas.

Data availability. X-ray crystallographic data for 4b and 6c can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) with the CCDC numbers 1589417 (4b) and 1589418 (6c) via its website (https://www.ccdc.cam.ac.uk/structures/). All other data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

S.M. and M.K. contributed equally. P.R., R.F., and D.T.G. conceived the project and supervised the experiments; M.K. designed, synthesized and characterized the precursor molecules; S.M. performed the on-surface synthesis and SPM experiments; C.A.P. supervised the experiments; M.K. designed, synthesized and characterized the precursor molecules; S.M. performed the on-surface synthesis and SPM experiments; C.A.P. performed the theoretical calculations. All authors contributed to writing the manuscript.

Additional information

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