CiQUS

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Bottom-up Approach to Nanographenes by Merging Organic Chemistry and On-Surface Synthesis

ESAM

1st European School on Advanced Materials

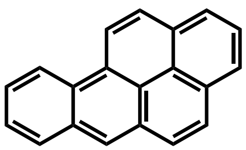
Diego Peña
CiQUS y Departamento de Química Orgánica
Universidade de Santiago de Compostela

Gandía
16/10/2023

PAHs: Polycyclic Aromatic Hydrocarbons

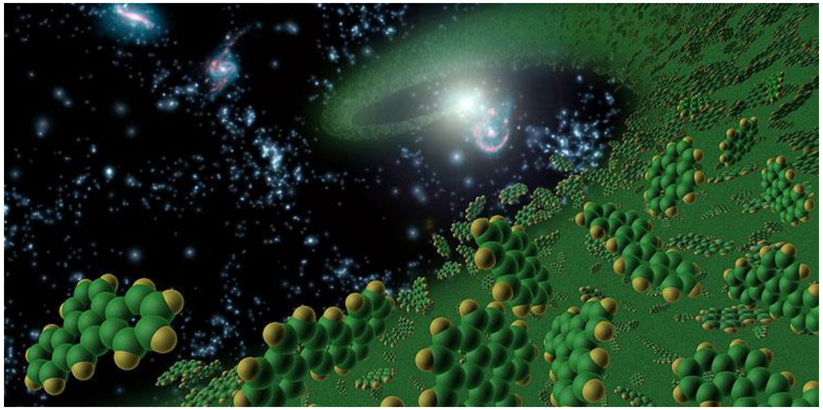
Hydrocarbons composed of multiple aromatic rings, mostly fused benzene rings

Bad reputation:
- Atmospheric pollutants
- Byproducts of fuel burning
- Carcinogenic



Benzo[*a*]pyrene

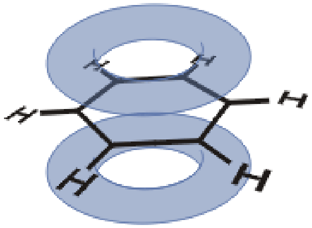
Chimney sweep (PAHs in soot)
First occupational cancer



- Abundant material in the interstellar medium
- **PAH World Hypothesis**: pre-RNA model of life's origin based on the self-organization of PAHs by π-stacking

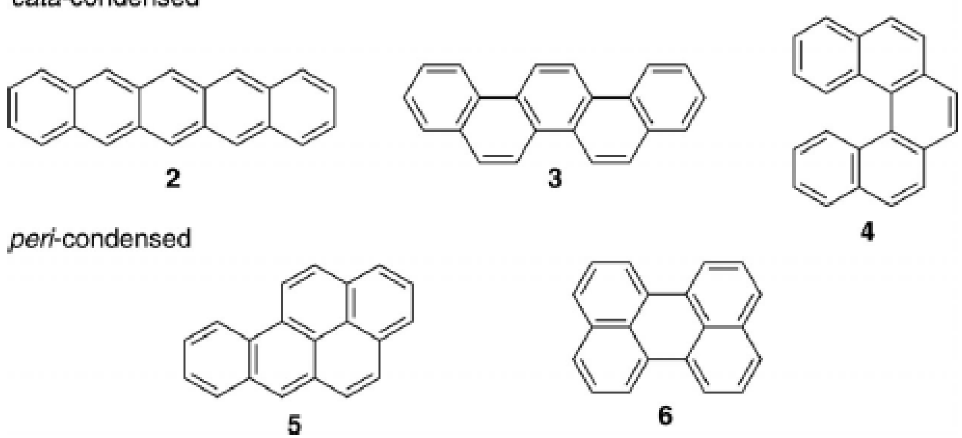
PAHs as Advanced Molecular Materials

How does a family of pollutants become a privileged advanced material?



π-electrons on aromatic rings make the difference

Importance of the geometry in PAHs



Pentacene (**2**)

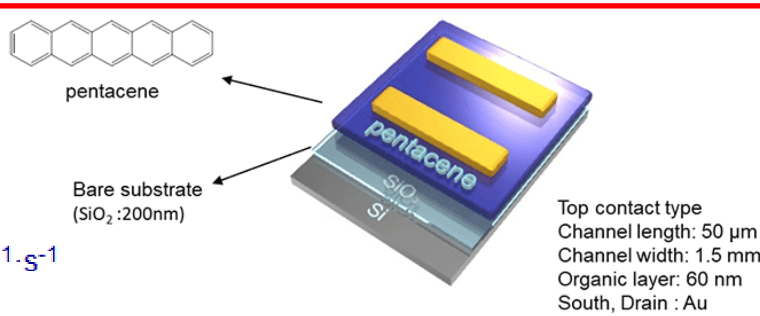
Picene (**3**)

Pentahelicene (**4**)

Benzo[*a*]pyrene (**5**)

Perylene (**6**)

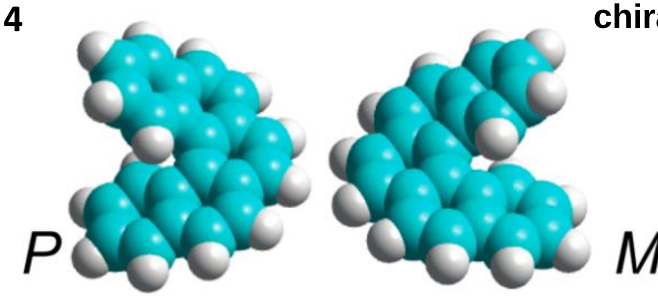
2



μ_{hole}: 5.5 cm^2· V^{-1}·s^{-1}

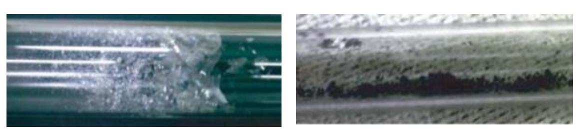
Gap: 1.9 eV

4 **chiral**



3

Picene | **K$_x$Picene**



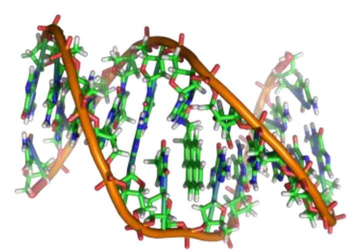
Insulator | ***Superconductor***

μ_{hole}: 3.0 cm^2·V^{-1}·s^{-1}

Gap: 3.2 eV

R. Mitsuhashi, et al. *Nature* **2010**, *464*, 76

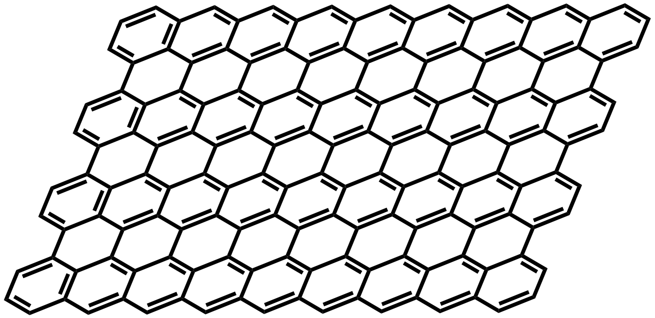
5



Mutagenic and Carcinogenic

6

Highly Fluorescent



GRAPHENE

-Unique combination of properties

The Nobel Prize in Physics 2010

Andre Geim, Konstantin Novoselov

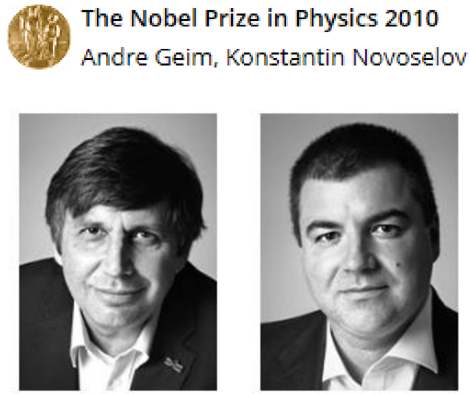
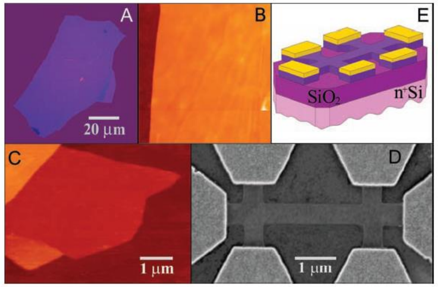


Photo: U. Montan
Andre Geim

Photo: U. Montan
Konstantin Novoselov

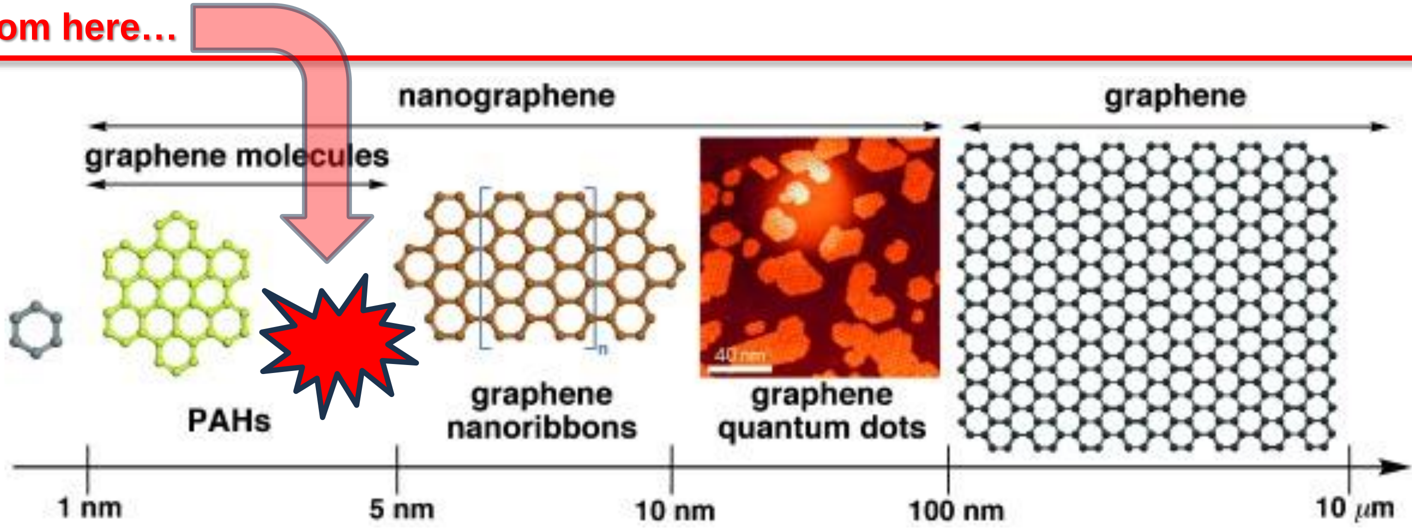
Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]



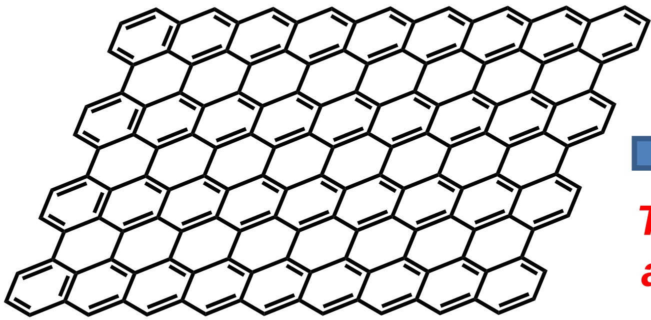
Science **2004**, *306*, 666

Plenty of room here…



Feng, Müllen and co, *Angew. Chem. Int. Ed.* **2012**, *51*, 7640

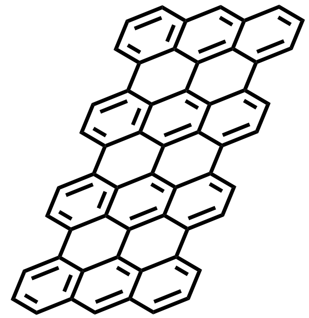
How does a family of pollutants become a privileged advanced material?



GRAPHENE

-Unique combination of properties

Top-down approach

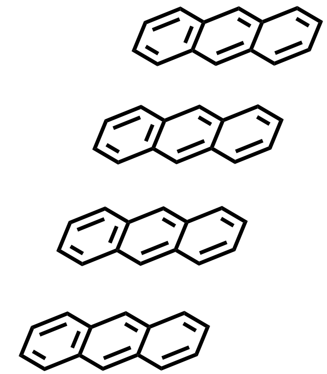


nanoGRAPHENE

-Properties depend on size & shape

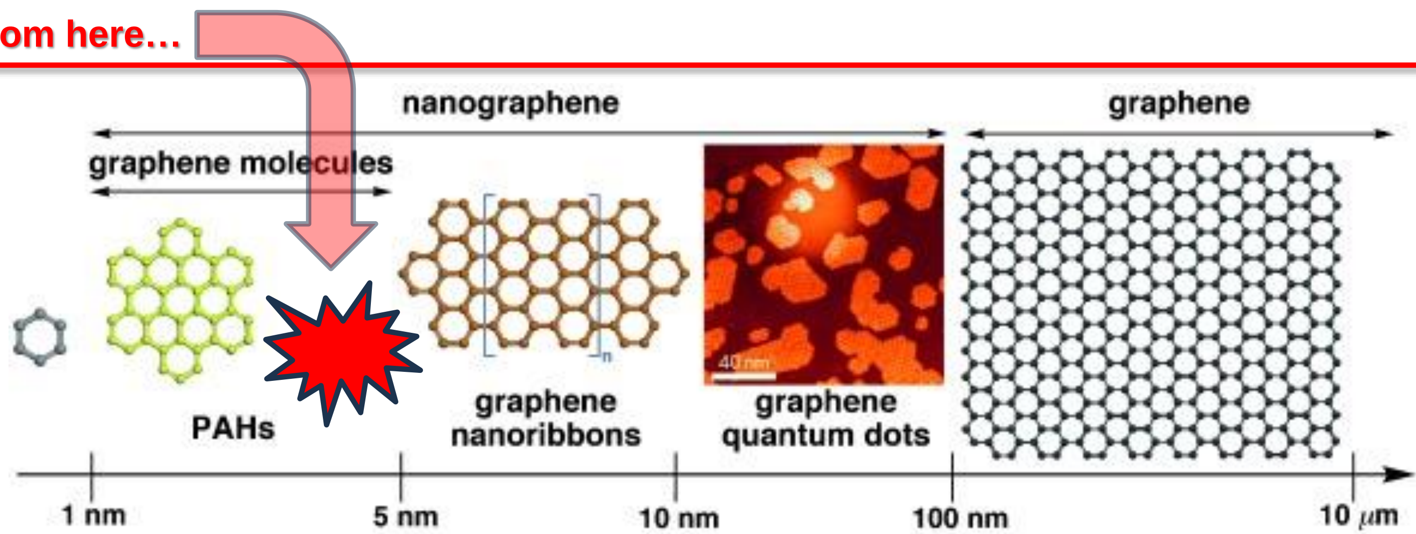
Organic Synthesis

Bottom-up approach



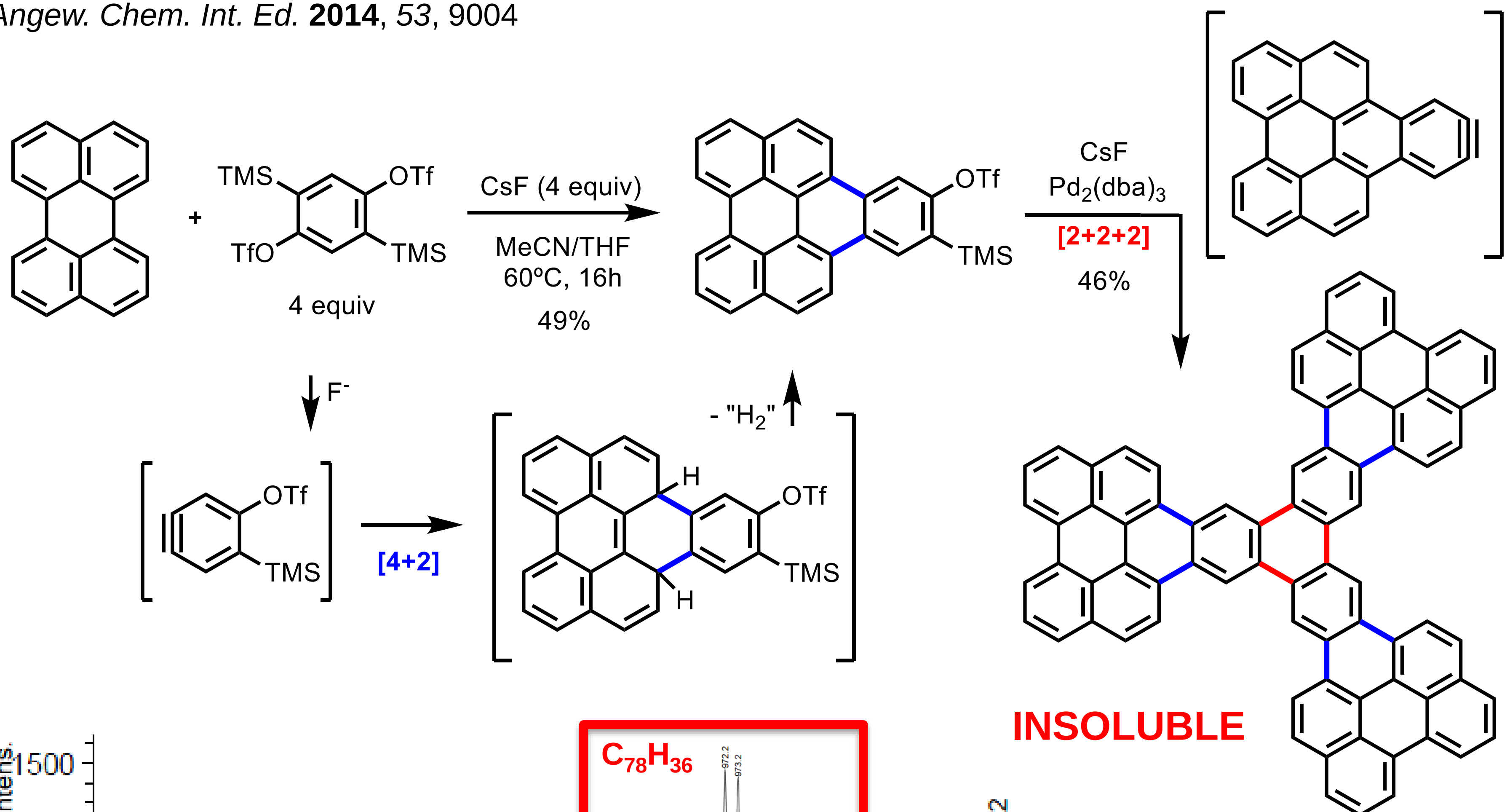
MOLECULES

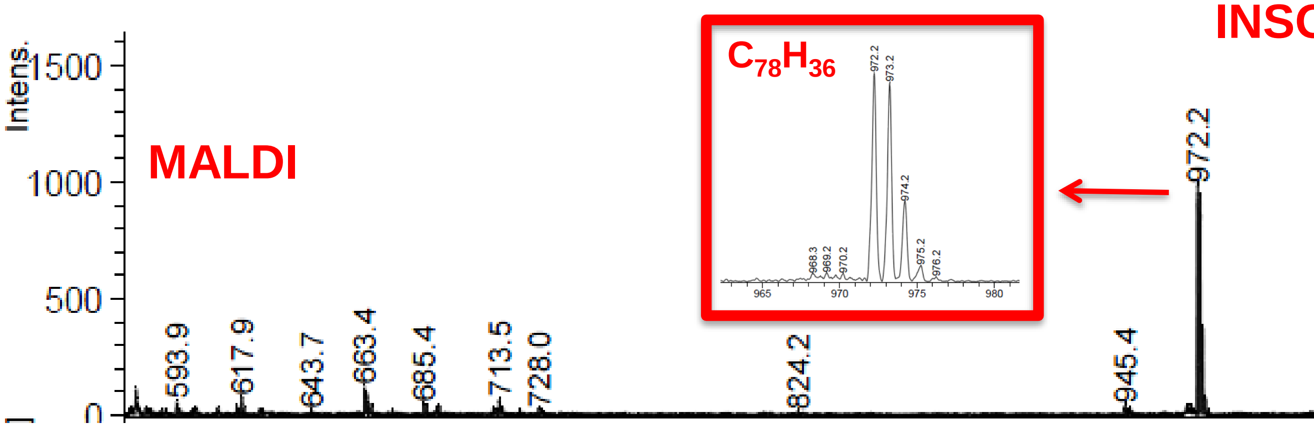
Plenty of room here…



Bottom-up approach to three-fold symmetric nanographenes

Angew. Chem. Int. Ed. **2014**, *53*, 9004



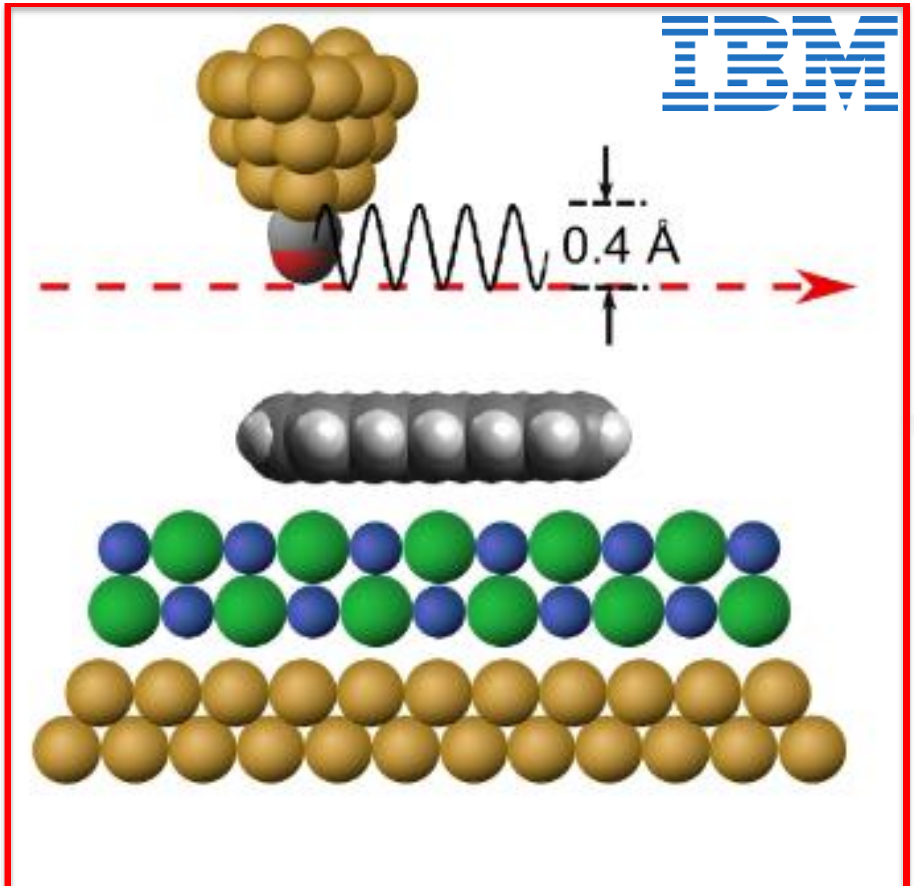


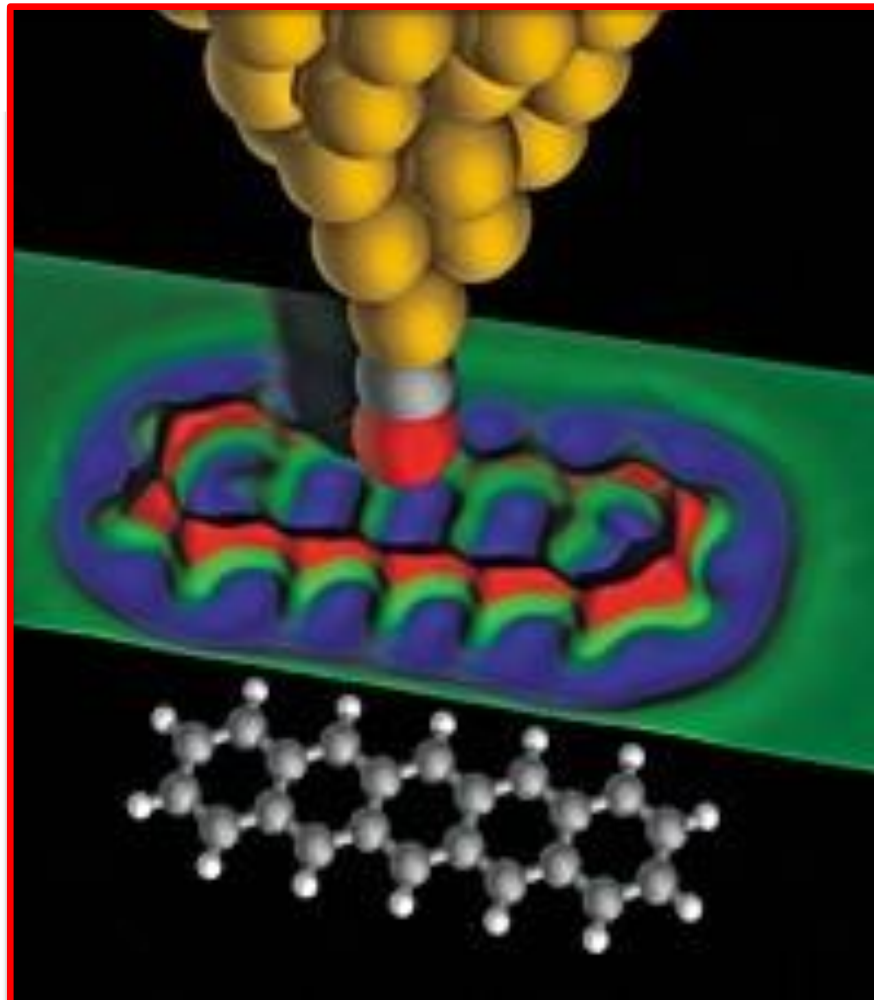
AFM with functionalized tips

The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

Leo Gross,[1*] Fabian Mohn,[1] Nikolaj Moll,[1] Peter Liljeroth,[1,2] Gerhard Meyer[1]

28 AUGUST 2009 VOL 325 SCIENCE



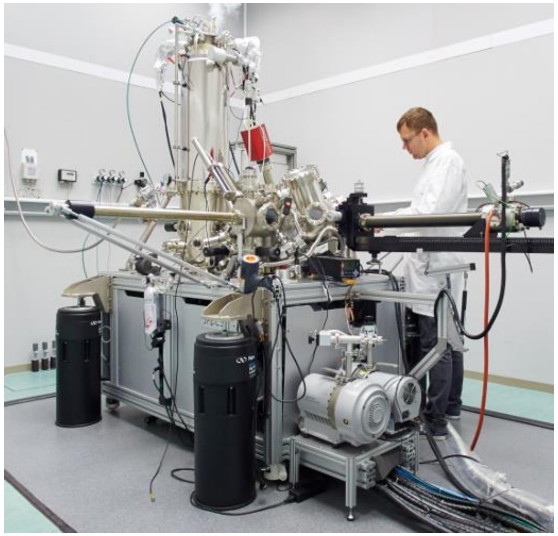


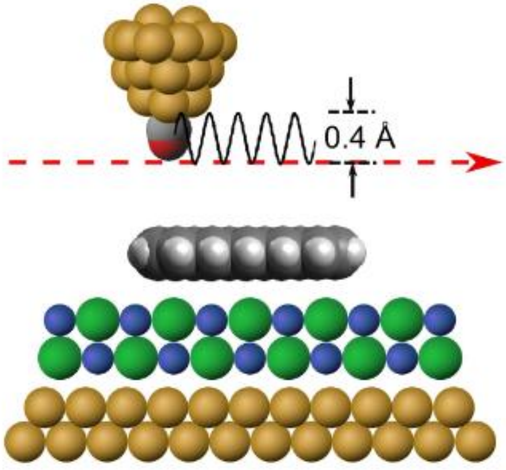
Pentacene ($C_{22}H_{14}$) on NaCl

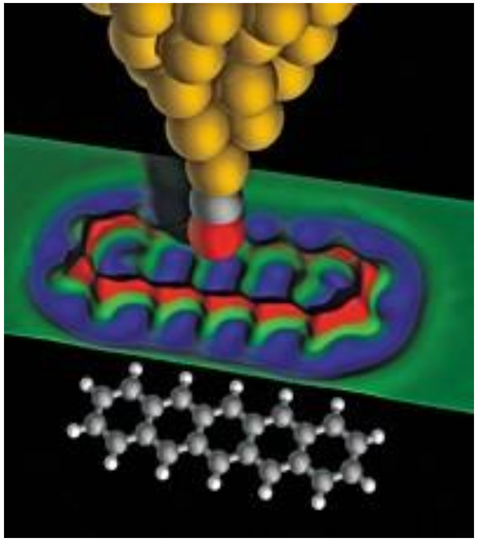
Ultra High Vacuum (UHV)

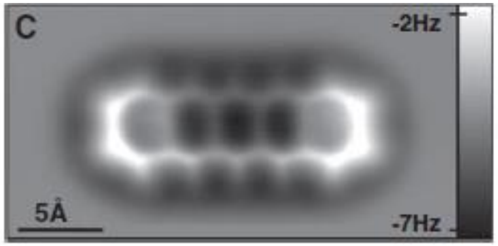
Cryogenic Temperature (5 K)

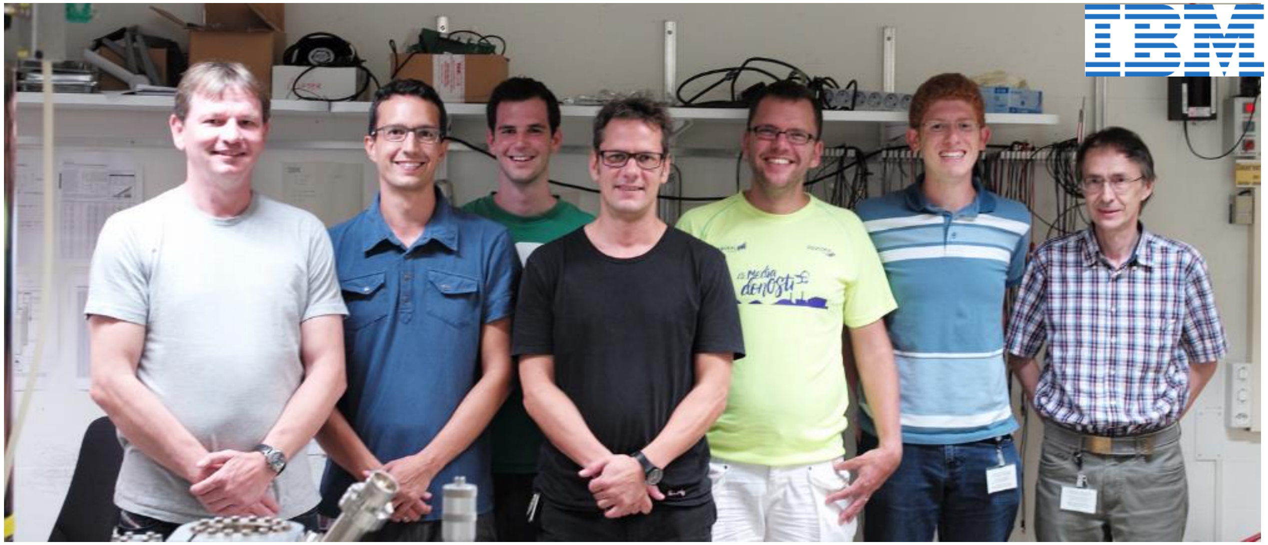
AFM with functionalized (UHV, 5K)







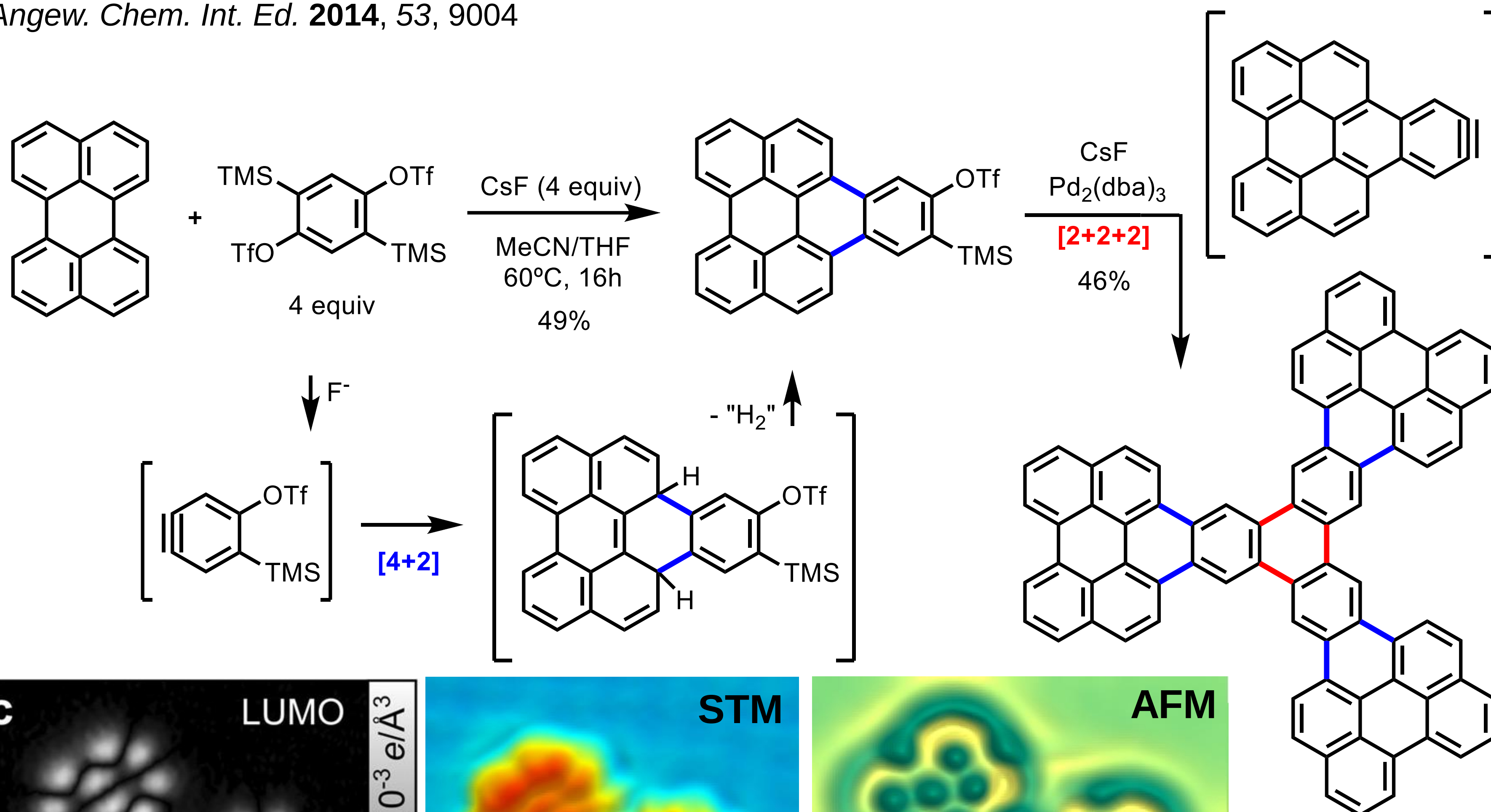


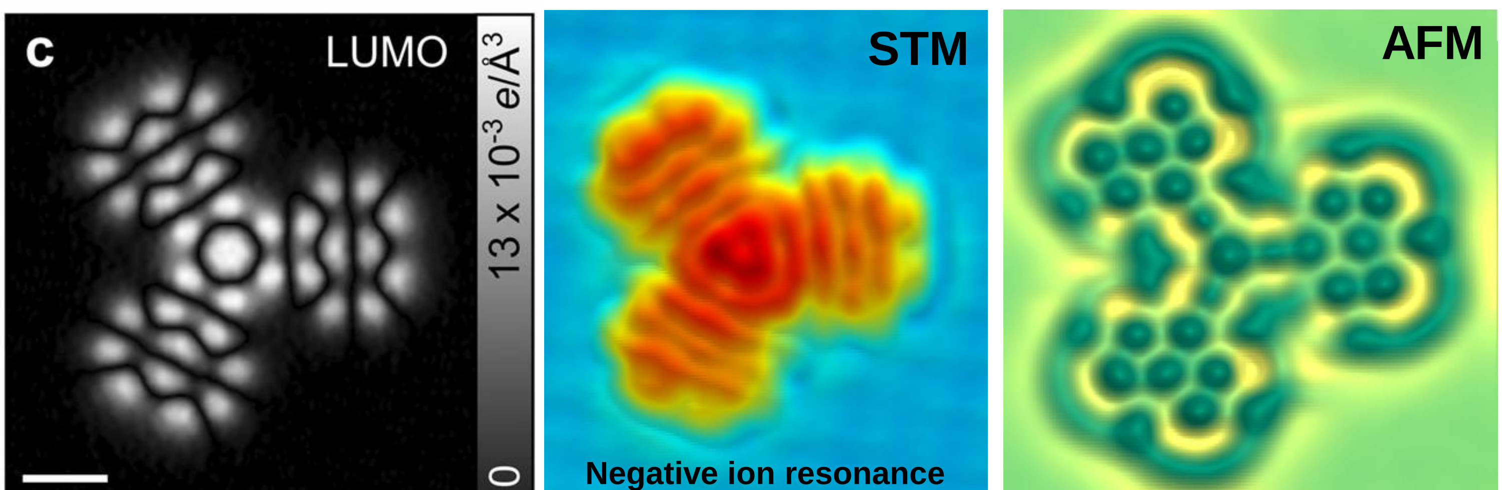


Leo Gross and coworkers
IBM Research Zurich

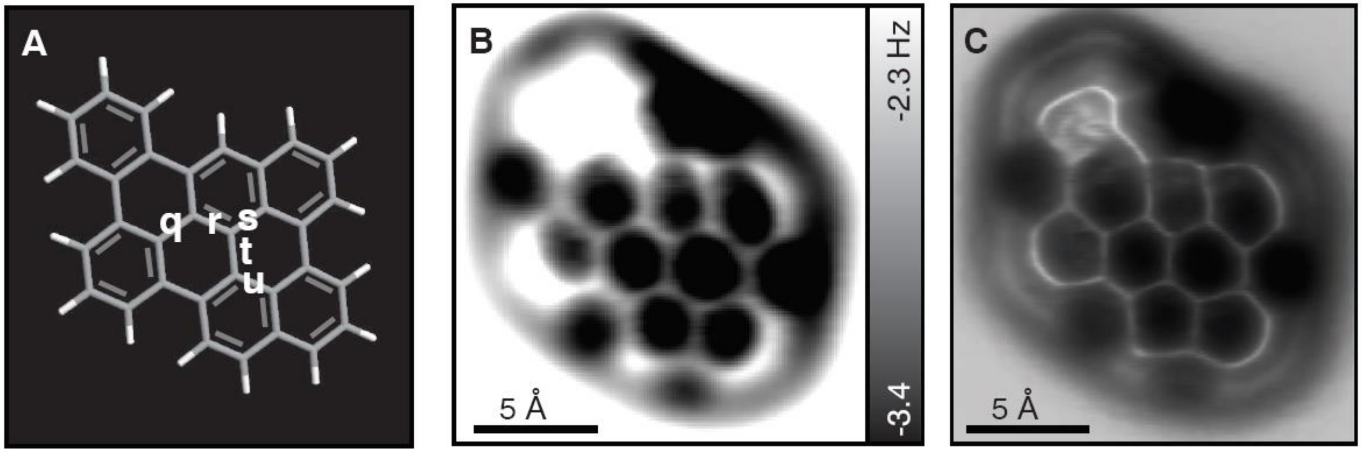
Bottom-up approach to three-fold symmetric nanographenes

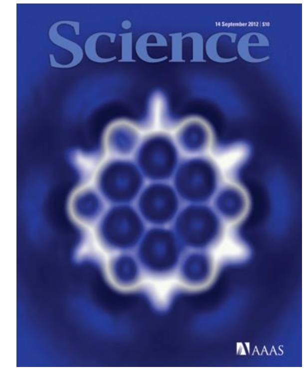
Angew. Chem. Int. Ed. **2014**, *53*, 9004



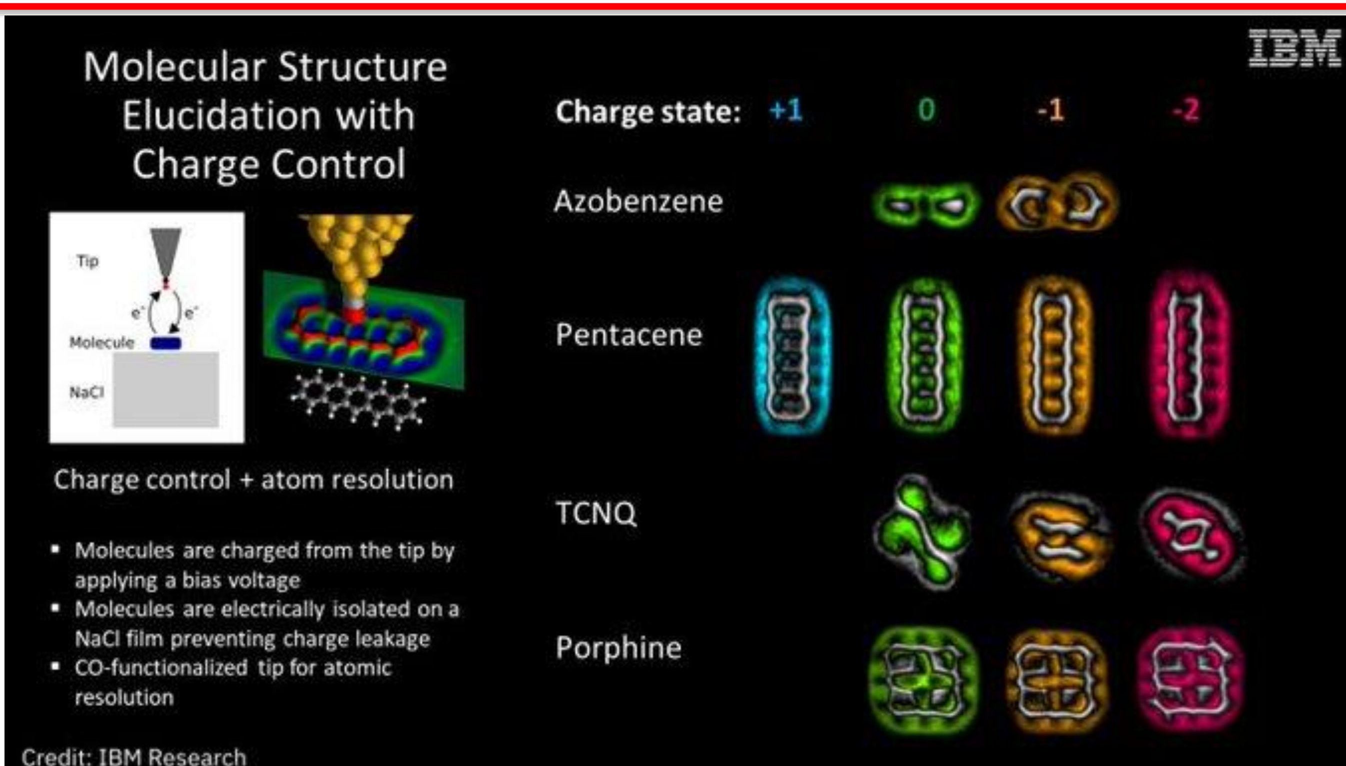


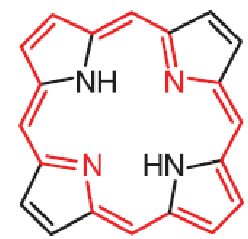
AFM with submolecular resolution

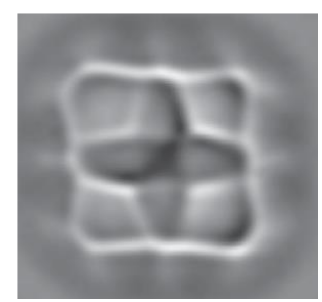




Science **2012**, *337*, 1326



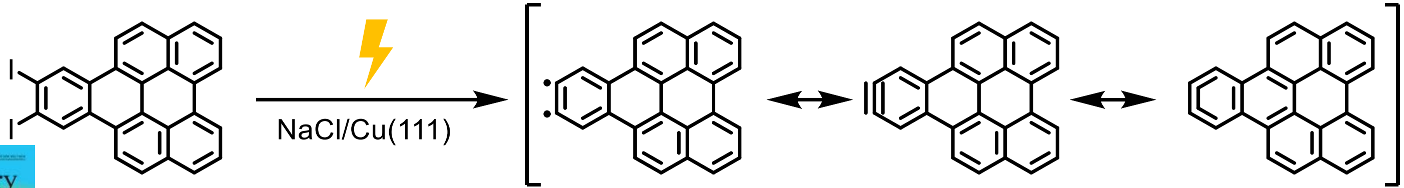




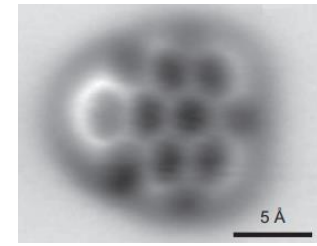
Science **2019**, *365*, 142

Single molecule reactions by voltage pulse

Aryne generation



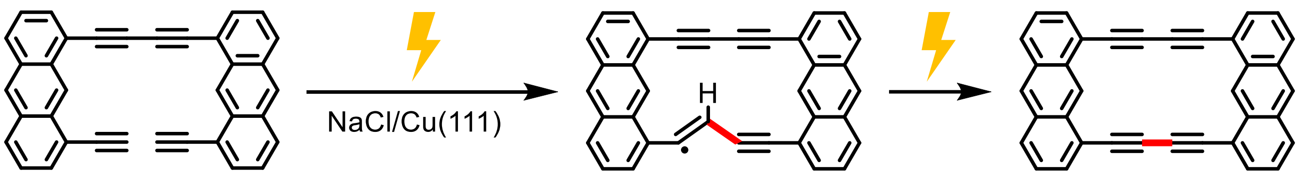
diradical alkyne cumulene

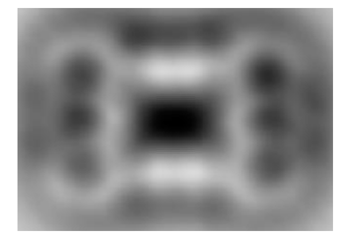


AFM (CO, UHV, 10 K)

Nature Chem. **2015**, *7*, 623

Glaser coupling

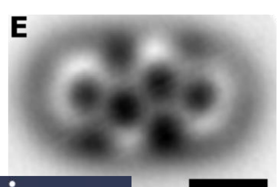


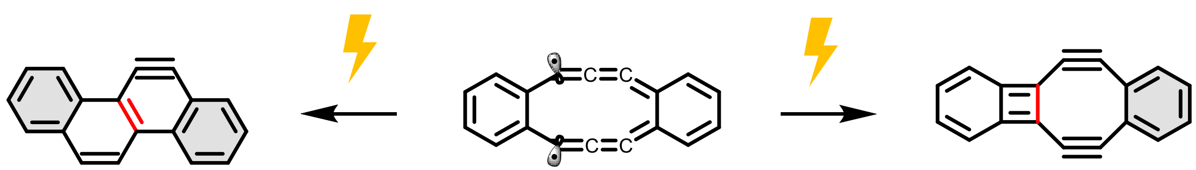


AFM (CO, UHV, 5 K)

Angew. Chem. Int. Ed. **2020**, *59*, 22989

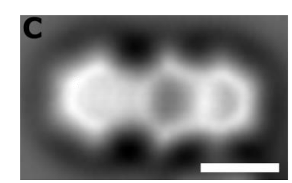
Molecular Rearrangements





V = -1.9 V

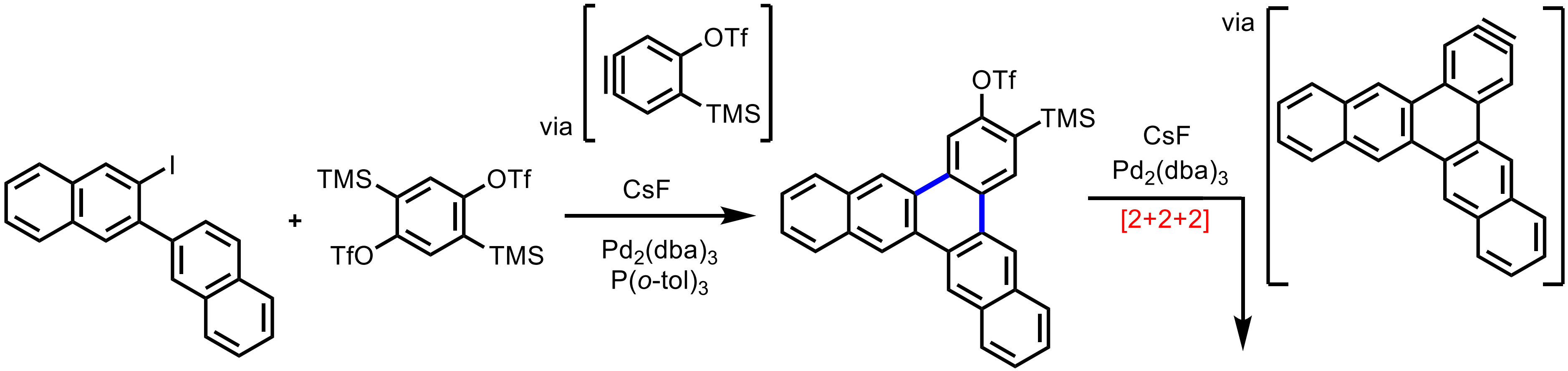
-1.7 V < *V* < - 0.9 V

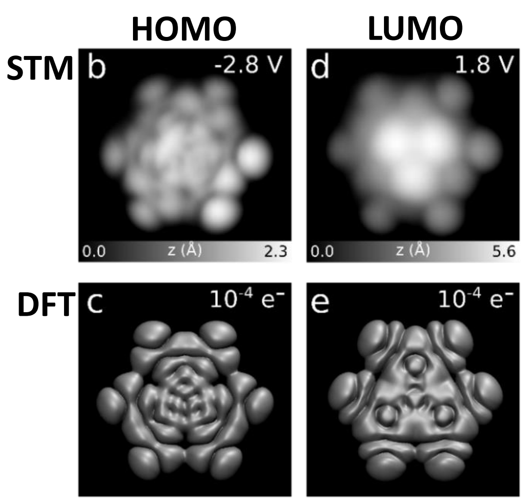


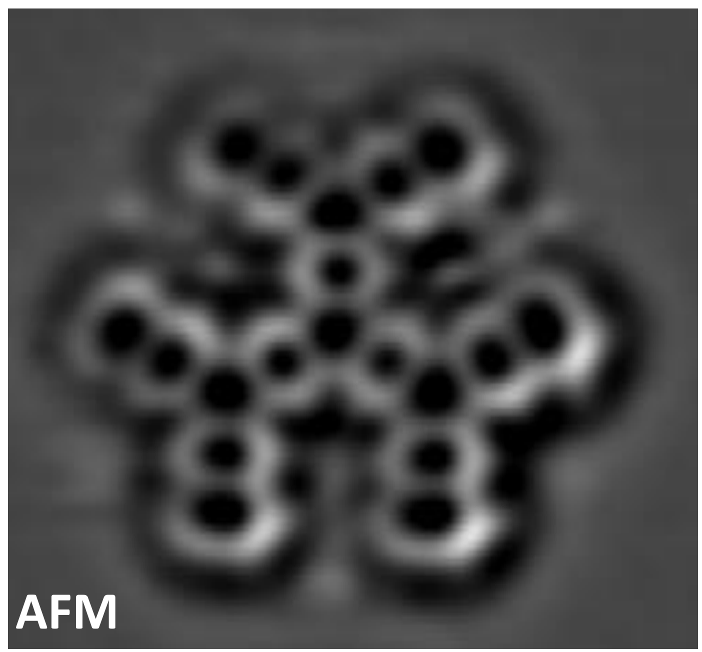
AFM (CO, UHV, 5 K)

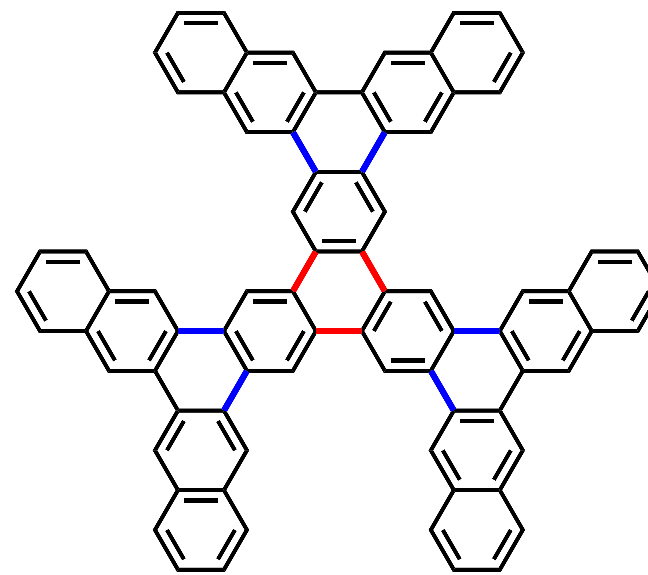
Science **2022**, *377*, 298

Dendritic Starphene

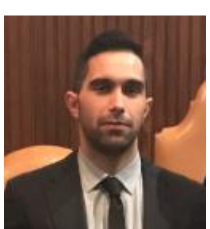








[19]Dendriphene
$C_{78}H_{42}$

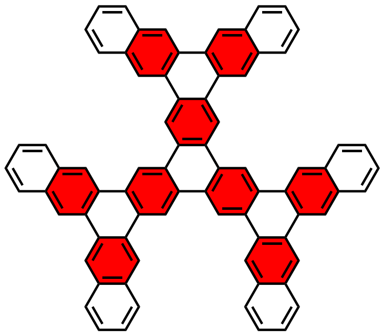


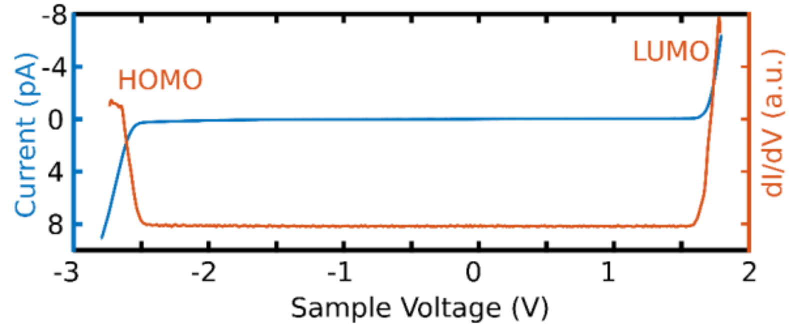
Manuel Vilas-Varela
Chem. Eur. J. **2018**, *24*, 17697

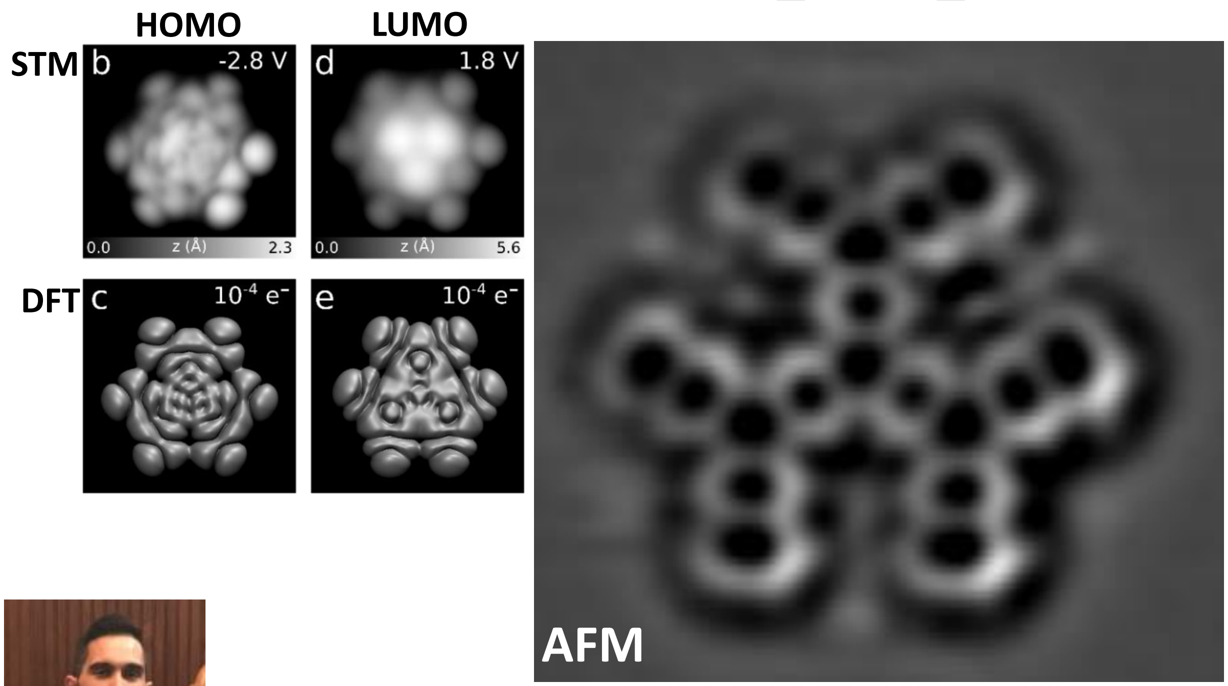
Dendritic Starphene

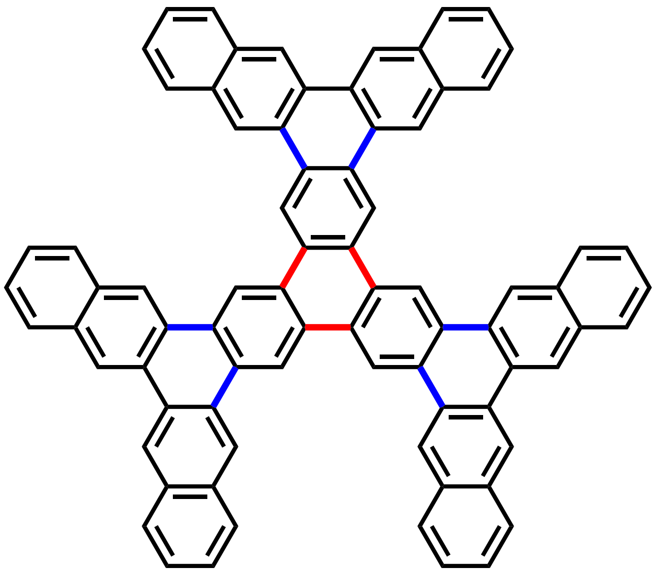
Scanning Tunneling Spectroscopy (STS)
HOMO-LUMO gap = 4.1 eV
9 Clar sextets

Clar's rule:
Predicts stability and gaps by grouping π-electrons into sextets within a ring





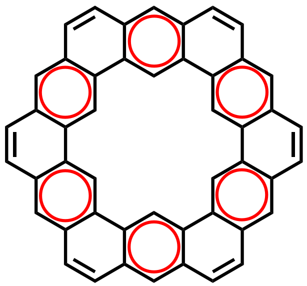




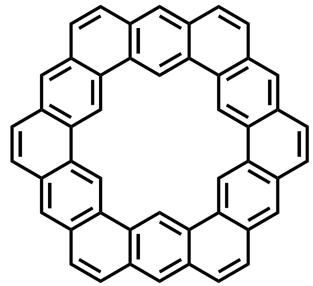
[19]Dendriphene
$C_{78}H_{42}$

Manuel Vilas-Varela
Chem. Eur. J. **2018**, *24*, 17697

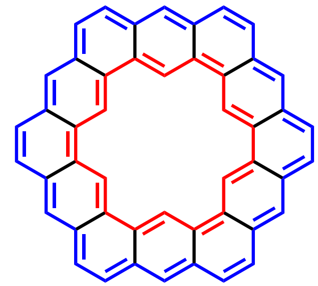
Revisiting an Iconic Molecule: Kekulene



Clar Model
sextet localization

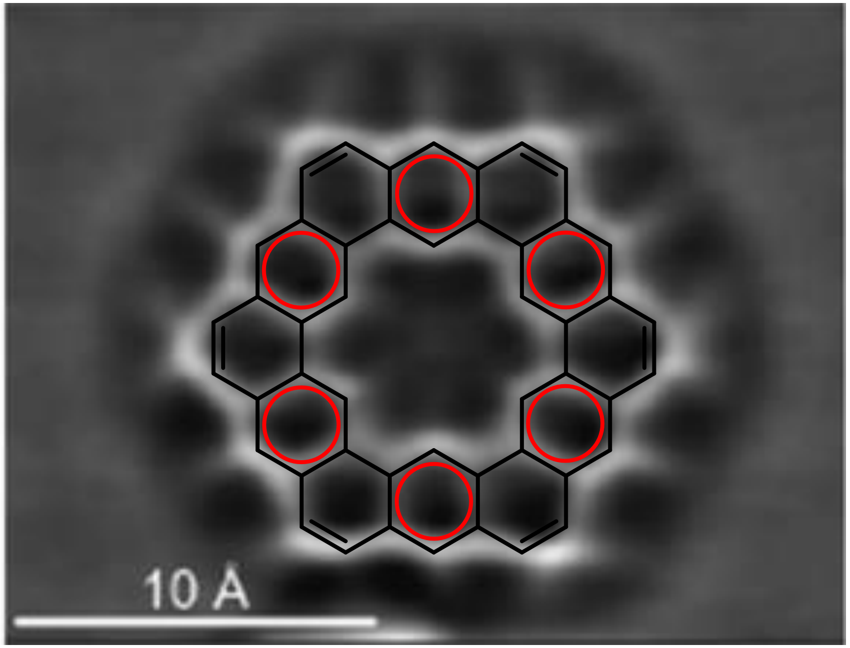


12 rings
[18]annulene pore



Annulene Model
global delocalization

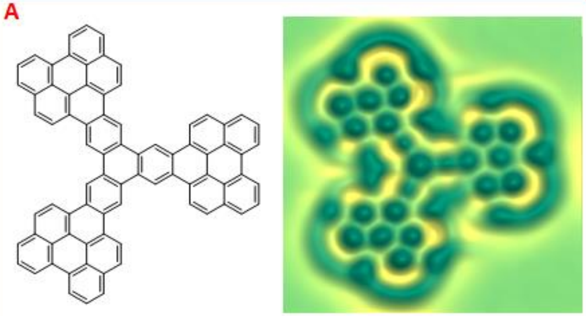
Iago Pozo



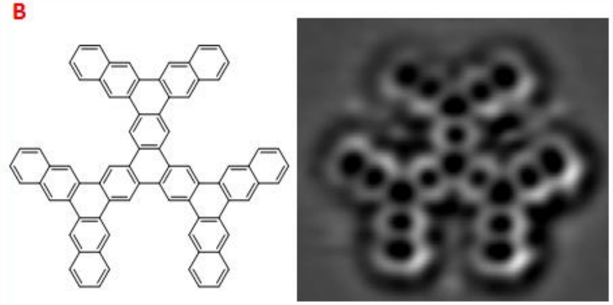
I. Pozo, Z. Majzik, N. Pavlicek, M. Melle-Franco, E. Guitián, D. Peña, L. Gross, D. Pérez *J. Am. Chem. Soc.* **2019**, *141*, 15488

AFM to characterize insoluble nanographenes and mixtures

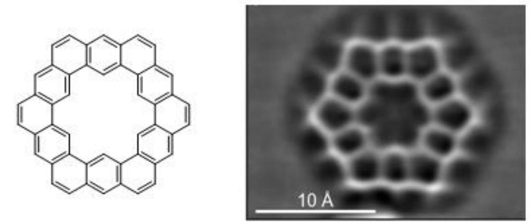
A

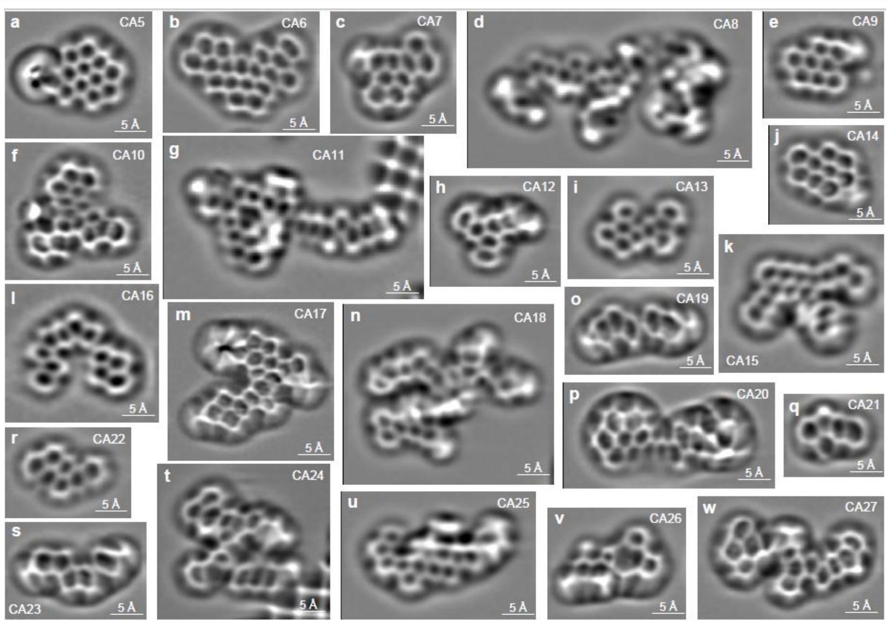


B



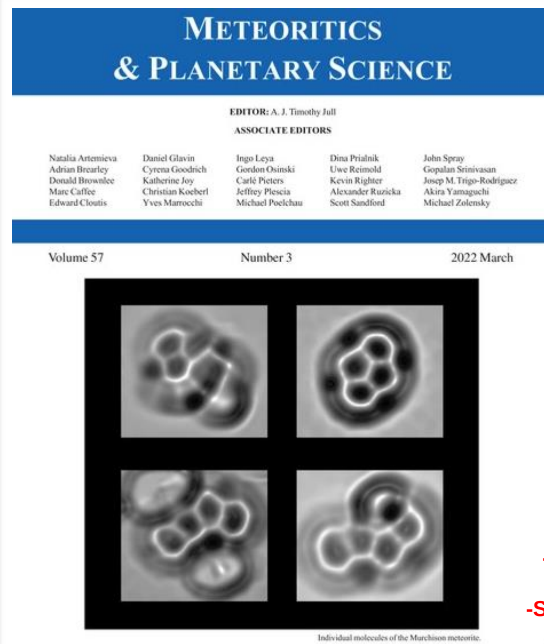
C





Molecular Structure of Asphaltenes
"The Choresterol of Oil Refineries"

J. Am. Chem. Soc. **2015**, *137*, 9870



METEORITICS
& PLANETARY SCIENCE

EDITOR: A. J. Timothy Jull

ASSOCIATE EDITORS

Natalia Artemieva, Adrian Brearley, Donald Brownlee, Marc Caffee, Edward Cloutis, Daniel Glavin, Cyrena Goodrich, Katherine Joy, Christian Koeberl, Yves Marrocchi, Ingo Leya, Gordon Osinski, Carlé Pieters, Jeffrey Plescia, Michael Poelchau, Dina Prialnik, Uwe Reimold, Kevin Righter, Alexander Ruzicka, Scott Sandford, John Spray, Gopalan Srinivasan, Josep M. Trigo-Rodriguez, Akira Yamaguchi, Michael Zolensky

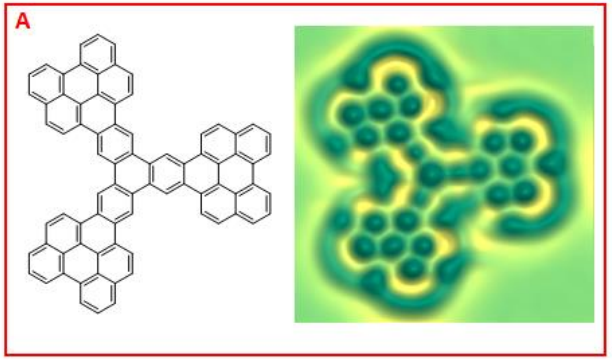
Volume 57 Number 3 2022 March

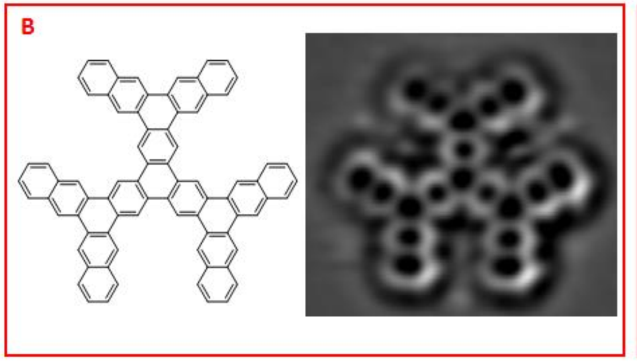
Individual molecules of the Murchison meteorite.

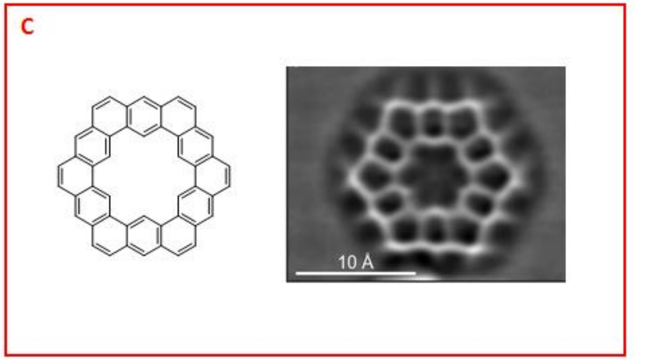
-Oldest material found on Earth
-Seven billion years-old
-Solar system: 4.5 billion years-old

Identification of PAHs in the Murchison Meteorite

Meteoritics & Planetary Science **2022**, *57*, 644





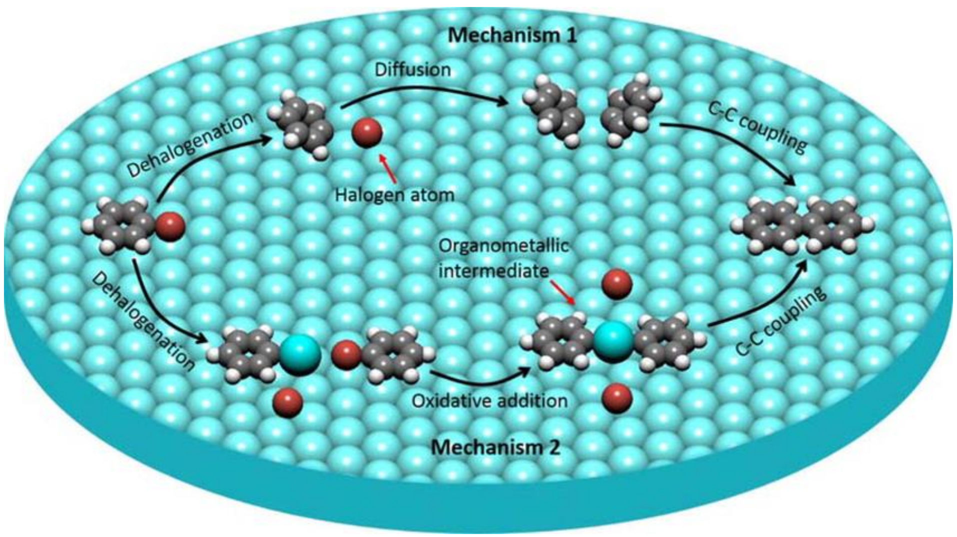


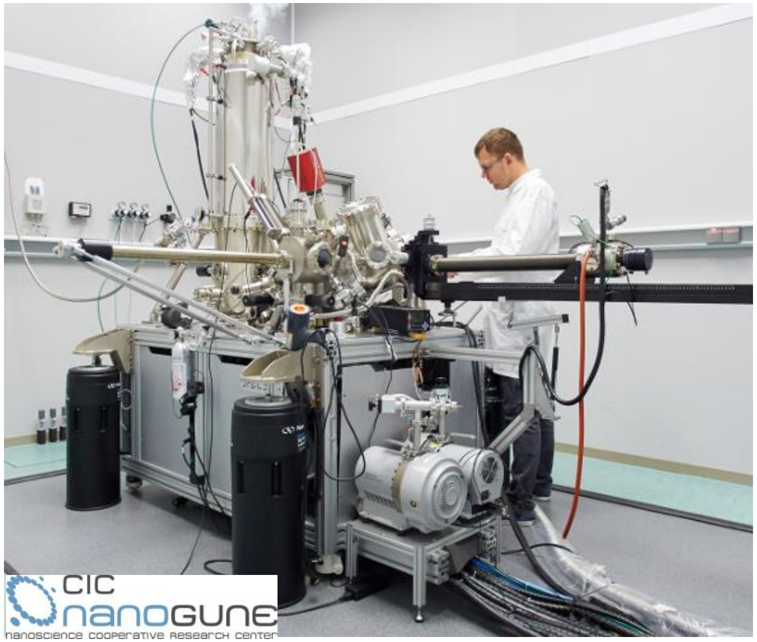
How to obtain larger/more exotic graphene molecules?

1) Characterization of graphene molecules

2) Combining solution and on-surface synthesis

-Last synthetic step on surface
-Annealing under UHV





Q. Fan, J. M. Gottfried, J. Zhu *Acc. Chem. Res.* **2015**, *48*, 2484

Combining In-Solution and On-Surface Synthesis

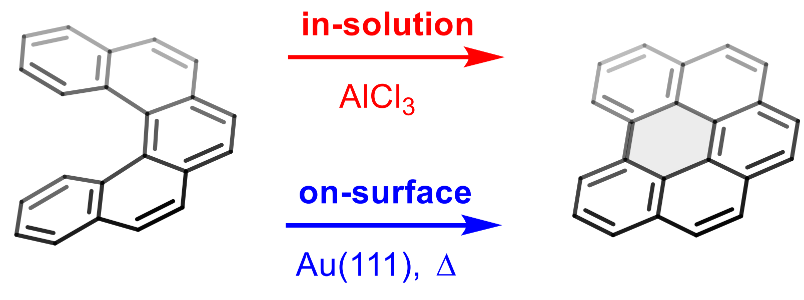
CiQUS

Table 1. Overview of successfully conducted on-surface reactions carried out in ultra-high vacuum.

Reaction name	Stimulus	Substrate and reference
Ullmann coupling	ΔT	Cu,[11, 14–20,42] Ag,[20–26, 42] Au,[13, 19,26–34,41,81] $CaCO_3$,[35–37] HOPG,[42] NaCl@Au,[38] h-BN@Ni[39] graphene@Ni[39]
Ullmann coupling	$h\nu$	Sapphire,[40] HOPG[71]
Glaser coupling	ΔT	Cu,[64,68, 69] Ag,[53, 63,65,66,68,69] Au,[68, 69]
Glaser coupling	$h\nu$	Cu,[53] Ag,[53] Au[53]
Bergman cyclization	ΔT	Cu,[60] Ag[58]
Huisgen cycloaddition	ΔT	Cu,[91] Au[94]
Scholl reaction	ΔT	Ag,[48, 26,47] Au,[26,49] Pt,[51, 52] Ru,[50] HOPG[71]
Ring-opening polymerization	ΔT	Cu[72]
NHC oligomerization	ΔT	Cu[56, 57]
Condensation reaction	ΔT	Cu,[80,83] Ag,[84,80, 82,85,87–89] Au[73–75,77–81]
Condensation reaction	ΔT	Ag[86]
Carbonyl-analogue addition	ΔT	Au,[90] Ag,[96] NaCl@Ag[96]
McMurry reaction	ΔT	Au[54]
[2+2+2] cycloaddition	ΔT	Au[61]
[2+2] cycloaddition	ΔT	Au[95]
[2+2] cycloaddition	$h\nu$	$CaCO_3$[97]
Decarboxylative polymerization	ΔT	Cu,[67] Ag[67]
Desulfurization + recyclization	ΔT	Ni[46]

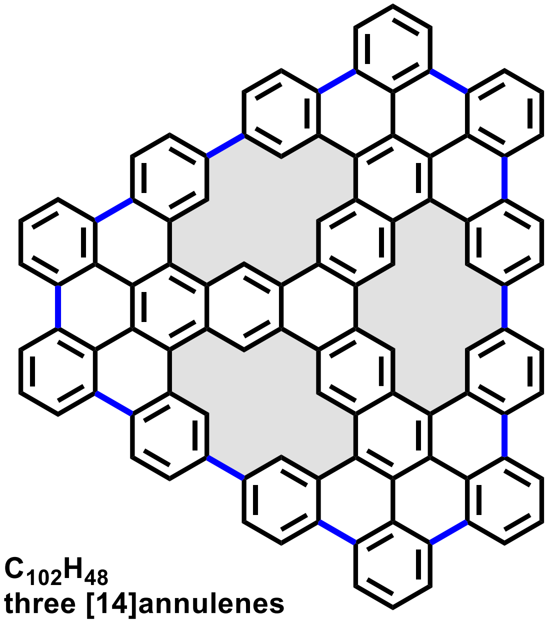
Lindner, R.; Kühnle, A. *ChemPhysChem* **2015**, *16*, 1582

SCHOLL REACTION



CYCLODEHYDROGENATION

Exotic molecules: three-pore nanographene

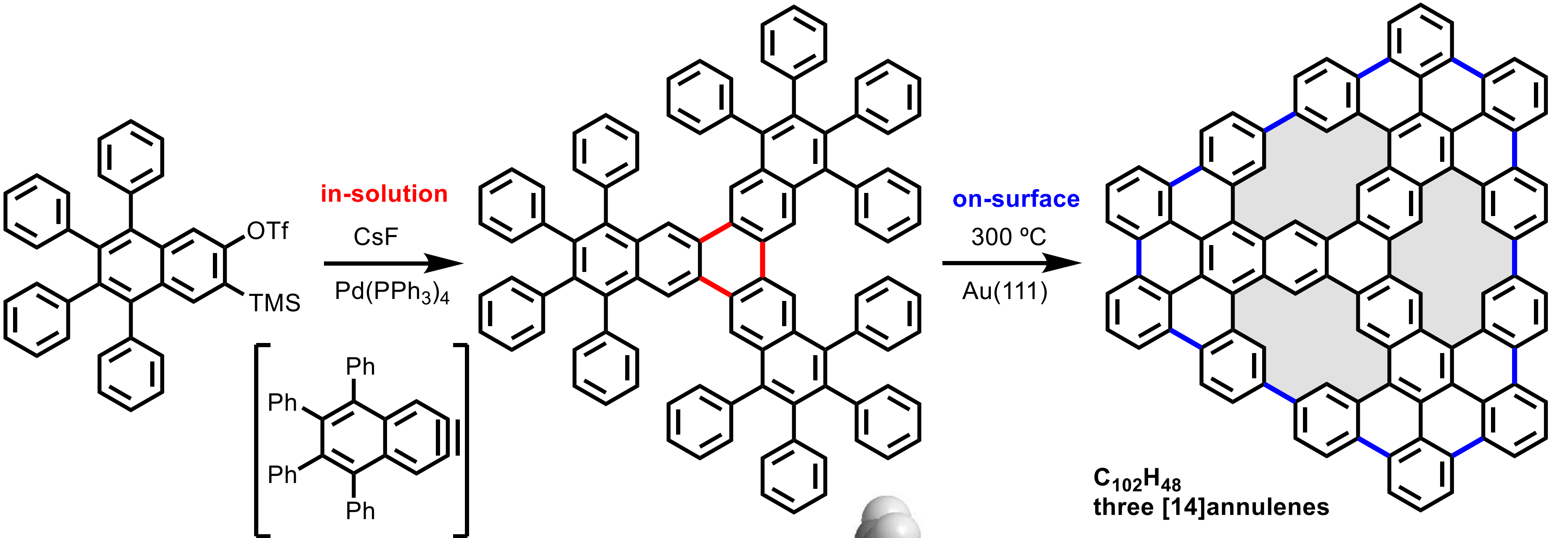


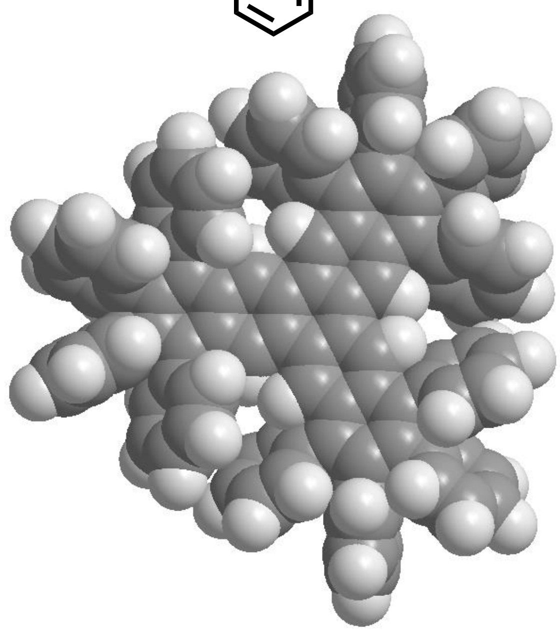
$C_{102}H_{48}$
three [14]annulenes

With Szymon Godlewski & co (JU Krakow) and Aran García-Lekue (DIPC)

Exotic molecules: three-pore nanographene

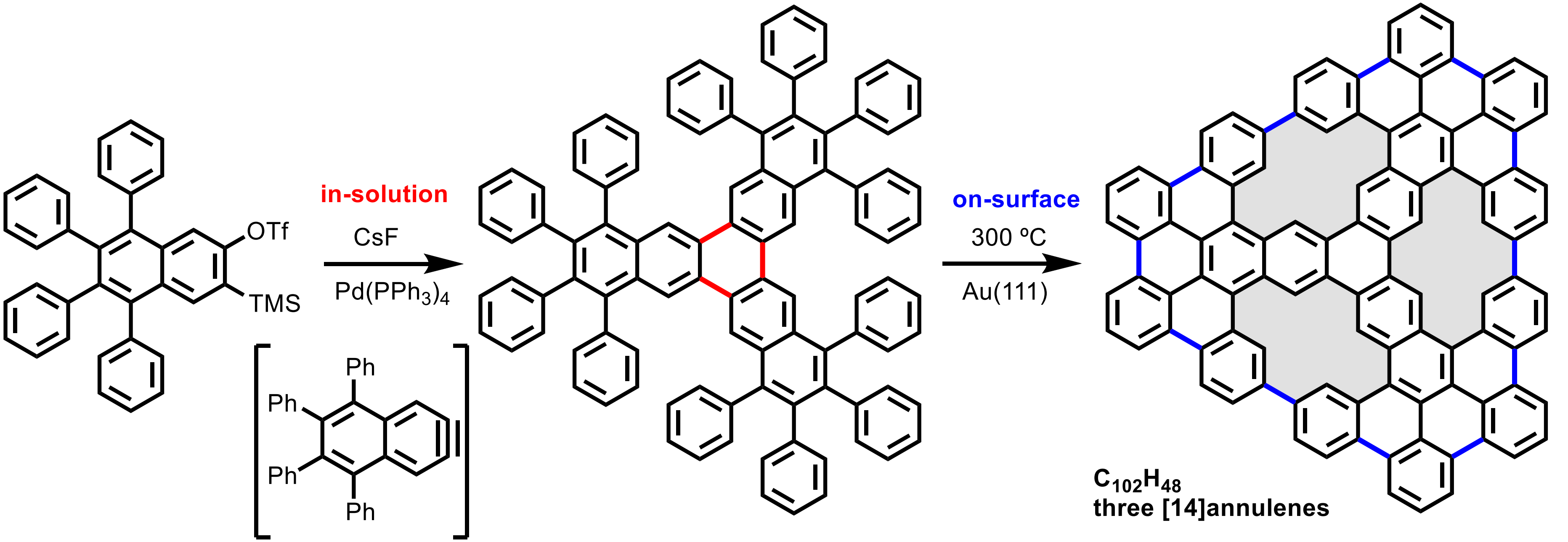
CiQUS

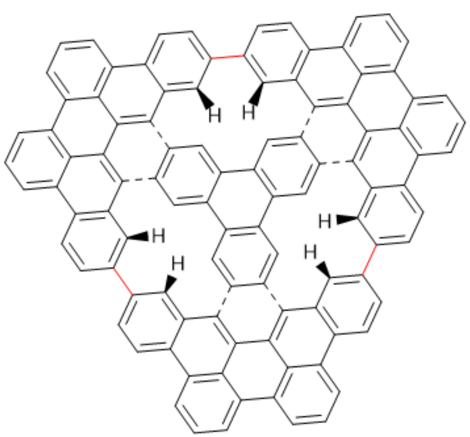


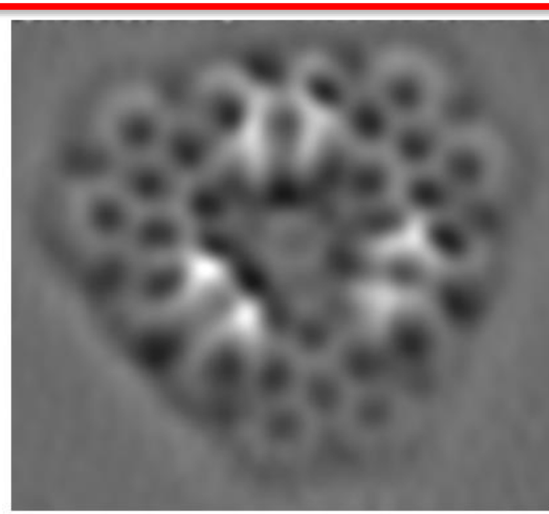


With Szymon Godlewski & co (JU Krakow) and Aran García-Lekue (DIPC)

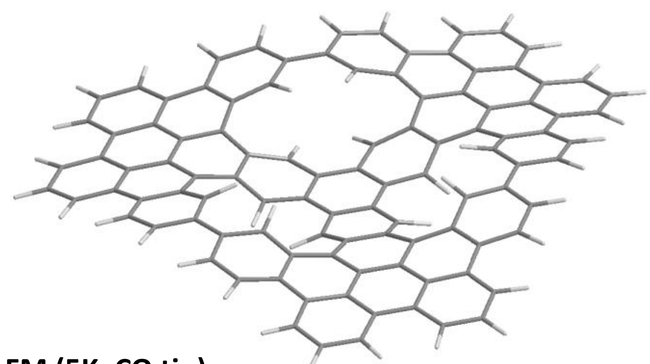
Exotic molecules: three-pore nanographene







AFM (5K, CO tip)
on Au(111)



With Szymon Godlewski & co (JU Krakow) and Aran García-Lekue (DIPC)

Ullmann Coupling

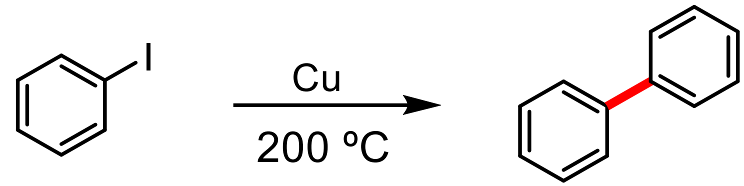
CiQUS

Ueber symmetrische Biphenylderivate;

von *Fritz Ullmann*,

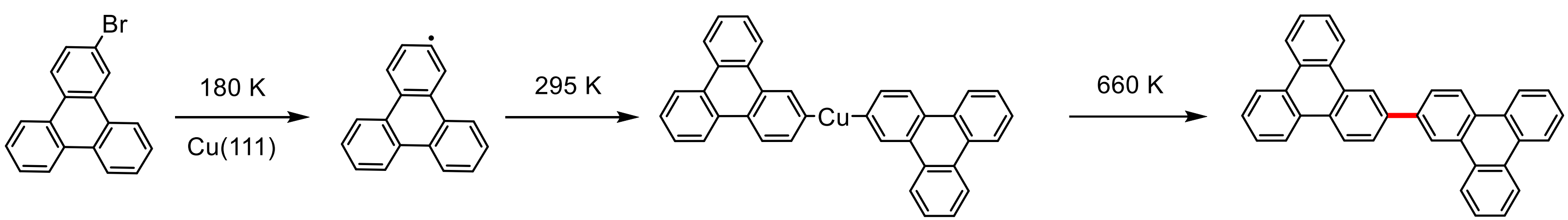
unter Mitwirkung von *Gustav M. Meyer* [1]), *Oscar Loewenthal* [2]) und *Emilio Gilli* [3]).

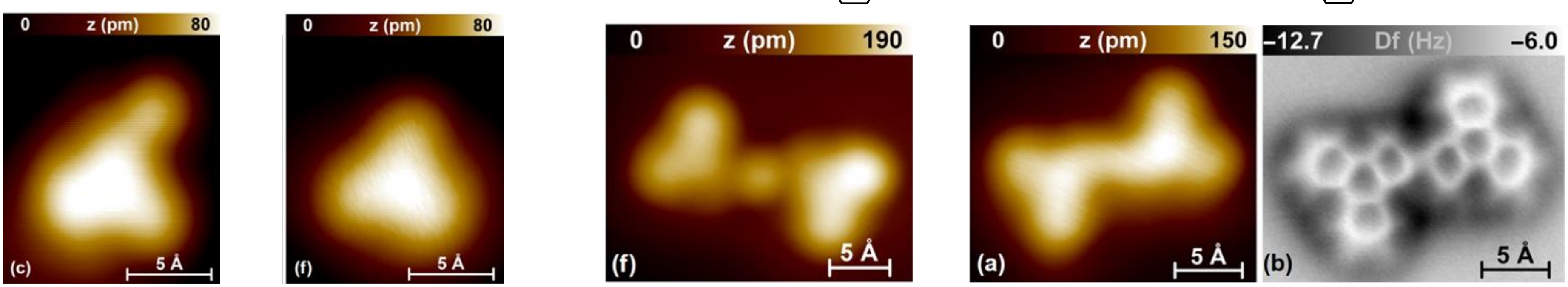
Erhitzt man Jodbenzol mit Kupfer, so beobachtet man, dass das Metall nach einiger Zeit seinen Glanz verloren hat und dass das Reactionsproduct fast reines Biphenyl darstellt,



Ullmann, F. *Justus Liebigs Ann. Chem.* **1904**, *332*, 38

Thermally induced on-surface Ullmann coupling





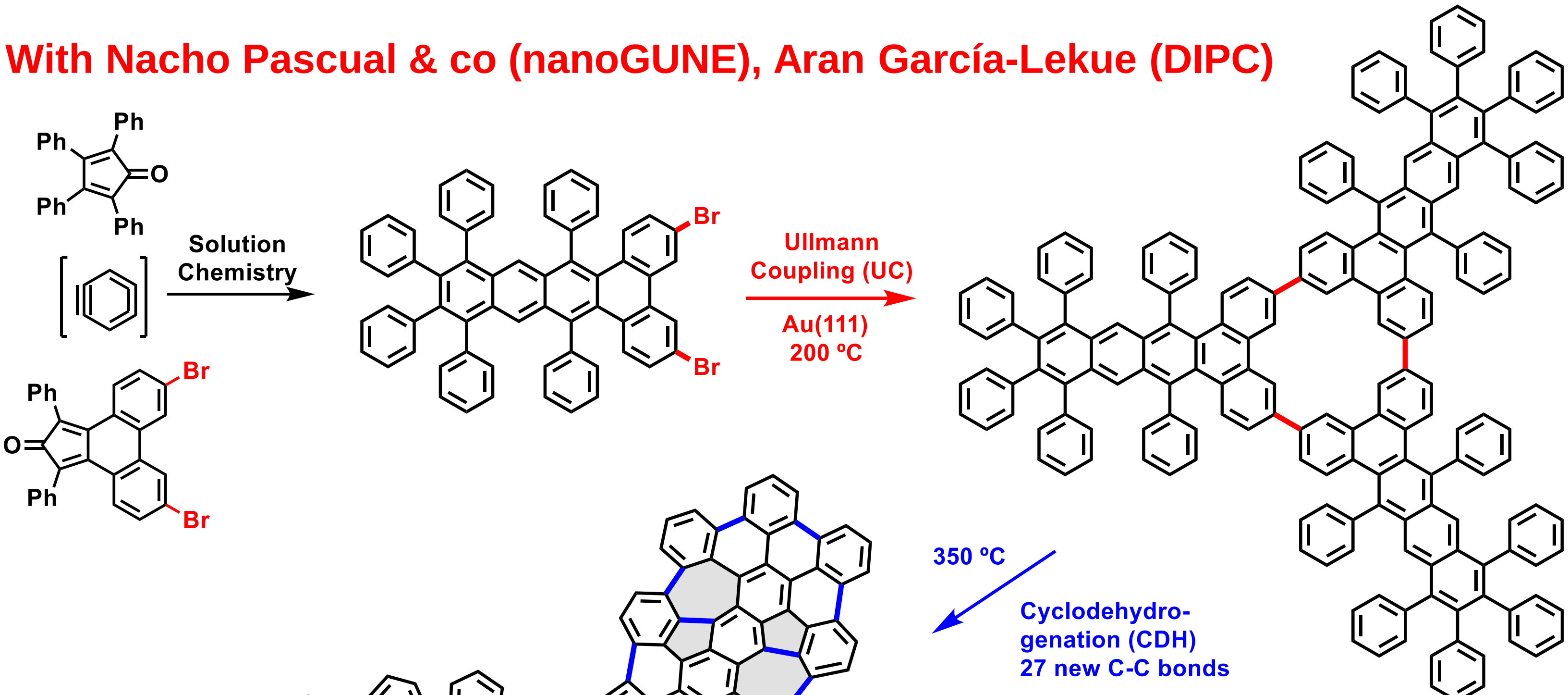
STM **AFM (CO tip)**

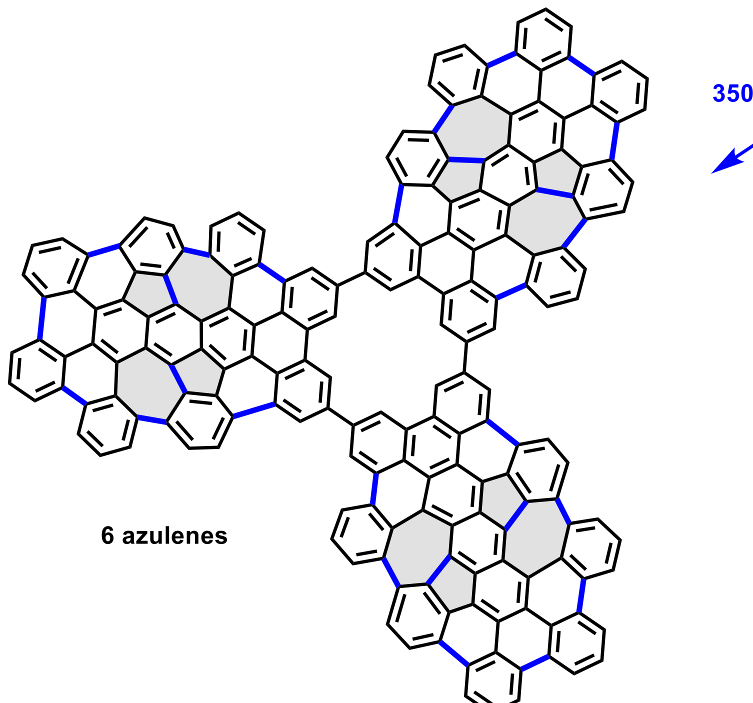
S. Zint *et al. ACS Nano* **2017**, *11*, 4183

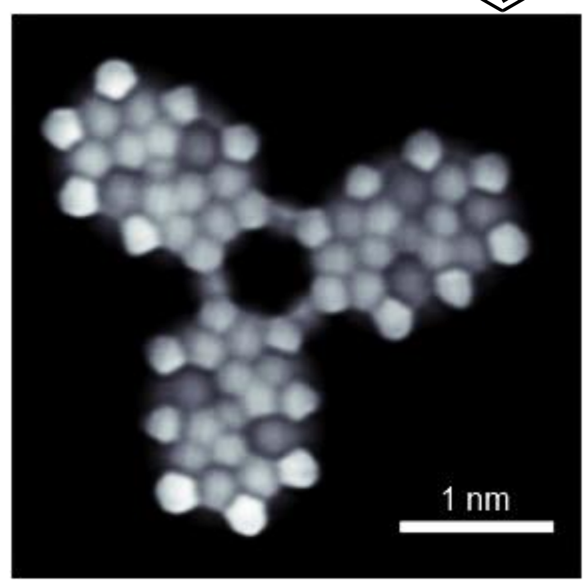
A nanographene with [18]annulene pore

CIC nanoGUNE — nanoscience cooperative research center | CiQUS

With Nacho Pascual & co (nanoGUNE), Aran García-Lekue (DIPC)







STM (5K, CO tip) on Au(111)

Hieulle, J.; Carbonell-Sanromà, E.; Vilas-Varela, M.; Garcia-Lekue, A.; Guitián, E.; Peña, D.; Pascual, J. I. *Nano Lett.* **2018**, *18*, 418

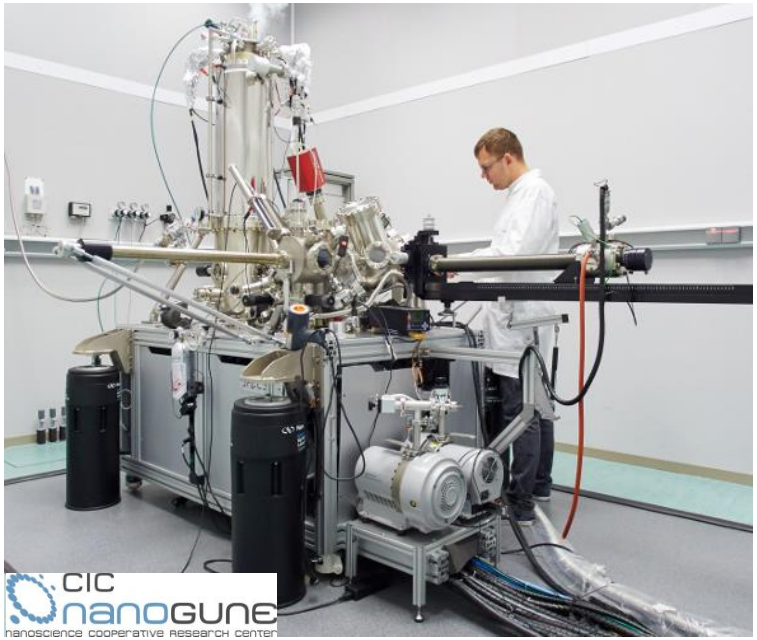
CiQUS

1) Characterization of graphene molecules

2) Combining solution and on-surface synthesis

3) Elusive graphene nanostructures

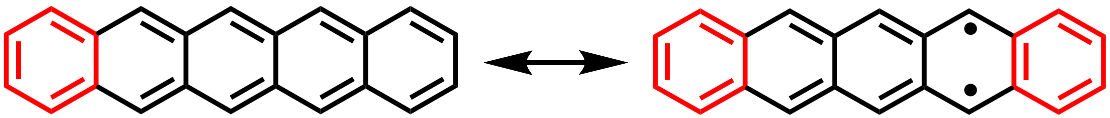
AFM/STM under ultra-high vacuum conditions



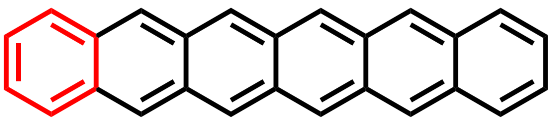
Synthesis of Large Acenes

CiQUS

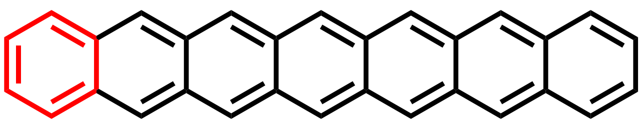
-Linear fusion of benzene rings: narrowest *zig-zag* GNRs
-One Clar sextet: the larger the length, the smaller the HOMO-LUMO gap
-Diradical character: unstable under ambient conditions



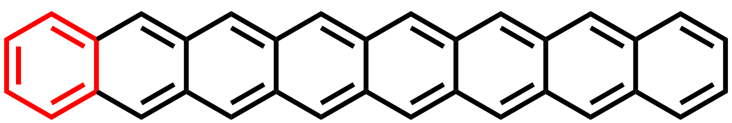
Pentacene: Paradigmatic organic semiconductor



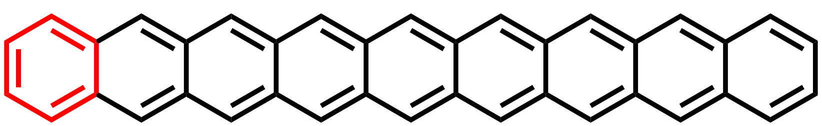
Hexacene:
Isolated in the solid state, M. Watanabe et al. *Nat. Chem.* **2012**, *4*, 574
Generated on Ni surface, D. F. Perepichka, F. Rosei et al. *ACS Nano* **2013**, *7*,1652



Heptacene: Isolated in the solid state
R. Einholz et al. *J. Am. Chem. Soc.* **2017**, *139*, 4435

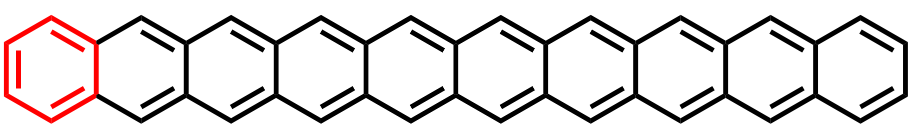


Octacene



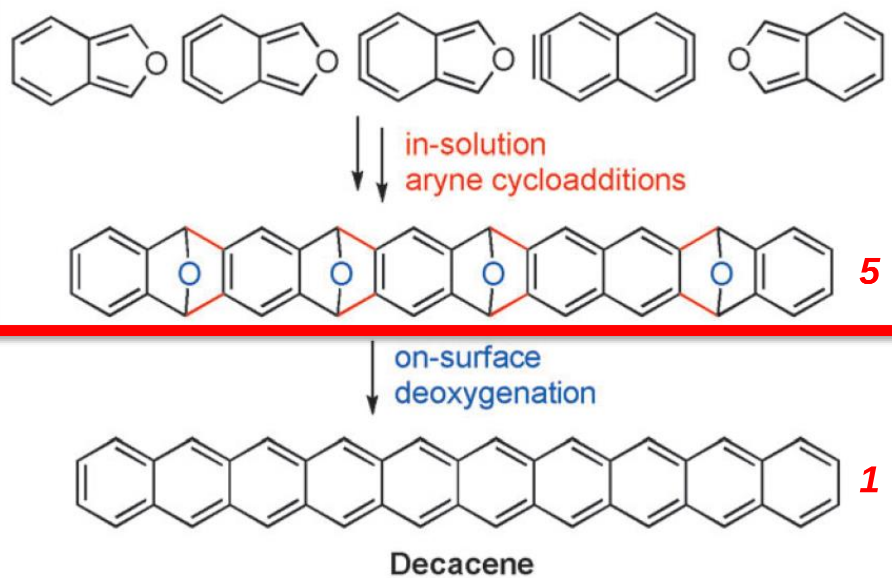
Nonacene

Generated in cryogenic noble gas matrices
C. Tönshoff, H. F. Bettinger
Angew. Chem. Int. Ed. **2010**, *122*, 4219



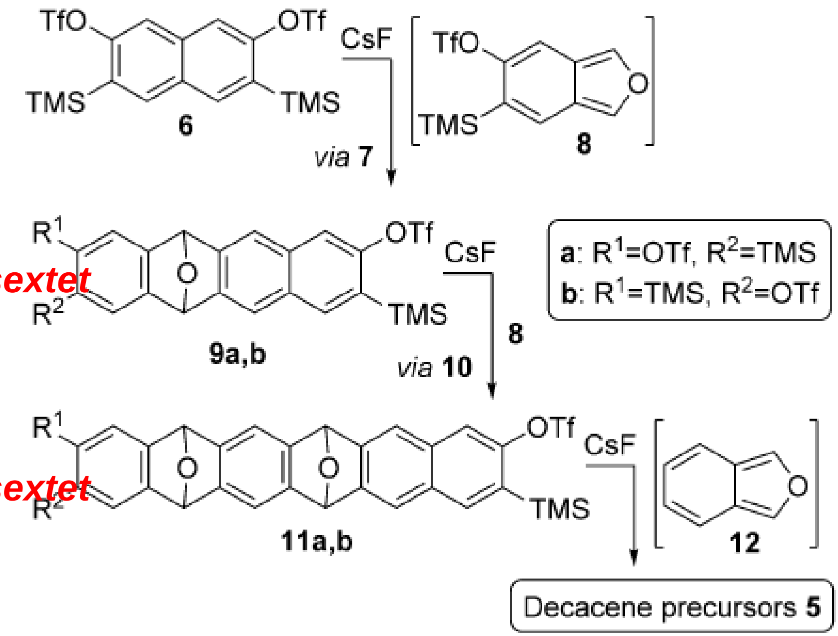
Decacene?

On-Surface Synthesis of Decacene



5 Clar sextet

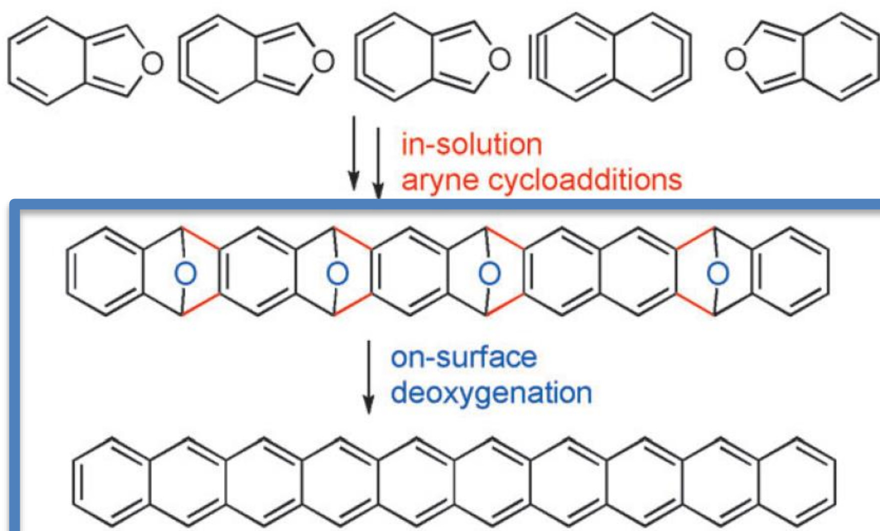
1 Clar sextet



Fátima García

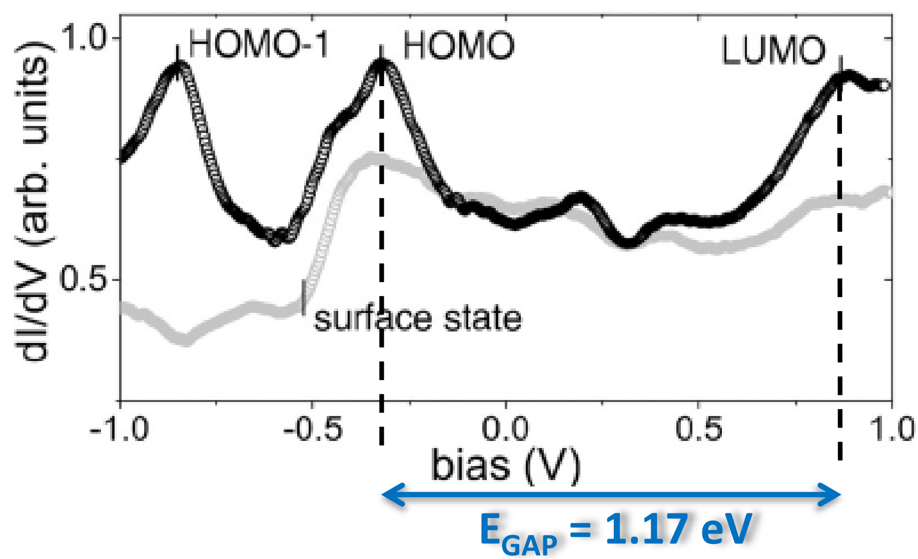
Angew. Chem. Int. Ed. **2017**, *56*, 11945

On-Surface Synthesis of Decacene



Decacene

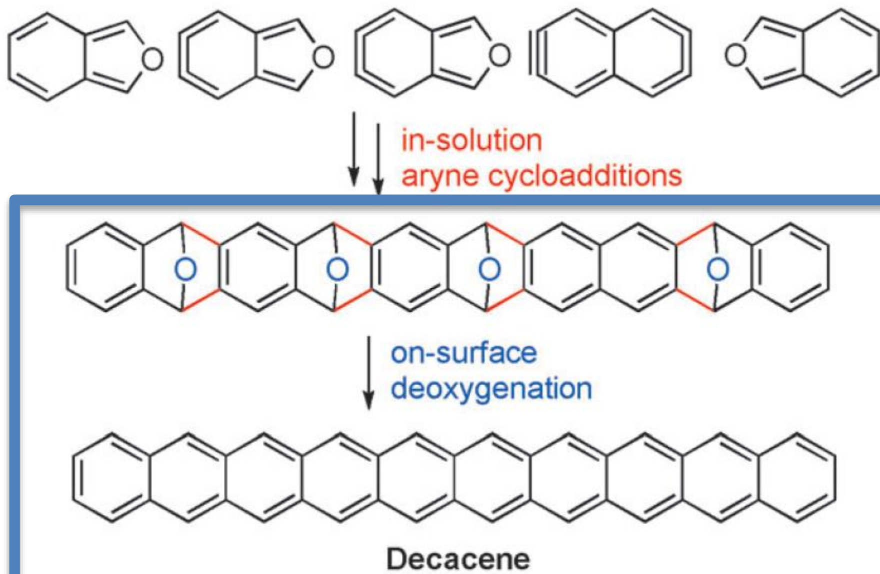
With F. Moresco & co (TU Dresden)



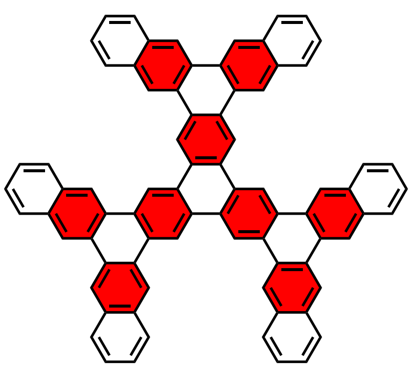
Fátima García

Angew. Chem. Int. Ed. **2017**, *56*, 11945

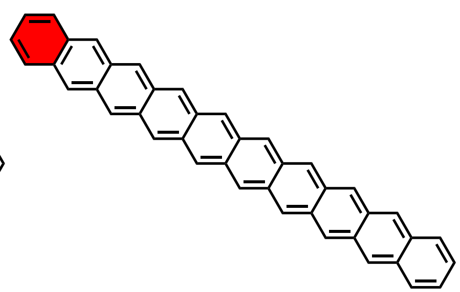
On-Surface Synthesis of Decacene



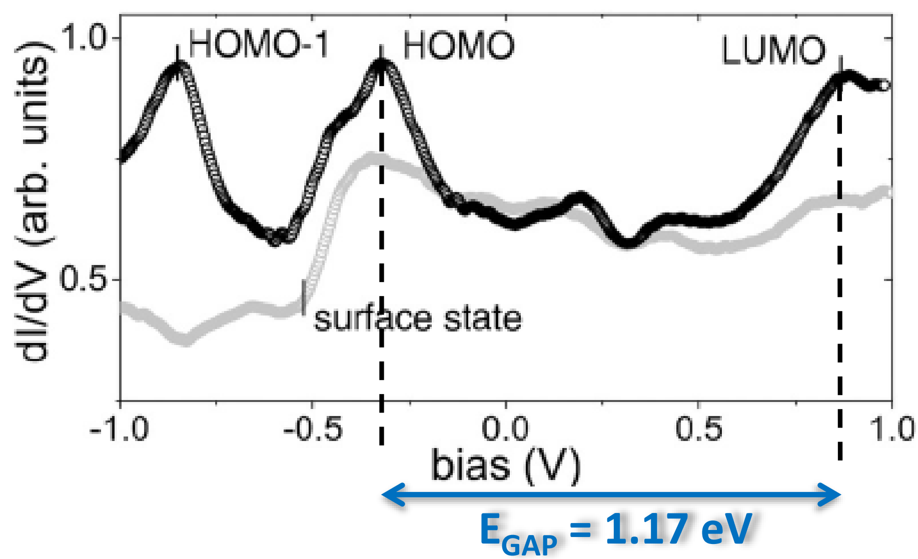
With F. Moresco & co (TU Dresden)



Gap = 4.1 eV
9 Clar sextets

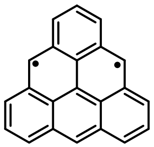


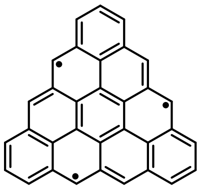
Gap = 1.2 eV
1 Clar sextet

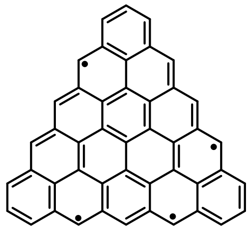


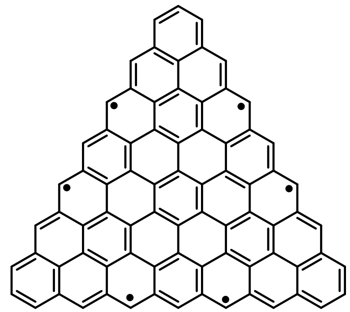
Open-shell nanographenes

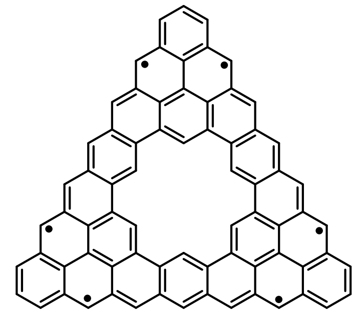
Triangulene derivatives

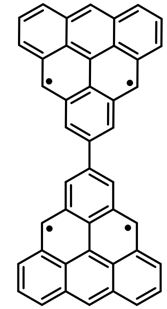

[3]triangulene
2 unpaired electrons (2 ue)

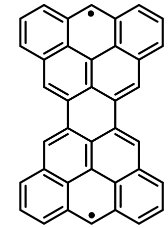

[4]triangulene
3 ue

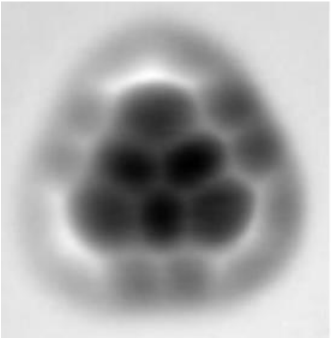

[5]triangulene
4 ue


[7]triangulene
6 ue

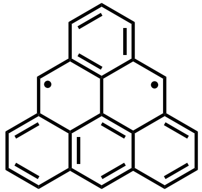

[7]triangulene ring
6 ue


[3]triangulene dimer
4 ue


Clar's goblet
2 ue

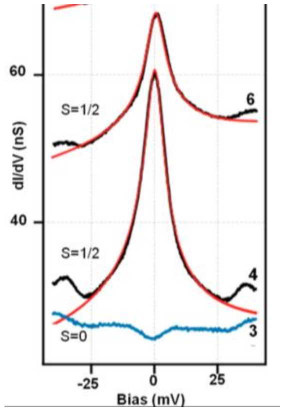


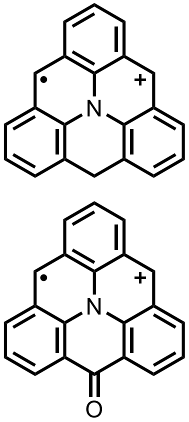
[3]triangulene



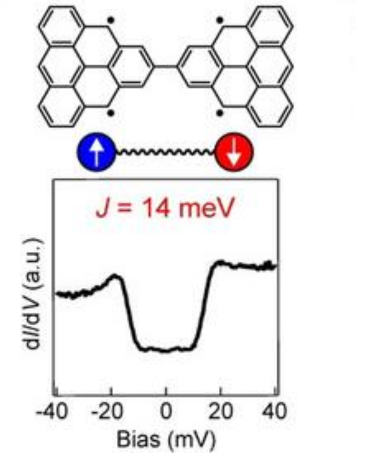
S = 1
Triplet ground state

L. Gross and co.
Nature Nanotech. **2016**, *12*, 308





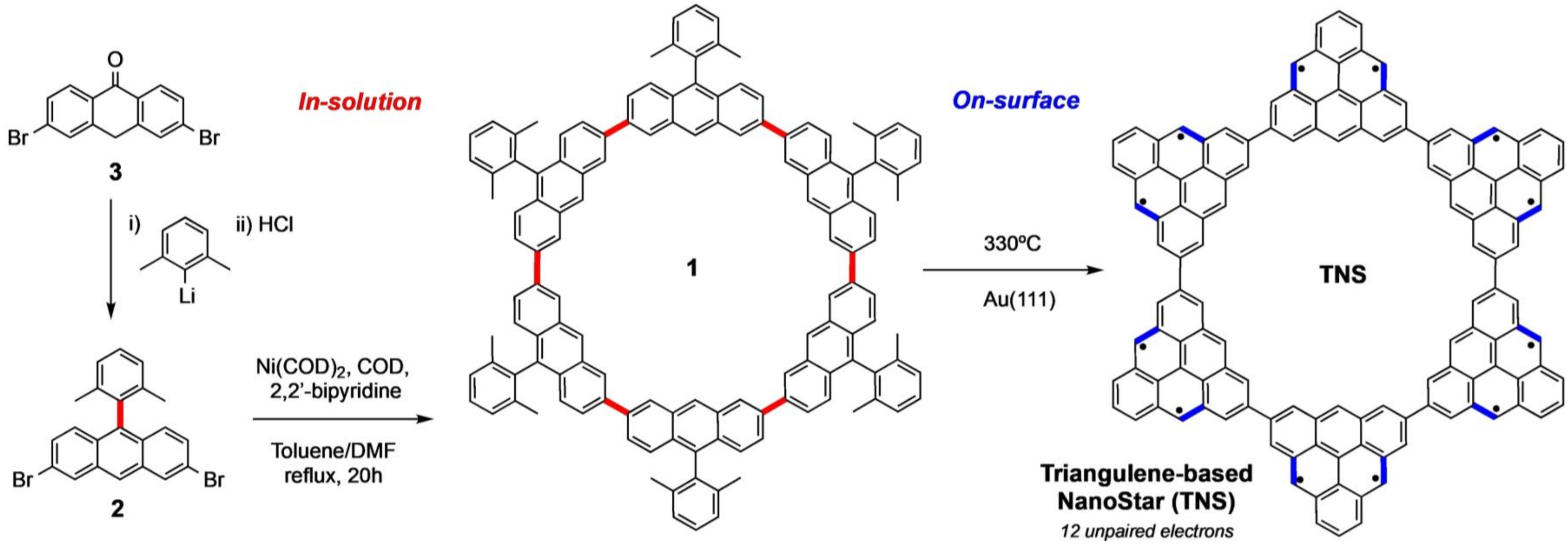
Kondo resonances
Unpaired spins-conduction electrons



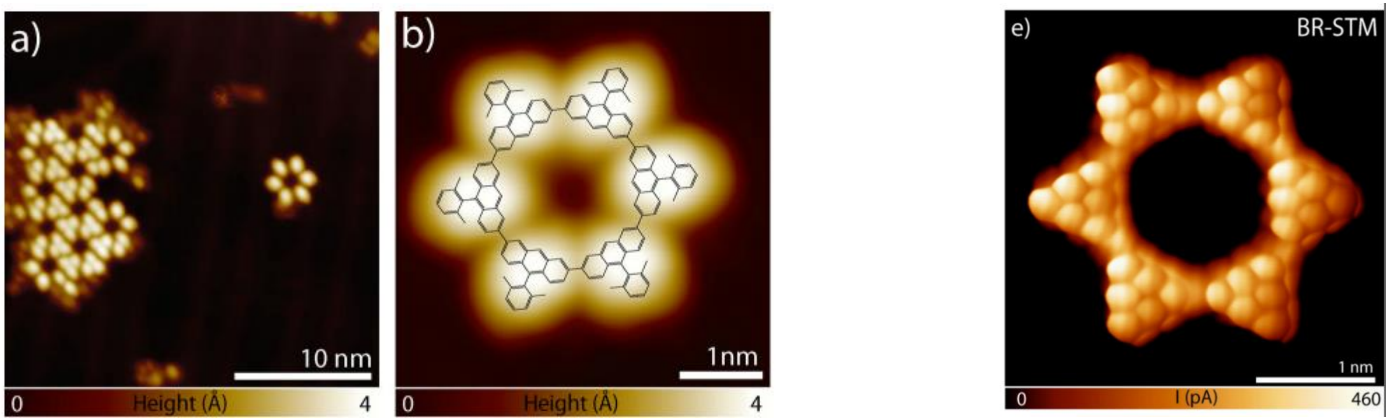
Inelastic excitations
Singlet-triplet spin excitations
Exchange interactions

Triangulene-based NanoStar

With Nacho Pascual and coworkers (nanoGUNE)



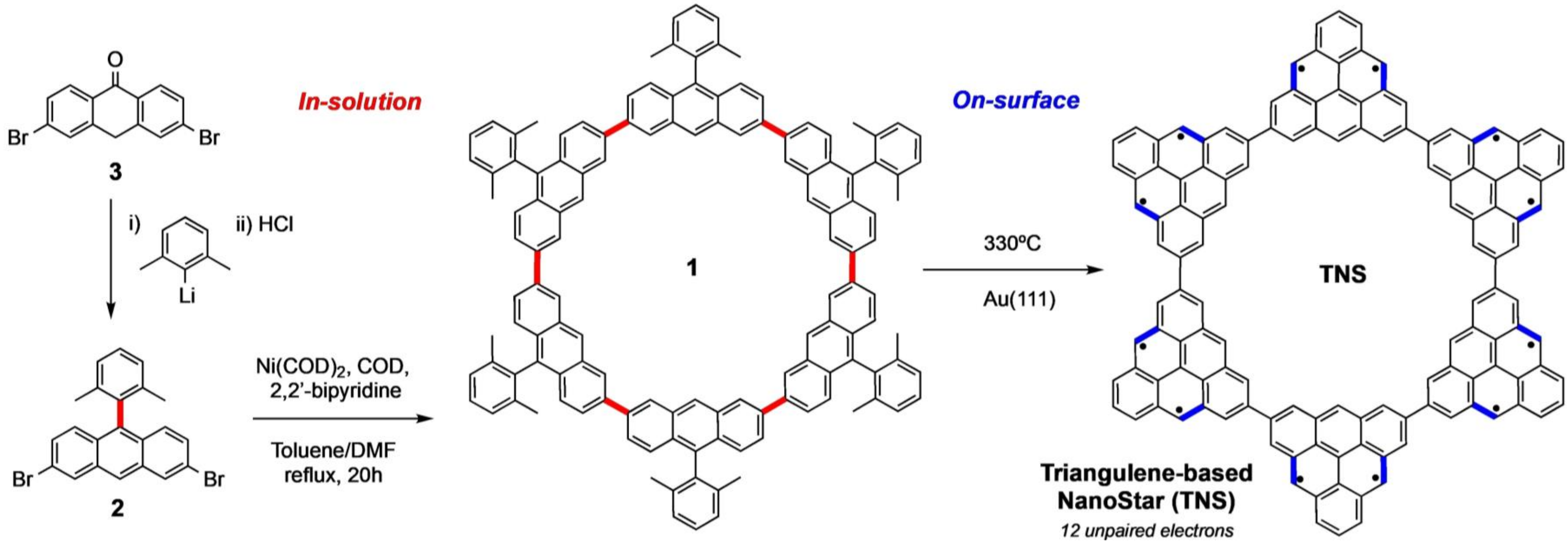
Silvia Castro

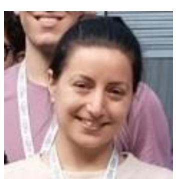


Angew. Chem. Int. Ed. **2021**, *60*, 25224

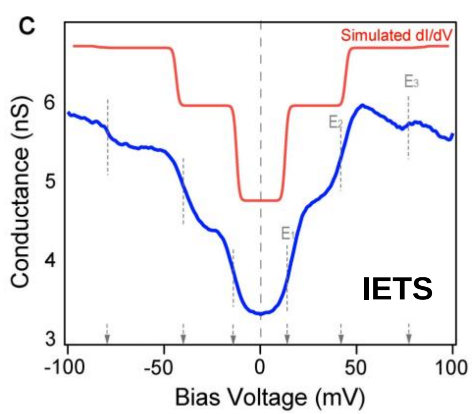
Triangulene-based NanoStar

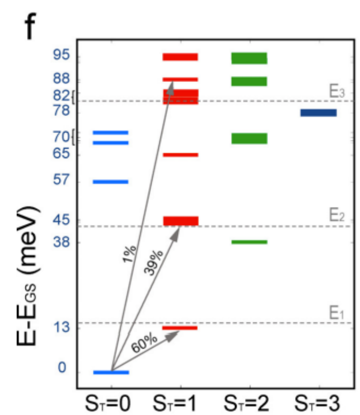
With Nacho Pascual and coworkers (nanoGUNE)



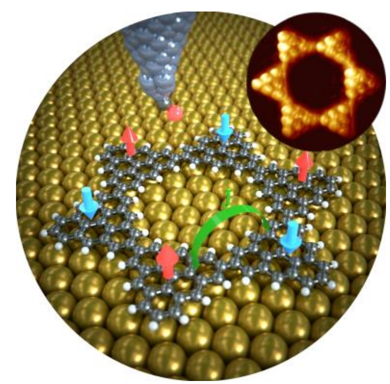


Silvia Castro





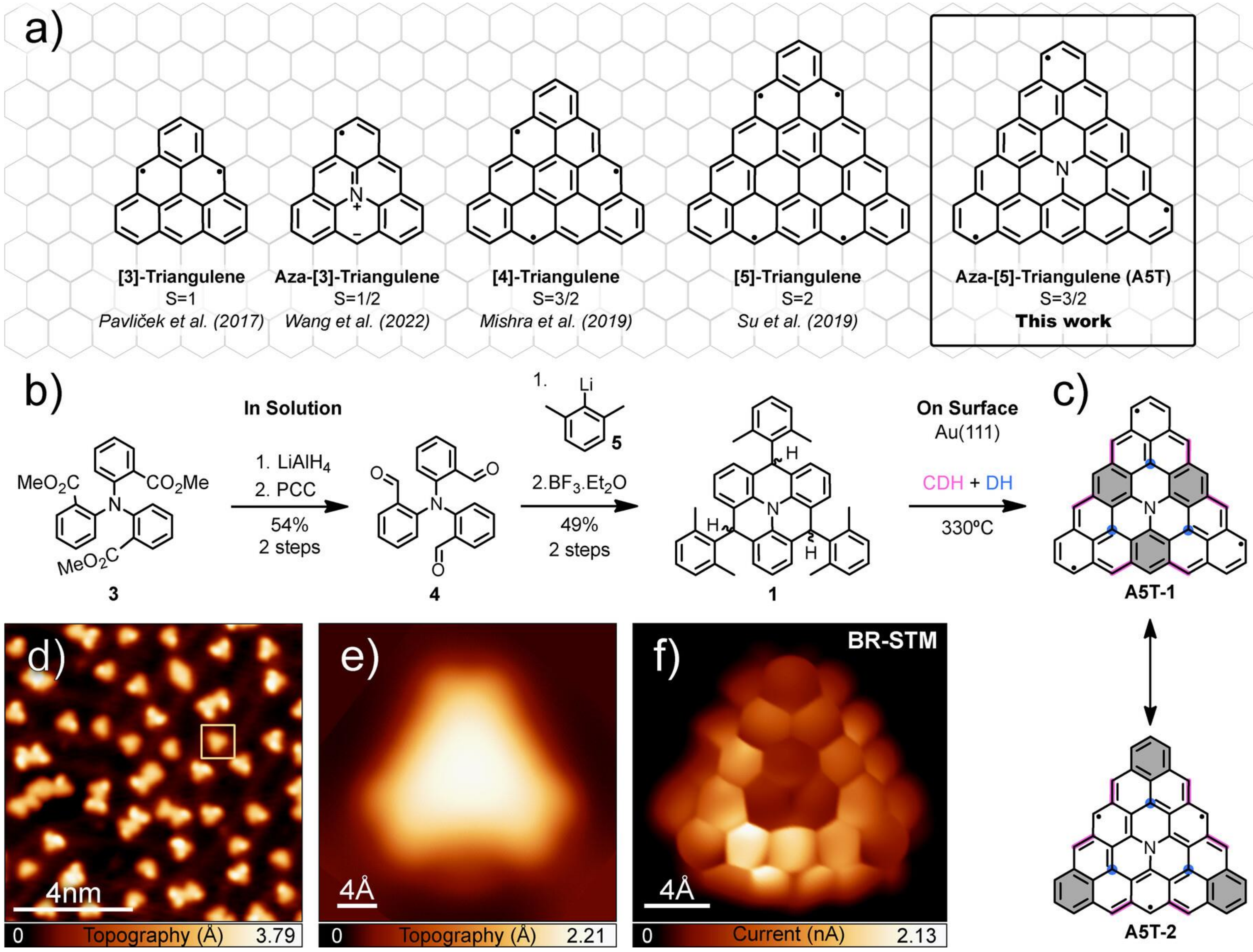
Collective spin excitations



Antiferromagnetic ordering of six S = 1 units

Angew. Chem. Int. Ed. **2021**, *60*, 25224

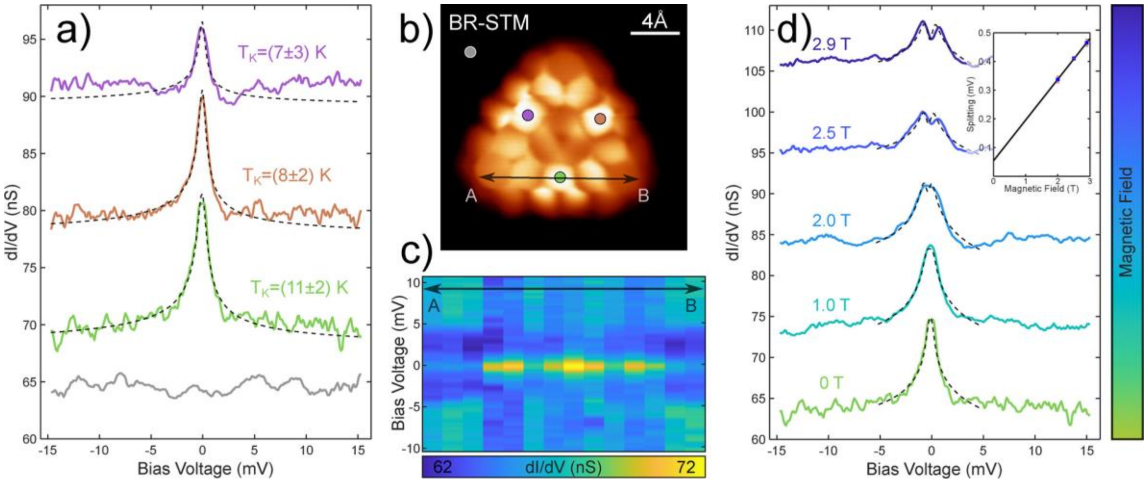
Aza-[5]-Triangulene

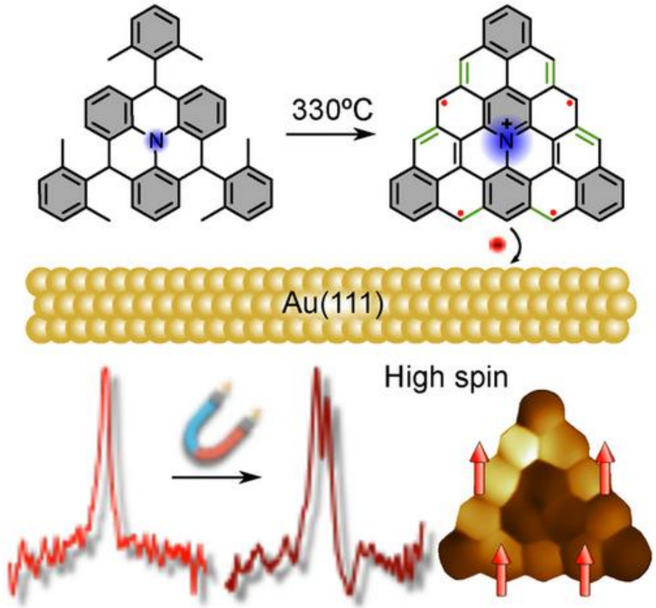


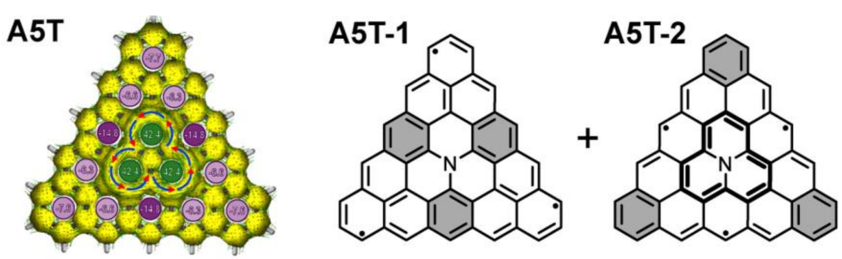
Angew. Chem. Int. Ed. **2023**, *ASAP*

With Nacho Pascual and coworkers (nanoGUNE)

Aza-[5]-Triangulene

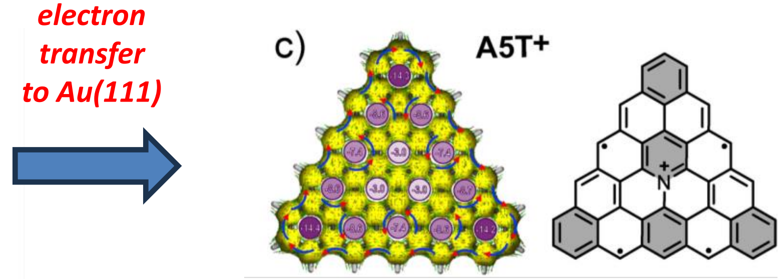






S = 3/2

electron transfer to Au(111)



S = 2

Angew. Chem. Int. Ed. **2023**, *ASAP*

With Nacho Pascual and coworkers (nanoGUNE)

CiQUS

1) *Characterization of graphene molecules*

2) *Combining solution and on-surface synthesis*

3) *Elusive graphene nanostructures*

4) *Bottom-up approach to graphene nanoribbons and nanoporous graphene*

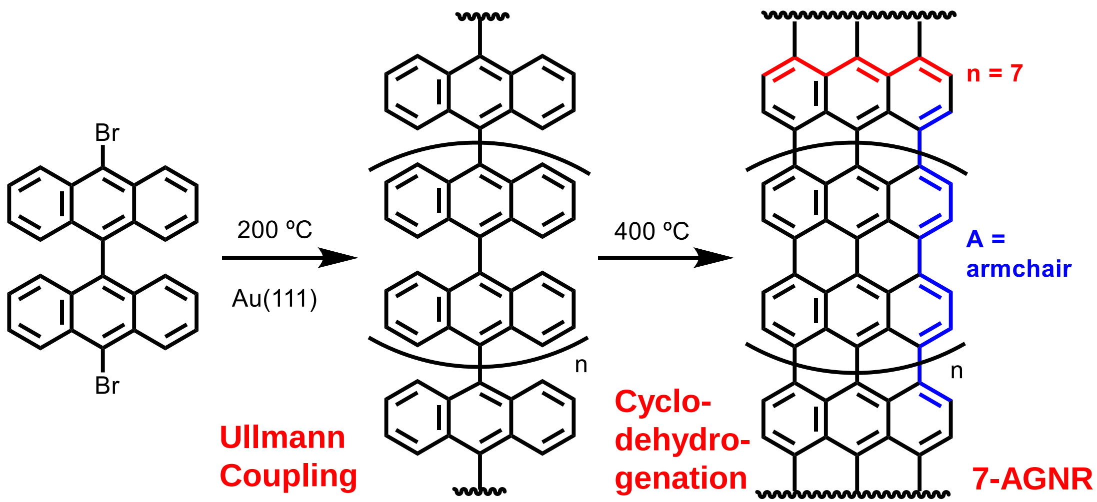
2-5 nm is OK…what about 10-100 nm?

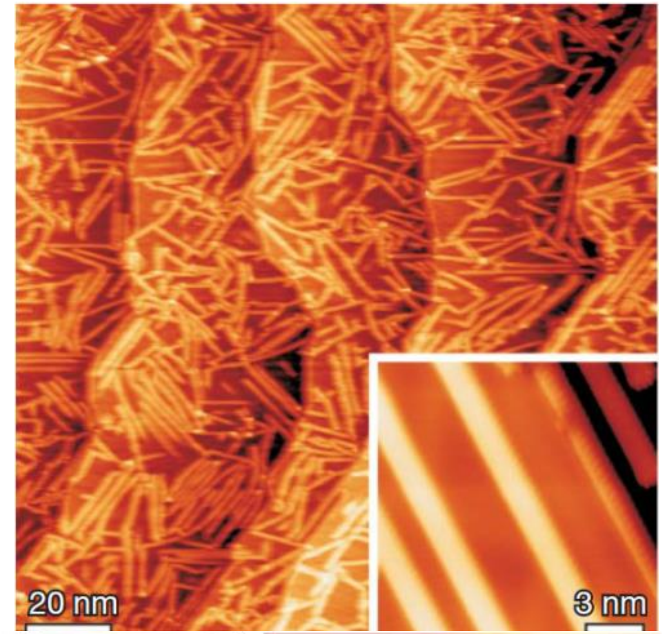
On-Surface Synthesis of GNRs

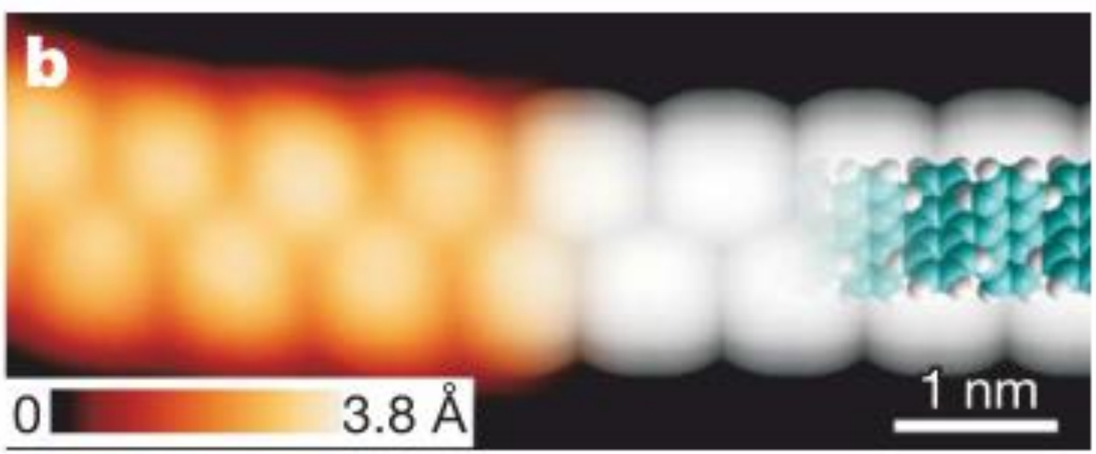
Atomically Precise Bottom-Up Fabrication of Graphene Nanoribbons

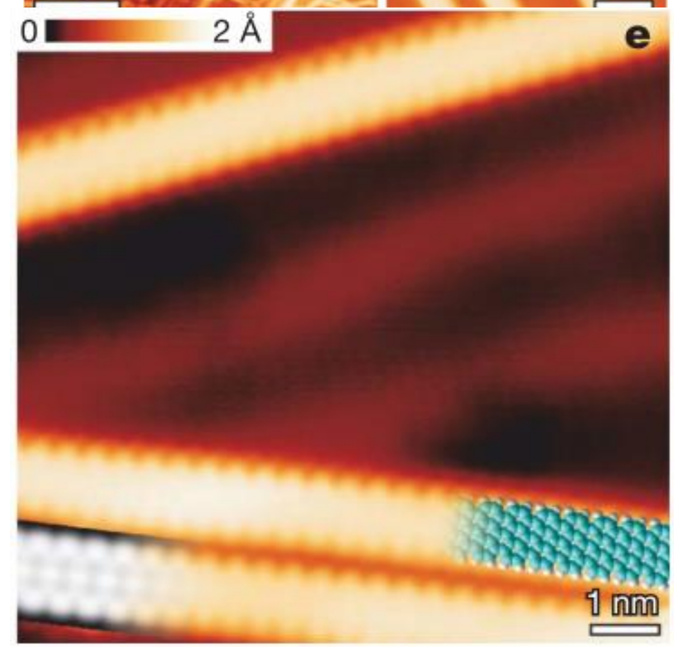
Müllen, Fasel et al. *Nature* **2010**, *466*, 470

Band gap = 2.50 eV









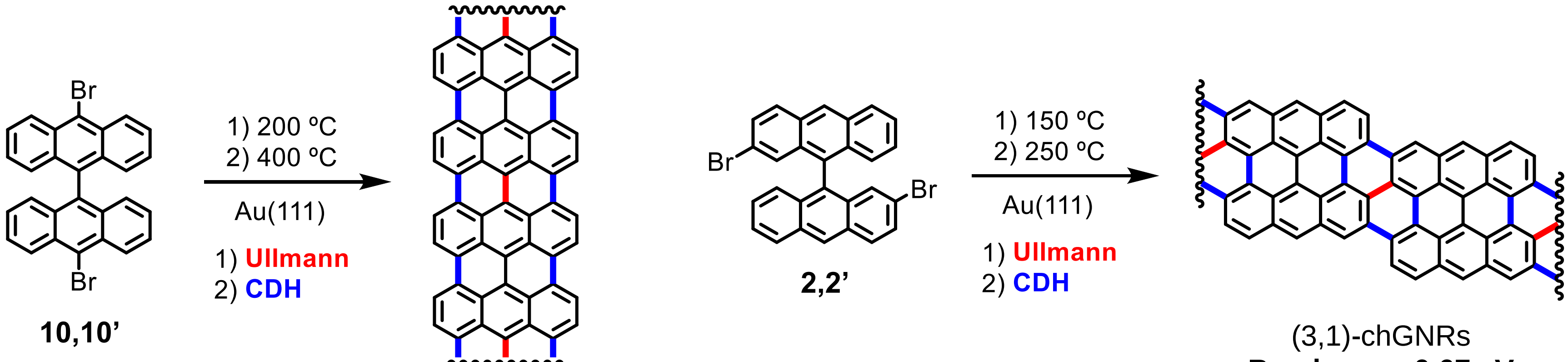
STM, 5K, Au(111)

On-Surface Synthesis of GNRs

CiQUS

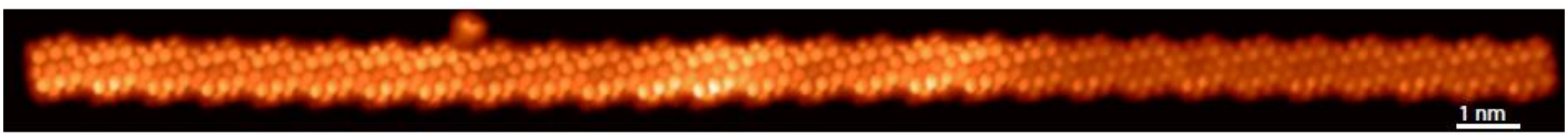
Substrate-Independent Growth of Atomically Precise Chiral Graphene Nanoribbons

With D. de Oteyza (CFM), J. I. Pascual (nanoGUNE), A. García-Lekue (DIPC) and co.



(3,1)-chGNRs
Band gap = 0.67 eV

7-AGNRs
Band gap = 2.50 eV



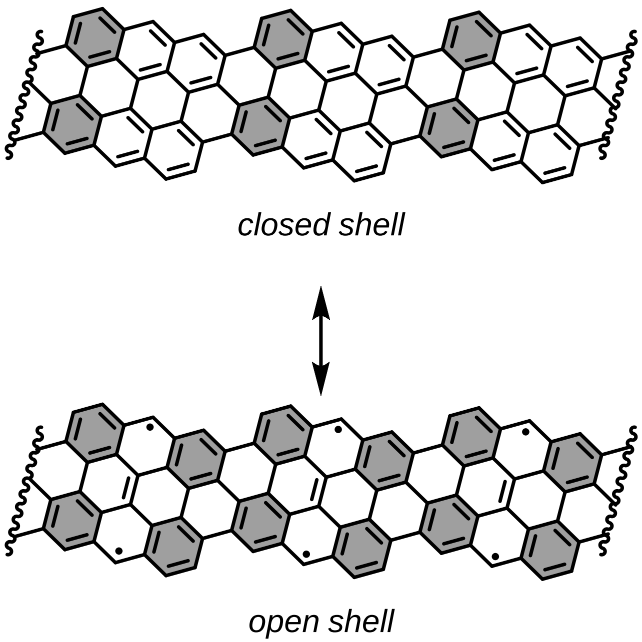
(3,1)-chGNRs **STM (5K, CO tip) on Au(111)**

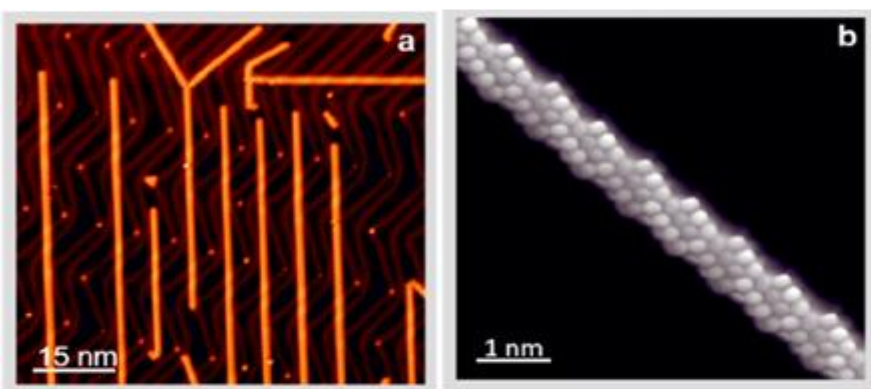
ACS Nano **2016**, *10*, 9000

Stability of GNRs

With Dimas de Oteyza (CFM), Pavel Jelinek (FZU) and co

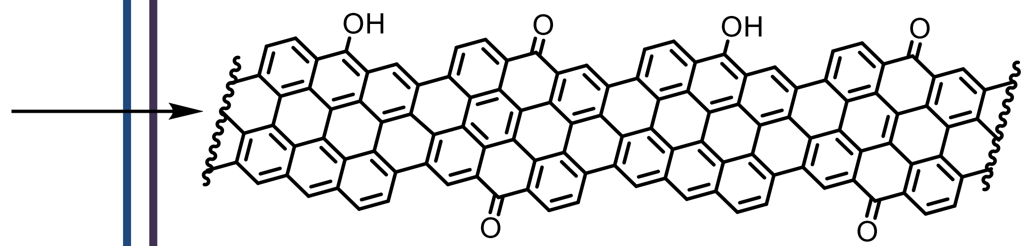
(3,1)-chGNRs



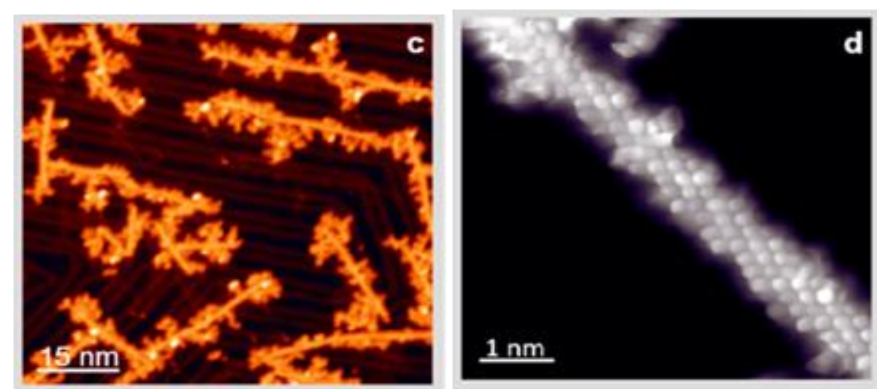


STM (UHV, 4 K) AFM (UHV, 4 K, CO tip)

Air exposure



ACS Nano, **2021**, *15*, 5610

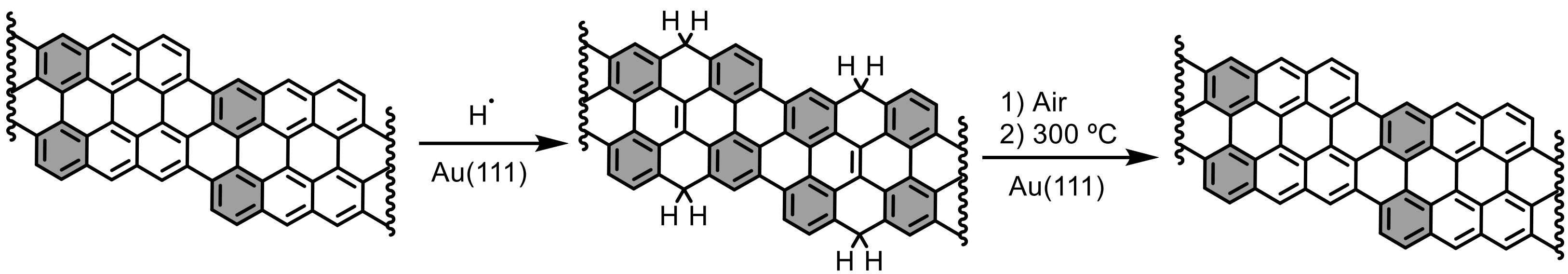


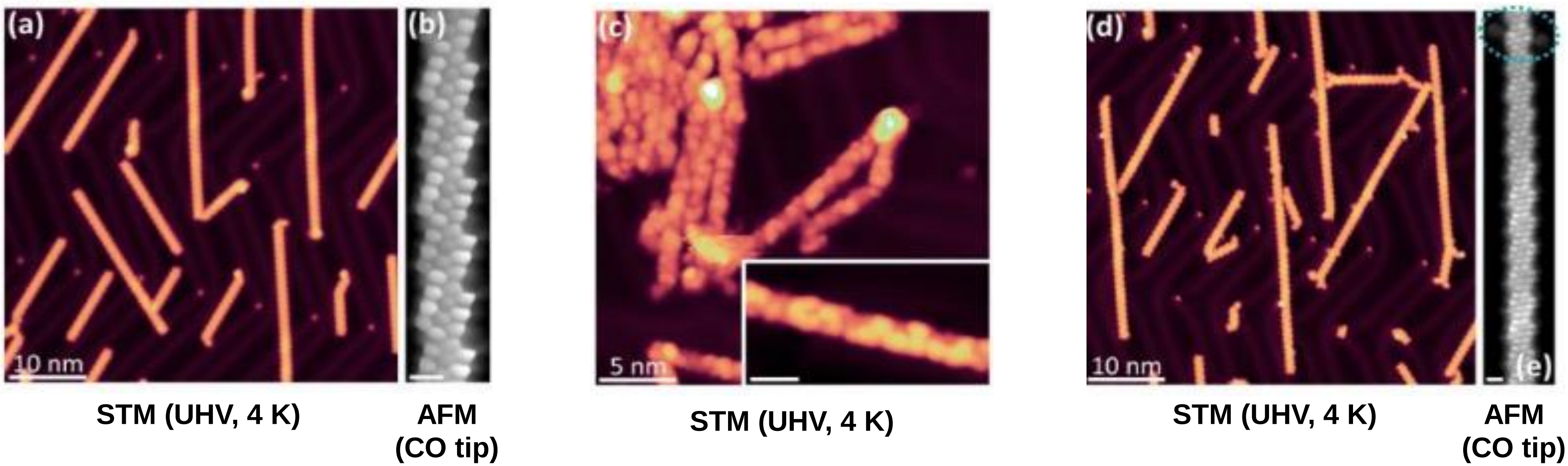
STM (UHV, 4 K) AFM (UHV, 4 K, CO tip)

Stability of GNRs

With Dimas de Oteyza (CFM), Pavel Jelinek (FZU) and co

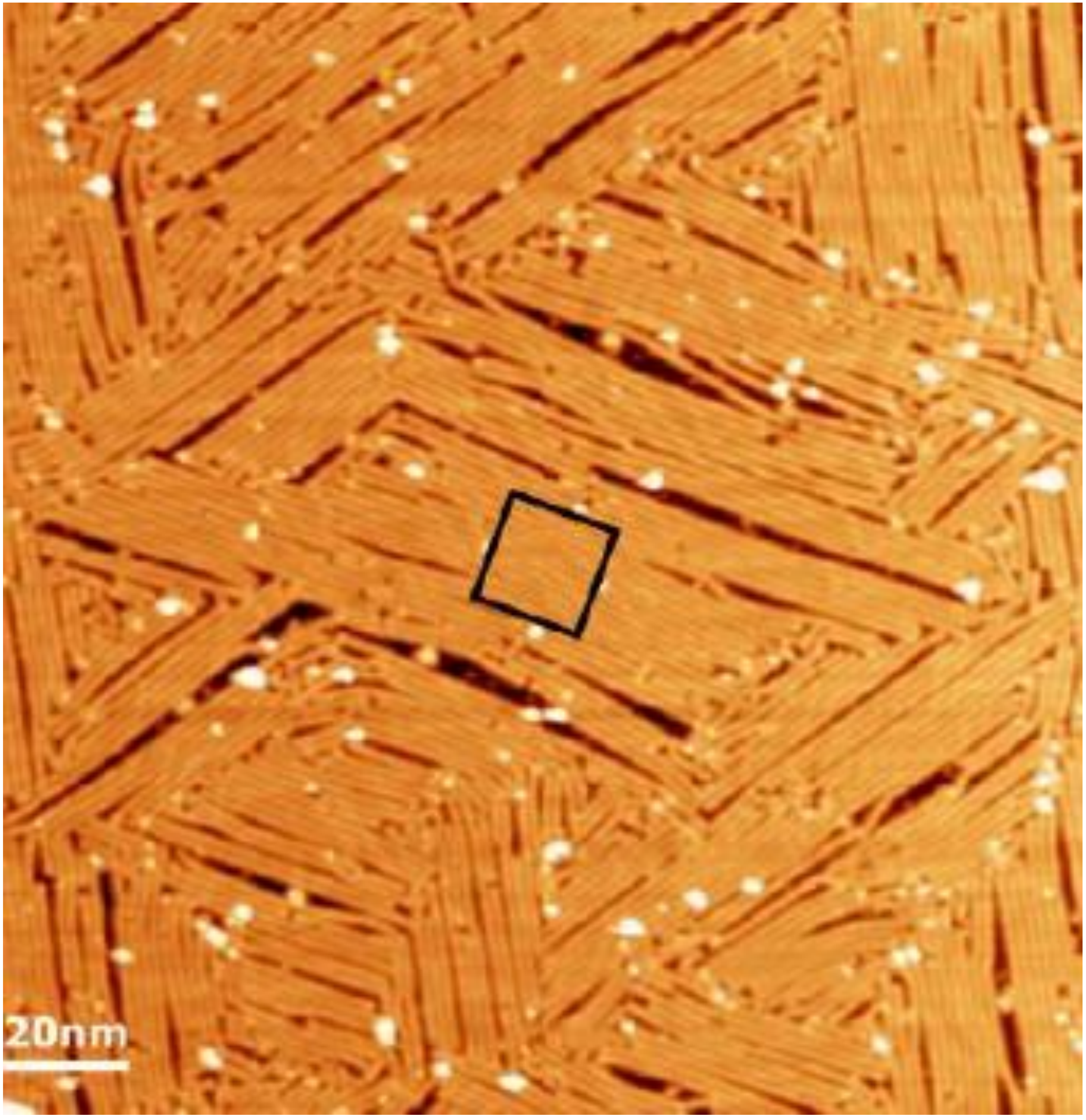
Protection/deprotection strategy



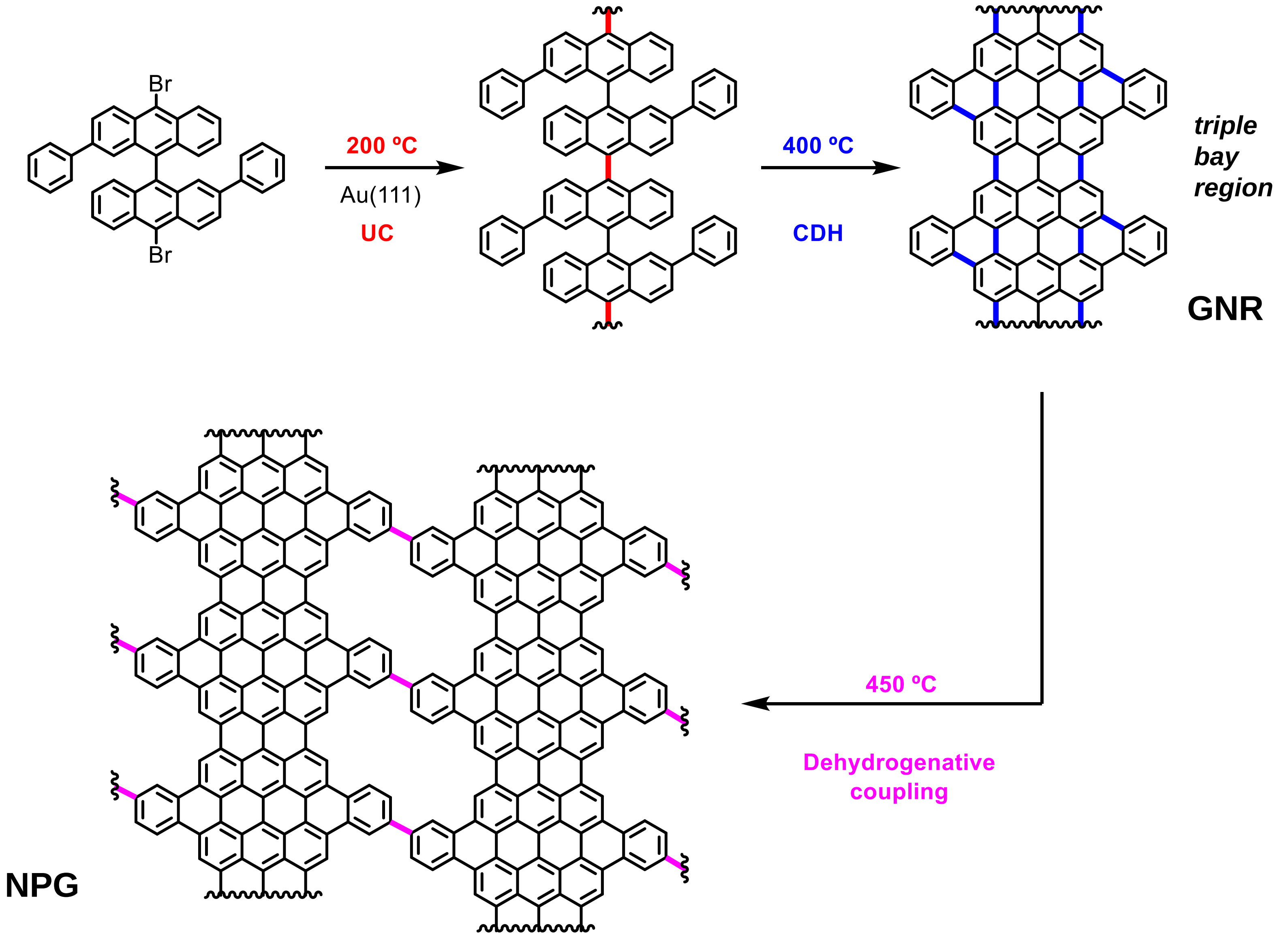


Nature Chem. **2022**, *14*, 1451

Lateral Fusion of Graphene Nanoribbons



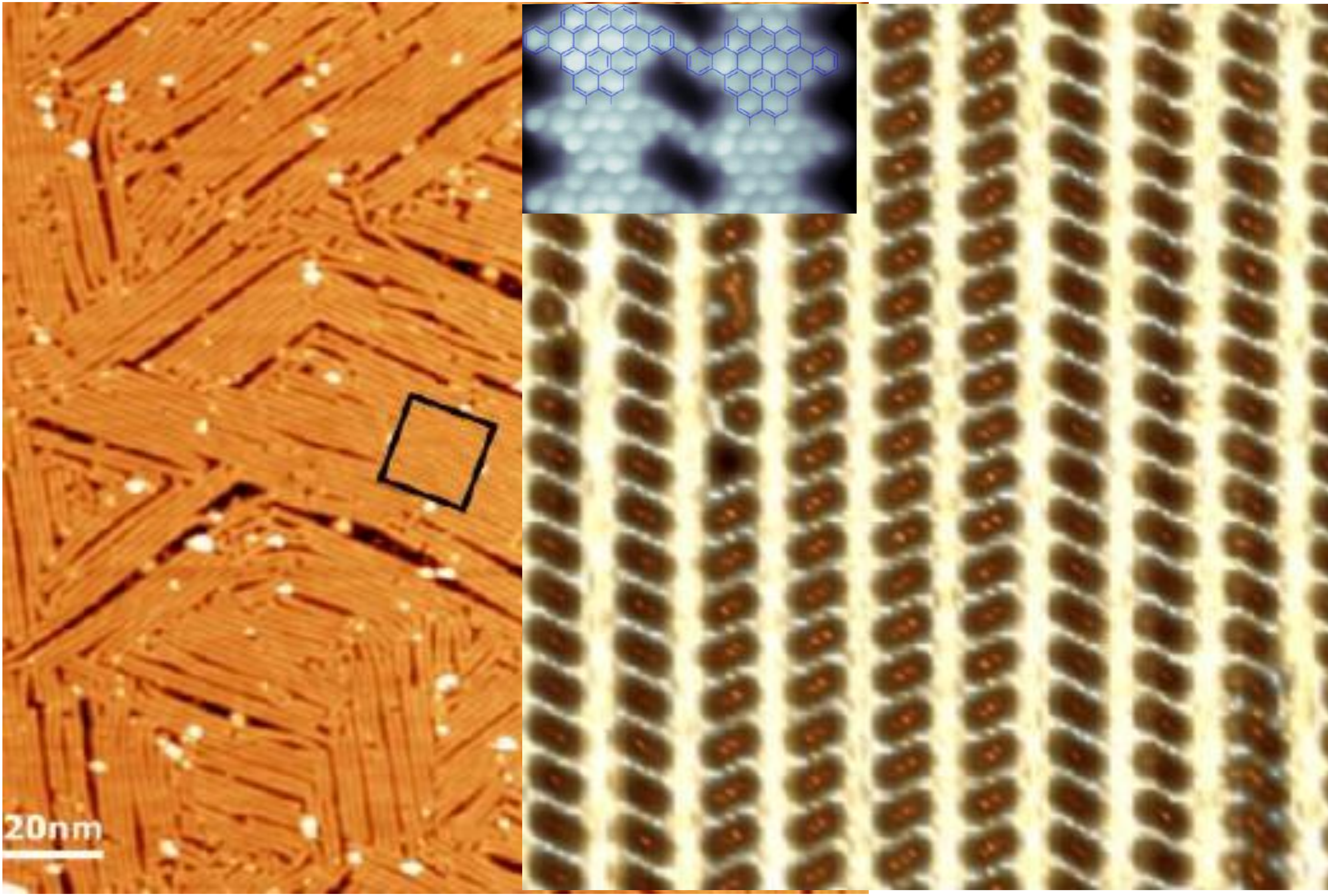
Nanoporous Graphene



Science **2018**, *360,* 199

with Aitor Mugarza, Cesar Moreno and co (ICN2-Barcelona) and Aran García-Leuke (DIPC-San Sebastián)

Nanoporous Graphene

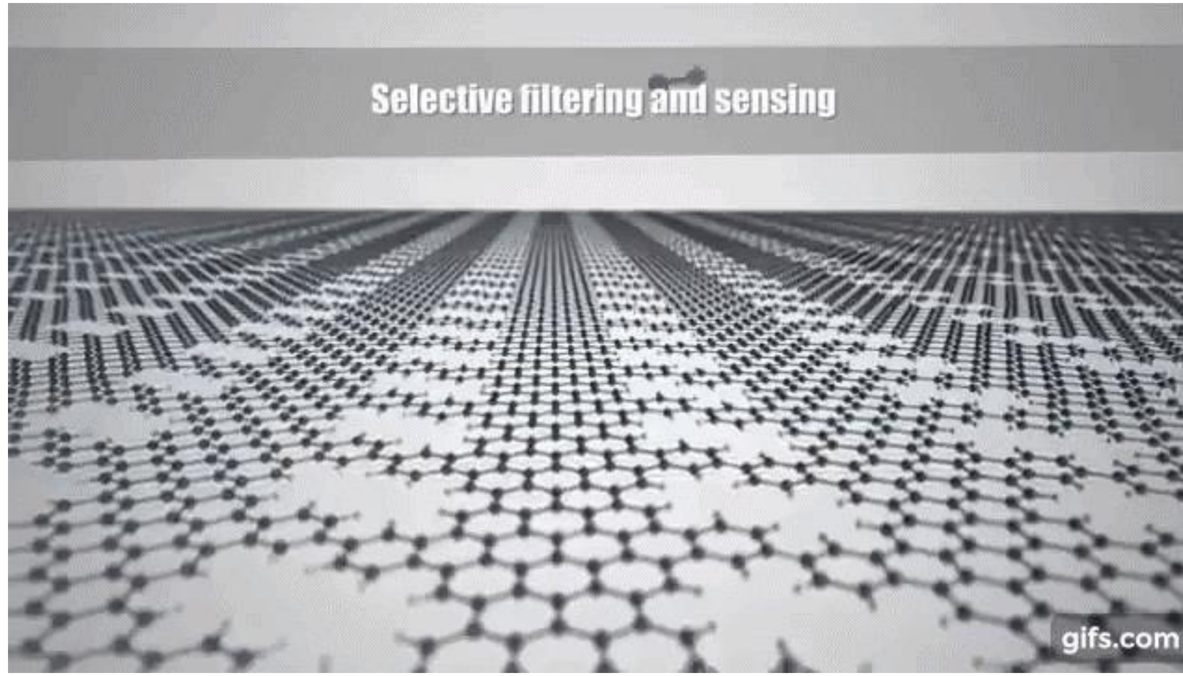


Nanoporous Graphene

-Semipermeable
-Semiconductor (1.0 eV)

-Molecular Filter
-Sensor

-Gas separation
-Water desalinisation



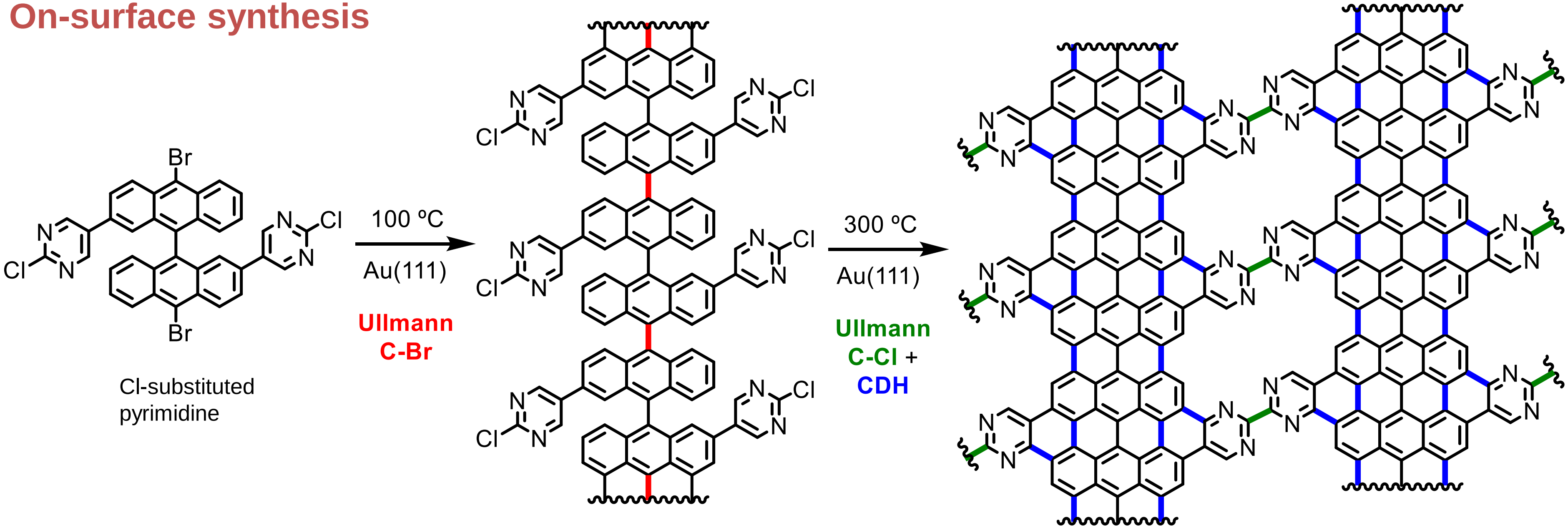
GRAPHENE FLAGSHIP

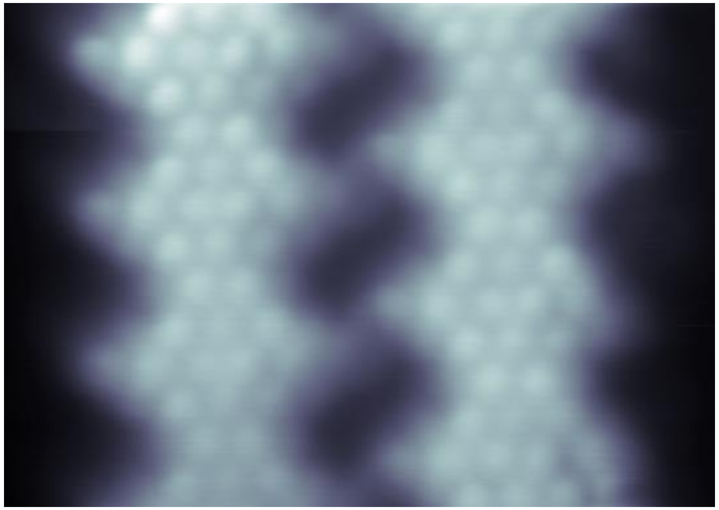
LEGOCHIP
Nanoporous Graphene Integration in Operational Nanophotonic Biosensors

Bottom-up synthesis of multifunctional nanoporous graphene
C. Moreno, M. Vilas-Varela, B. Kretz, A. Garcia-Lekue, M. V. Costache, M. Paradinas, M. Panighel, G. Ceballos, S. O. Valenzuela, D. Peña, A. Mugarza
Science **2018**, *360*, 199-203

Nitrogen-doped Nanoporous Graphene

On-surface synthesis



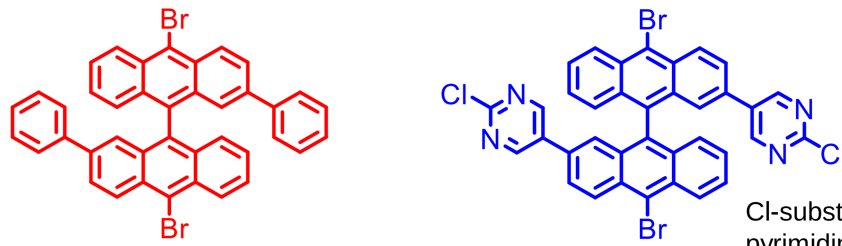


STM (UHV, 4 K, CO tip)

Jesus Castro

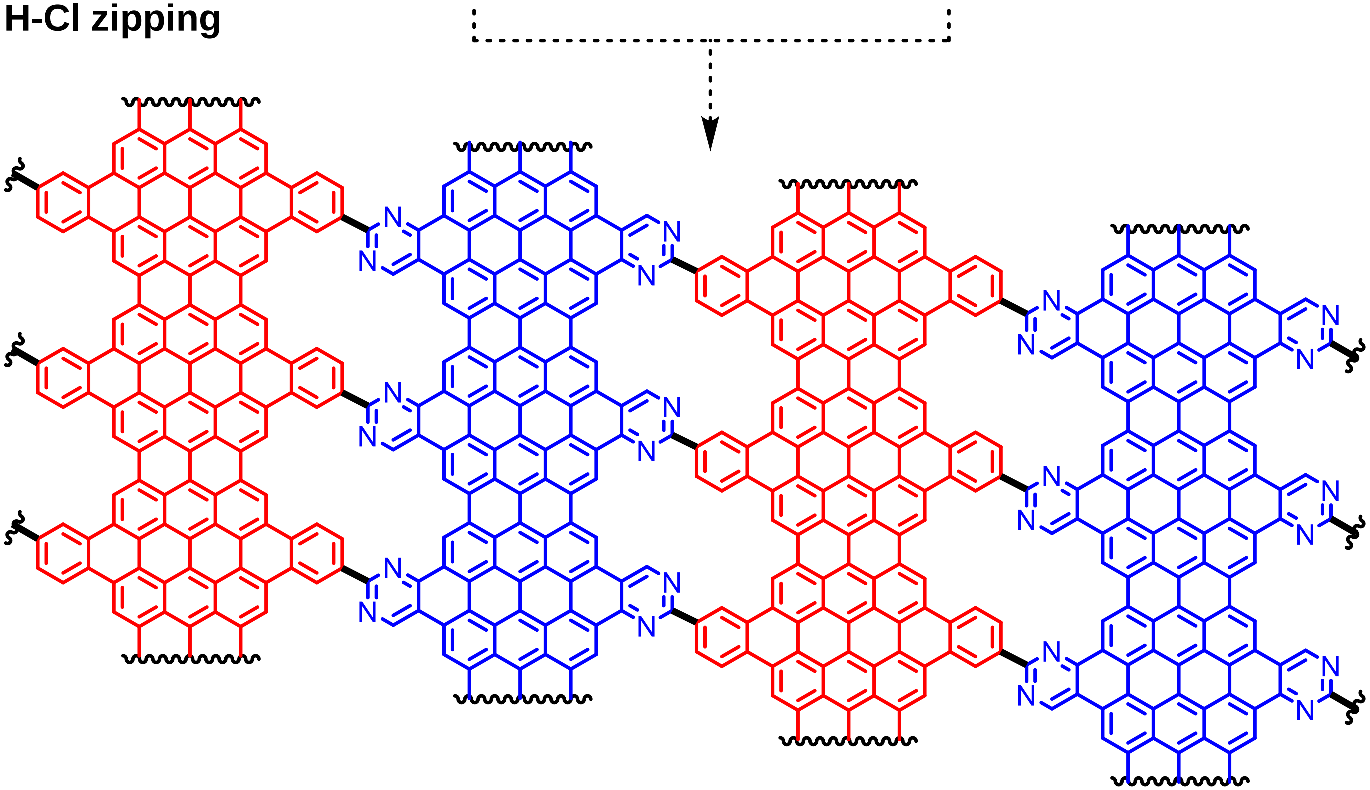
Hybrid Nanoporous Graphene

Combining precursors:



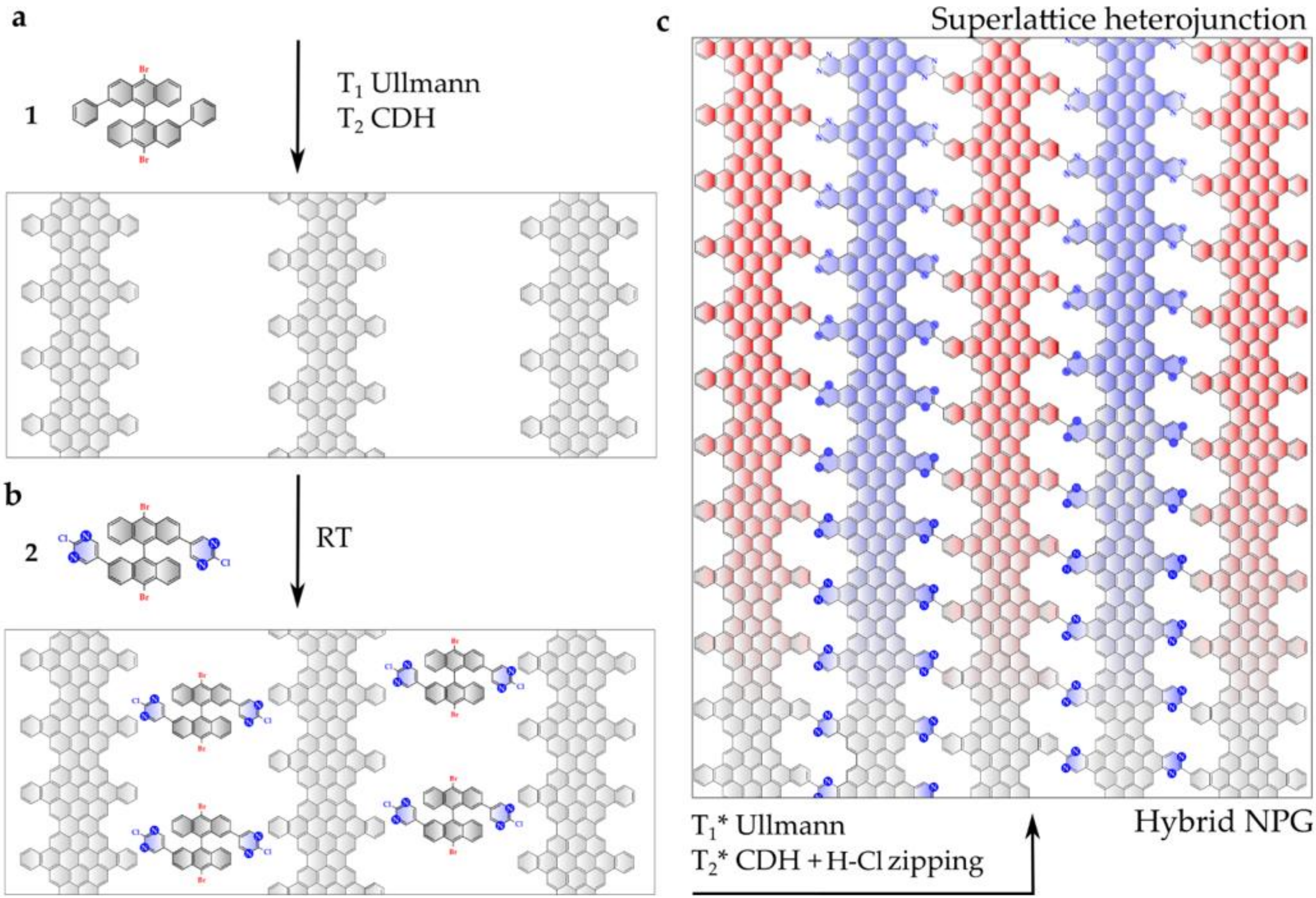
Jesus Castro

Hierarchical growth:
UC / CDH / **H-Cl zipping**



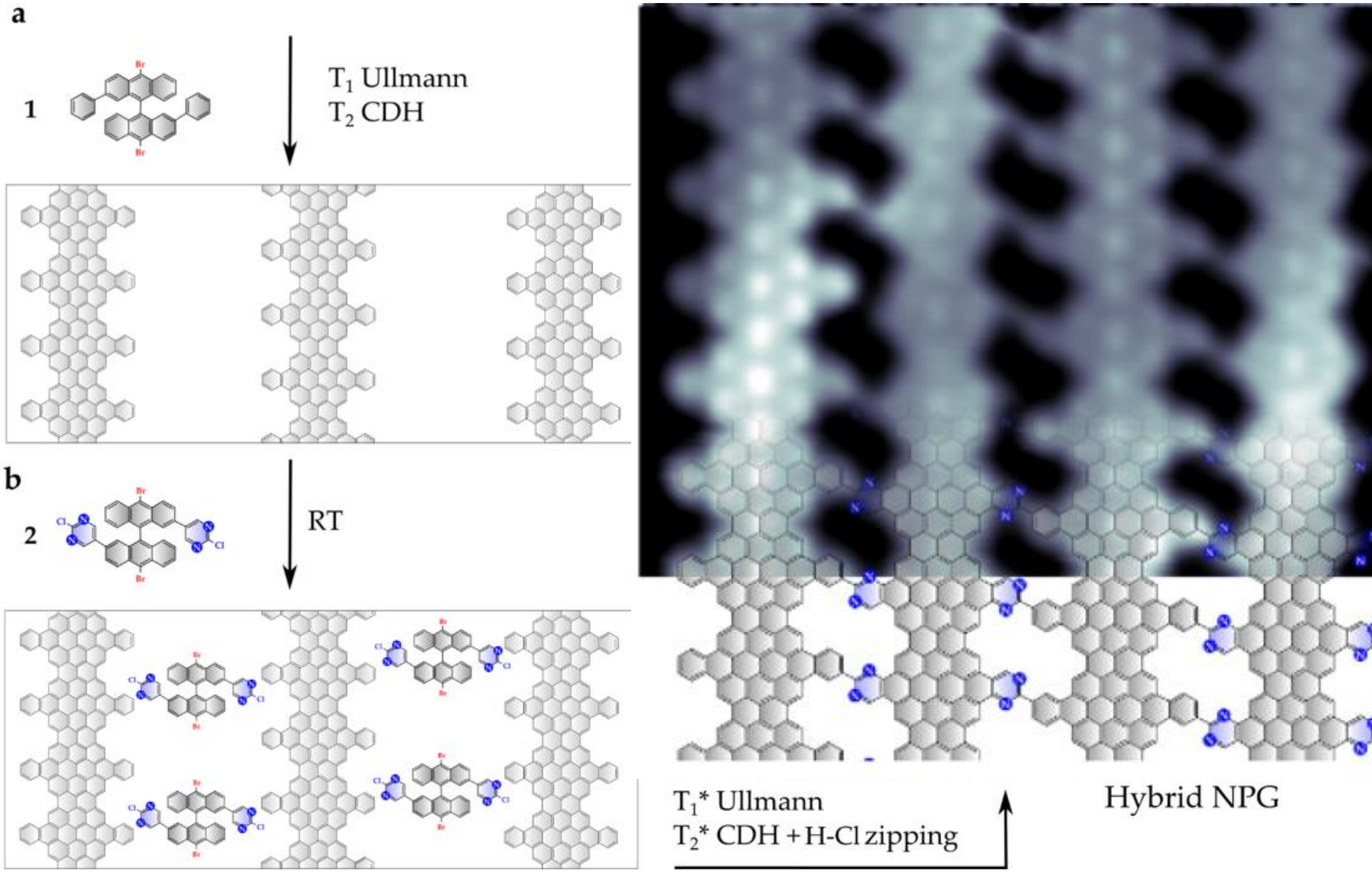
Atomically Sharp Lateral Superlattice Heterojunctions Build-in Nitrogen-doped Nanoporous Graphene
with A. Mugarza and coworkers *Advanced Materials* **2022**, *34*, 2110099

Hybrid Nanoporous Graphene



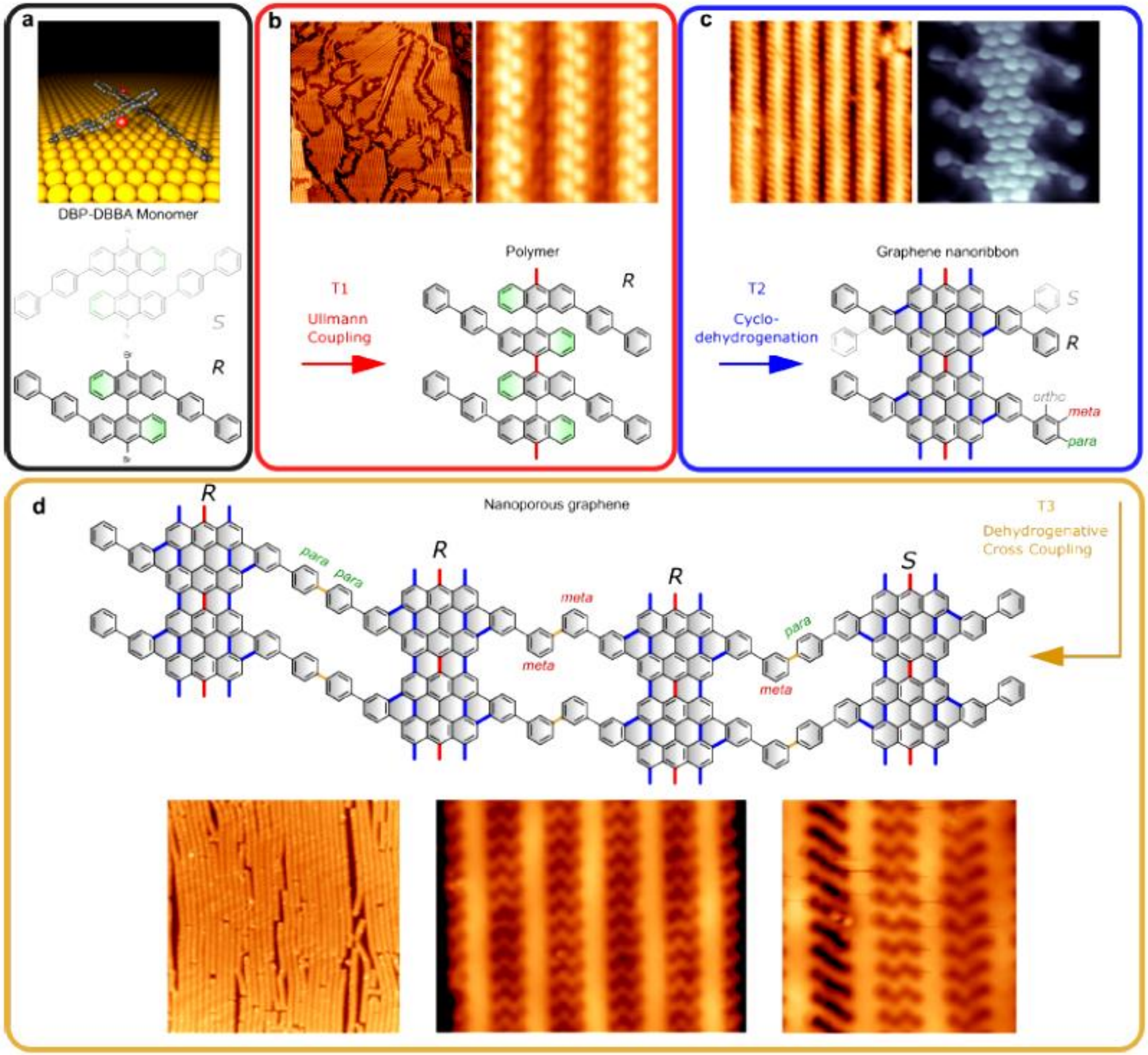
Atomically Sharp Lateral Superlattice Heterojunctions Build-in Nitrogen-doped Nanoporous Graphene
with A. Mugarza and coworkers *Advanced Materials* **2022**, *34*, 2110099

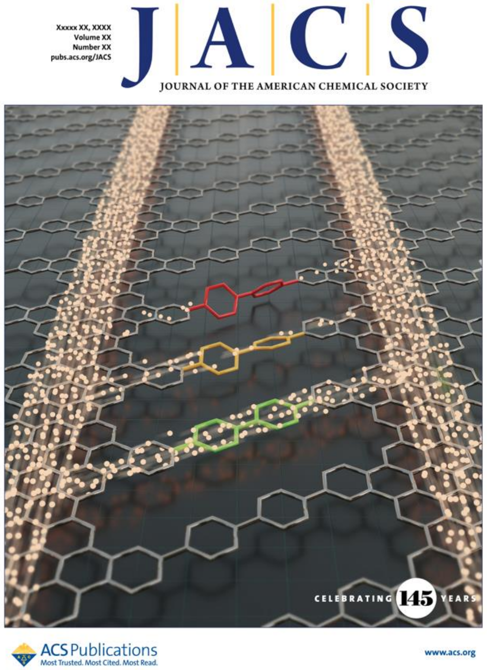
Hybrid Nanoporous Graphene



Atomically Sharp Lateral Superlattice Heterojunctions Build-in Nitrogen-doped Nanoporous Graphene
with A. Mugarza and coworkers *Advanced Materials* **2022**, *34*, 2110099

Larger Pores in NPG





Molecular Bridge Engineering in Nanoporous Graphene

J. Am. Chem. Soc. **2023**, *145*, 8988

THANKS!

IBM Research Zurich

Leo Gross, Gerhard Meyer, Bruno Schuler, Niko Pavlicek, Nikolaj Moll, Zsolt Majzik, Fabian Schulz, Shadi Fatayer, Florian Albrecht

nanoGUNE, DIPC, CFM San Sebastián

Nacho Pascual, Dimas de Oteyza, Aran García-Lekue, Martina Corso, D. Sánchez Portal
Jigcheng Li, Néstor Merino, Niklas Friedrich, Guillaume Vasseur, Eduard Carbonell, Enrique Ortega, Celia Rogero, Jeremy Hieulle,, Pedro Brandimarte, Mads Engelund

ICN2 Barcelona

Aitor Mugarza, César Moreno, Gustavo Ceballos, Markos Paradinas, Mirko Panighel, María Tenorio

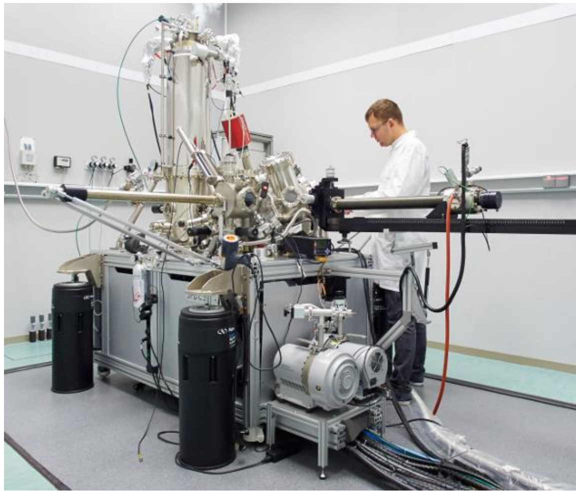
TU Dresden

Francesca Moresco, Justus Krüger, Thomas Lehman, Frank Eisenhut, Dimitry Skidin, Gianaurelio Cuniberti

Jagiellonian University Krakow

Szymon Godlewski, Marek Szymonski, Rafal Zuzak, Marek Kolmer

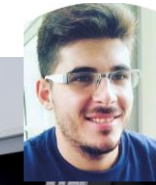
AFM/STM under ultra-high vacuum conditions



COMMO (Catálisis Organometálica y Materiales Moleculares Orgánicos)

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

CiQUS



10 YEARS CiQUS

XUNTA DE GALICIA
CONSELLERÍA DE EDUCACIÓN E ORDENACIÓN UNIVERSITARIA
ED431C 2020/22

GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
PID2019-110037GB-I00
PID2019-107338RB-C62

European Commission HORIZON 2020
H2020 FET-OPEN #863098

SPRING

MolDAM

FLAG-ERA

LEGOCHIP
Nanoporous Graphene Integration in Operational Nanophotonic Biosensors

PCI2019-111933-2

erc
ERC-2020-SyG-951519