RZ 3943 (# ZUR1806-048) 15/06/2018
Physical Sciences 5 pages

Research Report

[19]Dendriphene: a 19-Ring Dendritic Nanographene

Manuel Vilas-Varela*, Shadi Fatayer**, Zsolt Majzik**, Dolores Pérez*, Enrique Guitián*, Leo Gross**, Diego Peña*

* Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Spain

**IBM Research-Zurich, Rüschlikon 8803, Switzerland

Research
Africa • Almaden • Austin • Australia • Brazil • China • Haifa • India • Ireland • Tokyo • Watson • Zurich

[19]Dendriphene: a 19-Ring Dendritic Nanographene**

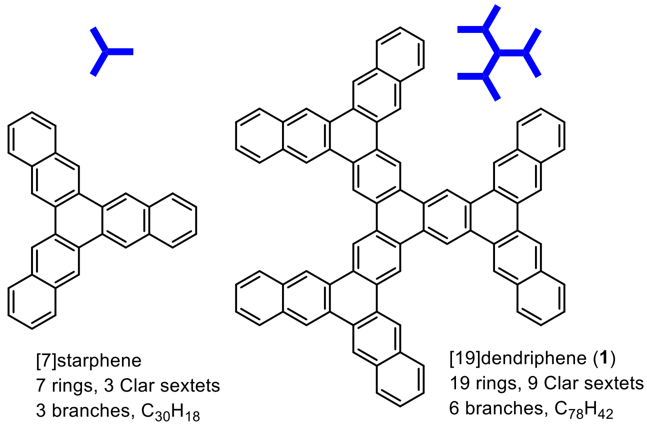
*Manuel Vilas-Varela, Shadi Fatayer, Zsolt Majzik, Dolores Pérez, Enrique Guitián, Leo Gross, Diego Peña**

Dedicated to Professor Luis Castedo on the occasion of his 80th birthday

***Abstract**: The synthesis of a threefold symmetric nanographene with 19 cata-fused benzene rings distributed within six branches is reported. This flat dendritic starphene, which is the largest unsubstituted cata-condensed PAH that has been obtained to date, was prepared in solution by means of a palladium-catalyzed aryne cyclotrimerization reaction and it was characterized on surface by scanning probe microscopy with atomic resolution.*

In 1968, Erich Clar, the admired pioneer in the field of polycyclic aromatic hydrocarbons (PAHs), introduced the term starphene to refer to benzologues of triphenylene in which three branches are annellated to a central ring and radiate outwards in a linear manner (e.g. [7]starphene, Figure 1).[1] Besides their appealing three-fold symmetric structure, starphenes have recently attracted interest in surface science as molecular logic gates and as planar reaction partners to study the reactivity of surface dangling bonds.[2] This interest has encouraged the development of synthetic methods to obtain new starphenes, in particular, nanosized derivatives.[3] However, the extremely low solubility of large planar aromatic hydrocarbons makes it difficult to characterize and manipulate these compounds. To some extent this problem can be solved by introducing substituents in the periphery of the molecule, as demonstrated in the synthesis of an alkyne-substituted [16]starphene.[4] But since these substituents can have a detrimental effect on the molecule-surface interaction, the preparation of unsubstituted *cata*-condensed PAHs such as starphenes is a highly desired but challenging goal. An interesting alternative is the on-surface generation of these large molecules from smaller precursors, as shown recently with the preparation of [13]starphene[5a] and [13]cloverphene.[5b-d] Recently, on-surface synthesis has also allowed the preparation of highly reactive linear *cata*-condensed PAHs such as [10] [6a] and [11]acene.[6b-c] Notably, the largest unsubstituted *cata*-condensed PAHs that had been obtained by solution chemistry prior to this work were two helicene-based molecules formed by the fusion of 16 benzene rings.[7]

Herein we report the synthesis and characterization of nanographene **1** (Figure 1), a 2D dendritic starphene formed by 19 *cata*-condensed benzene rings which are distributed within six branches.[8] Compound **1** is formed by the fusion of three [7]starphene moieties sharing one central benzene ring. We anticipated a reasonable stability for this molecule, since it is possible to identify nine Clar sextets in its structure. Based on its dendrimer-like structure we propose the trivial name dendriphene to refer to this novel PAH and its analogues. [19]Dendriphene (**1**) is the largest unsubstituted *cata*-condensed PAH which has been obtained to date by solution chemistry.



[7]starphene
7 rings, 3 Clar sextets
3 branches, $C_{30}H_{18}$

[19]dendriphene (**1**)
19 rings, 9 Clar sextets
6 branches, $C_{78}H_{42}$

Figure 1. Structure of [7]starphene and [19]dendriphene (**1**).

Twenty years ago, some of us introduced the palladium-catalyzed cyclotrimerization of arynes as an efficient synthetic procedure to obtain triphenylene derivatives.[9a] For years, this method allowed the preparation of large three fold-symmetric PAHs such as starphenes and cloverphenes.[5d,7c,9b,10] When exploring the limits of this methodology as a bottom-up approach to obtain nanographenes by solution chemistry we encountered serious limitations to characterize the corresponding products. In particular, the extreme insolubility precluded the analysis of the obtained solids by conventional techniques such as NMR spectroscopy. However, the introduction of non-contact atomic force microscopy with functionalized tips allows the identification of flat and insoluble graphene molecules.[11] With this unique characterization tool in hands we decided to attempt the synthesis of [19]dendriphene (**1**) by means of Pd-catalyzed cyclotrimerization of aryne **2**, generated by fluoride-induced decomposition of triflate **3** (Scheme 1).

---

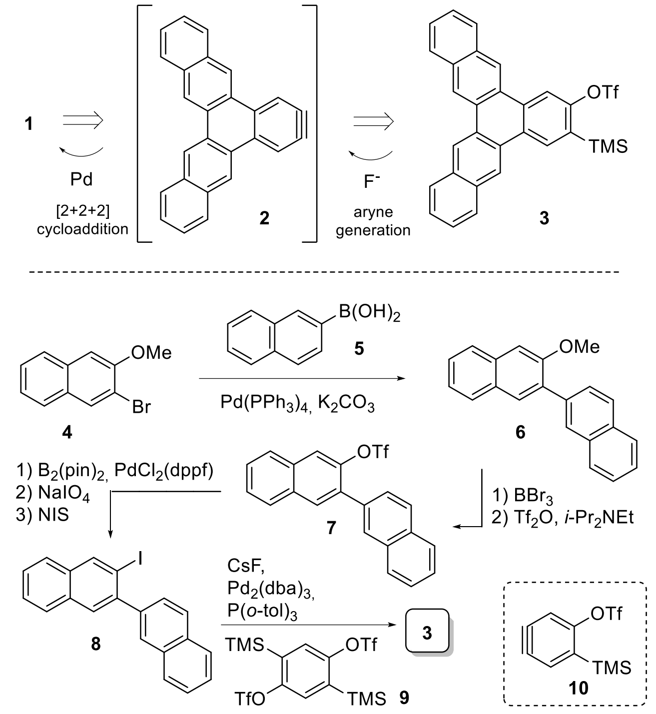
[*] M. Vilas-Varela, Prof. Dr. D. Pérez, Prof. Dr. E. Guitián, Prof. Dr. D. Peña
Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela
15782-Santiago de Compostela, Spain
Fax: (+34) 981591014
E-mail: diego.pena@usc.es

S. Fatayer, Dr. Z. Majzik, Dr. L. Gross
IBM Research - Zurich
CH-8803 Rüschlikon, Switzerland

[**] We thank Gerhard Meyer for discussions and support in the STM/AFM experiments. We thank the European Union (Project PAMS, contract no. 610446), Agencia Estatal de Investigación (MAT2016-78293-C6-3-R and CTQ2016-78157-R), Xunta de Galicia (Centro singular de investigación de Galicia, accreditation 2016-2019, ED431G/09), Fondo Europeo de Desarrollo Regional (FEDER) and the European Research Council consolidator grant AMSEL for financial support.

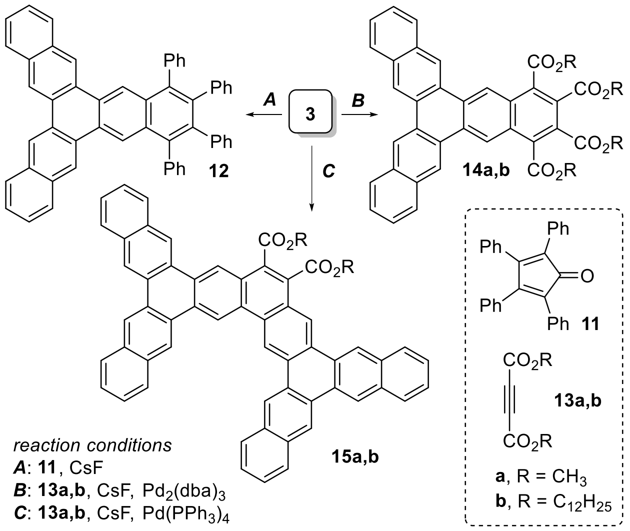
Supporting information for this article is available on the WWW

Aryne **2** is a didehydrogenated derivative of benzo[*h*]pentaphene or [6]starphene(2.2.1). The preparation of starphyne precursor **3** was performed in seven steps from 2-bromo-3-methoxynaphthalene (**4**). First, a Pd-catalyzed Suzuki-Miyaura coupling between compound **4** and boronic acid **5** led to the isolation of methoxybinaphthalene **6** in 96% yield. Then, BBr_3-promoted demethylation followed by triflation with Tf_2O afforded compound **7** in 75% yield. Triflate **7** was transformed in the corresponding boronic ester which was then converted to iodobinaphthalene **8** in 74% yield, by sequential treatment with $NaIO_4$[12] and N-iodosuccinimide (NIS). Finally, substituted [6]starphene **3** was obtained by reaction of compound **8** with bistriflate **9**, by means of Pd-catalyzed annulation of aryne **10** with iodobinaphthalene **8** in 19% yield.[13] Presumably, this low yield is associated with the difficulties involved in the selective generation of monoaryne **10** in the reaction mixture.



Scheme 1. Retrosynthesis of [19]dendriphene (**1**) and synthesis of precursor **3**.

Then, we decided to explore the ability of triflate **3** to generate aryne **2** and to access diverse starphene derivatives (Scheme 2). Treatment of triflate **3** with CsF in the presence of dienone **11** led to the synthesis of tetraphenyl[7]starphene **12** in 52% yield. This compound is formed by an aryne [4+2] cycloaddition followed by *in situ* CO extrusion. To further explore the utility of aryne **2**, we studied its palladium-catalyzed cocyclotrimerization with dimethyl acetylenedicarboxylate (**13a**).[9b] Treatment of triflate **3** with CsF in the presence of **13a** and 5 mol% of $Pd_2(dba)_3$ led to the isolation of compound **14a** in 54% yield, resulting from the [2+2+2] cocycloaddition of one aryne **2** with two alkynes **13a**. Similar reaction but using alkyne **13b** bearing dodecyl alkyl chains afforded starphene **14b** in 36% yield. Alternatively, treatment of triflate **3** with CsF in the presence of **13a-b** and 10 mol% of $Pd(PPh_3)_4$ led to the isolation of starphene derivatives **15a-b** in 33% and 50% yield, respectively. These molecules, resulting from the reaction of two arynes with one alkyne, are formed by the fusion of two [7]starphene moieties sharing one central benzene ring, in such manner that the 13 *cata*-condensed benzene rings are distributed within four branches. Notably, while compound **15a** proved to be highly insoluble in most organic solvents, starphene **15b** was soluble enough to allow its spectroscopic characterization.[14]



Scheme 2. Synthesis of substituted [7]starphene derivatives.

Once demonstrated the utility of triflate **3** to access large starphene derivatives, we decided to attempt the synthesis of [19]dendriphene (**1**). Triflate **3** was treated with CsF in the presence of catalytic amounts of $Pd_2(dba)_3$ in MeCN/THF at 60 ºC for 16 h. The resulting solid was filtered off and thoroughly washed with H_2O, MeOH, Et_2O, $CHCl_3$, 1,1,2,2-tetrachloroethane and *ortho*-dichlorobenzene to afford an extremely insoluble black solid. The MALDI mass spectrum showed a peak at *m/z* 978.3 which is consistent with the composition of dendriphene **1** ($C_{78}H_{42}$). However, the high insolubility of the solid precluded the use of NMR spectroscopy for structure elucidation. Therefore, we decided to characterize compound **1** with a combined scanning tunneling microscope/atomic force microscope (STM/AFM).[11c]

The washed solid obtained in the cyclotrimerization reaction was sublimated from a Si wafer [15] to a two monolayer (ML) NaCl film grown on the Cu(111) substrate.[16] The sample was held at 10 K during deposition. CO molecules were adsorbed to the surface to allow for the establishment of CO functionalized tips.[17,18] All surveyed molecules in the surface presented the 3-fold symmetry of the structure of [19]dendriphene (**1**, Figure 1). Detailed inspection of the molecules by constant-height AFM with a CO-functionalized tip[18,19] allowed the definitive confirmation of the molecular structure of compound **1** (Figure 2).[20]

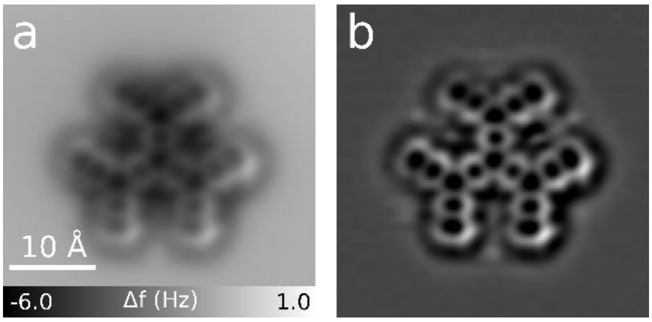


Figure 2. Atomic force microscopy characterization of dendriphene **1** on NaCl (2ML)/Cu(111). a) Constant-height AFM image with a CO functionalized tip (Sample voltage V = 0 V and z_{offset} = -0.4 Å from tunnelling conditions, V = 0.2 V

and tunneling current I = 1 pA). b) Laplace-filtered version of b) to highlight the structure of the molecule.

The electronic characterization of dendriphene **1** by STM is exemplified with images of the molecule in the middle of the gap (Figure 3a) as well as at the positive and negative ion resonances,[21] shown in Figures 3b and 3d, respectively. These images correspond to the orbital density at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. The calculated squared orbital density for the HOMO and the LUMO of compound **1** (Figure 3c and 3e, respectively) agrees with the STM measurements.[20]

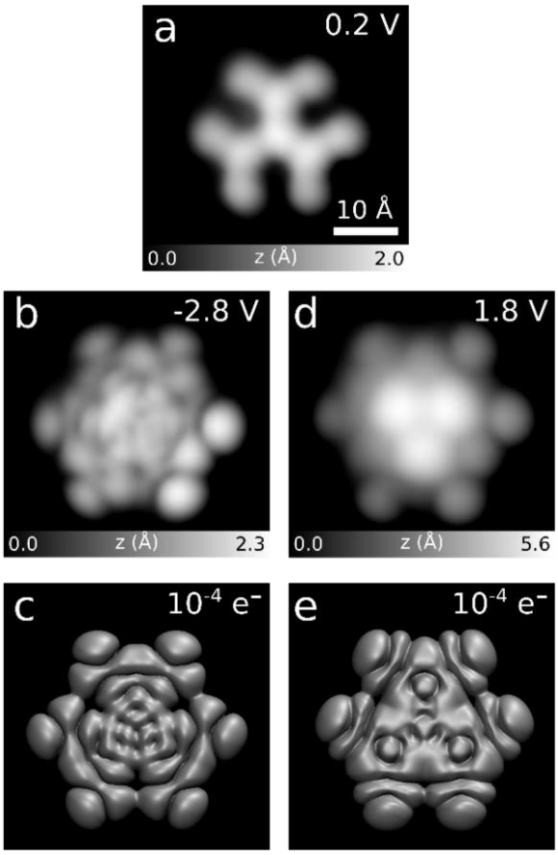


Figure 3. Scanning tunneling microscopy characterization of dendriphene **1** on NaCl (2ML)/Cu(111). a) STM image of **1** in the HOMO-LUMO gap (Sample voltage V = 0.2 V, tunneling current I = 1 pA). b) STM image of **1** at the positive ion resonance (V = -2.8 V, I = 1 pA). c) DFT calculated HOMO orbital of **1**. d) STM image of **1** at the negative ion resonance (V = 1.8 V, I = 1 pA). e) DFT calculated LUMO orbital of **1**.

As expected based on the presence of 9 Clar sextets in the structure of nanographene **1**, the differential conductance spectroscopy showed a substantial transport gap of approximately 4.1 eV,[14] which is considerably larger than those reported for other families of *cata*-fused PAHs such as acenes, which present one single Clar sextet (e.g. 1.17 eV for decacene on Au(111)).[6a] It should be mentioned that DFT calculations of dendriphene **1**, at the B3LYP/6-31G* level, estimated a HOMO-LUMO gap of 3.5 eV.

The next generation of this family of starphene-based dendrimers is [43]dendriphene, a non-planar *cata*-condensed PAH with molecular formula $C_{174}H_{90}$ (Figure 4). Although the preparation of such a huge PAH would be extremely demanding, we consider that the structural attractiveness of [43]dendriphene may someday motivate its challenging synthesis.

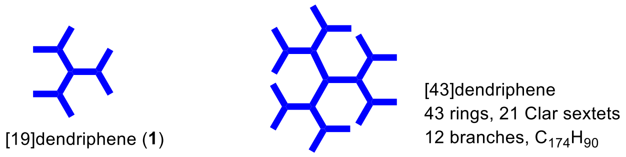


Figure 4. Comparison of two generations of starphene-based dendrimers.

In conclusion, we have obtained the largest unsubstituted *cata*-condensed PAH which has been synthesized to date: [19]dendriphene (**1**). This three-fold symmetric starphene-based 2D dendrimer is formed by 19 *cata*-condensed benzene rings which are distributed within six branches. This flat geometry could be particularly useful to use this compound as single molecular nanojunction with six contacts. We have unambiguously characterized nanographene **1** with submolecular resolution by STM/AFM, allowing the visualization of HOMO and LUMO molecular orbitals. Additionally, the synthetic procedure to obtain dendriphene **1**, which is based on a Pd-catalyzed aryne cyclotrimerization, provides access to different large starphene derivatives with interesting structures.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: arynes • nanographenes • scanning probe microscopy • starphenes • dendrimers

---

[1] E. Clar, A. Mullen, *Tetrahedron* **1968**, *24*, 6719-6724.

[2] a) W.-H. Soe, C. Manzano, N. Renaud, P. de Mendoza, A. De Sarkar, F. Ample, M. Hliwa, A. M. Echavarren, N. Chandrasekhar, C. Joachim, *ACS Nano* **2011**, *5*, 1436-1440; b) S. Godlewski, M. Kolmer, H. Kawai, B. Such, R. Zuzak, M. Saeys, P. de Mendoza, A. M. Echavarren, C. Joachim, M. Szymonski, *ACS Nano* **2013**, *7*, 10105-10111; c) S. Godlewski, H. Kawai, M. Kolmer, R. Zuzak, A. M. Echavarren, C. Joachim, M. Szymonski, M. Saeys, *ACS Nano* **2016**, *10*, 8499-8507.

[3] For a recent synthesis of [10]starphene, see: O. Guillermet, S. Gauthier, C. Joachim, P. de Mendoza, T. Lauterbach, A. Echavarren, *Chem. Phys. Lett.* **2011**, *511*, 482-485.

[4] E. C. Rüdiger, M. Porz, M. Schaffroth, F. Rominger, U. H. F. Bunz, *Chem. Eur. J.* **2014**, *20*, 12725-12728.

[5] a) C. Sánchez-Sánchez, A. Nicolaï, F. Rossel, J. Cai, J. Liu, X. Feng, K. Müllen, P. Ruffieux, R. Fasel, V. Meunier, *J. Am. Chem. Soc.* **2017**, *139*, 17617-17623; b) Q. Fan, S. Werner, J. Tschakert, D. Ebeling, A. Schirmeisen, G. Hilt, W. Hieringer, J. M. Gottfried, *J. Am. Chem. Soc.* **2018**, *140*, 7526-7532. For the preparation of [13]cloverphenes by solution chemistry, see: c) T. Yatabe, M. A. Harbison, J. D. Brand, M. Wagner, K. Müllen, P. Samori, J. P. Rabe, *J. Mater. Chem.* **2000**, *10*, 1519-1525; d) C. Romero, D. Peña, D. Pérez, E. Guitián, *Chem. Eur. J.* **2006**, *12*, 5677-5684.

[6] a) J. Krüger, F. García, F. Eisenhut, D. Skidin, J. M. Alonso, E. Guitián, D. Pérez, G. Cuniberti, F. Moresco, D. Peña, *Angew. Chem. Int. Ed.* **2017**, *56*, 11945-11948; b) R. Zuzak, R. Dorel, M. Kolmer, M. Szymonski, S. Godlewski, A. M. Echavarren *Angew. Chem. Int. Ed.* **2018**, *57*, 10500-10505; c) For the recent generation of [11]acene on a polymer matrix, see: B. Shen, J. Tatchen, E. Sánchez-García, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2018**, *57*,10506-10509.

[7] a) K. Mori, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2015**, *54*, 6847-6851; b) V. Berezhnaia, M. Roy, N. Vanthuyne, M. Villa, J.-V. Naubron, J. Rodriguez, Y. Coquerel, M. Gingras, *J. Am. Chem. Soc.* **2017**, *139*, 18508-18511; c) T. Hosokawa, Y. Takahashi, T. Matsushima, S. Watanabe, S. Kikkawa, I. Azumaya, A. Tsurusaki, K. Kamikawa, *J. Am. Chem. Soc.* **2017**, *139*, 18512-18521.

[8] a) Hexabenzotriphenylene or [10]cloverphene can also be considered as a dendritic PAH, in this case derived from triphenylene, as proposed in: L. Barnett, D. M. Ho, K. K. Baldridge, R. A. Pascal Jr.,

J. Am. Chem. Soc. **1999**, *121*, 727-733. b) For a review on selected applications of dendritic structures, see: D. Astruc, E. Boisselier, C. Ornelas, *Chem. Rev.* **2010**, *110*, 1857-1959.

[9] a) D. Peña, S. Escudero, D. Pérez, E. Guitián, L. Castedo, *Angew. Chem. Int. Ed.* **1998**, *37*, 2659-2661; b) D. Peña, D. Pérez, E. Guitián, *Chem. Rec.* **2007**, *7*, 326-333.

[10] See for example: a) P. T. Lynett, K. E. Maly, *Org. Lett.* **2009**, *11*, 3726-3729; b) J. M. Alonso, A. E. Díaz-Álvarez, A. Criado, D. Pérez, D. Peña, E. Guitián, *Angew. Chem. Int. Ed.* **2012**, *51*, 173-177; c) B. Schuler, S. Collazos, L. Gross, G. Meyer, D. Pérez, E. Guitián, D. Peña, *Angew. Chem. Int. Ed.* **2014**, *53*, 9004-9006.

[11] See for example: a) L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Peña, A. Gourdon, G. Meyer, *Science* **2012**, *337*, 1326-1329; b) D. G. de Oteyza, P. Gorman, Y.-C. Chen, S. Wickenburg, A. Riss, D. J. Mowbray, G. Etkin, Z. Pedramrazi, H.-Z. Tsai, A. Rubio, M. F. Crommie, F. R. Fischer, *Science* **2013**, *340*, 1434-1437; c) 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*, 15143-15146; d) S. Kawai, V. Haapasilta, B. D. Lindner, K. Tahara, P. Spijker, J. A. Buitendijk, R. Pawlak, T. Meier, Y. Tobe, A. S. Foster, E. Meyer, *Nat. Commun.* **2016**, *7*, 12711; e) O. Stetsovych, M. Svec, J. Vacek, J. V. Chocholousova, A. Jančarik, J. Rybáček, K. Kosmider, I. G. Stará, P. Jelínek, I. Starý *Nat. Chem.* **2017**, *9*, 213-218. f) P. H. Jacobse, A. van den Hoogenband, M.-E. Moret, R. J. M. K. Gebbink, I. Swart, *Angew. Chem. Int. Ed.* **2016**, *55*, 13052-13055; g) H. Mönig, D. R. Hermoso, O. D. Arado, M. Todorovic, A. Timmer, S. Scüer, G. Langewisch, R. Pérez, H. Fuchs, *ACS Nano* **2016**, *10*, 1201-1209. For a recent review, see: h) L. Gross, B. Schuler, N. Pavliček, Z. Majzik, N. Moll, D. Peña, G. Meyer, *Angew. Chem. Int. Ed.* **2018**, *57*, 3888-3908.

[12] J. M. Murphy, C. C. Tzschucke, J. F. Hartwig, *Org. Lett.* **2007**, *9*, 757-760.

[13] Z. Liu, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2005**, *127*, 15716-15717.

[14] See the Supporting Information for details

[15] B. Schuler, G. Meyer, D. Peña, O. C. Mullins, L. Gross, *J. Am. Chem. Soc.* **2015**, *137*, 9870–9876.

[16] R. Bennewitz, V. Barwich, M. Bammerlin, C. Loppacher, M. Guggisberg, A. Baratoff, E. Meyer, H.-J. Güntherodt, *Surf. Sci.* **1999**, *438*, 289–296.

[17] L. Bartels, G. Meyer, K.-H. Rieder, *Appl. Phys. Lett.* **1997**, *71*, 213–215.

[18] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **2009**, *325*, 1110–1114.

[19] L. Gross, F. Mohn, N. Moll, G. Meyer, R. Ebel, W. M. Abdel-Mageed, M. Jaspars, *Nat. Chem* **2010**, *2*, 821–825.

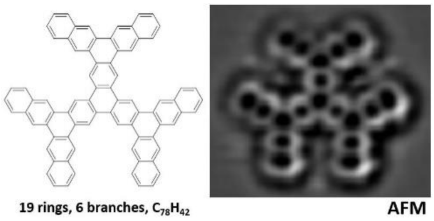
[20] For AFM images at different heights and a comparison with the simulated AFM image, see the Supporting Information.

[21] J. Repp, G. Meyer, S. M. Stojković, A. Gourdon, C. Joachim, *Phys. Rev. Lett.* **2005**, *94*, 026803.

Nanographenes

M. Vilas-Varela, S. Fatayer, Z. Majzik,
D. Pérez, E. Guitián, L. Gross, D. Peña*
_______ **Page – Page**

[19]Dendriphene: a 19-Ring Dendritic Nanographene



The successful synthesis of a dendritic nanographene is reported. [19]Dendriphene, which is the largest unsubstituted *cata*-condensed nanographene obtained by solution chemistry, was characterized on-surface by scanning probe microscopy.