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

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The chemistry of graphene is attracting enormous interest owing to the exceptional properties of this material. Recently, a collaboration between chemists at Centro de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS, University of Santiago de Compostela, Spain) and physicists from IBM Research – Zurich (Switzerland) resulted in the discovery of a novel synthetic approach to graphene fragments, which may be used for the fabrication of electronic devices. The graphene templates were subsequently characterized by atomic force microscopy (AFM). The research team from CIQUS, which included Professors Diego Peña, Enrique Guitián and Dolores Pérez, and PhD student Sara Collazos, developed the synthetic methodology to obtain nanographenes by chemical methods in solution, while the IBM team, which involved Drs. Leo Gross and Gerhard Meyer, and PhD student Bruno Schuler, characterized these molecules by AFM. The research was coordinated by Professor Peña (CIQUS) and Dr. Gross (IBM). Both groups are partners in the Large European Project PAMS (*http://pams-project.eu/*, Planar Atomic and Molecular Scale Devices), whose main objective is the development, fabrication and characterization of planar atomic and molecular scale electronic devices.

Professor Peña said: "Graphene is considered a unique material, which is leading to the emergence of a completely new technology. One of the biggest challenges in this new field is the development of methodologies for the preparation of this material with nanometric size and high quality: if we can gain perfect control over their size and geometry, then we could explore new applications for high-performance electronic devices." The method reported in this paper allows well-defined nanographenes to be obtained in one pot from perylene, a very common organic compound. The preparation of these materials with different shapes and sizes could be crucial for building graphene-based electronic circuits, molecular machinery and/or single molecule electronic devices.

Professor Peña explained: "This method is based on the reactivity of arynes, which can act as a 'molecular glue' to paste graphene fragments together. In particular, we employed two sequential cycloaddition reactions involving arynes: a Diels–Alder reaction on the bay region of perylene, followed by a Pd-catalyzed cyclotrimerization. Since the clover-shaped nanographenes obtained in this transformation were extremely insoluble, characterization by classical methods (e.g. NMR) was not an option, so we proposed that our colleagues in IBM should attempt the identification by atomic-resolved AFM. Notably, besides the characterization of the anticipated graphene molecule they were able to detect some unexpected and interesting byproducts."

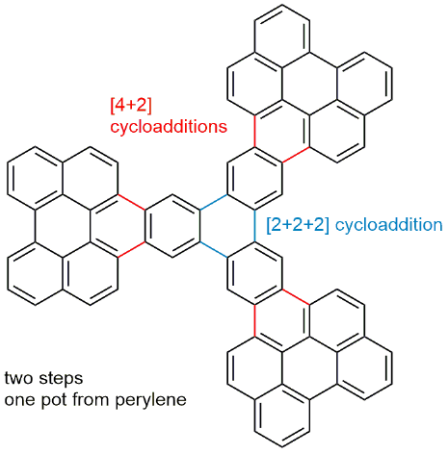

Figure 1 *Three-fold symmetric nanographene*

Dr. Gross continued: "We achieved the first atomic-resolved atomic force microscopy (AFM) images of molecules in 2009. The key was the termination of the scanning probe tip by a single CO molecule. Soon after, we tried to make use of that technique for molecular structure identification and we also refined the technique to increase the information that can be obtained."

Using AFM, the authors identified natural products that could not be solved using standard techniques such as mass spectrometry and nuclear magnetic resonance alone. They also obtained additional information by AFM, including the exact adsorption geometry of molecules, information about the bond order of individual bonds within molecules, the charge distribution within molecules, some information related to element specificity and identification of byproducts.

Dr. Gross concluded: "In terms of a wider applicability of AFM for structure identification, one challenge is to expand

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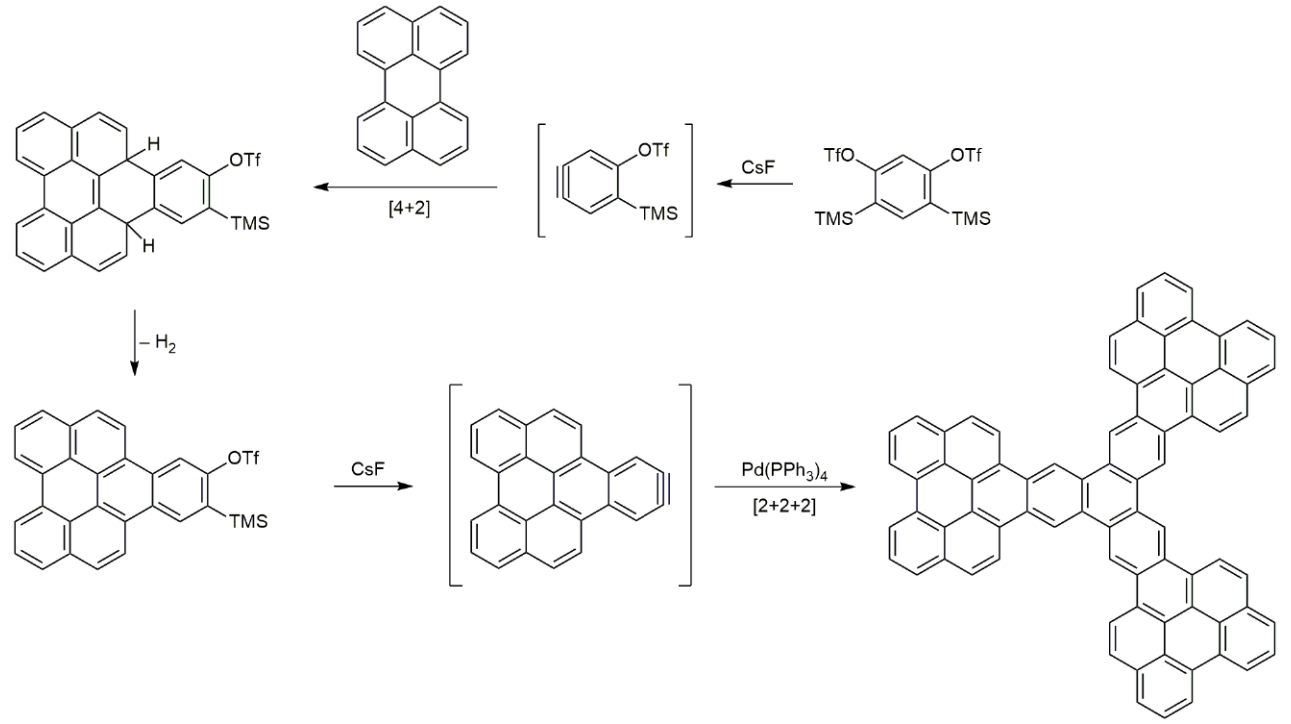

Scheme 1 *Synthetic route*

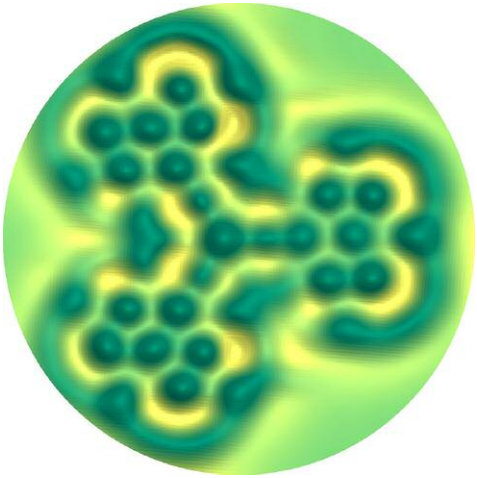

Figure 2 *Atomic force microscopy (AFM) image of a clover-shaped nanographene (Credit: Bruno Schuler, IBM)*

the classes of molecules that can be studied. The recent case, namely a 22-ring aromatic molecule, was the largest molecule that we have been able to resolve so far. However, with this molecule we reached about the size of molecules that can be thermally evaporated. A challenge for the future is to switch to other preparation methods, for example, electrospray deposition, that would allow us to deposit even larger molecules without breaking them."

Matteo Zanda

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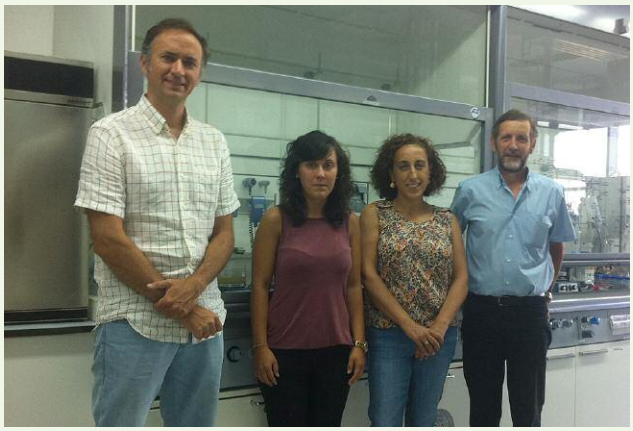
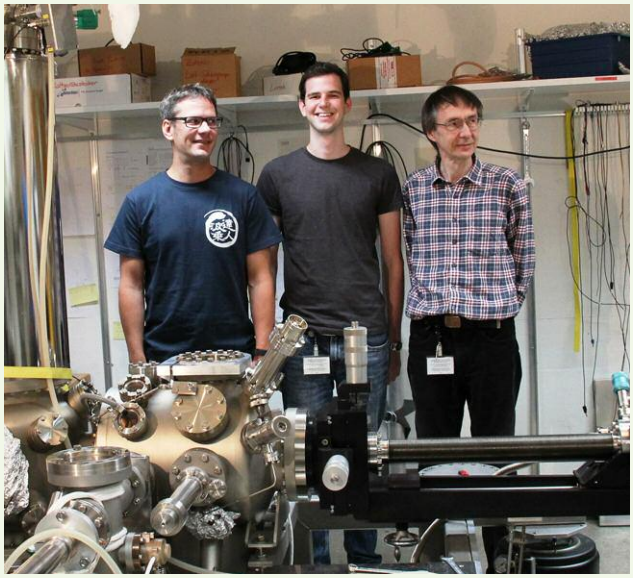
About the authors



CIQUS group, from left: Prof. D Peña, S. Collazos, Dr. D. Pérez, Prof. E. Guitián



IBM group, from left: Dr. L. Gross, B. Schuler, Dr. G. Meyer

Diego Peña Gil was born in Santiago de Compostela (Spain) in 1974. He graduated in Chemistry at the University of Santiago de Compostela in 1998, where he also obtained his PhD under the guidance of Professors Enrique Guitián and Dolores Pérez, working on transition-metal-catalyzed cycloaddition reactions of arynes (2001, Special Doctorate Award). He spent short predoctoral stays in the groups of Professors Eric N. Jacobsen (1999, Harvard University, USA), Paul Knochel (2000, LMU, Munich, Germany) and Antonio M. Echavarren (2001, UAM, Madrid, Spain). During 2002 and 2003 he joined the group of Ben L. Feringa (Groningen University, The Netherlands) as a Marie Curie Postdoctoral Fellow working on asymmetric catalysis, with short research stays in the group of Johannes G. de Vries (DSM, Geleen, The Netherlands). In 2004 he returned to the University of Santiago de Compostela as Ramón y Cajal researcher, where he has been Associate Professor since 2008. His main research interests are focused on the development of new synthetic methodologies, metal-based homogeneous catalysis, the chemistry of organic intermediates such as arynes, the synthesis of nano-sized polycyclic aromatic compounds and nanographenes, and their study as new molecular materials.

Sara Collazos Suárez was born in Pontevedra (Spain) in 1987. She graduated in Chemistry at the University of Santiago de Compostela (Spain) in 2010, where she is working as PhD student on the synthesis of large aromatic compounds and nanographenes.

Dolores Pérez Meirás was born in Ferrol (A Coruña, Spain). She graduated (with honors) in Chemistry at the University of Santiago de Compostela (Spain), where she also carried out her graduate studies under Professors Luis Castedo and Enrique Guitián. After obtaining her PhD in 1991, she did a two-year postdoctoral stay as a Fullbright Fellow at the University of California at Berkeley (USA) in the group of Professor K. Peter C. Vollhardt, and a shorter stay in the group of Professor Stephen L. Buchwald at the Massachusetts Institute of Technology (USA). In 1995 she joined the Faculty of the University of Santiago de Compostela as Assistant Professor and since 2000 she has been Associate Professor of Organic Chemistry. Her main research interests are the discovery of new metal-catalyzed reactions of synthetic interest, the development of aryne chemistry and, in particular, its application to the synthesis of complex polycyclic aromatic systems of interest in the field of materials science. She is the Deputy Director of the Centre for Research in Biological Chemistry and Molecular Materials (CIQUS) at the University of Santiago de Compostela.

Enrique Guitián Rivera received his PhD from the University of Santiago de Compostela (Spain) in 1981 for work in the field of natural product synthesis under Professor Luis Castedo. After a postdoctoral stay at the University of Hannover (Germany) under Professor Ekkehard Winterfeldt, he continued his career at Santiago (Associate Professor, 1985–1992; Full Professor, 1992). His main research interests lie in the fields of natural product synthesis and aryne chemistry, especially pericyclic and transition-metal-catalyzed reactions of arynes.

Bruno Schuler is working as a PhD student at IBM Research – Zurich Laboratory (Switzerland). The main focus of his work is molecular structure determination using atomic force microscopy. In 2011, he joined the IBM Research – Zurich Laboratory and the group of Gerhard Meyer for his Masters' thesis. He obtained

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his Masters and Bachelor degrees from ETH Zurich (Switzerland).

Leo Gross, a native of Berlin (Germany), has been a research staff member at the IBM Research – Zurich Laboratory since 2009. He is working on atomic/molecular manipulation by scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and on nanostencil lithography. He has been with the IBM Research – Zurich Laboratory since 2005, having originally joined IBM Research as a postdoctoral fellow in the group of Gerhard Meyer. Leo Gross received his PhD in Physics in 2005 from the Free University of Berlin (Germany) in the group of Professor Karl-Heinz Rieder and the Master's (Diploma) degree in Physics in 2001 from the University of Muenster (Germany) in the group of Professor Harald Fuchs. He received the Feynman Prize for Experiment in 2012 and the Gerhard Ertl Young Investigator Award in 2010.

Gerhard Meyer is research staff member in the 'Physics of Nanoscale Systems' group at the IBM Research – Zurich Laboratory. His main research interests are in the area of scanning probe microscopy and epitaxial growth, in particular low-temperature scanning tunneling microscopy and atomic force microscopy, atomic/molecular manipulation and studies on the growth of/on ultrathin insulating films. He received his PhD from the University of Hannover (Germany) in 1987. Following a postdoctoral fellowship at the IBM Research Laboratory in Yorktown Heights (USA) he joined the group of Prof. Karl-Heinz Rieder at the Free University Berlin, starting a project on low-temperature scanning probe microscopy. In 2000 he became staff member of the Paul Drude Institut für Festkörperelektronik, Berlin (Germany) until 2002 when he moved to the IBM Research – Zurich Laboratory. For his work in scanning probe microscopy he received several IBM awards including an IBM Corporate Award, the German Nano-Science Prize (2002) and the Robert Wichard Pohl Prize of the German Physical Society (2011). Since 2009, he has been Fellow of the American Physical Society. In 2012 he received the Feynman Prize for Experiment. He has published more than 120 publications and presented more than 100 invited talks in the area of surface science and nanoscience. His research projects have been supported by several national and EU projects fostering international collaborations and recently, in 2011, he was awarded an ERC advanced grant.

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