On-Surface Synthesis of Dibenzohexacenohexacene and Dibenzopentaphenoheptaphene

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Abstract

We report the on-surface synthesis and gas-phase theoretical studies of two novel nanographenes, namely, dibenzohexacenohexacene and dibenzopentaphenoheptaphene, using 8,8'-dibromo-5,5'-bibenzo[*rst*]pentaphene as a precursor. These nanographenes display a combination of armchair and zigzag edges, as shown by noncontact atomic force microscopy (nc-AFM), and their electronic properties are elucidated by density functional theory (DFT) calculations which reveal relatively low HOMO-LUMO energy gaps of about 1.75 eV.

Keywords: Nanographene, Polycyclic Aromatic Hydrocarbon, On-Surface synthesis

1. Introduction

On-surface synthesis has emerged as a powerful method to obtain atomically precise carbon nanostructures, which allows for in-situ visualization by high-resolution scanning probe microscopy (SPM) and characterizations by different surface-sensitive spectroscopy methods, including scanning tunneling spectroscopy and X-ray photoelectron spectroscopy.[1-4] In particular, on-surface synthesis of quasi-zero-dimensional nanographenes (NGs), namely large polycyclic aromatic hydrocarbons (PAHs), and quasi-one-dimensional graphene nanoribbons (GNRs) has attracted attention for their intriguing, structure-dependent electronic and magnetic properties.[5-8] Different NGs and GNRs have thus far been achieved on surface. For example, in 2015, Crommie, Fischer and their colleagues demonstrated the formation of peripentacene through on-surface cyclodehydrogenation of 6,6'-bipentacene as the precursor,[9] and we have described an on-surface synthesis of OBO-doped perihexacene in 2017, which showed unique row-like self-assembly due to hydrogen bonding or coordination with a gold atom.[10] Unsubstituted [3]-[11], [4]-[12], and [5]-triangulenes[13] have more recently been achieved on-surfaces, displaying open-shell biradical character. Moreover, bowtie-shaped PAH consisting of two fused [3]triangulenes was also obtained on surface, exhibiting strong antiferromagnetic character and indicating the

potential of the on-surface synthesis for future molecular spintronics applications.[14] On the other hand, after the first report about the on-surface synthesis of N = 7 armchair GNR (7-AGNRs; N denotes the number of carbon atoms across the GNR width) in 2010[15], GNRs with various structures have been achieved, including AGNRs with different widths (N = 5, 7, 9, 13, 15, and 17 without laterally fusing more than one GNRs)[16-20], chiral GNR[21], chevron-type GNRs[15], zigzag GNRs,[22] and heteroatom-doped GNRs[23, 24].

Nevertheless, the variety of NGs and GNRs available by the on-surface synthesis is still limited. In particular, among the low-bandgap GNRs, the 8-AGNR is predicted to show a very small bandgap (0.57 eV)[25], and is thus promising for electronic device applications. However, its synthesis on surface, apart from local formation via lateral fusion of 3- and 5-AGNRs[26], has remained elusive. To this end, we have designed 8,8'-dibromo-5,5'-bibenzo[*rst*]pentaphene (**4**) as a potential precursor of 8-AGNR (Scheme 1). Although its polymerization toward 8-AGNR did not proceed, thermal on-surface activation of **4** provided novel dibenzohexacenohexacene (**NG-I**) and dibenzopentaphenoheptaphene (**NG-II**) with combinations of zigzag and armchair edges. Here we report the synthesis of precursor **4** and its on-surface planarization to **NG-I** and **NG-II**, which were clearly visualized by noncontact atomic force microscopy (nc-AFM).
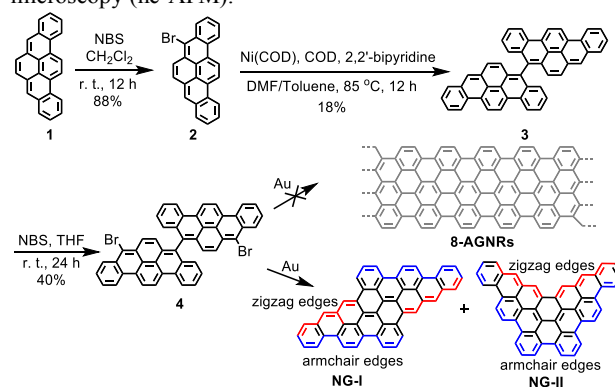
Scheme 1. The synthetic route toward **NG-I** and **NG-II**.

2. Results and Discussion

The synthesis of precursor **4** was started from benzo[*rst*]pentaphene (**1**), which was prepared through the so-called dehydrative π-extension (DPEX) reaction, following the report by Maier, Amsharov, and their colleagues[27]. Then, 5-bromobenzo[*rst*]pentaphene (**2**) was obtained by bromination of

1 in 88% yield using an equivalent amount of *N*-bromosuccinimide (NBS). 5,5'-Bibenzo[*rst*]pentaphene (**3**) was obtained by Yamamoto coupling reaction in 18% yield, where the low yield could be due to the steric effect. Finally, **3** was brominated by NBS to afford **4** in 41% yield. The chemical structure of **4** was validated by ^{1}H NMR and high-resolution matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (see Supporting Information).

Precursor **4** was deposited onto the Au(111) surface held at room temperature (RT) under ultra-high vacuum (UHV) conditions (Figure S6). The surface was subsequently annealed to 180 °C and investigated by means of scanning tunneling microscopy (STM, Figure 1a-c) and nc-AFM with a CO-functionalized tip[28, 29](Figure 1d,e). We expected the debromination and polymerization of **4** after annealing at 180 °C[30]. However, no indication of covalent aryl-aryl coupling between the monomers was found, and we only observed planar molecular species (Figure 1a) with two regular shapes: the majority species **NG-I** with a parallelogram-like shape (~87% of the molecules; Figure 1b,d; see Figure S7 for the statistics) and the minority species **NG-II** with a butterfly-like appearance (~13% of the molecules; Figures 1c,e and S7). The observed disparity between the two NGs can be ascribed to the thermodynamically stable conformation of precursor **4** upon deposition on the Au surface, considering the high sublimation temperature, leading to **NG-I**. The conformational change of **4** to "flip" the benzopentaphene unit can be excluded at room temperature and while annealing to 180 °C. The comparatively low cyclodehydrogenation temperature presumably derives from the strong van der Waals interaction between the benzopentaphene units and the underlying metal surface, which energetically favors a flatter conformation[31], and in turn strains the C-H bonds, lowering the activation barrier toward the C-C bond formation[32].
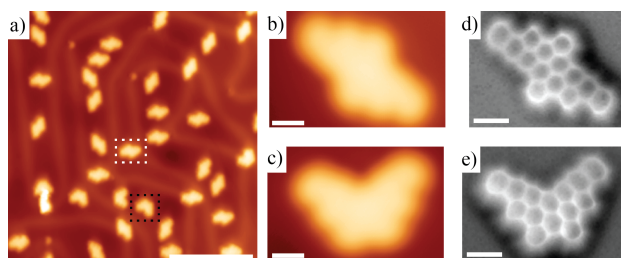

Figure 1. a) STM image of the Au(111) surface with precursor **4** after annealing to 180 °C (I_t = 100 pA, V_b = –1 V). The white box indicates the main product **NG-I** (~87%) and the black box the minor product **NG-II** (~13%). **b,c)** STM images of b) **NG-I** and c) **NG-II** (I_t = 50 pA, V_b = –0.1 V). **d,e)** nc-AFM images of d) **NG-I** and e) **NG-II** acquired with a CO-functionalized tip.(Scale bars: a:10 nm; b-e: 0.5 nm)

Nc-AFM with a CO-functionalized tip allows for exact chemical identification of the obtained products via bond resolved images. The nc-AFM image of **NG-I** (Figure 1d) clearly reveals a structure of benzo[*fg*]benzo[5,6]hexaceno[2,1,16,15,14,13-*stuvwxyza*]hexacene, which is an expected product after the debromination and intramolecular cyclodehydrogenation of precursor **4**. **NG-I** can be thought of as a short segment of an 8-AGNR. On the other hand, the structure of **NG-II** can be elucidated as dibenzo[5,6:7,8]pentapheno[2,1,14,13,12,11-*fghijklmn*]heptaphene from its nc-AFM image (Figure 1e),

which is an isomer of **NG-I**, most probably resulting from the adsorption of **4** on the surface with two different conformations.

Both species have been passivated with hydrogen atoms at the positions originally functionalized with bromo groups, and no coupling product was observed in the STM images. Since the adsorption configuration of **4** leading to **NG-I** should in principle be able to afford intermolecular coupling after the generation of diradical species upon the debromination, we tentatively ascribe the complete absence of such coupling product to steric problems. This might also be related to the fact that the radical sites on the zigzag edges could point towards the metal surface, resulting in a stronger binding and immobilization. In the case of the on-surface synthesis of 7-AGNRs using the dibromobianthracene (DBBA) precursor, the radical sites are kept away from the surface by the twisted adsorption configuration of the molecules, thus preventing such interaction of the radical sites with the surface[15]. Moreover, the π-extended structure of **4** in comparison to DBBA probably also leads to a stronger van der Waals interaction with the surface, which hinders the diradical species from moving to achieve the coupling.
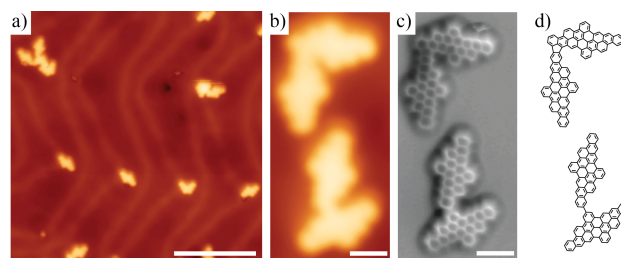

Figure 2. a) STM image of the surface after annealing to 330 °C (I_t = 50 pA, V_b = –0.1 V). **b)** STM image of a pair of fused molecules (I_t = 50 pA, V_b = –0.1 V). **c)** Bond resolved nc-AFM image of the species shown in (b) reveals that the coupling can occur by the formation single C-H bond and by the formation of a 5-membered ring. **d)** The assigned chemical structure of the fused species. (Scale bars: a: 10 nm; b-c: 1 nm)

With the aim of verifying whether further intermolecular reactions could be activated at higher temperatures, we annealed the surface to 330 °C, and found that >50% of the molecules desorbed (Figure 2a). Non-selective activation of the C-H bonds occurred at this temperature on the Au(111) surface, leading to covalently bonded dimers of the NGs (Figure 2b). A nc-AFM image of two representative dimers of **NG-I** revealed distinct types of coupling motifs (Figure 2c,d), featuring the formation of 1) a single C-C bond between the apexes of the two NGs, or 2) two C-C bonds to make a five-membered ring on the zigzag edge of one of the NGs.
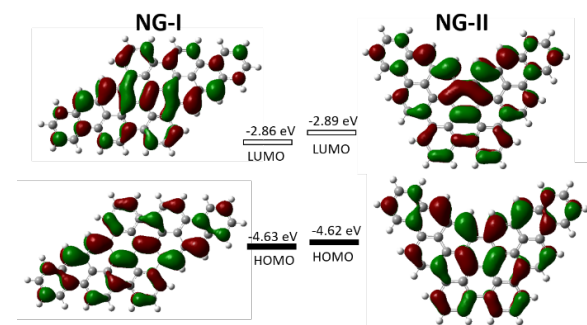

Figure 3. Frontier molecular orbitals and energy diagrams of **NG-I** and **NG-II** calculated by DFT at the B3LYP/6-311G(d,p) level.

To estimate the orbital energies of **NG-I** and **NG-II**, density functional theory (DFT) calculations were performed at the

B3LYP/6-311G(d,p) level of theory (Figure 3). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **NG-I** are found at –4.63 and –2.86 eV, respectively, translating into a HOMO-LUMO energy gap of 1.77 eV. The HOMO and LUMO levels of **NG-II** are comparable to those of **NG-I** with a HOMO-LUMO gap of 1.73 eV. These HOMO-LUMO energy gaps of **NG-I** and **NG-II** are smaller than for example that calculated for dibenzo[*hi,st*]ovalene derivatives (2.1 eV), which exhibited promising optical properties such as strong red fluorescence, stimulated emission, fluorescence blinking suitable for the application in modern super-resolution microscopy techniques[7,33]. These on-surface experimental and theoretical results motivated us to synthesize **NG-I** and **NG-II** also via solution chemistry for further characterizations and applications.

3. Conclusion

In summary, we have investigated the on-surface reactions of 8,8'-dibromo-5,5'-bibenzo[*rst*]pentaphene (**4**) as a possible precursor for 8-AGNRs, and demonstrated the formation of parallelogram-shaped dibenzohexacenohexacene (**NG-I**) and butterfly-shaped dibenzopentaphenoheptaphene (**NG-II**), representing novel NGs with combinations of armchair and zigzag edges. Their structures were unambiguously revealed by STM and nc-AFM. DFT calculations revealed HOMO-LUMO energy gaps of approximately 1.77 and 1.73 eV, respectively, suggesting potential interest of such NGs for applications as optoelectronic materials, for example with near-infrared emission. Solution synthesis of these NGs is ongoing in our laboratory in addition to further attempts to develop suitable molecular precursors for the on-surface synthesis of 8-AGNRs.

References

1 S. Clair, D. G. de Oteyza, *Chem. Rev.* **2019**, *119*, 4717.

2 X. C. Li, H. M. Zhang, L. F. Chi, *Adv. Mater.* **2019**, *31*, 1804087.

3 Q. Shen, H. Y. Gao, H. Fuchs, *Nano Today* **2017**, *13*, 77.

4 L. Gross, B. Schuler, N. Pavlicek, S. Fatayer, Z. Majzik, N. Moll, D. Pena, G. Meyer, *Angew. Chem. Int. Ed.* **2018**, *57*, 3888.

5 Z. P. Chen, A. Narita, K. Müllen, *Adv. Mater.* **2020**, *32*, 2001893.

6 J. Z. Liu, X. L. Feng, *Angew. Chem. Int. Ed.* **2020**, *59*, 2.

7 X. S. Xu, K. Müllen, A. Narita, *Bull. Chem. Soc. Jpn.* **2020**, *93*, 490.

8 Y. Yano, N. Mitoma, H. Ito, K. Itami, *J. Org. Chem.* **2020**, *85*, 4.

9 C. Rogers, C. Chen, Z. Pedramrazi, A. A. Omrani, H. Z. Tsai, H. S. Jung, S. Lin, M. F. Crommie, F. R. Fischer, *Angew. Chem. Int. Ed.* **2015**, *54*, 15143.

10 X. Y. Wang, T. Dienel, M. Di Giovannantonio, G. B. Barin, N. Kharche, O. Deniz, J. I. Urgel, R. Widmer, S. Stolz, L. H. De Lima, M. Muntwiler, M. Tommasini, V. Meunier, P. Ruffieux, X. Feng, R. Fasel, K. Müllen, A. Narita, *J. Am. Chem. Soc.* **2017**, *139*, 4671.

11 N. Pavlicek, A. Mistry, Z. Majzik, N. Moll, G. Meyer, D. J. Fox, L. Gross, *Nat. Nanotechnol.* **2017**, *12*, 308.

12 S. Mishra, D. Beyer, K. Eimre, J. Z. Liu, R. Berger, O. Groning, C. A. Pignedoli, K. Müllen, R. Fasel, X. L. Feng, P. Ruffieux, *J. Am. Chem. Soc.* **2019**, *141*, 10621.

13 J. Su, M. Telychko, P. Hu, G. Macam, P. Mutombo, H. J. Zhang, Y. Bao, F. Cheng, Z. Q. Huang, Z. Z. Qiu, S. J. R. Tan, H. Lin, P. Jelinek, F. C. Chuang, J. S. Wu, J. Lu, *Sci. Adv.* **2019**, *5*, eaav7717.

14 S. Mishra, D. Beyer, K. Eimre, S. Kezilebieke, R. Berger, O. Gröning, C. A. Pignedoli, K. Müllen, P. Liljeroth, P. Ruffieux, X. L. Feng, R. Fasel, *Nat. Nanotechnol.* **2020**, *15*, 22.

15 J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, *Nature* **2010**, *466*, 470.

16 L. Talirz, H. Söde, T. Dumslaff, S. Wang, J. R. Sanchez-Valencia, J. Liu, P. Shinde, C. A. Pignedoli, L. Liang, V. Meunier, N. C. Plumb, M. Shi, X. Feng, A. Narita, K. Müllen, R. Fasel, P. Ruffieux, *ACS Nano* **2017**, *11*, 1380.

17 Y. C. Chen, D. G. de Oteyza, Z. Pedramrazi, C. Chen, F. R. Fischer, M. F. Crommie, *ACS Nano* **2013**, *7*, 6123.

18 A. Kimouche, M. M. Ervasti, R. Drost, S. Halonen, A. Harju, P. M. Joensuu, J. Sainio, P. Liljeroth, *Nat. Commun.* **2015**, *6*, 10177.

19 N. Abdurakhmanova, N. Amsharov, S. Stepanow, M. Jansen, K. Kern, K. Amsharov, *Carbon* **2014**, *77*, 1187.

20 J. Yamaguchi, H. Hayashi, H. Jippo, A. Shiotari, M. Ohtomo, M. Sakakura, N. Hieda, N. Aratani, M. Ohfuchi, Y. Sugimoto, H. Yamada, S. Sato, *Comms. Mater.* **2020**, *1*, 36.

21 P. Han, K. Akagi, F. Federici Canova, H. Mutoh, S. Shiraki, K. Iwaya, P. S. Weiss, N. Asao, T. Hitosugi, *ACS Nano* **2014**, *8*, 9181.

22 P. Ruffieux, S. Wang, B. Yang, C. Sánchez Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, R. Fasel, *Nature* **2016**, *531*, 489.

23 C. Bronner, S. Stremlau, M. Gille, F. Brauße, A. Haase, S. Hecht, P. Tegeder, *Angew. Chem. Int. Ed.* **2013**, *52*, 4422.

24 X. Y. Wang, X. Yao, A. Narita, K. Müllen, *Acc. Chem. Res.* **2019**, *52*, 2491.

25 D. Prezzi, D. Varsano, A. Ruini, A. Marini, E. Molinari, *Phys. Rev. B* **2008**, *77*, 041404.

26 K. W. Sun, P. H. Ji, J. J. Zhang, J. X. Wang, X. C. Li, X. Xu, H. M. Zhang, L. F. Chi, *Small* **2019**, *15*, 1804526.

27 D. Lungerich, O. Papaianina, M. Feofanov, J. Liu, M. Devarajulu, S. I. Troyanov, S. Maier, K. Amsharov, *Nat. Commun.* **2018**, *9*, 4756.

28 L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **2009**, *325*, 1110.

29 L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitian, D. Pena, A. Gourdon, G. Meyer, *Science* **2012**, *337*, 1326.

30 M. Di Giovannantonio, O. Deniz, J. I. Urgel, R. Widmer, T. Dienel, S. Stolz, C. Sánchez Sánchez, M. Muntwiler, T. Dumslaff, R. Berger, A. Narita, X. Feng, K. Müllen, P. Ruffieux, R. Fasel, *ACS Nano* **2018**, *12*, 74.

31 J. Bjork, S. Stafstrom, F. Hanke, *J. Am. Chem. Soc.* **2011**, *133*, 14884.

32 S. Blankenburg, J. Cai, P. Ruffieux, R. Jaafar, D. Passerone, X. Feng, K. Müllen, R. Fasel, C. A. Pignedoli, *ACS Nano* **2012**, *6*, 2020.

33 G. M. Paternò, Q. Chen, X.-Y. Wang, J. Liu, S. G. Motti, A. Petrozza, X. Feng, G. Lanzani, K. Müllen, A. Narita, F. Scotognella, *Angew. Chem. Int. Ed.* **2017**, *56*, 6753.

Graphical Abstract

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Parallelogram-shaped dibenzohexacenohexacene and butterfly-shaped dibenzopentaphenoheptaphene with combinations of armchair and zigzag edges were prepared via on-surface synthesis, and their structures were unambiguously revealed by STM and nc-AFM. DFT calculations further elucidated their relatively low HOMO-LUMO energy gaps.