Benzo-Fused Periacenes or Double Helicenes? Different Cyclodehydrogenation Pathways on Surface and in Solution

Qiangzhong Zhang,†‡ Yunbin Hu,§∥ Kaifeng Niu,† Haiming Zhang,† Biao Yang,†¶ Daniel Ebeling,‡† Jalmar Tschakert,† Tao Cheng,‡ André Schirmeisen,‡ Akimitsu Narita,*§⊥ Klaus Müllen,*§∥ and Lifeng Chi*†

†Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Joint International Research Laboratory of Carbon-Based Functional Materials and Devices, Soochow University, Suzhou 215123, China
‡Institute of Applied Physics, Justus-Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany
§Max Planck Institute for Polymer Research, 55128 Mainz, Germany
∥Department of Organic and Polymer Chemistry, College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China
¶Organic and Carbon Nanomaterials Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa 904-0495, Japan
*Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

ABSTRACT: Controlling the regioselectivity of C–H activation in unimolecular reactions is of great significance for the rational synthesis of functional graphene nanostructures, which are called nanographenes. Here, we demonstrate that the adsorption of tetranaphthyl-p-terphenyl precursors on metal surfaces can completely change the cyclodehydrogenation route and lead to obtaining planar benzo-fused periacenes rather than double [7]helicenes during solution synthesis. The course of the on-surface planarization reactions is monitored using scanning probe microscopy, which unambiguously reveals the formation of dibenzo-periacenes and the structures of reaction intermediates. The regioselective planarization can be attributed to the flattened adsorption geometries and the reduced flexibility of the precursors on the surfaces, in addition to the different mechanism of the on-surface cyclodehydrogenation from that of the solution counterpart. We have further achieved the on-surface synthesis of dibenzo-periacene by employing a tetra-anthryl-p-terphenyl precursor. The energy gaps of the new nanographenes are measured to be approximately 2.1 eV (dibenzo-periacene) and 1.3 eV (dibenzo-periacene) on a Au(111) surface. Our findings shed new light on the regioselectivity in cyclodehydrogenation reactions, which will be important for exploring the synthesis of unprecedented nanographenes.

INTRODUCTION

Nanographenes (NGs) are regarded as segments of graphene featuring nanometer sizes in one or two dimensions.¹ The size control, especially at the sub-10 nm scale, has been proven to induce a quantum confinement effect and allow for the tuning of the electronic band gap.²³ The unique, structure-dependent properties of NGs qualify them for various applications in molecular electronics,⁴ spintronics,⁵ and optoelectronics.⁶ Since the electronic properties of NGs sensitively depend on their size² and edge geometries,⁸ it is mandatory to fabricate NGs with atomic precision. To this end, bottom-up molecular synthesis is the most suitable approach for providing NG molecules, i.e., large polycyclic aromatic hydrocarbons (PAHs) with uniform and defined chemical structures. The synthesis of NG molecules has typically been carried out through the oxidative cyclodehydrogenation of tailor-made oligoarylene precursors in solution in the presence of Lewis acids and oxidants.⁹−¹⁹ Nevertheless, the cyclodehydrogenation in solution is sometimes hampered by side reactions furnishing undesired and often inseparable mixtures of products.²⁰−²⁴ On the other hand, cyclodehydrogenation on metal surfaces has emerged during the past decade as an alternative and complementary method enabling the synthesis of atomically precise NG molecules under ultrahigh vacuum (UHV) conditions.²⁵−²⁷ The on-surface cyclodehydrogenation proceeds at elevated temperatures, typically at >400 °C, with the help of the catalytic effect of the metal surfaces such as.
Au(111), Ag(111), and Cu(111). This process is most likely accompanied by the release of hydrogen, which is in contrast to the solution reaction that is regarded to include cationic intermediates with the elimination of protons; however, the mechanisms of both cases are not yet fully understood. On-surface synthesis allowed for the formation of unstable PAHs, in particular, higher acenes, which could not be obtained in solution. It is essential, therefore, that the resulting product structures can be visualized at an atomic resolution using in situ scanning probe microscopy (SPM). However, little is known about the influence of metal surfaces on the selectivity of the cyclodehydrogenation reaction, especially when different isomers can be envisaged.

Periacenes, which are zigzag-edge NG molecules with two rows of peri-fused linear acenes, are highly attractive due to their intriguing properties, such as low energy gaps and open-shell biradical character. In addition to the smallest periacenes, perylene, and bisanthene, the synthesis of peritetracene with bulky substituents was recently achieved in solution. It is essential, therefore, that the resulting product structure along the reaction combined with density functional theory (DFT) calculations provided insights into the structures along the reaction.

RESULTS AND DISCUSSION

First, we deposited a submonolayer of 4,4-di-tert-butyl-2,2′,6,6′-tetra(2-naphthyl)-p-terphenyl (TNTP-tBu, 1a) onto a room temperature Cu(110) surface using molecular sublimation at 620 K. As seen in Figure 2a, the molecules were scattered on the Cu(110) surfaces without forming a regular assembly. Most of the molecules of 1a (with the axis across the two tert-butyl (tBu) groups) were adsorbed parallel to the [1 1 0] direction of Cu(110). As shown in Figure 2d, g, and j and Figure S1, the four naphthyl branches were arranged nearly parallel to each other. This configuration is advantageous for the C–C bond formation at the β-position of the naphthyl group (highlighted in pink in Figure 1) because the reaction at the α-position (highlighted in blue in Figure 1) would involve an extra flipping process of the naphthyl group. Two naphthyl groups (the upper two in Figure 2d and g) were relatively flat, making them invisible to AFM imaging with a constant height at the tip height +50 pm (Figure 2g) and a constant-current mode (Figure S1b and c). In contrast, the other two naphthyl groups and the central benzene ring were tilted with respect to the surface plane due to intramolecular steric hindrance. This configuration of adsorbed TNTP-tBu molecules was verified by the DFT calculated structures (Figures 3a and b) and the simulated AFM image (Figure 3c). Interestingly, a 90° rotation of the molecules was observed after annealing at 460 K for 30 min, but pristine TNTP-tBu was still predominant (Figure S2b and Figure S3a–d).

To our delight, C–C bond formation at the β-positions of the naphthyl groups was observed when annealing the sample...
at 530 K or higher, thereby leading to the formation of dibenzopiperhexacene 3a instead of double [7]helicene 2a, as previously obtained in the solution synthesis (Figure 2; see Figure S2 for the whole annealing processes). Between 530 and 590 K, intermediates such as 4, resulting from the incomplete cyclodehydrogenation, were detected with different adsorption geometries and orientations. The chemical structures of the intermediates were confirmed by high-resolution AFM images and computer simulations (Figures 3e–h and S3e–h).

Intermediate 4 was more distorted than the pristine precursor 1a, thus leaving two of the four naphthyl groups appearing as bright lobes in the STM image (Figure 2e); they are highlighted by the two yellow ovals in Figure 2k, while the other two naphthyl groups are fused to the central benzene ring. At 590 K, molecules with only one remaining naphthyl group were also found, e.g., in Figure S3i–l. Nevertheless, no other intermediate structure was found, indicating that the planarization of each naphthyl group from structure 4 was accompanied by subsequent or simultaneous formation of three C–C bonds. Elevating the annealing temperature to 620 K induced the complete planarization of some molecules (∼10% (5/52), as seen in Figure 2c, f, i, and l). After annealing at 640 K, most of the molecules have been planarized. Some of the molecules were connected with each other due to the removal of the tert-butyl groups followed by intermolecular C–C bond formation (Figure S2f). It should be noted that the dibenzopiperhexacene structure of 3a is not completely flat because of the bulkiness of the fBu groups, which makes the middle part of the molecule higher while the two sides are bent down due to the strong interaction with the substrate, as shown in Figure 2i and Figure 3j and k.

As mentioned above, precursor 1a was distributed separately on Cu(110) surfaces, thus implying that there is a stronger molecule–surface interaction than molecule–molecule interaction. To exclude possible special template and/or catalytic effects of Cu(110) as the driving force for the planarization, control experiments on Cu(111) and Au(111) were conducted. Unlike the scattered distribution on Cu(110), precursor 1a initially assembled into a two-dimensional monolayer on Cu(111) and Au(111) (see Figure S4c and d). The molecules were adsorbed in a more twisted shape presumably because of the interplay of a weaker molecule–surface interaction on Cu(111)/Au(111) and the intra-molecular geometric relaxation. The same planarized products were observed when annealing at approximately 620 K on Cu(111) (Figure S5c and Figure S6c and d) and at 700 K on Au(111) (Figure S5d).

Notably, the benzo-fused double [7]helicene 2a that was obtained from precursor 1a in the solution synthesis was not observed at all in the on-surface experiments. Instead, the same precursor exclusively led to benzo-fused perhexacene 3a. The rotation around the C–C bond between the naphthyl group and the inner benzene unit of the p-terphenyl is relatively free in solution. Thus, bond formation seems possible at both the α- and the β-positions of the naphthyl moiety. Nevertheless, assuming that the oxidative cyclodehydrogenation of precursor 1a proceeds after the initial electron transfer, thus generating...
its radical cation of species, the formation of 2a in solution can be ascribed to the higher spin density at the α-position according to the DFT calculation at the UB3LYP/6-31G(d, p) level (Figure S7). On the other hand, while not being perfectly flat, precursor 1a adopts a conformation that maximizes the contacts between the π-systems and the surface, as observed using STM (see Figure 2a, d, and g). Maintaining these contacts throughout the reaction will facilitate a flat product structure, namely, dibenzoperihexacene 3a. The adsorption energy of 1a on the Cu(110) surface was estimated to be −2.48 eV from the reactive force field (ReaxFF) simulation (see Table S1), which is consistent with the observed conformation. Furthermore, the on-surface cyclodehydrogenation supposedly proceeds via the initial abstraction of a hydrogen atom, thereby generating free radical species of the naphthyl group, followed by the C=C bond formation with the central benzene ring. The reaction enthalpies and barriers for the hydrogen abstraction from naphthalene were calculated to be almost identical for the α- and β-positions, which can explain the observed difference in the region selectivity. Further, the rotation of the naphthyl groups on the surface is hindered by the higher rotation barriers of 0.44 eV on Au(111) and 0.46 eV on Cu(110) in comparison to that of 0.32 eV in solution (see Table S1). It is worth noting that the adsorption of 3a is much more stable than that of 2a-1 with a difference of −4.65 eV (Table S2), which also favors the planarization reaction. We propose the reaction processes as shown in Figure S8. Nonetheless, comprehensive calculations of the energy barrier of each reaction step as well as stabilization energy of each possible intermediate need to be done in future work to obtain deeper insights into the reaction pathways.

We noticed that a nonnegligible amount of the dibenzoperihexacene molecules were randomly connected to each other after annealing at 640 K (Figure S2f), probably because the fBu radicals were removed so that the cyclodehydrogenation was accompanied by intermolecular coupling. To suppress the oligomerization of the products, 2,2″,6,6″-tetra(2-naphthyl)-p-terphenyl (TNTP, 1b) was used as a precursor without fBu groups for comparison. TNTP 1b was synthesized via a fourfold Suzuki reaction between 2,2″,6,6″-tetrabromo-1,1′:4′,1″-terphenyl and 2-naphthylboronic acid, as displayed in Scheme S1. TNTP 1b was deposited onto Cu(110), Cu(111), and Au(111) (Figure S4e–h). When the same cyclodehydrogenation conditions as in the experiments with TNTP-fBu 1a were applied, the TNTP molecules were planarized to dibenzoperihexacene 3b with much fewer intermolecular reactions (Figure S5a–d vs Figure S5e–h). The yield of 3b on Au(111) was the highest compared to yields on other metal surfaces (32% on Cu(110), 30% on Cu(111), and 56% on Au(111), as shown in Figure S5f–h). We thus took the reactions on Au(111) as a representative example.

After thermal sublimation, TNTP precursor 1b was initially adsorbed in a more distorted conformation on Au(111) surfaces and self-assembled into one-dimensional (1D) molecular chains. The chains were not perfectly periodic, thereby indicating the coexistence of different adsorption geometries. As illustrated in Figure 4c and d, precursor 1b was transformed into dibenzoperihexacene 3b after annealing at 720 K for 30 min. Extending the annealing time leads to an increased yield of the planarization reaction. However, it also leads to an increase in intermolecular connections. Basing on trial-and-error experiments, we finally determined 30 min as the optimal annealing time. The majority of the planarized product molecules remained separate from each other (Figure 4b), in contrast to the randomly connected products that were obtained from TNTP-fBu 1a (see Figure S2f and Figure S5c and d). The exact chemical structure of dibenzoperihexacene 3b was determined using bond-resolution AFM (Figure 4f).

Finally, we exploited the on-surface regioselective cyclodehydrogenation to synthesize an even higher homologue of dibenzoperihexacene, namely, dibenzoperoctacene 6 (Figure 4b). To this end, 4,4″-di-tert-butyl-2,2″,6,6″-tetra(2-anthryl)-p-terphenyl (TATP-fBu, 5, Figure 5a) was designed as the precursor and synthesized via the fourfold Suzuki coupling between 2,2″,6,6″-tetrabromo-1,1′:4′,1″-terphenyl and 2-anthrylboronic acid, as described in Scheme S2. After sublimation at 720 K onto the Au(111) surface that was kept at room temperature, the TATP-fBu molecules dominantly self-assembled into 1D molecular chains (Figure 5c). The STM image of TATP-fBu 5 (Figure 5e) indicated that three of the four anthryl groups lie more or less flat while the remaining one is highly tilted. Annealing the sample at 690 K for 30 min promoted the transformation from 5 to dibenzoperoctacene 6, which was confirmed by the chemical bond imaging (Figure 5g).

The electronic structures of dibenzoperihexacenes 3a and 3b and dibenzoperoctacene 6 were characterized using scanning tunneling spectroscopy (STS) on the Au(111) surfaces. The STS curves in Figure 6a, e, and i recorded the dI/dV versus bias voltage in the range from −2 to 2 V at specific points that were marked in the STM images in Figure 6b, f, and j, respectively. The characteristic peaks at ~0.6 and 1.5 V in Figure 6a and e were assigned as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively, for both 3a and 3b.

Therefore, a HOMO–LUMO energy gap of approximately 2.1 eV was deduced for dibenzoperihexacenes 3a and 3b. Similarly,
with the decreased HOMO–LUMO gaps of the larger periacene.\textsuperscript{51–53} Moreover, two-dimensional STS maps of the HOMO and LUMO for dibenzoperihexacenes 3a (Figure 5c and d, respectively), 3b (Figure 5g and h, respectively), and dibenzoperiacene 6 (Figure 5k and l, respectively) were obtained at constant current. The spatially localized distribution of the electronic states indicated a weaker interference from the Au(111) surfaces compared to other more reactive surfaces, e.g., Cu(111) (see Figure S14), which enabled the detection of the molecular frontier orbitals. As seen in Figure 6c, g, and k, the HOMO of 3a, 3b, and 6 mainly exists at the zigzag edges, which is reminiscent of the edge states observed in the zigzag-edge graphene nanoribbons.\textsuperscript{54} The HOMO localized at the zigzag edges is enhanced in the middle, which is where the zigzag edges are fused with a benzene ring. The similarity in the electronic structures of 3a and 3b indicates that the influence of tBu groups on the molecular electronic properties is negligible.

\section*{CONCLUSION}

In summary, we demonstrate that the regioselectivity of the cyclodehydrogenation of 2,2′,6,6′-tetra(2-naphthyl)-p-terphenyl on metal surfaces is different from that in solution, thereby leading to an unprecedented synthesis of dibenzoperihexacene on Cu(110), Cu(111), and Au(111) in contrast to the previously reported double \textsuperscript{7}helicene generated through the solution synthesis. To the best of our knowledge, this is the first example to demonstrate different regioselectivity in similar reactions on the surface and in solution, thereby yielding different products from the same precursor. We have further developed a 2,2′,6,6′-tetra(2-anthryl)-p-terphenyl precursor to accomplish the on-surface synthesis of dibenzoperiacene as the largest periacene analogue with a small HOMO–LUMO gap of 1.3 eV. The current results provide new insight into the cyclodehydrogenation reactions on metal surfaces and a useful guideline for the design of new precursors, e.g., those having naphthyl and/or anthryl groups, for developing further varieties of nanographene structures. The structural extension to dibenzoperidecacene and the synthesis of benzo-fused zigzag graphene nanoribbons\textsuperscript{55} are planned for future investigation in our laboratories.

\section*{METHODS}

\textbf{Synthesis of Precursors.} 4,4′-Di-tert-butyl-2,2′,6,6′-tetra(2-naphthyl)-p-terphenyl (TNTP-tBu, 1a) was synthesized as described in our previous report.\textsuperscript{57} The details of the synthesis of 2,2′,6,6′-tetra(2-naphthyl)-p-terphenyl (TNTP, 1b) and 4,4′-di-tert-butyl-2,2′,6,6′-tetra(2-anthryl)-p-terphenyl (TATP-tBu, 5) are provided in Schemes S1 and S2, respectively.

\textbf{Sample Preparation.} The Cu(110)/Cu(111)/Au(111) crystals that were purchased from MTeck (Germany) were cleaned using combined sputtering/annealing cycles. The precursors were deposited onto the single crystal surfaces from a homemade molecule evaporator.\textsuperscript{56} Reactions were triggered by heating the sample at appropriate temperatures for 30 min. The prepared samples were transferred into an STM/AFM scanner where the base pressure is better than 1.0 × 10\textsuperscript{−9} mbar.

\textbf{STM/AFM and STS Measurements.} All of the STM/AFM images were measured at 5 K with a commercial LT-STM/AFM (Scicenta Omicron, Germany). The tip was grounded and a voltage bias was applied to the sample for STM imaging in the constant current mode. The STS spectra (di/dV vs bias voltage (V)) were acquired in the following steps: (i) Put the tip at the target positions with a tunneling set point of −1 V and 100 pA, (ii) switch off the tip-height feedback, and (iii) ramp V from −2 to 2 V and record the di/
the probe particle model from Hapala et al. and taking the DFT constant-height frequency shift AFM images were carried out using atomic force. The simulations of the calculations were performed using the Vienna Ab initio Simulation Package (VASP), in which the electron–ion interactions were described using the Projector Augmented-Wave (PAW) potentials. The exchange-correlation interactions were interpreted through the Perdew–Burke–Ernzerhof (PBE) of the Generalized Gradient Approximation (GGA) pseudopotentials. The cut-off energy for the plane wave was set as 400 eV. The vdW-D3 method developed by Grimme et al. was employed to describe the van der Waals interactions.

The Cu(110) surface was modeled using periodic cells. During the structural optimizations, the bottom two layers of Cu atoms were kept fixed, and all other atoms were relaxed until the atomic force was less than 0.01 eV/Å. The simulations of the constant-height frequency shift AFM images were carried out using the probe particle model from Hapala et al. and taking the DFT calculated molecular structures as input. A CO tip was used with a lateral stiffness of 0.5 N m⁻¹ and an oscillation amplitude of 1 Å.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b01267.

AFM experimental images, DFT calculations on the adsorption geometries and AFM simulation images of the initial, intermediate and final state of TNTP-Ibu on Cu(110). Additional STM overview of the reactions of Ia, Ib, and S on Cu(110), Cu(111), and Au(111), respectively. Calculations on the adsorption energy of Ia and the rotation barrier of the naphthyl groups in solution and on Au(111) and Cu(110). Calculations on the adsorption energy of 3a and 2a-1 on Cu(110). Spin density of the radical cation of precursor 1b. Proposed the reaction processes. Synthesis and characterization of precursors 1b and S. STM dI/dV spectroscopy of the planarized products 3a, 3b, and 6 on Cu(111). Figures S1–S14. Schemes S1 and S2. Tables S1 and S2 (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

*chili@suda.edu.cn

*muellen@mpip-mainz.mpg.de

*narita@mpip-mainz.mpg.de

ORCID

Yunbin Hu: 0000-0001-5346-7059

Dani Ebeling: 0000-0001-8582-170X

Akimitsu Narita: 0000-0002-3625-522X

Klaus Müller: 0000-0001-6630-8786

Lifeng Chi: 0000-0003-3835-2776

Present Address

§Physics Department E20, Technical University of Munich, James-Franck-Straße 1, D-85748 Garching, Germany

**Author Contributions**

Q.Z. and Y.H. contributed equally.

**Notes**

The authors declare no competing financial interest.

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