Nanographenes

DOI: 10.1002/ange.201403707

From Perylene to a 22-Ring Aromatic Hydrocarbon in One-Pot**

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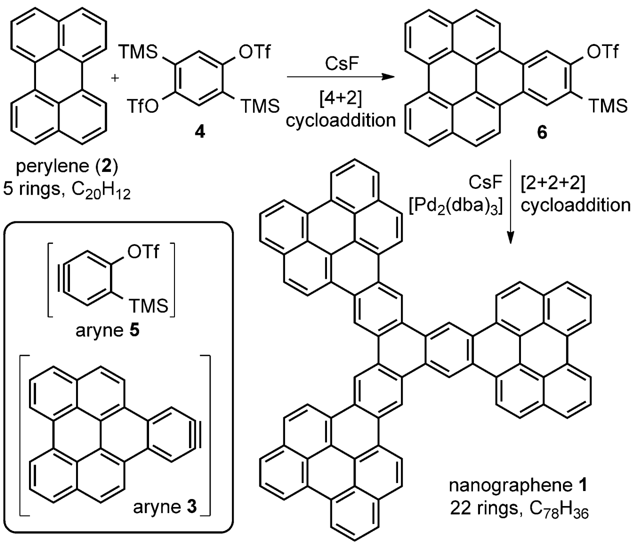
In memory of Juan Fernández Salgado

***Abstract:** The successful synthesis of a threefold symmetric $C_{78}H_{36}$ molecule with 22 fused benzene rings is reported. This clover-shaped nanographene was characterized on an ultrathin insulating film with atomic resolution by scanning probe microscopy.*

One of the biggest challenges in graphene science is the development of efficient methodologies for the preparation of this material with defined size, shape, and quality.[1] In this respect, organic chemistry methodologies in solution can be especially useful to obtain graphene molecules.[2] However, a number of drawbacks of these methodologies have been identified: 1) The extremely low solubility of planar aromatic molecules makes it difficult to characterize and manipulate these materials. 2) The lack of volatility due to the large size hampers the integration of molecules into devices. 3) The number of reactions that are suitable to obtain graphene molecules is very small and this limits the edges and shapes that can be achieved. Herein we report attempts to overcome these drawbacks by introducing the nanographene **1** (Scheme 1), a large polycyclic aromatic hydrocarbon (PAH) with 22 fused benzene rings, which was prepared in solution, isolated, sublimated, and characterized on a surface.

Arynes are privileged building blocks for the preparation of graphene molecules.[3] In 2012, we reported on the synthesis of a hexaphenyl-substituted threefold symmetric PAH with 16 fused benzene rings by palladium-catalyzed cyclotrimerization of an aryne.[4] Based on this result we decided to attempt the synthesis of nanographene **1** by means of cyclotrimerization of polycyclic aryne **3**. The absence of susbstituents attached to the aromatic core of compound **1** led us to anticipate severe difficulties in manipulating and characterizing this large molecule. However, if this synthetic route was found to be viable, it would provide access to a compound in which all of the 76 sp^2 carbon atoms of the molecule are part of a flat aromatic core, a situation similar to that in graphene itself.



Scheme 1. Synthesis of cyclotrimer **1**.

Recently, Fort and Scott reported the Diels–Alder cycloaddition of benzyne to the bay region of perylene to give naphthoperylene.[5] Inspired by this result, we decided to study the reaction of perylene (**2**) with bisbenzyne precursor **4**, a molecule that was previously employed by Wudl and coworkers to obtain large acenes by double aryne cycloaddition.[6] Remarkably, a judicious choice of the temperature and solvent mixture allowed us to control the solubility of the fluoride salt to generate aryne **5**, but at the same time to cause the precipitation of triflate **6** (49% yield) from the reaction mixture and thus to avoid the subsequent generation of aryne **3**. At that point, we decided to attempt the palladium-catalyzed [2+2+2] cycloaddition of aryne **3**. Triflate **6** was treated with CsF in the presence of catalytic amounts of $[Pd_2(dba)_3]$ (dba = dibenzylidene acetone) in MeCN/THF at 60 °C for 16 h. The resulting solid was filtered off and washed under sonication to afford a highly insoluble grayish solid. The MALDI mass spectrum showed a molecular ion with a mass of m/z 972.2 and the isotopic distribution was consistent with the composition of cyclotrimer **1** ($C_{78}H_{36}$,

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[**] We thank the European Union (Project PAMS, contract no. 610446), the Spanish Ministry of Economy and Competitiveness (MINECO, CTQ2010-18208), Xunta de Galicia (10PXIB2200222PR), Fondo Europeo de Desarrollo Regional (FEDER), and the European Research Council advanced grant CEMAS for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201403707.

46% yield). It is notable that this molecule can be obtained in a straightforward manner from both commercially available perylene (**2**) and bisbenzyne precursor **4** in one pot without the need to isolate aryne precursor **6**.

The extreme insolubility of this solid precluded characterization by conventional methods such as NMR spectroscopy. Encouraged by the recent advances in non-contact atomic force microscopy (NC-AFM),[7] we attempted the confirmation of the molecular structure of trimer **1** by this technique. Compound **1** was sublimated by rapid heating[8] from a Si wafer onto the sample held at $T = 10$ K. The sample employed was Cu(111) with islands of bilayer NaCl, denoted as NaCl(2ML)/Cu(111) (ML = monolayer). CO and Xe were also adsorbed to functionalize the tip[9] and scanning tunneling microscopy (STM) and AFM were employed to characterize the adsorbents. Most adsorbents we assigned to fragments of compound **1**, which one would expect to decompose when heated to its sublimation temperature due to its large size. However, evidence for some cloverleaf shaped molecules was found and detailed inspection by AFM with a CO-functionalized tip confirmed the presence of nanographene **1** (Figure 1a,b). STM (Figure 2a,b) was also carried out in order to obtain molecular orbital images[10] and CO tips were again employed to increase resolution.[11] The measured image of the negative ion resonance (Figure 2b) corresponds to the lowest unoccupied molecular orbital (LUMO) of compound **1** as seen by comparison with the calculation of its orbital density squared (Figure 2c), thus confirming the presence of intact trimer **1**. DFT calculations at the B3LYP/6-31G (d) level estimated the energy of the HOMO–LUMO energy gap to be 2.95 eV ($E_{\mathrm{HOMO}} = -5.01$ eV, $E_{\mathrm{LUMO}} = -2.06$ eV) and this is in good agreement with the values corresponding to nanographenes of the same size.[2d,12] The UV/Vis spectrum of compound **1** exhibited long absorption bands at 424, 456 and 485 nm. The emission spectrum under excitation at 355 nm showed fluorescence bands at 490 and 522 nm.[13]

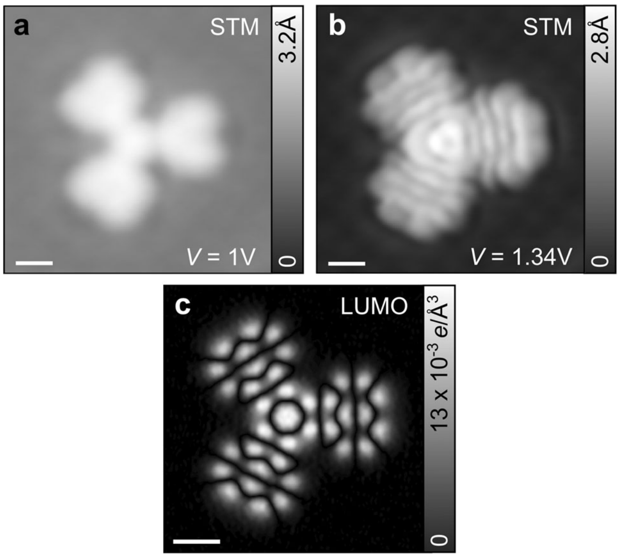

Figure 2. a,b) Constant-current STM measurements (tunnel current $I = 2$ pA, $T = 5$ K) of trimer **1** on NaCl(2ML)/Cu(111) using a CO tip. Measurements were acquired at sample voltages of $V = 1.0$ V, i.e., in the gap below the onset of the LUMO in (a), and at $V = 1.34$ V, i.e., at the onset of the LUMO in (b). c) Calculated orbital density squared of the LUMO at a distance of 1.2 Å above the molecular plane. The scale bars are 5 Å.

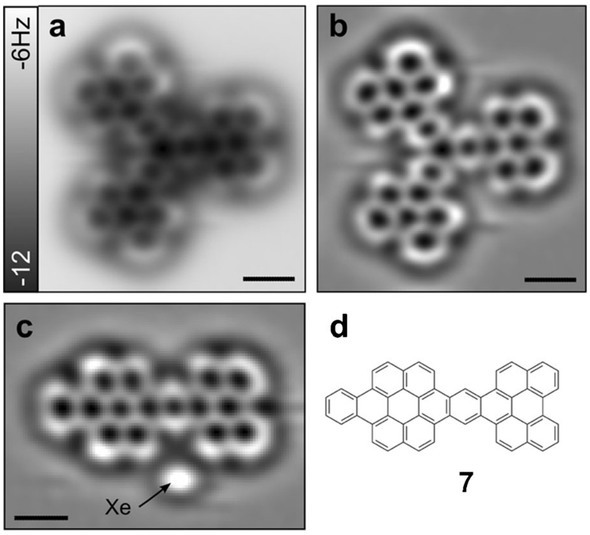

Figure 1. a) Constant-height AFM measurement of trimer **1** on NaCl(2ML)/Cu(111) using a CO-functionalized tip (sample voltage $V = 0$ V, oscillation amplitude $A = 0.4$ Å, at $T = 5$ K). b) Laplace filtered data of (a). c) AFM measurement of dimer **7** (and a nearby Xe atom). The scale bars are 5 Å. d) Structure of aryne dimer **7**.

Surprisingly, the AFM experiments revealed the presence of tetranaphthoheptacene **7** (Figure 1c,d), a 15-ring PAH which is not a fragment of cyclotrimer **1**. It is plausible that this compound was obtained by a sequence of reactions initiated with the [4+2] cycloadddition of aryne **3** with a bay region of triflate **6**.[13] The isolation of this face-to-edge dimer of aryne **3** is particularly interesting, since the iterative version of this transformation could provide a new bottom-up approach to graphene nanoribbons (GNRs), which regularly combine zig-zag and armchair edges.

In conclusion, large PAHs can be obtained from perylene by following an extremely simple procedure. This example demonstrates the potential and simplicity of aryne chemistry in solution to build nanographenes by a bottom-up approach, in which the formal triple bond of the aryne acts as a "molecular glue" to paste aromatic fragments together. Additionally, the work described here shows how atomic-resolution scanning probe microscopy techniques can provide synthetic chemists with unique tools for the identification of insoluble graphene molecules.

Received: March 25, 2014
Revised: May 21, 2014
Published online: July 1, 2014

Keywords: arynes · cycloadditions · nanographenes · polyarenes · scanning probe microscopy

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