The awakening of on-surface synthesis

David Écija
www.ecijalab.com

www.nanoscience.imdea.org

www.nanoscience.imdea.org

OUTLINE

1.- The group

2.- On-surface synthesis.

3.- Emergence of π-magnetism in nanographenes.

4.- Topology and magnetism in π-conjugated 1D polymers.

5.- Conclusions and outlook

www.nanoscience.imdea.org

OUTLINE

1.- The group

2.- On-surface synthesis.

3.- Emergence of pi-magnetism in nanographenes.

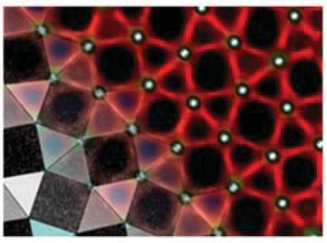
4.- Topology and magnetism in π-conjugated 1D polymers.

5.- Conclusions and outlook.

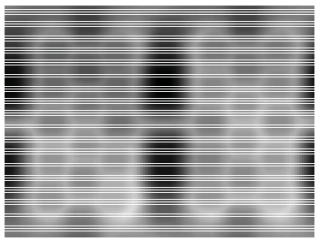
institute IMdea nanoscience

THE GROUP: NANOARCHITECTONICS AT SURFACES

Supramolecular chemistry



Covalent chemistry



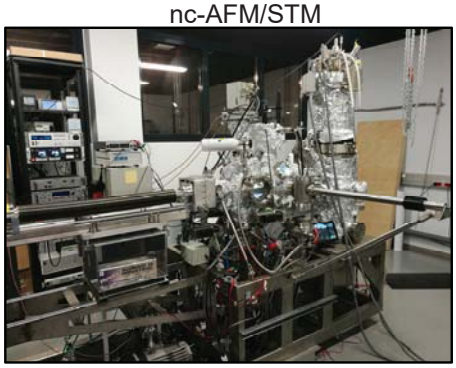
Molecular Nanoscience at Interfaces

Model catalysts for circular economy

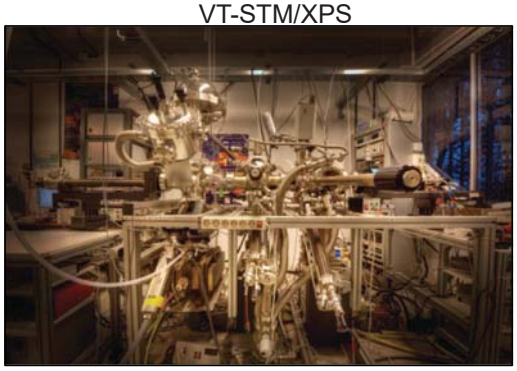
www.nanoscience.imdea.org

The group: Instrumentation

nc-AFM/STM

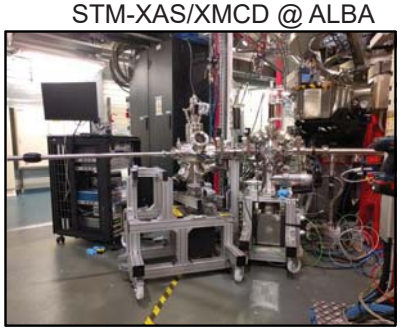


VT-STM/XPS



Device-STM

STM-XAS/XMCD @ ALBA



State-of-the-art facilities for topographic, electronic, and magnetic inspection at the nanoscale

www.nanoscience.imdea.org

THE GROUP: PEOPLE

Interdisciplinar team of physicists, chemists and engineers

OUTREACH

POSITION	TEAM NAME	COUNTRY	DISTANCE	# TURNS	INCIDENTS
1	MADRID-LINDKÖPING		678 nm	54	Changing lane for overpassing - Crash at 5.30 pm
1	TSUKUBA		1054 nm	54	Cross a trench and go back - jump across a trench *8
3	STRASBOURG		476 nm	28	Cross a trench * 3
4	GRAZ-HOUSTON		403 nm	15	Cross a trench * 2 Crash
5	DRESDEN		160 nm	9	Molecule jump onto the tip
6	TOULOUSE-NARA		150 nm	10	Molecule is lost again
7	OHIO		136 nm	17	Cross a trench * 2, one wheel
8	SAN SEBASTIAN		29 nm	0	

institute IMdea nanoscience

OUTLINE

1.- The group

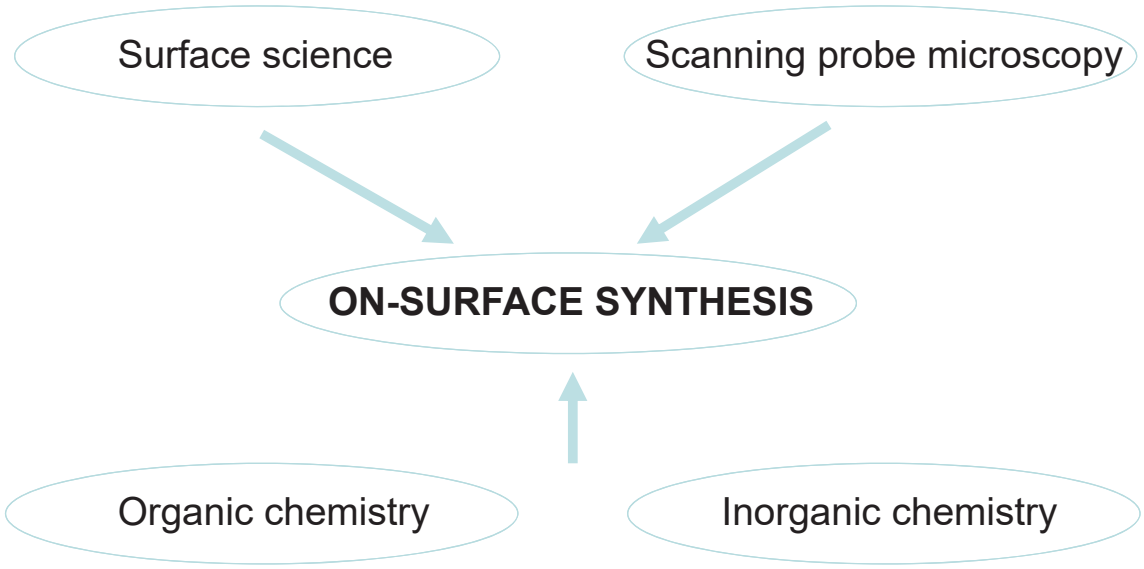
2.- On-surface synthesis.

3.- Emergence of π-magnetism in nanographenes.

4.- Topology and magnetism in π-conjugated 1D polymers.

5.- Conclusions and outlook.

www.nanoscience.imdea.org



institute IMdea nanoscience

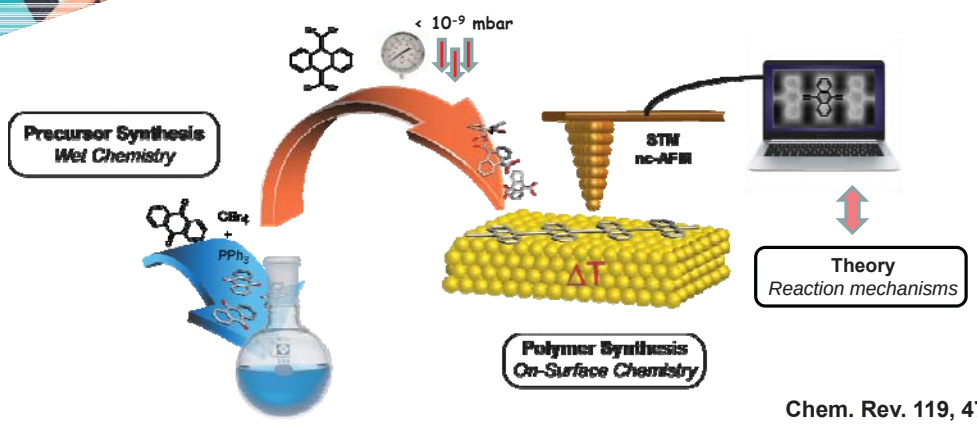
ON-SURFACE SYNTHESIS

- Heterogenous catalysis
- On-surface supramolecular synthesis
- On-surface covalent synthesis

www.nanoscience.imdea.org

What is on-surface covalent synthesis?

- Evaporation of small organic molecules at ultra high vacuum (UHV)
- Deposition on 2D metallic substrates: Au, Ag, Cu, Pt…
- Direct observation & study of chemical reactivity and electronic properties



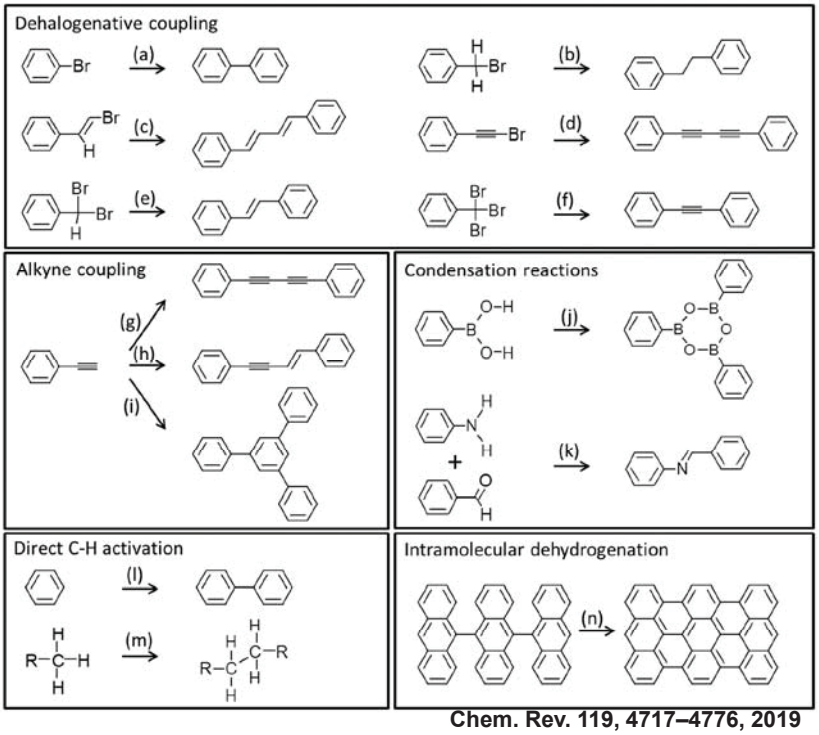
Chem. Rev. 119, 4717–4776, 2019

ON-SURFACE COVALENT SYNTHESIS

Why on-surface covalent synthesis?

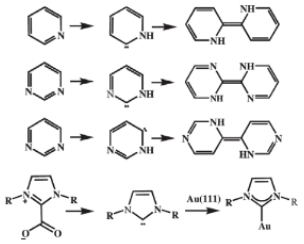
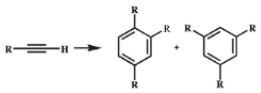
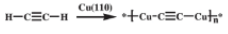
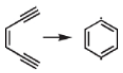
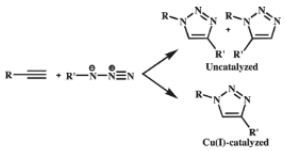
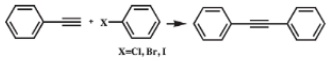
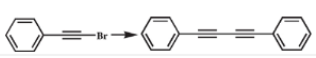
- Original reaction mechanisms → On-surface organic wonders
  - Oligophenylene macrocycles
  - Polyacenes
  - Open-shell nanographenes
- 1D polymers and conjugated ladder polymers (nanoribbons)
- 2D polymers and networks
- Characterization at the atomic scale with surface science

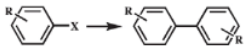
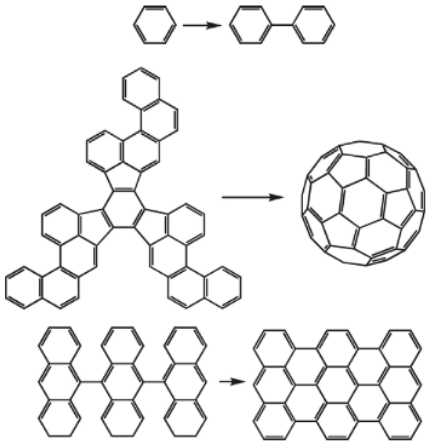
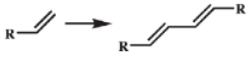
Reaction mechanisms

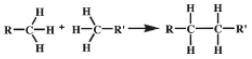
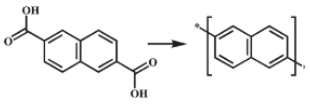
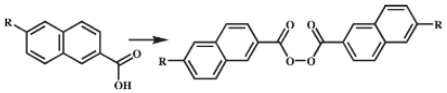
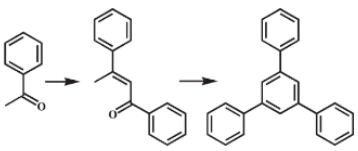
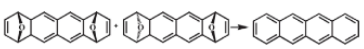
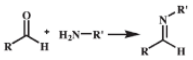
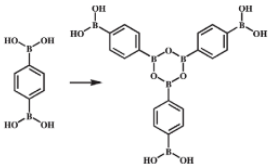


Chem. Rev. 119, 4717–4776, 2019

www.nanoscience.imdea.org

Category	Reaction name	Chemical equation
SP^0-C	N-heterocyclic carbenes formation and dimerization	
SP^1-C	Glaser coupling	
	Alkyne cyclotrimerization	
	Metalated carbyne	
	Bergman reaction	
	Azide–alkyne cycloaddition	
	Sonogashira coupling	
	Dehalogenative homocoupling	

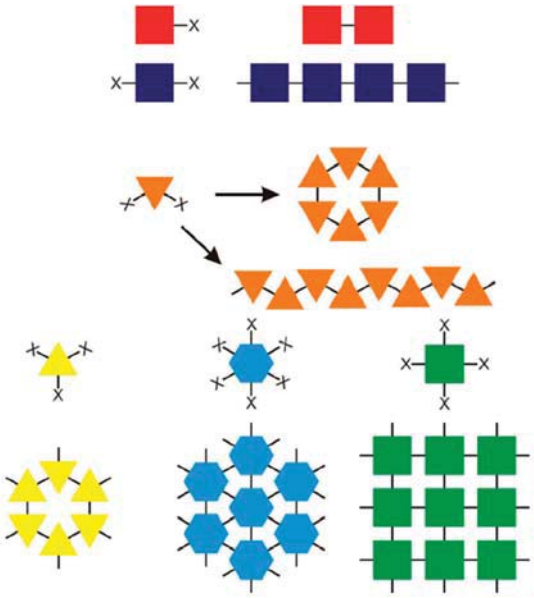
SP^2-C	Ullmann coupling	
	Aryl–aryl dehydrogenation coupling	
	Dehydrogenative homocoupling of terminal alkene	

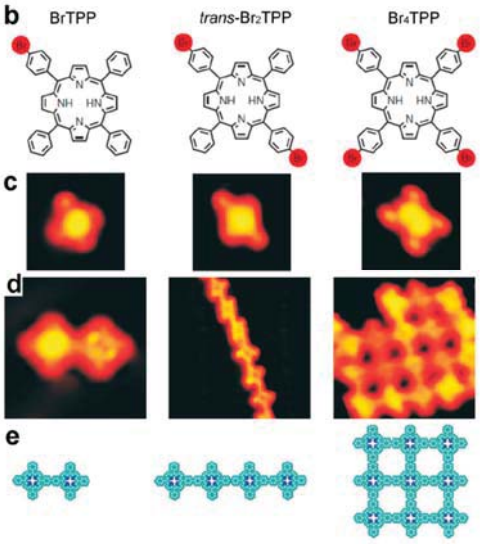
SP^3-C	Wurtz coupling	
	Linear alkane polymerization	
Carboxylic acid/ester/ether/acetyls (C—O, C=O)	Decarboxylative polymerization	
	Dehydrogenative coupling	
	Dimerization and cyclotrimerization of acetyls	
	Dealkylation of ethers to alcohols	
	Reduction	
	Schiff-base reaction (imine formation)	
Others	Boronic acid condensation	

ON-SURFACE COVALENT SYNTHESIS

Key role of the precursor!

- Structural Topology
- Functional group



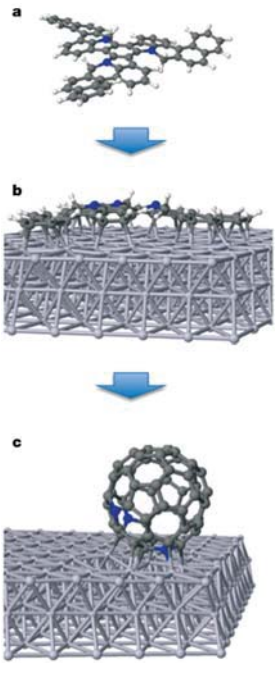


Nat. Nanotechnol. 2007, 2, 687-691

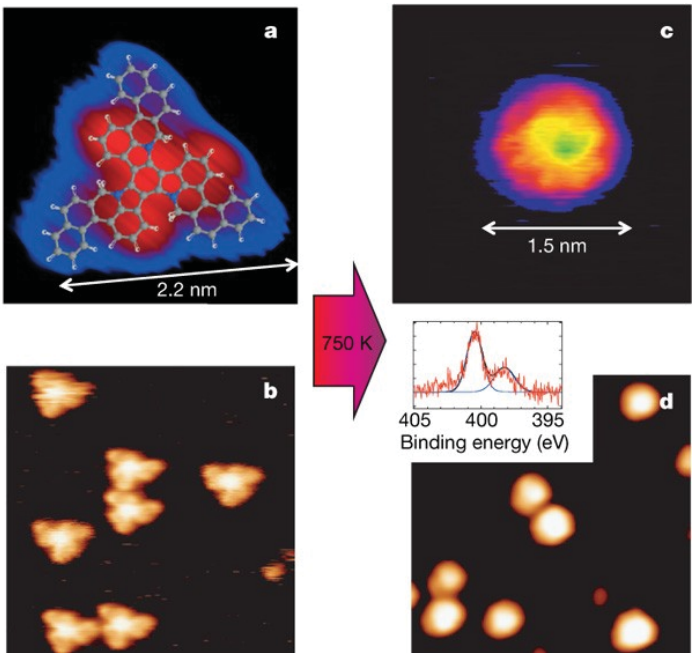
www.nanoscience.imdea.org

ON-SURFACE COVALENT SYNTHESIS

The on-surface organic wonders: Synthesis of fullerenes



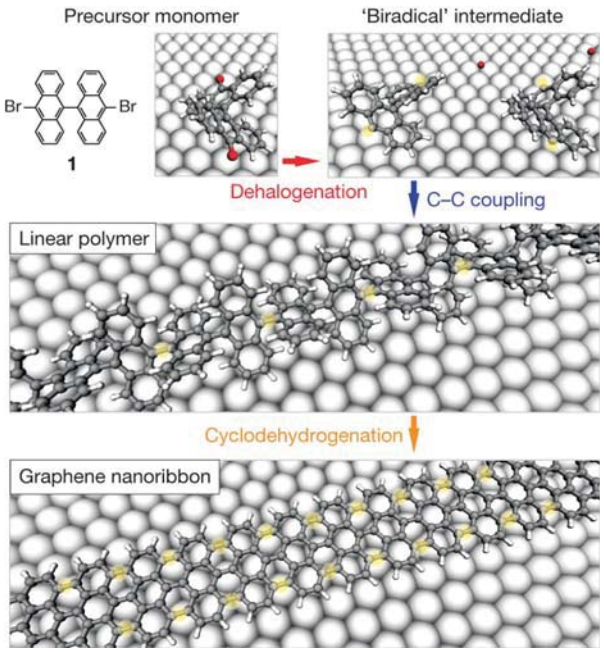
Pt (111)

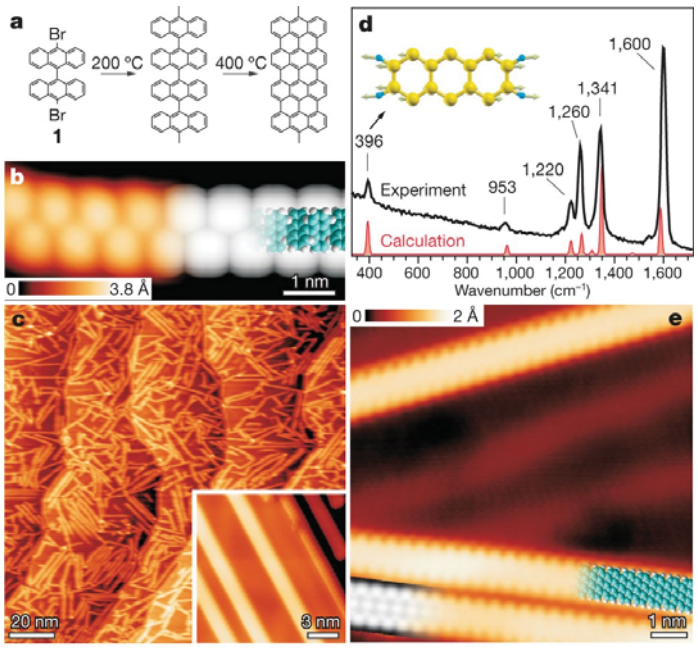


Nature 454, 865–868 (2008)

ON-SURFACE COVALENT SYNTHESIS

The on-surface organic wonders: Nanorribons



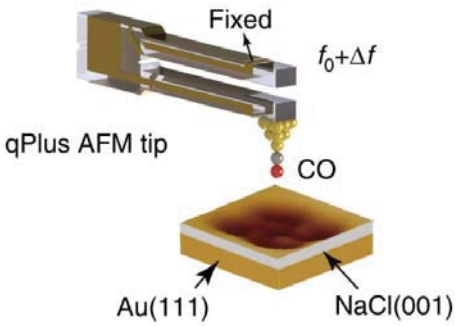


Nature 466, 470–473 (2010)

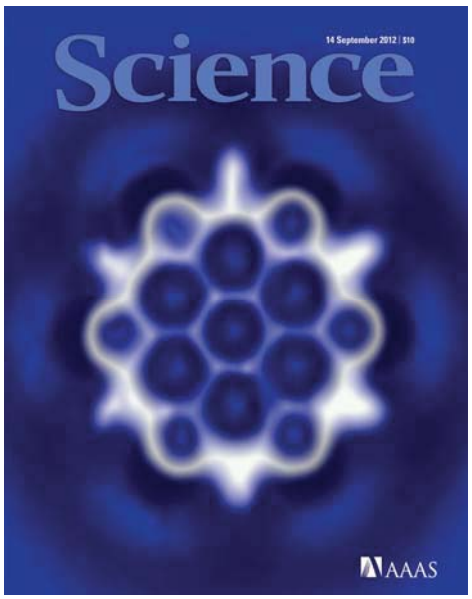
www.nanoscience.imdea.org

ON-SURFACE COVALENT SYNTHESIS

NC-AFM: Elucidating the chemical backbone of molecular species

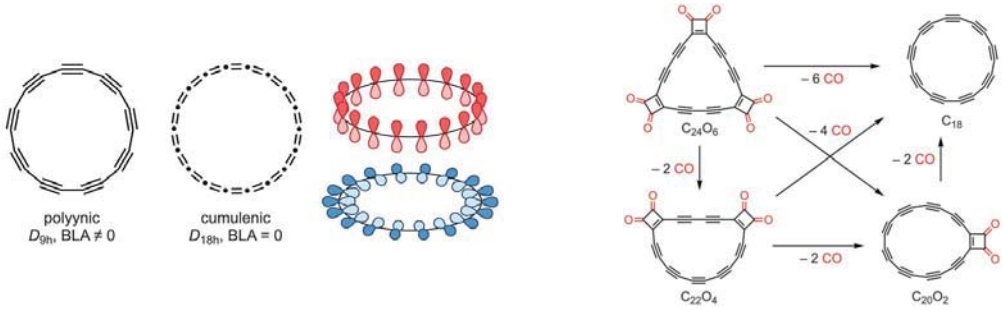


Science 325 (5944), 1110-1114, (2009)

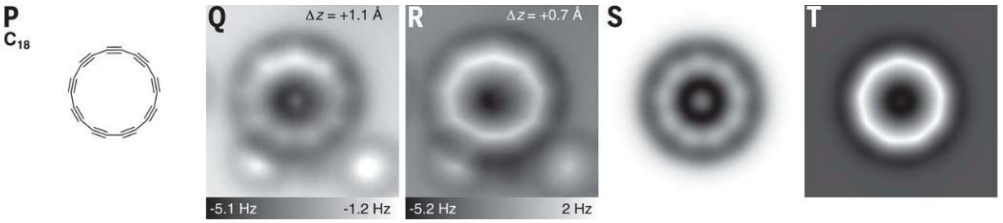


Science 337 (6200), 1326-1329, (2012)

The on-surface organic wonders: A new carbon allotrope, C18



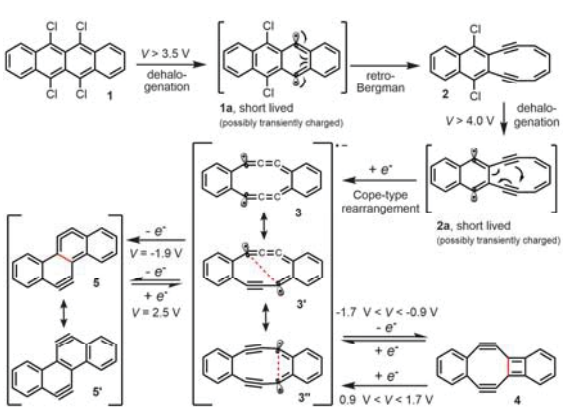
Pulses on precursor on NaCl

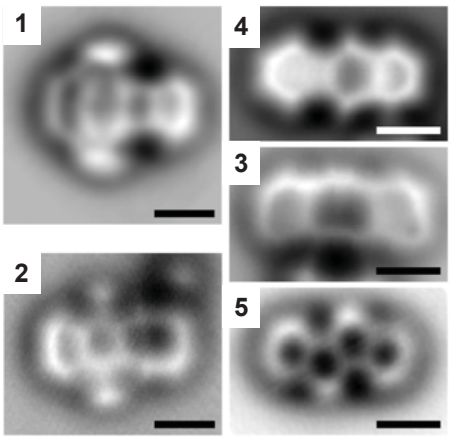


Science 365 (6459), 1299-1301

ON-SURFACE COVALENT SYNTHESIS

The on-surface organic wonders: Driving reactions by pulses

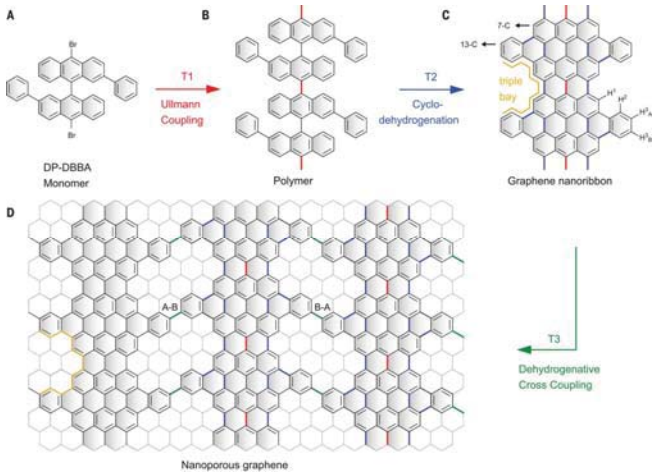


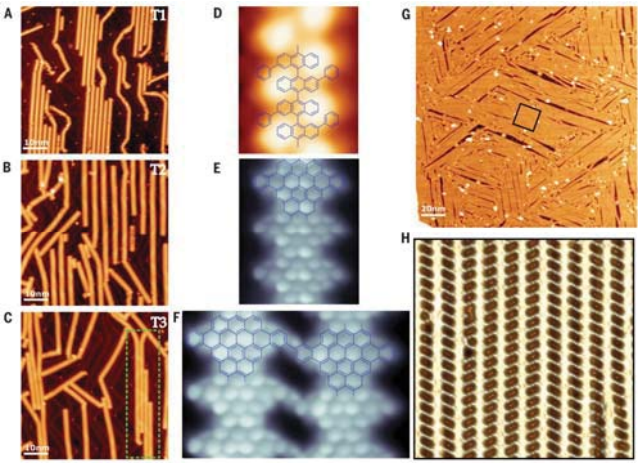


Science 377 (6603), 298, 2022

ON-SURFACE COVALENT SYNTHESIS

The on-surface organic wonders: Porous graphene



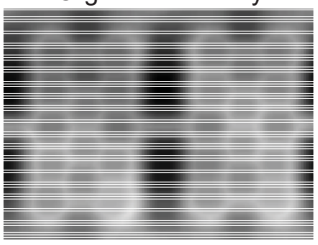


www.nanoscience.imdea.org

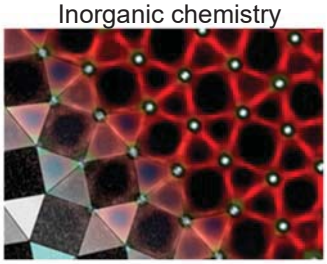
GOAL OF THE TALK

To visualize and understand the importance of π-conjugation on materials and on surfaces

Organic chemistry



Inorganic chemistry



OUTLINE

1.- The group

2.- On-surface synthesis.

3.- Emergence of π-magnetism in nanographenes.

4.- Topology and magnetism in π-conjugated 1D polymers.

5.- 2D conductive π-conjugated metal-organic networks.

institute IMdea nanoscience

Motivation: π-magnetism in nanographenes

♦ Magnetism is typically associated to d- or f-block elements

• It can also appear in carbon-based materials (π-magnetism)

♦ Why is magnetism interesting at all in carbon materials?

• Chemical properties:
  - Versatility, flexibility and biocompatibility

• Physical properties:
  - Low spin-orbit and hyperfine couplings
  - Absence of traditional channels for spin relaxation and decoherence
  - High spin stiffness
  - Electrical field control of magnetization

W. Zeng et al., Chem 7 (2), 358-386

www.nanoscience.imdea.org

Sources of π-magnetism in nanographenes

- Sublattice imbalance

  Nat. Nanotechnol. 12, 308, 2017

  JACS 141 (27), 10621-10625, 2019

  Sci. Adv. 2019, eaav7717

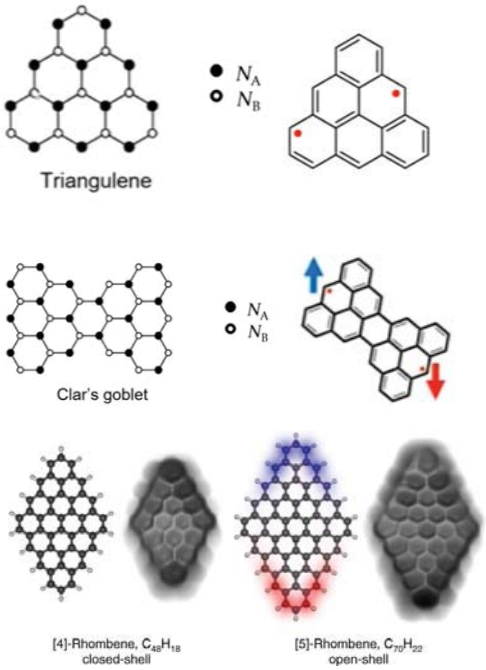
  PRL 124, 177201, 2020

- Topological frustration

  Nat. Nanotechnol.15 (1), 22-28, 2020

- Polarization of low energy states

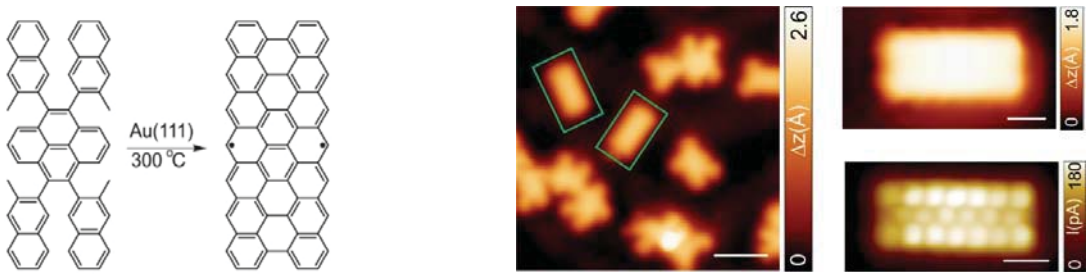
  Nat. Chem. 13 (6), 581-586, 2021



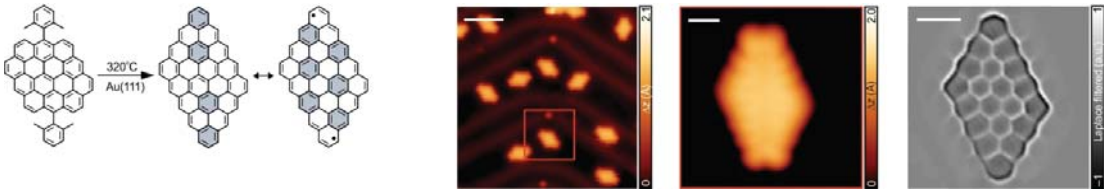
Π-MAGNETISM IN NANOGRAPHENES

Towards a record value of exchange coupling in nanographenes

A glimpse of the general idea



Biswas, Kalyan, et al. *ACIE*, e202114983 (2022)

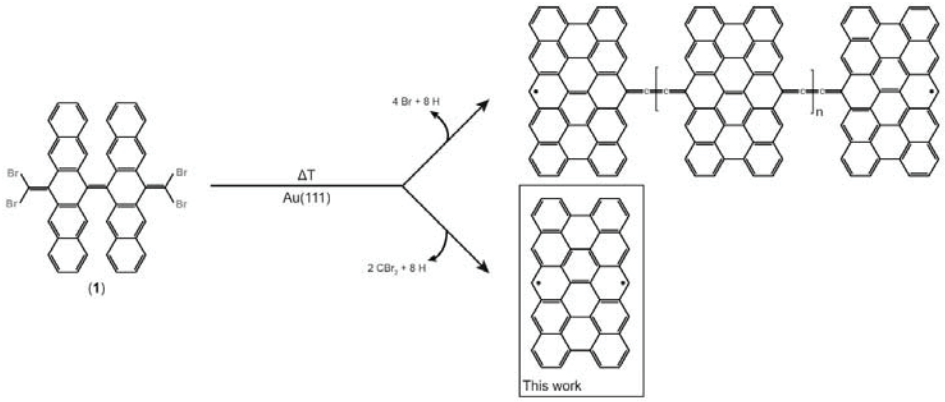


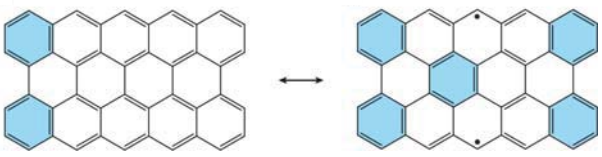
Biswas, Kalyan, et al. *JACS* (2022)

institute IMdea nanoscience
Π-MAGNETISM IN NANOGRAPHENES

www.nanoscience.imdea.org

Peripentacene

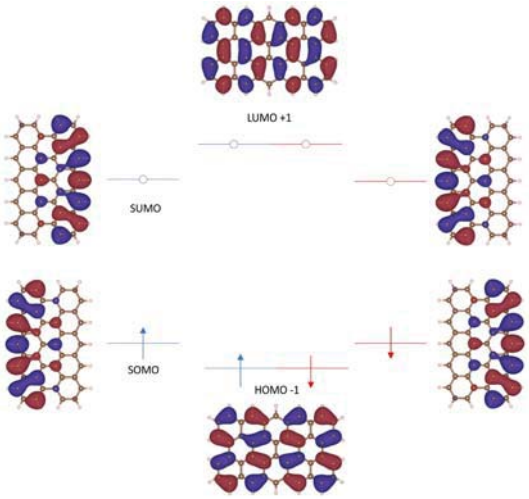




J. Phys. Chem. Lett. 330, 12, 2020

- Closed-shell or open-shell on Au(111)?!?

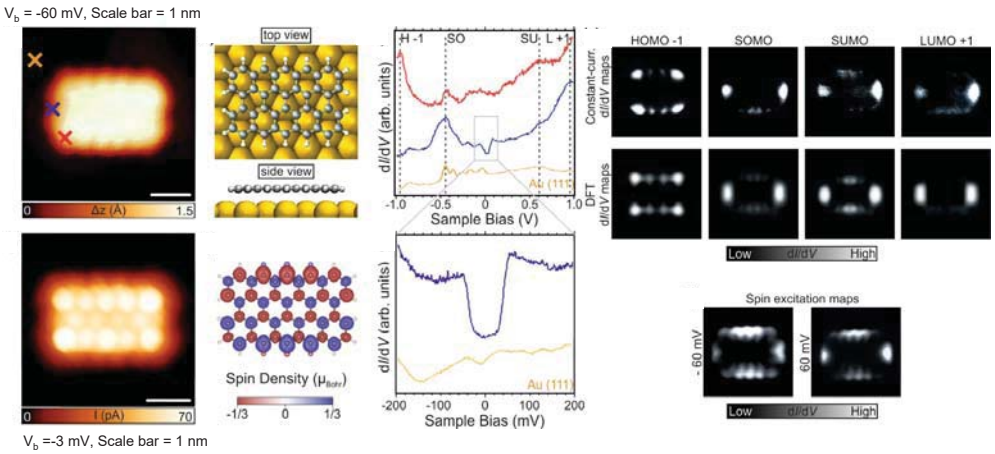
Peripentacene



- Polarization of low energy levels give rise to open-shell character

Π-MAGNETISM IN NANOGRAPHENES

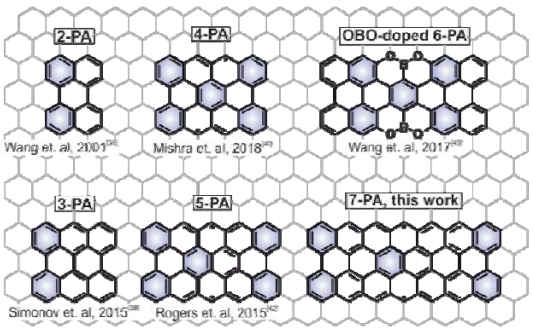
Peripentacene

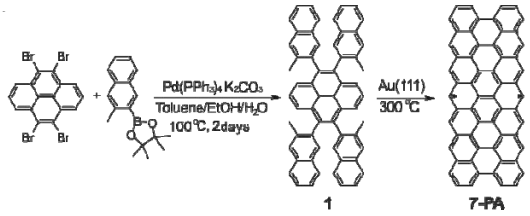


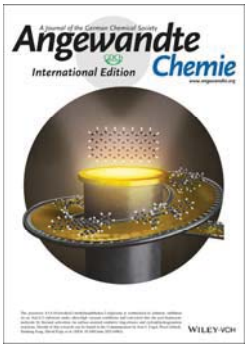
J. Phys. Chem. Lett. 330, 12, 2020

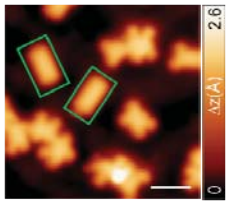
- Open-shell character with J = 60 meV

Periheptacene

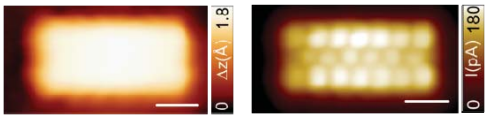








V_b = 900 mV, Scale bar = 2 nm



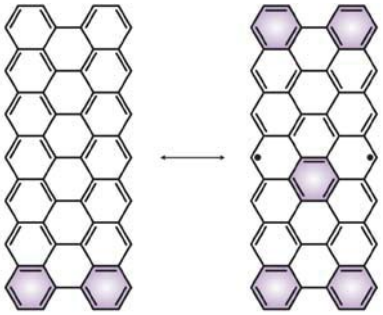
V_b = 5 mV, Scale bar = 0.5 nm

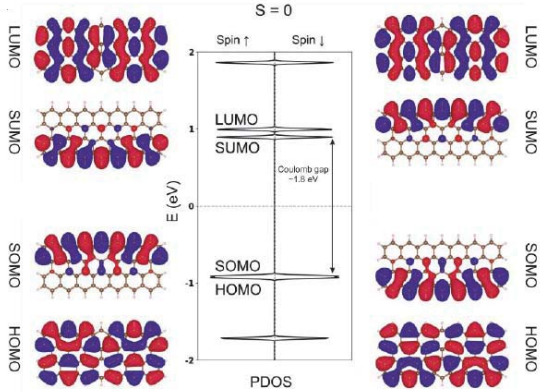
Angew. Chem. Int. Ed. 2022, 61, e 202114983

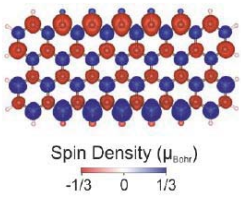
institute IMdea nanoscience

Π-MAGNETISM IN NANOGRAPHENES

Periheptacene





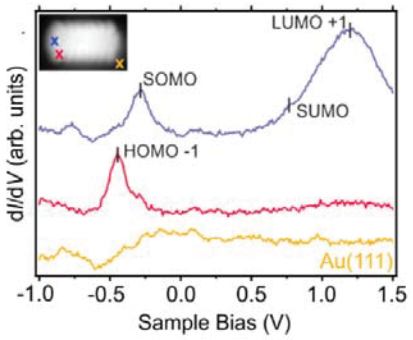


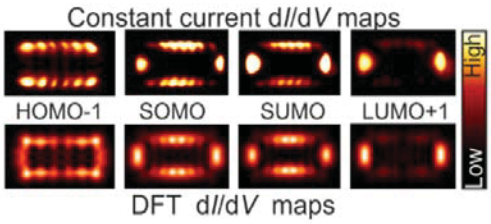
- Predicted open-shell ground state

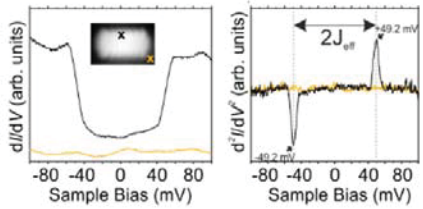
www.nanoscience.imdea.org

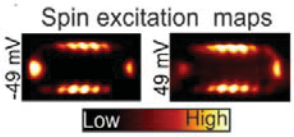
Π-MAGNETISM IN NANOGRAPHENES

Periheptacene





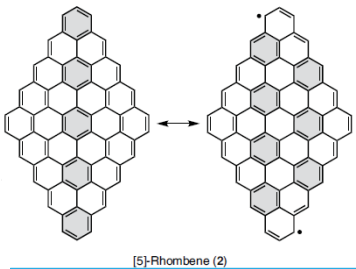




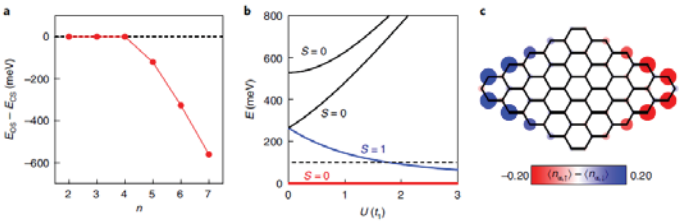
• Open-shell ground state with J = 49.2 meV

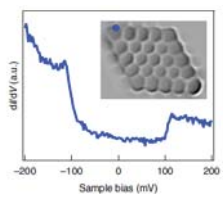
ON-SURFACE SYNTHESIS

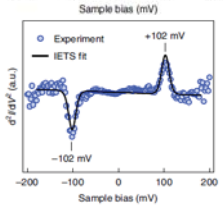
Rhombenes: Giant magnetic exchange coupling



Nat. Chem. 13 (6), 581-586, 2021



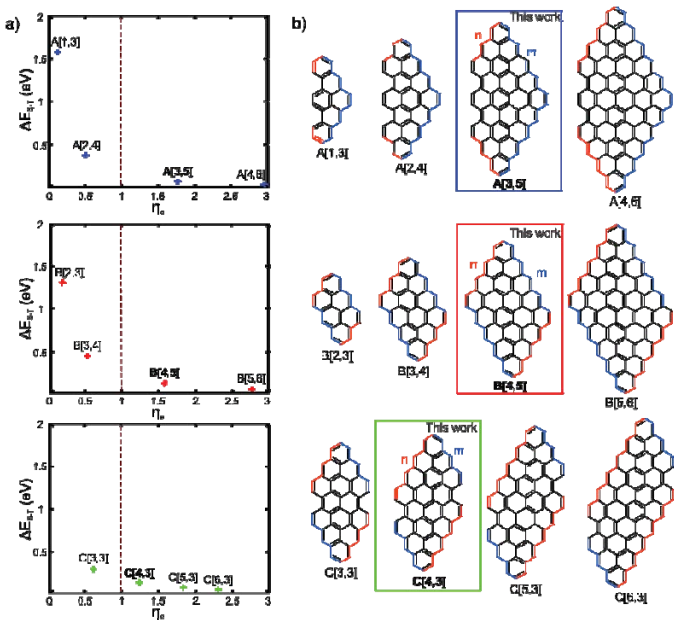




J=102 meV !

Π-MAGNETISM IN NANOGRAPHENES

Giant magnetic exchange coupling: Theoretical benchmarking

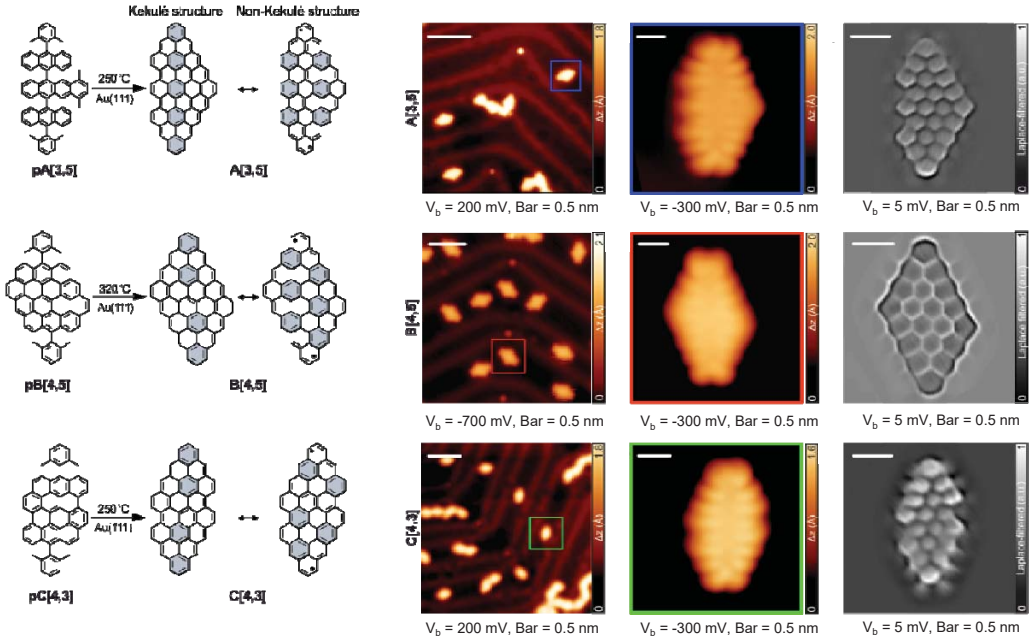


- Closed-shell to open-shell transition with size

www.nanoscience.imdea.org

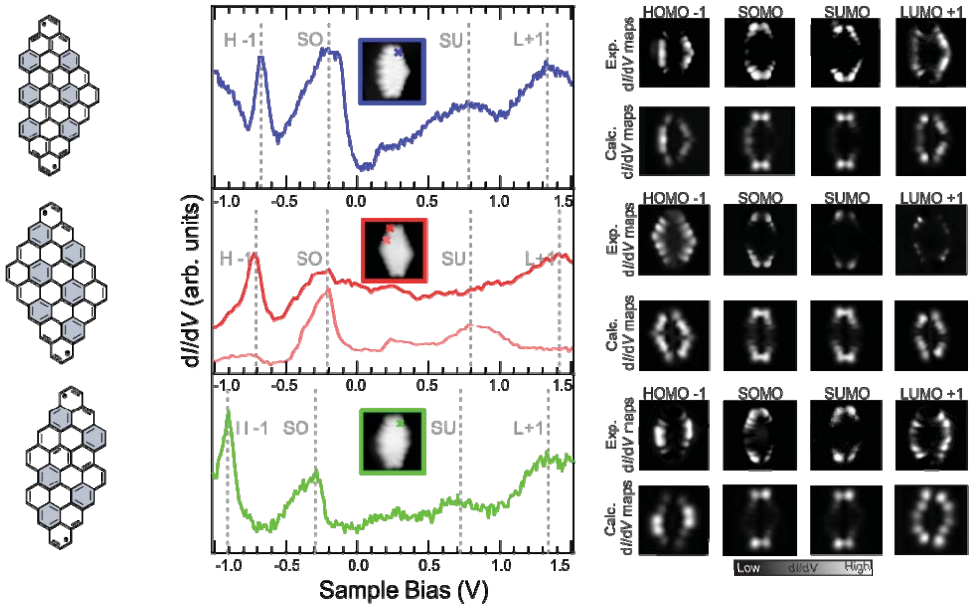
Π-MAGNETISM IN NANOGRAPHENES

Giant magnetic exchange coupling: Ziz-zag nanographenes (NGs)



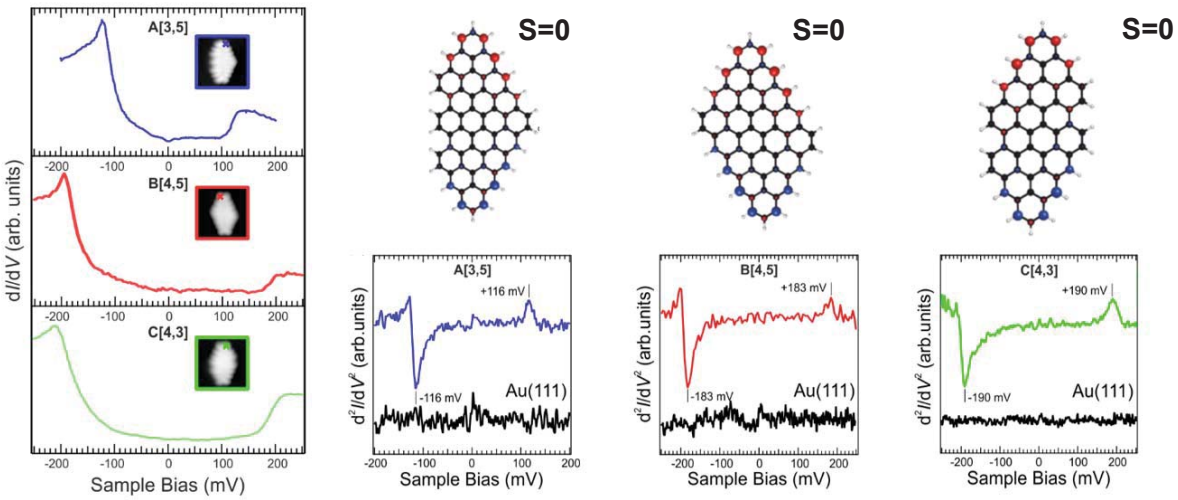
- On-surface synthesis of nanographenes featuring zig-zag peripheries

Giant magnetic exchange coupling: Electronic structrure of zig-zag NGs



- Identification of HOMO-1, SOMO, SUMO and LUMO+1 by DFT

Giant magnetic exchange coupling: Magnetic structure of zig-zag NGs



- Giant magnetic exchange couplings:
  - A[3,5]: 116 meV
  - B[4,5]: 183 meV
  - C[4,3]: 190 meV

J. Am. Chem. Soc. 2023, 145, 2968-2974

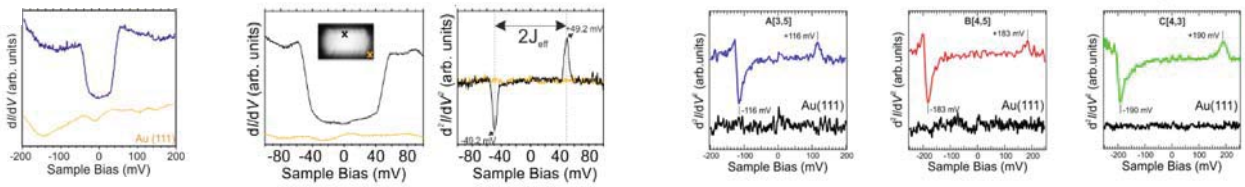
Conclusions

- Successful synthesis of unprecedented families of open-shell nanographenes

- Polarization of low energy states –> π- Magnetism

- Emergence of π –magnetism with very high magnetic exchange coupling:

Importance of the proximity to the open-shell to close-shell transition



- On-going: Direct magnetic characterization with Nickelocene tips

1.- The group

2.- On-surface synthesis.

3.- Emergence of π-magnetism in nanographenes.

4.- Topology and magnetism in π-conjugated 1D polymers.

5.- Conclusions and outlook.

PART I: Fundaments of π-conjugated polymers

www.nanoscience.imdea.org

Motivation: π-conjugated polymers

…a bite of history…

- 1973: Accidental synthesis of highly doped polyacetylene
- 1977: Report on conducting properties of doped polyacetylene

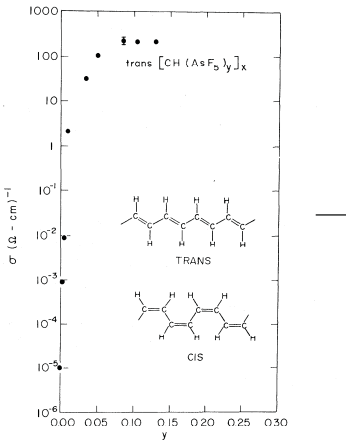


FIG. 1. Electrical conductivity of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

Heeger, Shirakawa and MacDiarmid, PRL 1977

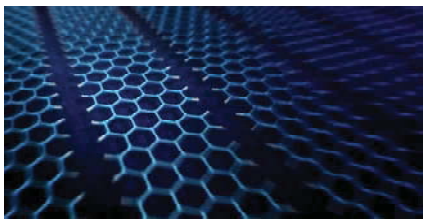
- Theoretical science
- Polymer synthesis
- Commercial interest

Nobel Prize in Chemistry 2000

Motivation: π - conjugated polymers

- Used in OLEDS, thin-film transistors and solar cells.

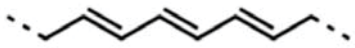
- Limited knowledge of structure-property relationships, due to inability to design defect free materials.
- Importance of lower bandgaps for emerging applications.
- On-surface synthesis rises as a new strategy for synthesizing previously precluded π-conjugated nanomaterials.



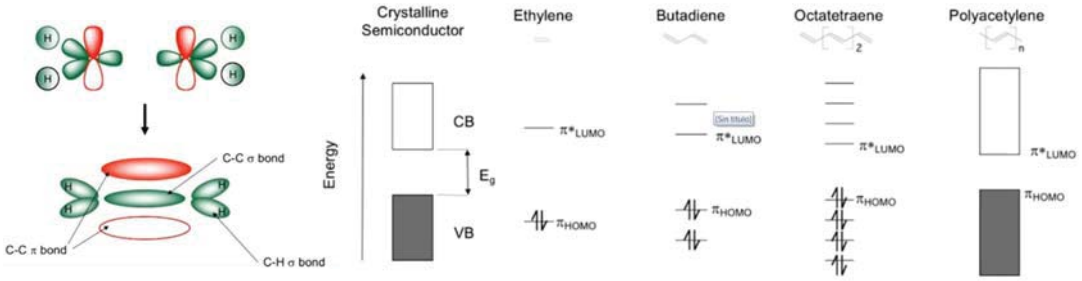
www.nanoscience.imdea.org

Fundaments of π-conjugated polymers

π-conjugated polymer

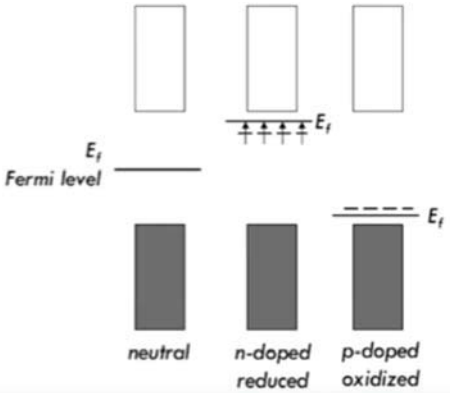


Alternating σ and π bonds allows for delocalization of electrons, which occurs through the overlap of the p_z orbitals



Fundaments of π-conjugated polymers

- π-Conjugated polymers are not intrinsically conducting!



- $\sigma = \sum ne\mu$

  σ = conductivity

  n = charge carrier concentration

  μ = charge carrier mobility

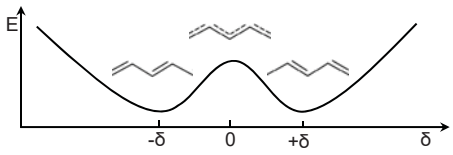
- In neutral state, n is low

- Need to dope to make the polymer conducting!

www.nanoscience.imdea.org

Fundaments: The Su-Schrieffer-Heeger Hamiltonian

Polyacetylene

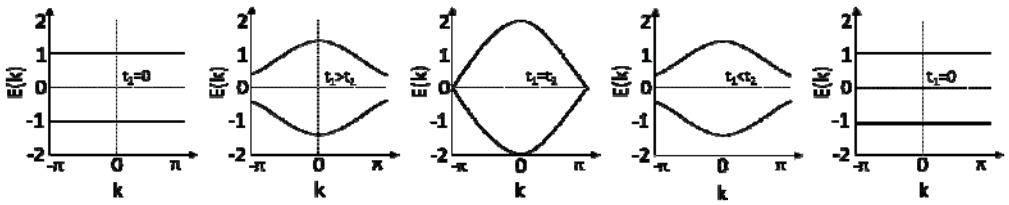


Hamiltonian of infinite 1D chain

$$\mathcal{H}(k) = \begin{pmatrix} \varepsilon_A & t_1 + t_2 e^{-ik} \\ t_1 + t_2 e^{ik} & \varepsilon_B \end{pmatrix}$$

Solution $(\varepsilon_A = \varepsilon_B = 0);\ k = (-\pi, \pi)$:

$$\varepsilon_{\pm}(k) = \pm\sqrt{t_1^2 + t_2^2 + 2t_1 t_2 \cos(k)}$$

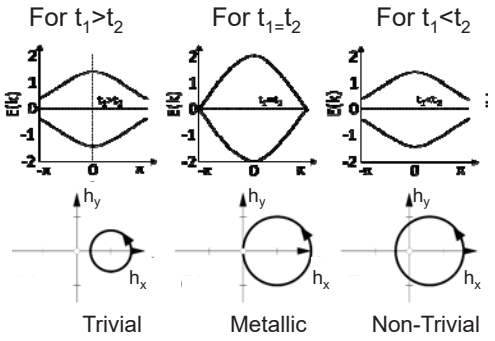


Variation of the band gap $E_g(k)$ with the ratio t_1/t_2; **metallic state $E_g(\pi)=0$ when $t_1=t_2$**

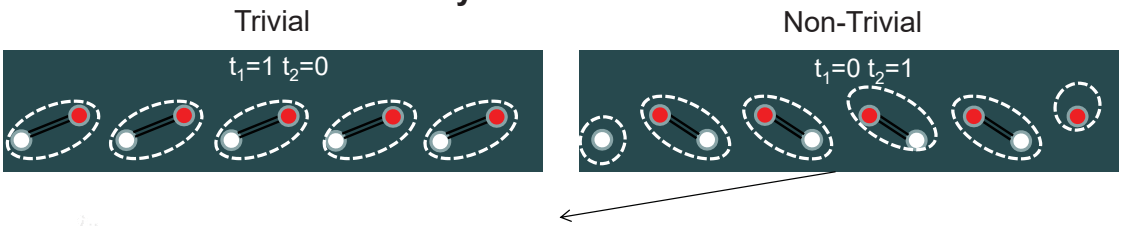
$$\mathcal{H}(k) = \begin{pmatrix} \varepsilon_A & t_1 + t_2 e^{-ik} \\ t_1 + t_2 e^{ik} & \varepsilon_B \end{pmatrix}$$

$$H(k) = \vec{h}(k)\hat{\sigma}$$

$$h_x(k) = t_1 + t_2 \cos k$$
$$h_y(k) = t_2 \sin k$$
$$h_z(k) = 0$$



Fully dimerized limit



Unpaired edge states -> the origin of the edge states

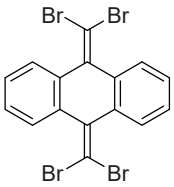
J. K. Asbóth et al., A Short Course on Topological Insulators, Springer (2015)

PART II: Can we tailor π-conjugation in a polymer?

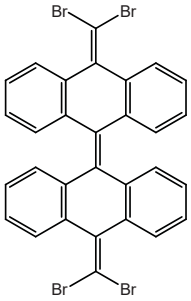
A. Sánchez-Grande et al., Angew. Chem. Int. Ed., 2019
B. Cirera et. al., Nature Nanotechnology, 2020
A. Sánchez-Grande et al., Angew. Chem. Int. Ed., 2020
B. de la Torre et al., Nat. Commun., 2020
A. Sánchez-Grande et al., J. Phys. Chem. Lett., 2021
H. González Herrero et al, Adv. Mater., 2021

Tunability of π-conjugation

n= 3

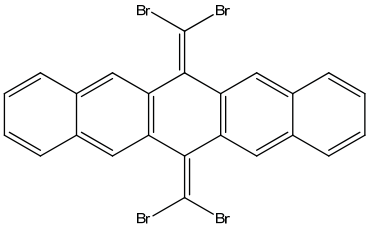


9,10-bis(dibromomethylene)-9,10-dihydroanthracene

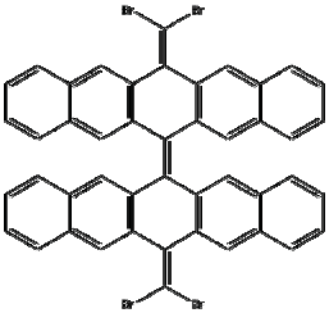


10,10'-bis(dibromomethylene)-10H,10'H-9,9'
bianthracenylidene

n= 5



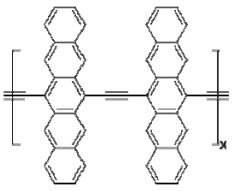
6,13-bis(dibromomethylene)-6,13-dihydropentacene



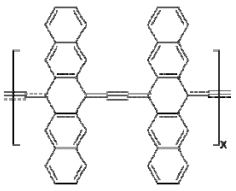
13,13'-bis(dibromomethylene)-6,6',13,13'-
tetrahydro-6,6'-bipentacene

www.nanoscience.imdea.org

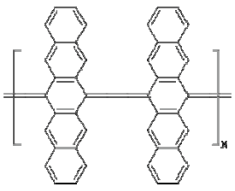
Tunability of π-conjugation



Aromatic/ethynylene

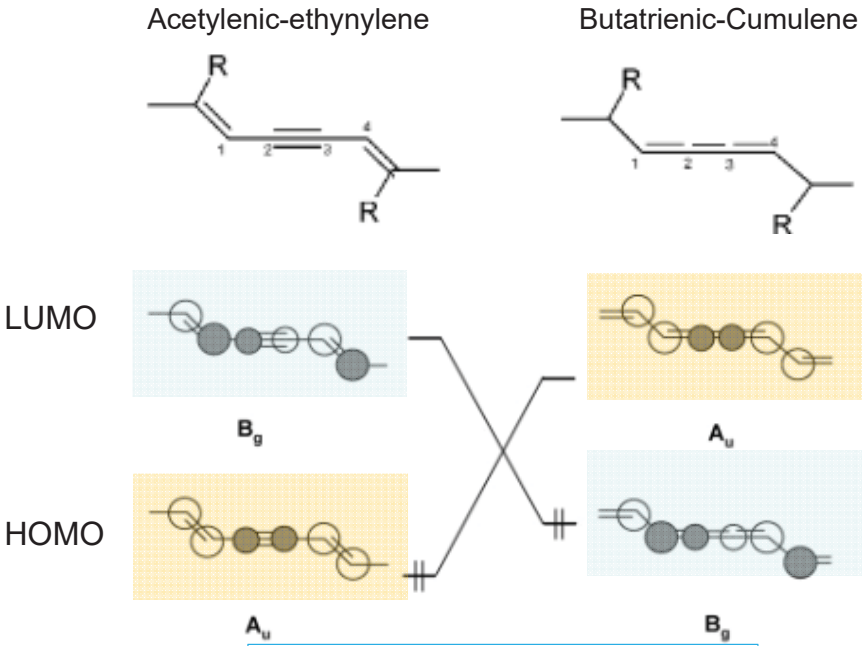


Quinoid enhanced/cumulene-like



Quinoid/cumulene

Tunability of π-conjugation

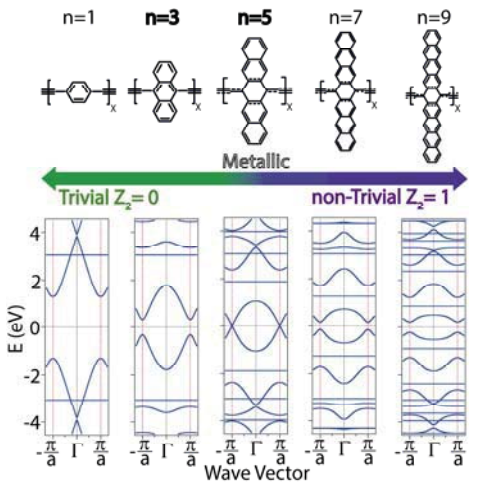


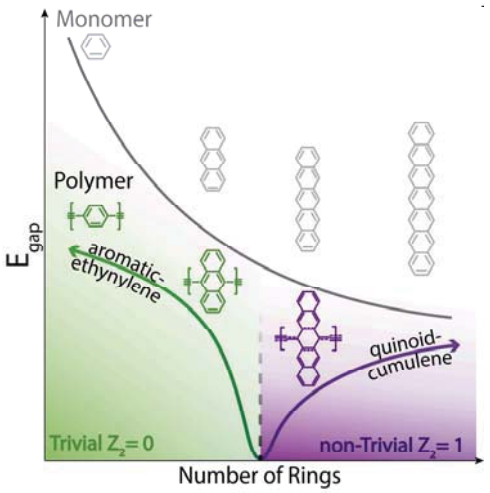
Chemical Reviews, 2005, Vol. 105, No. 10

❑ Orbital level crossing mechanism → Conical intersection

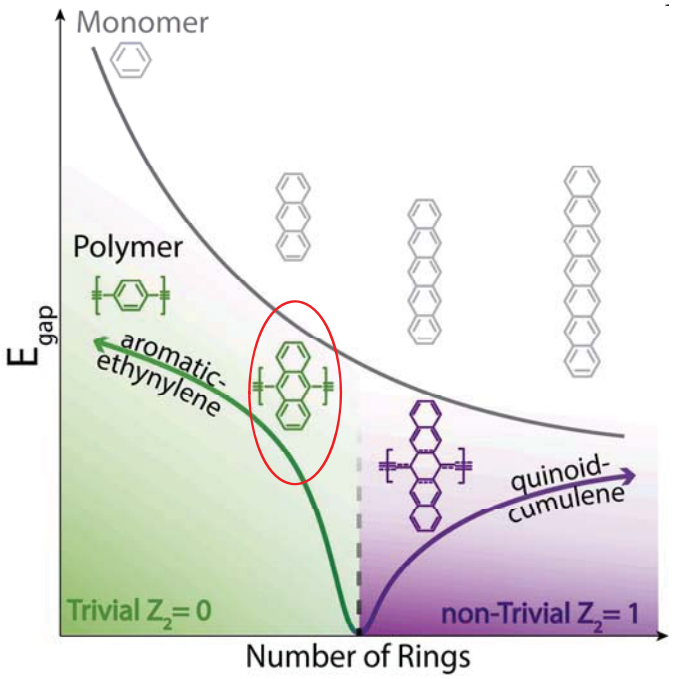
www.nanoscience.imdea.org

Topological transition in π-conjugated polymers



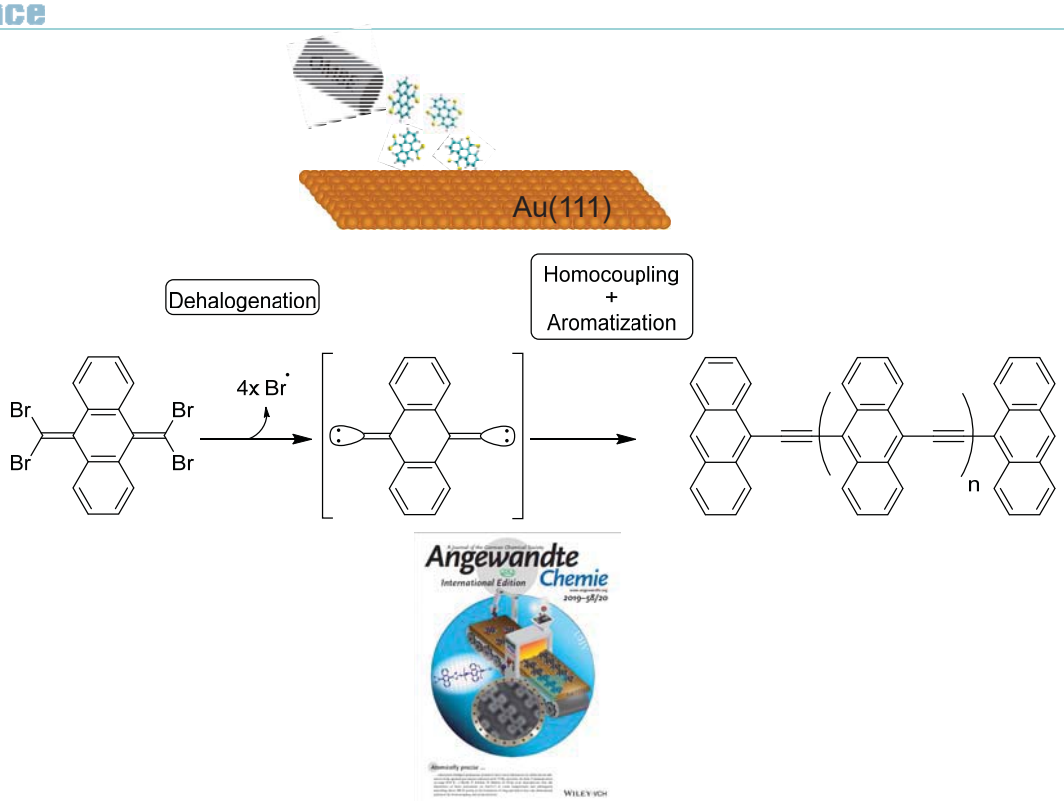


Ethynylene bridged anthracene polymers



institute IMdea nanoscience

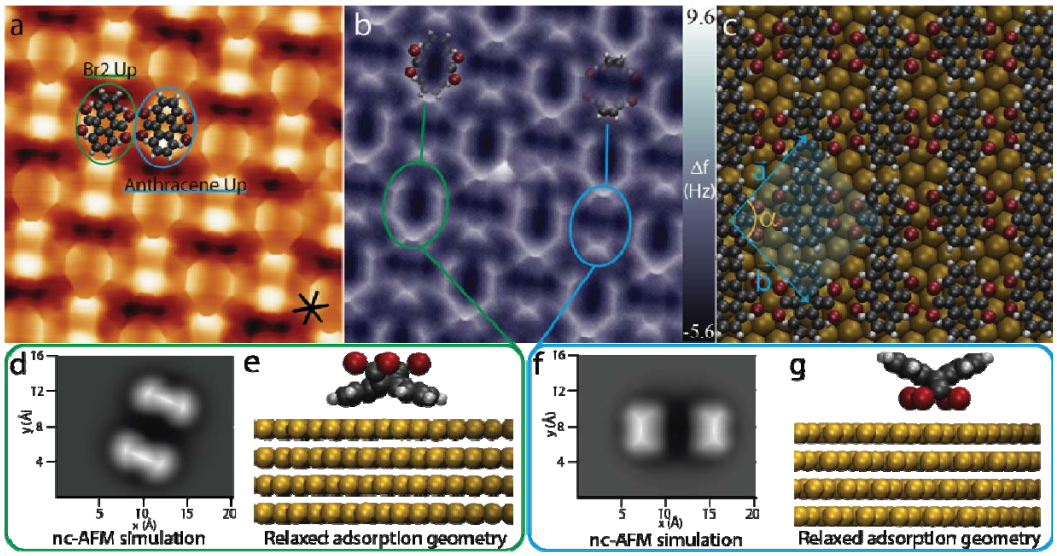
Ethynylene bridged anthracene polymers



www.nanoscience.imdea.org

Ethynylene bridged anthracene polymers

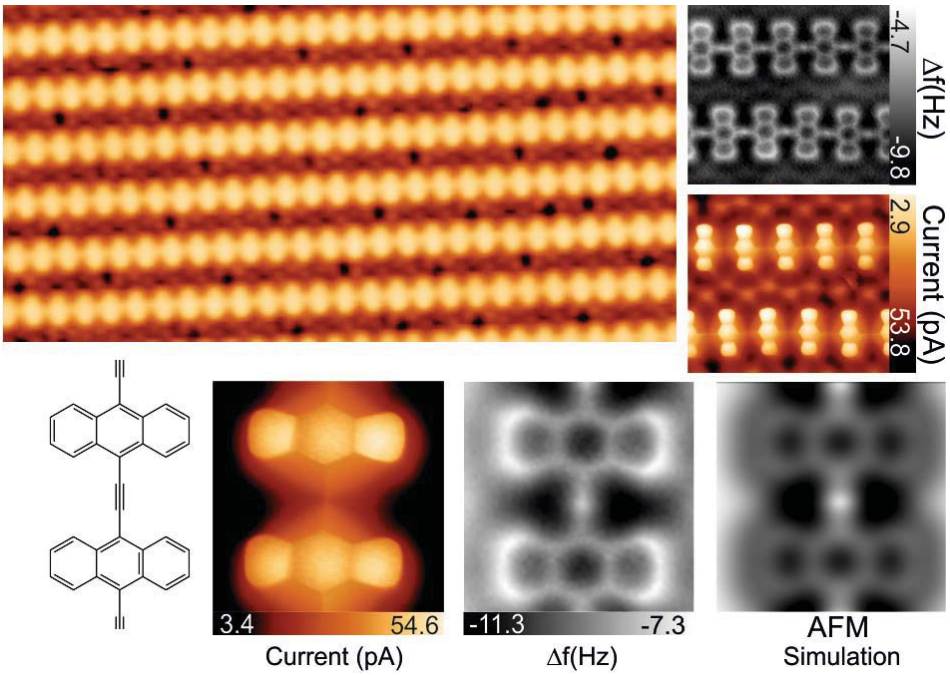
Step 1. Deposition at room temperature. Self-assembly



www.nanoscience.imdea.org

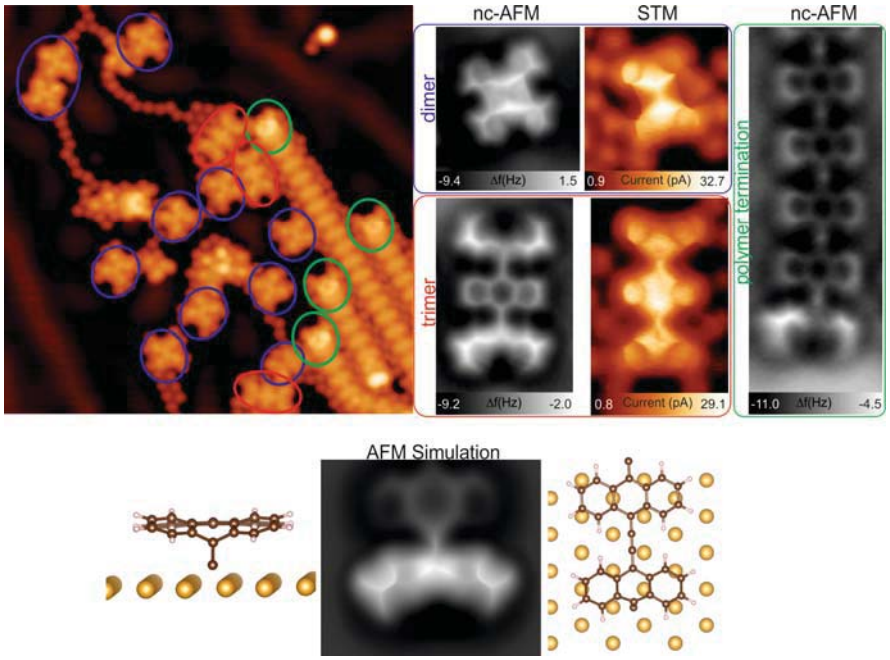
Ethynylene bridged anthracene polymers

Step 2. Annealing at 400 K. Debromination and coupling



Ethynylene bridged anthracene polymers

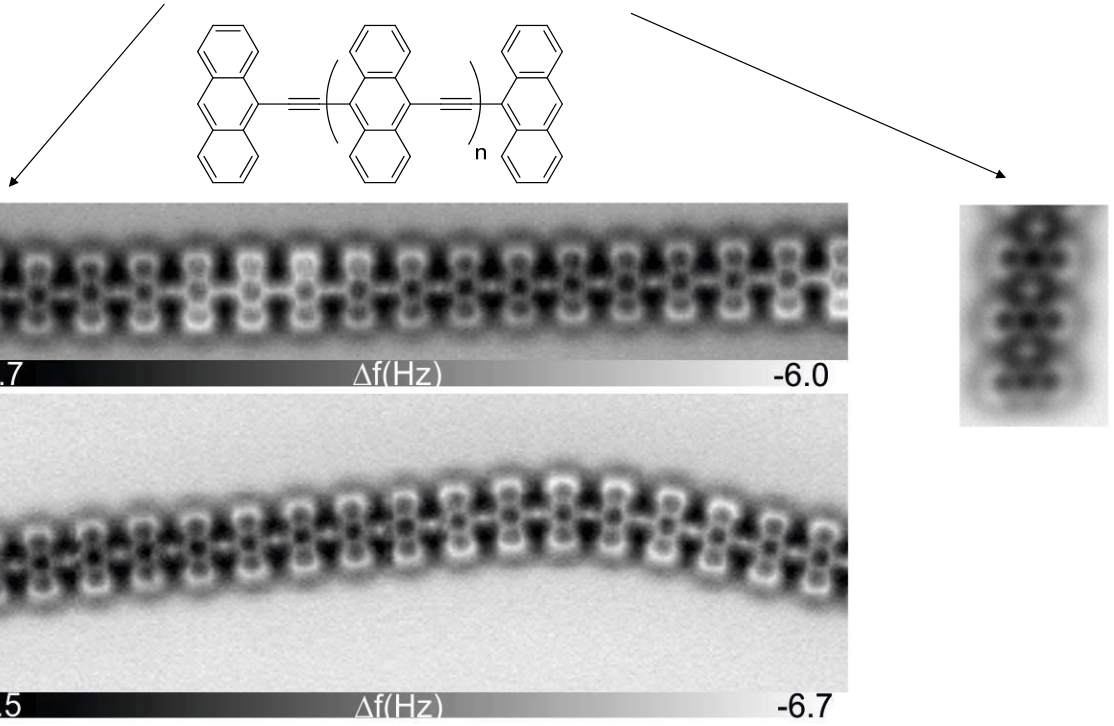
Step 2: Termini



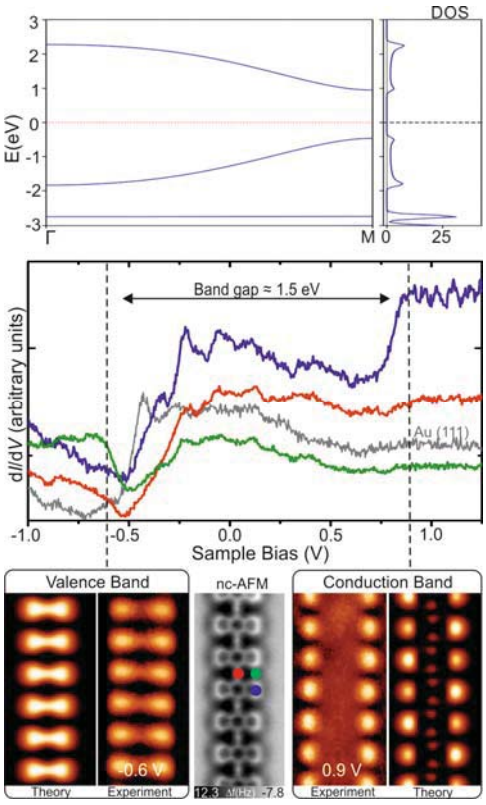
www.nanoscience.imdea.org

Ethynylene bridged anthracene polymers

Step 3: Desorption of bromine and hydrogen passivation



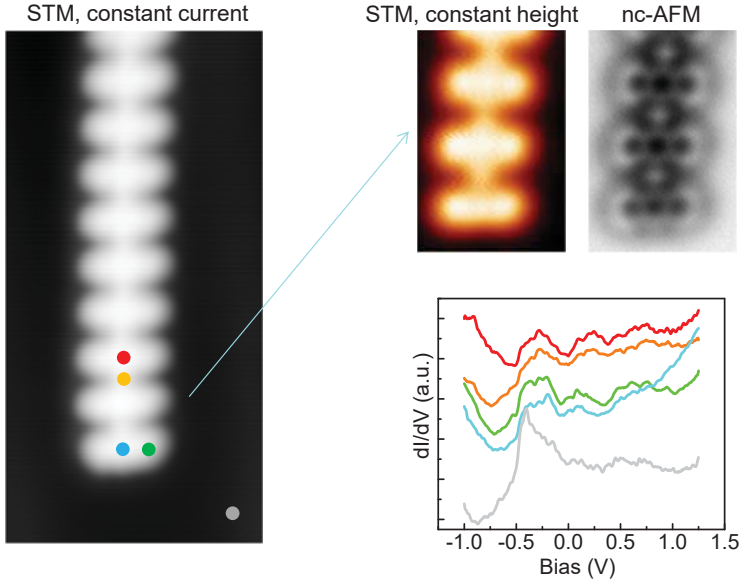
Ethynylene bridged anthracene polymers

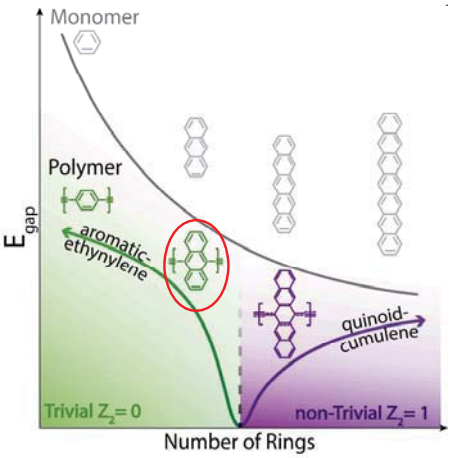


www.nanoscience.imdea.org

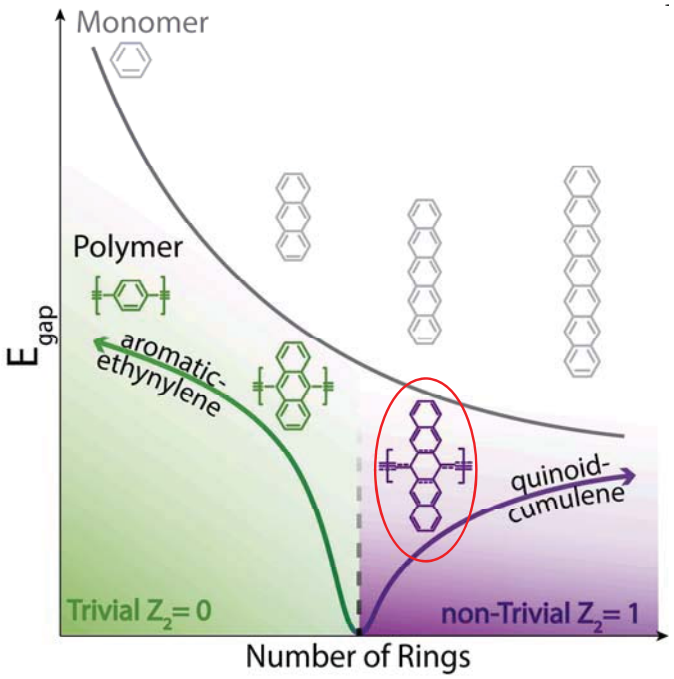
Ethynylene bridged anthracene polymers

- From topology $Z_2 = 0$: no end states.
- Experiments confirm theory: no end states.



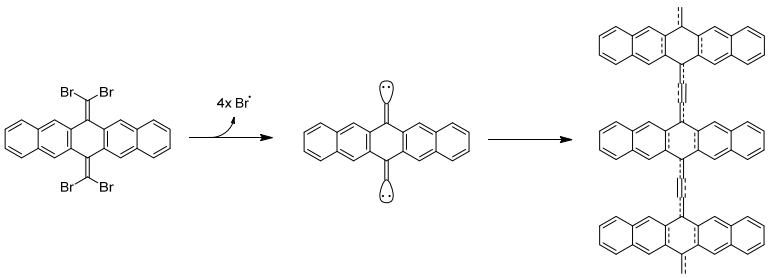


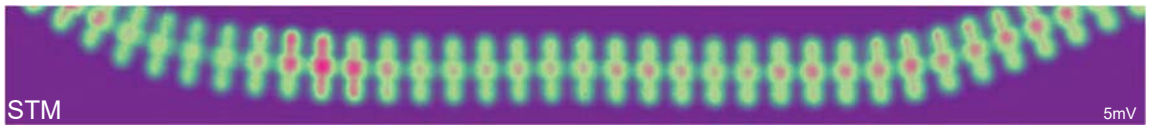
Pentacene polymers



institute IMdea nanoscience

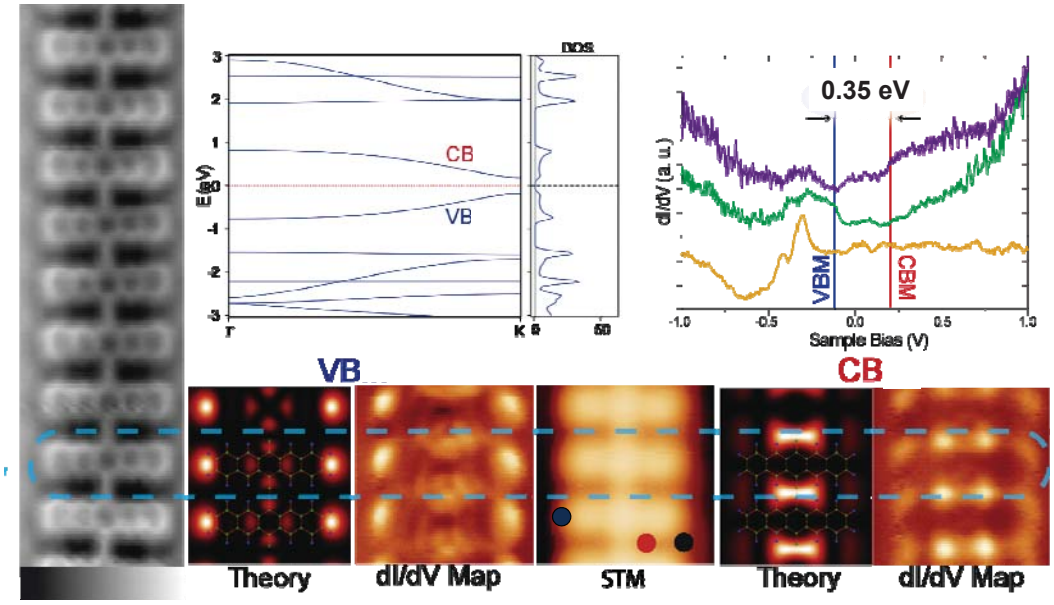
Pentacene polymers





www.nanoscience.imdea.org

Pentacene polymers

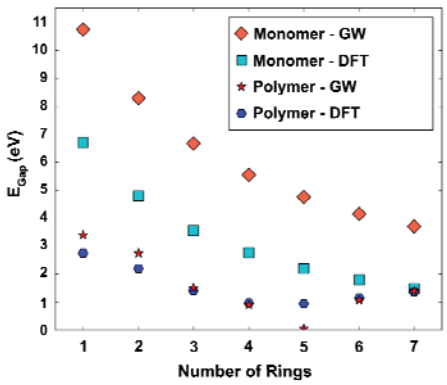


❑ Very narrow bandgap

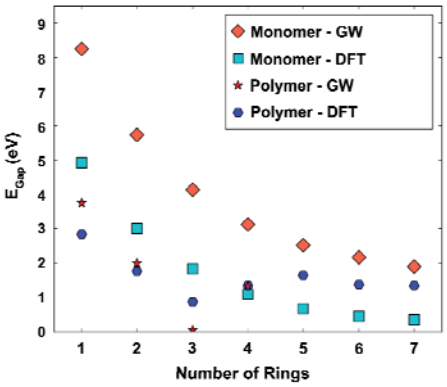
www.nanoscience.imdea.org

Theoretical study of bandgap

Acene family



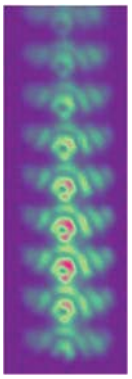
Periacene family

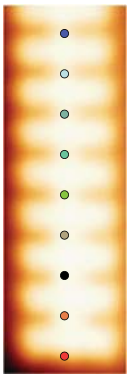


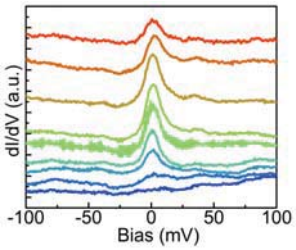
❑ **GW calculations: 50 meV for pentacene polymers!**

Pentacene polymers: Termini

- From topology $Z_2 = 1$: end states.



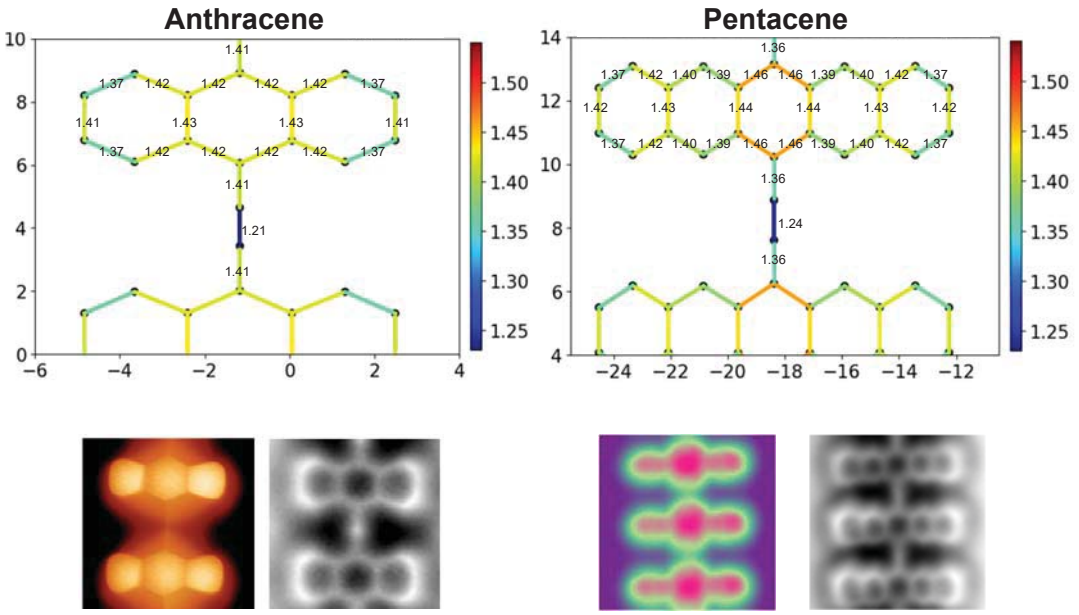




- Experiments confirm theory: end state at zero bias.

www.nanoscience.imdea.org

What is the origin of the topological transition?

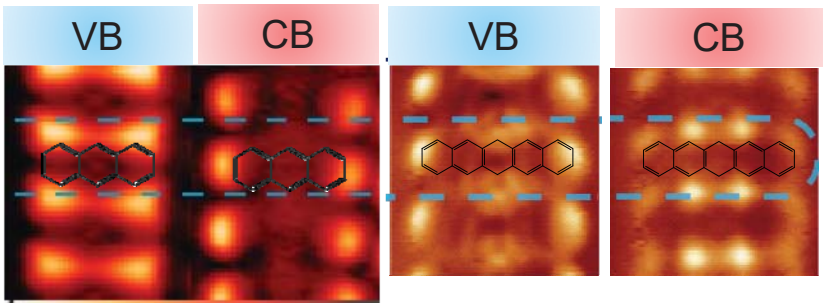


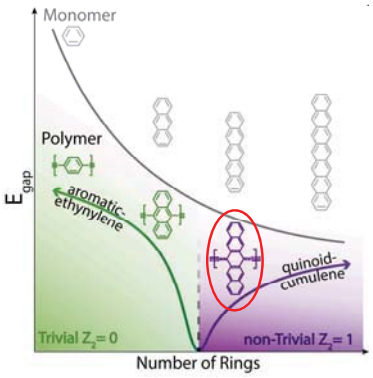
- Ethynylene/Aromatic → Cumulene-like/Quinoidal

What is the origin of the topological transition?

❑ Crossing level mechanism

Anthracene Polymer Pentacene Polymer





Ethynylene/Aromatic → 'Cumulene/Quinoid'

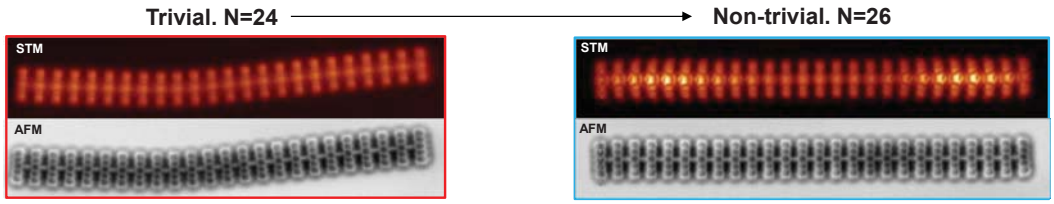
Crossing level

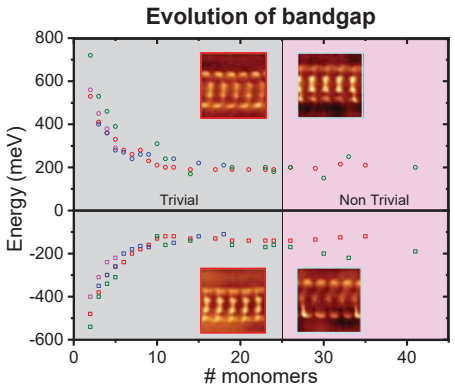
Change of topological class

www.nanoscience.imdea.org

Does the length of the polymer matter?

Topological transition induced by length





@ Jelinek´s lab

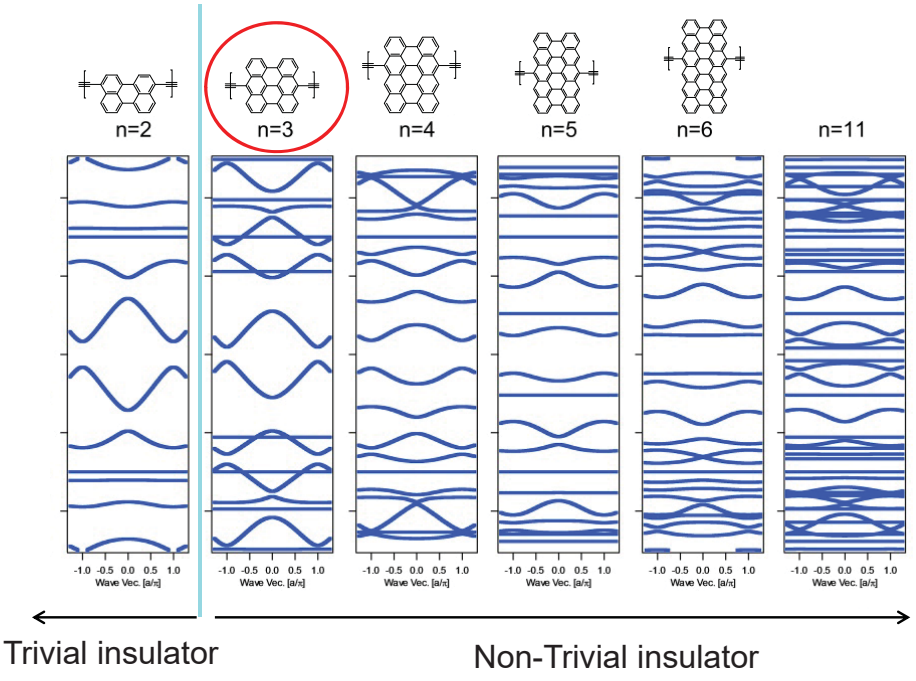
❑ Topological quantum phase transition from N=24 to N=26

institute IMdea nanoscience

Is this approach valid for other polymers?

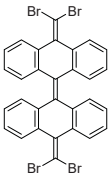
www.nanoscience.imdea.org

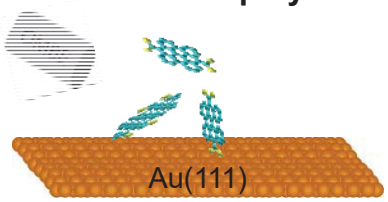
‘Fused-acenes’ polymers

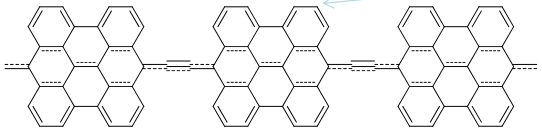


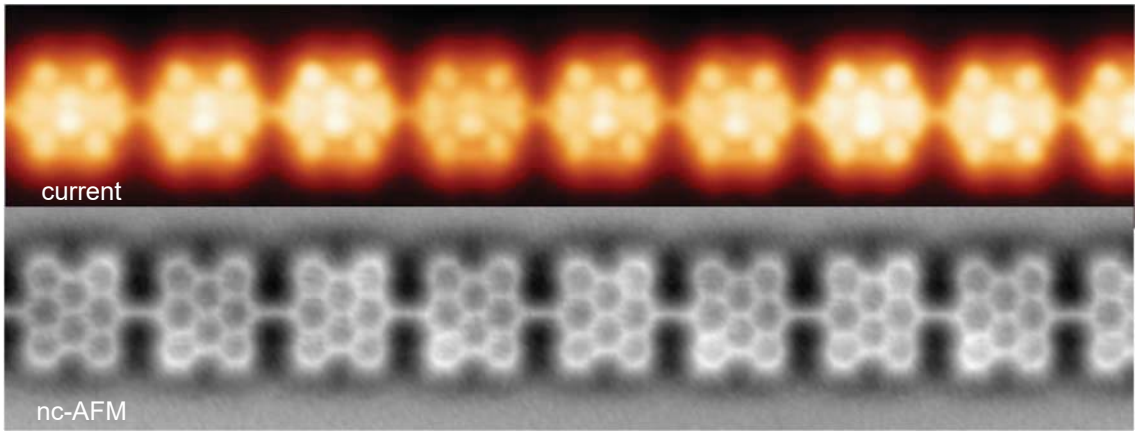
www.nanoscience.imdea.org

Bisanthene polymers

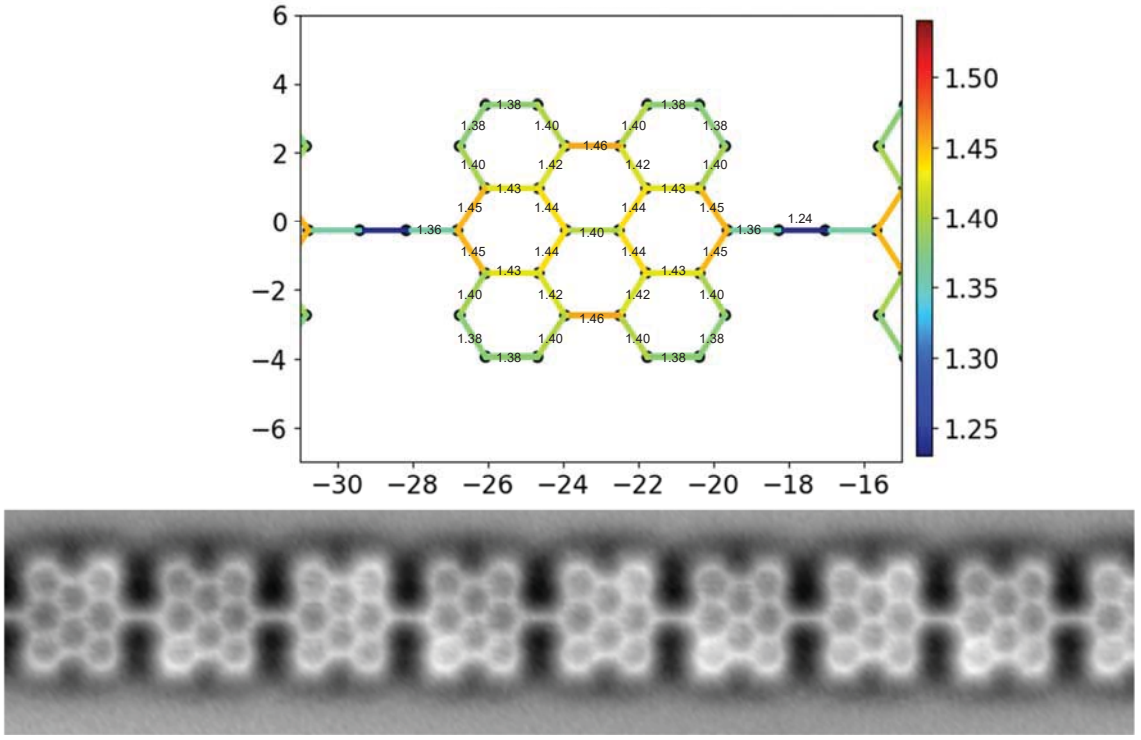






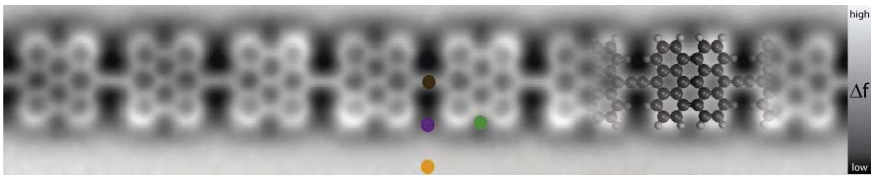


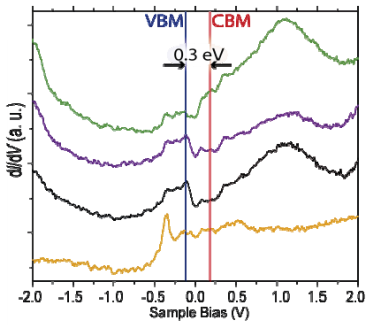
Bisanthene polymers

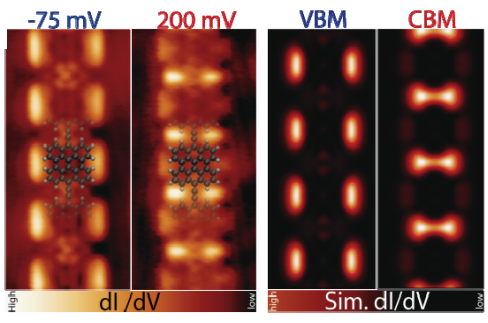


www.nanoscience.imdea.org

Bisanthene polymers

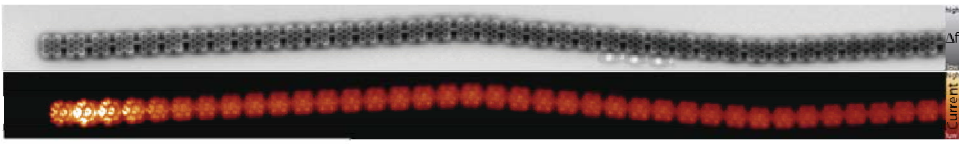


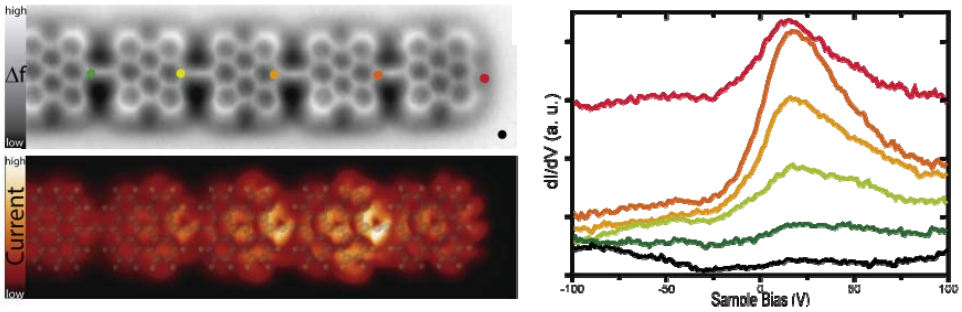




- ❑ Very narrow bandgap
- ❑ GW calculations: 30 meV

Bisanthene polymers

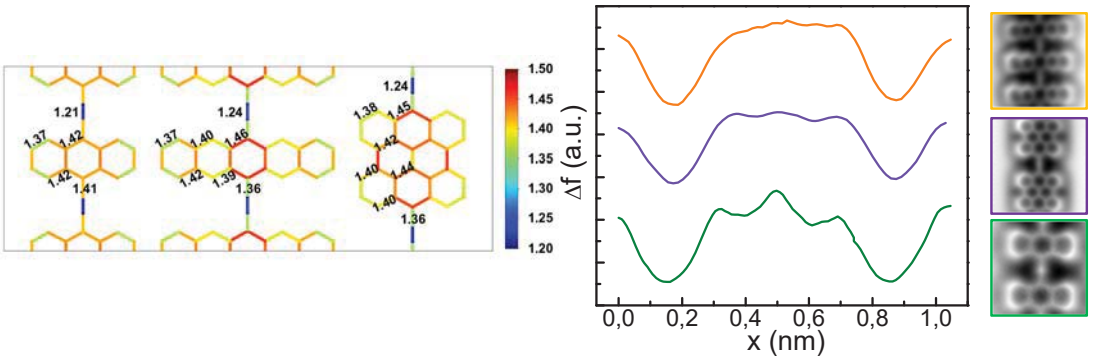


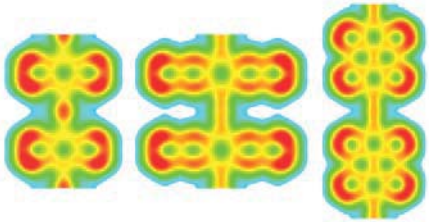


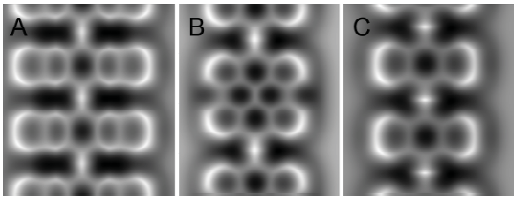
❑ Topological non trivial 1D insulator: Z_2=1 and end state

www.nanoscience.imdea.org

WHY?







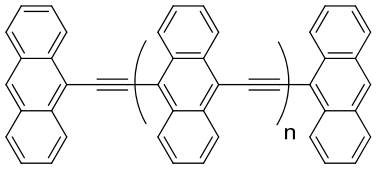
Ethynylene/Aromatic → 'Cumulene/Quinoid'

PART II: Can we steer new chemical intramolecular reactions based on specific π-conjugation?

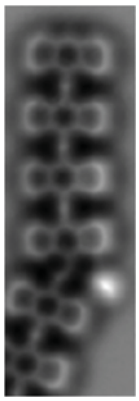
B. de la Torre et al., Nature Communications, 2020

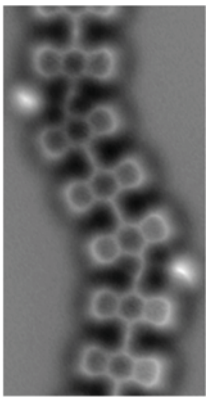
www.nanoscience.imdea.org

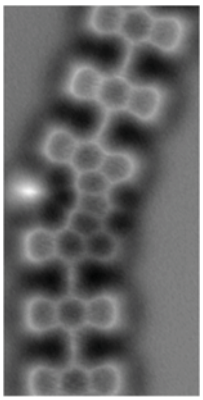
Annealing the ethynylene-bridge



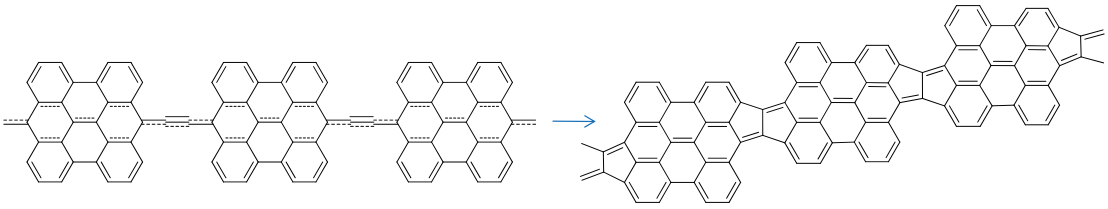
Irregular polymer



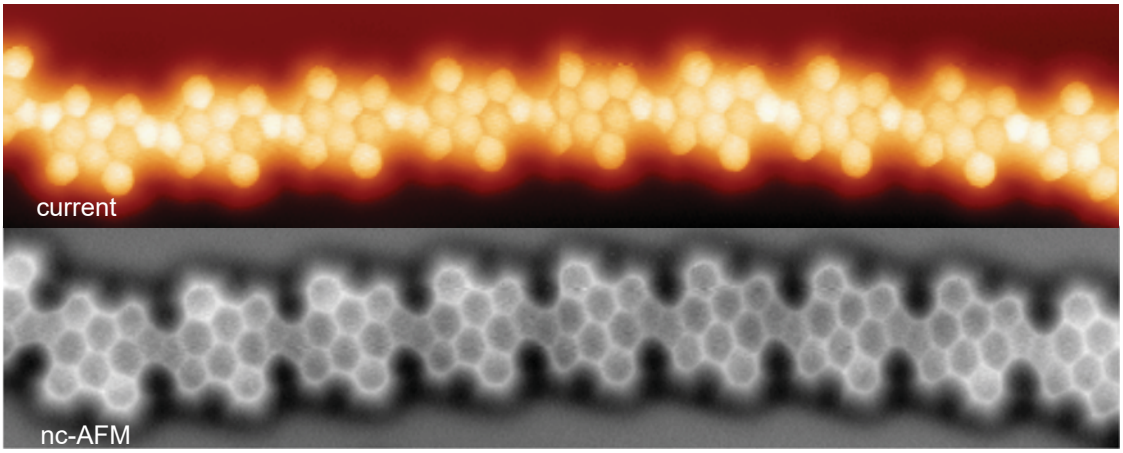




Annealing the cumulene-like bridge

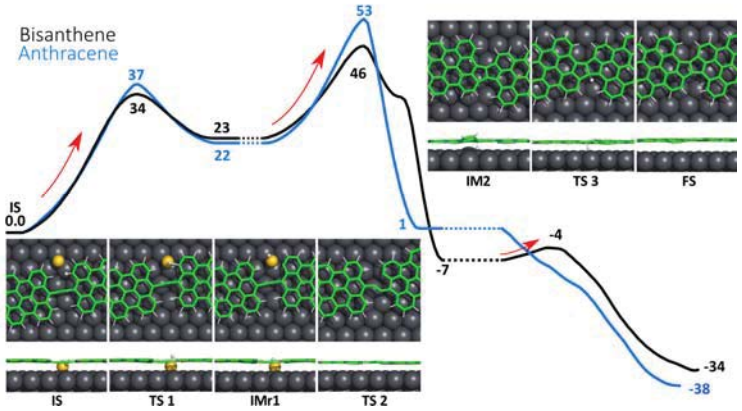


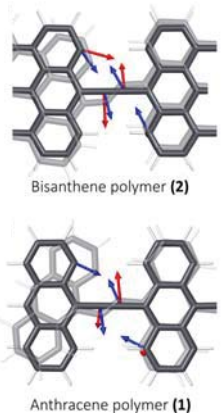
Pentalene-bridged π-conjugated ladder polymer



www.nanoscience.imdea.org

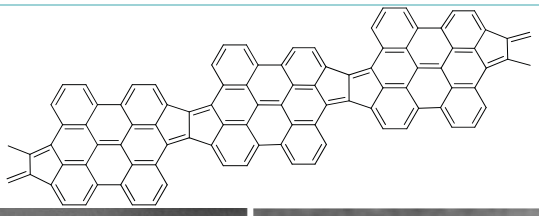
Homocoupling beyond transition state theory

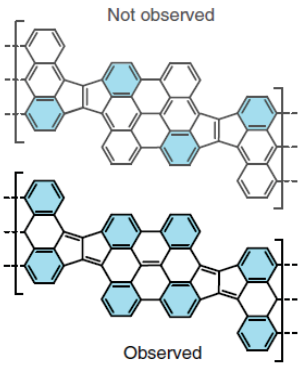


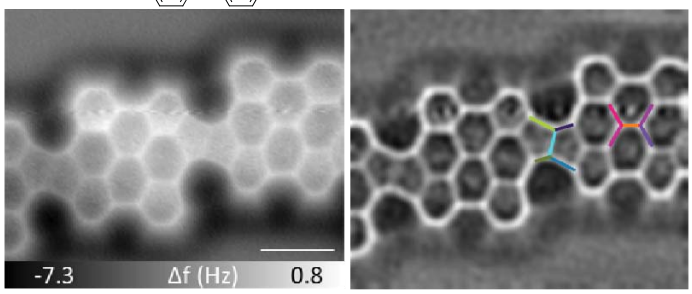


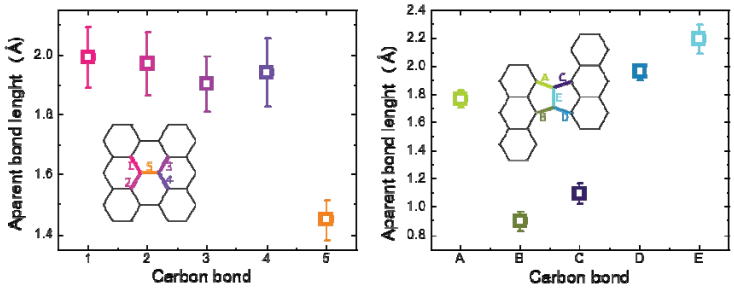
Vibrational modes come into play!

Bond order analysis of pentalene bridged polymers



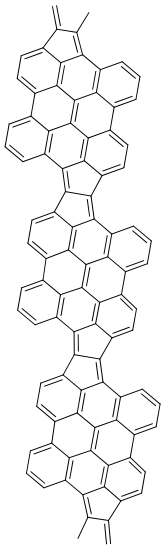


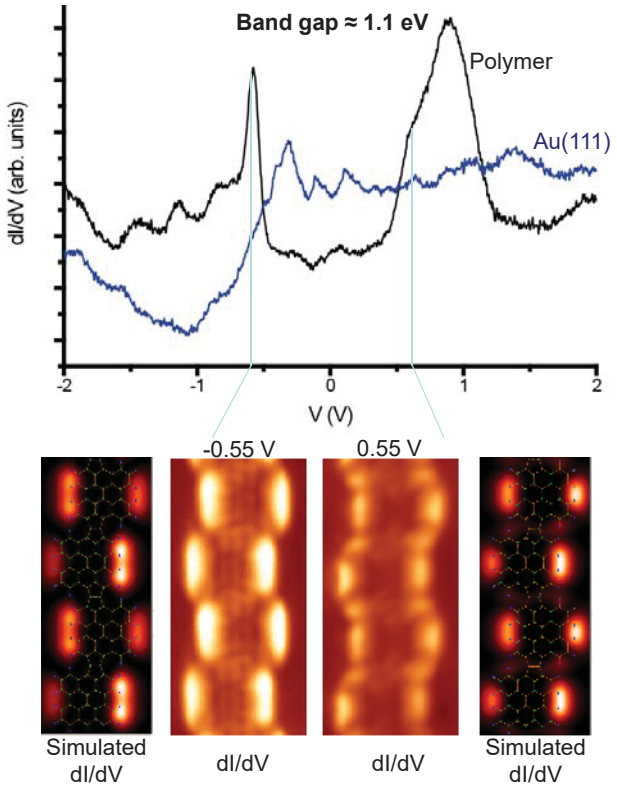




www.nanoscience.imdea.org

Annealing the cumulene-like bridge

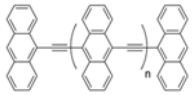


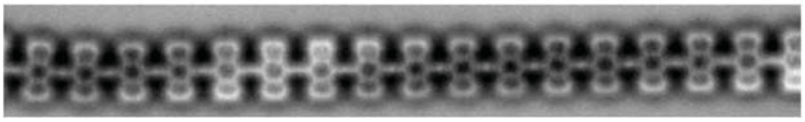


Summary: All-carbon based polymers

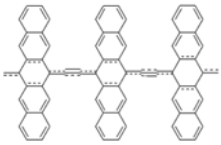
1D acene- and periacene-based polymers

Anthracene (*ACIE* 2019)

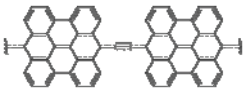


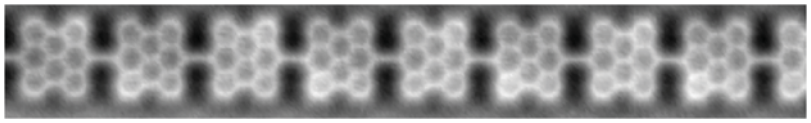


Pentacene (*Nat. Nanotechnol*. 2020)

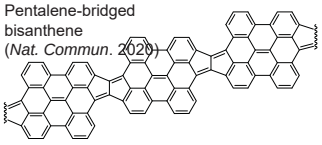


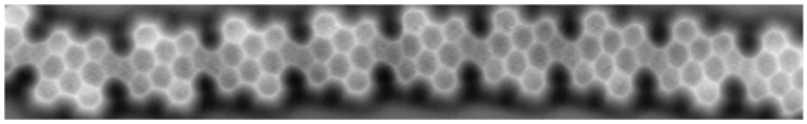
Bisanthene (*Nat. Nanotechnol*. 2020)



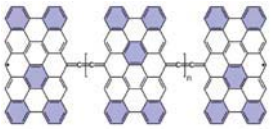


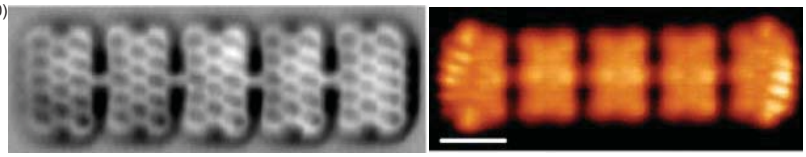
Pentalene-bridged bisanthene (*Nat. Commun*. 2020)





Peripentacene biradical polymers (*ACIE* 2020)

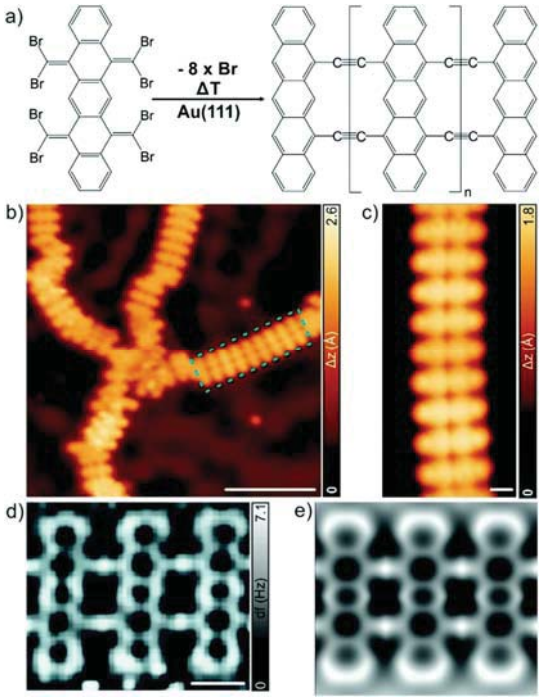




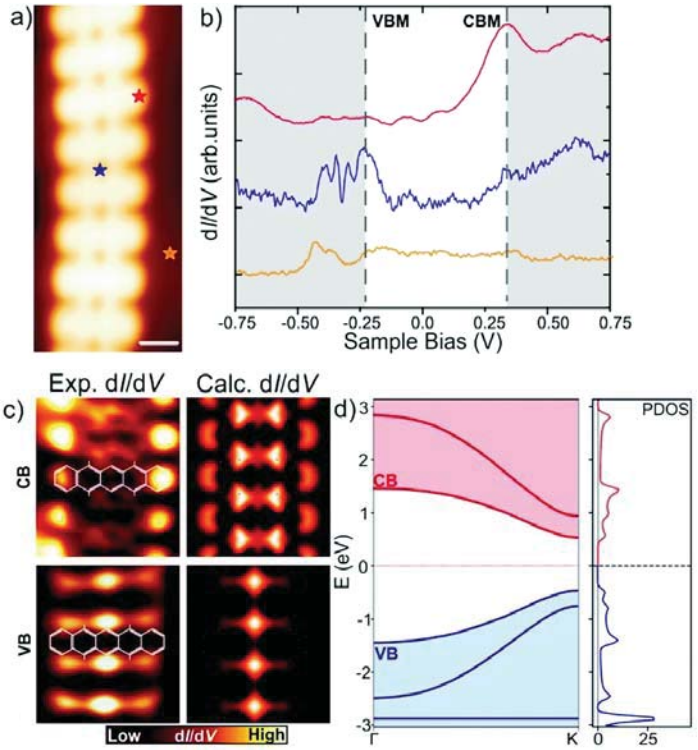
www.nanoscience.imdea.org

PART III: Can we increase the number of connections?!?

Increasing the number of connections



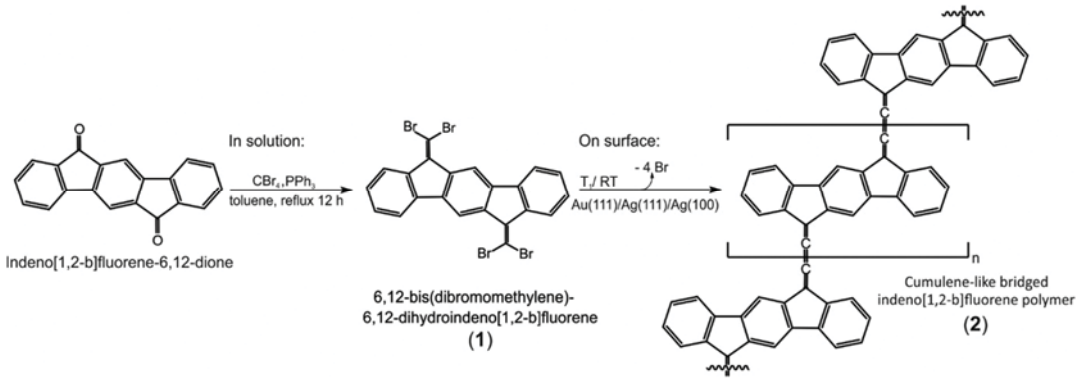
K. Biswas et al, Chem. Commun. 2022

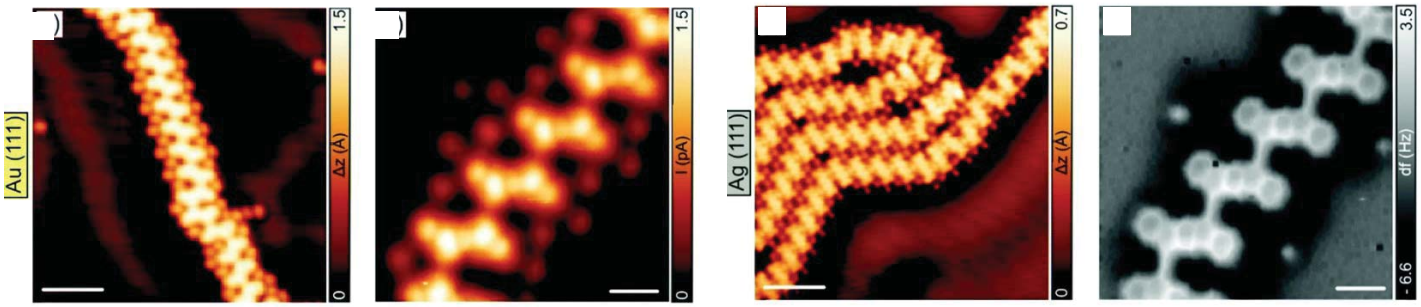


www.nanoscience.imdea.org

PART IV: Can we exploit $=CBr_2$ functional group in odd-member rings?

=CBr_2 as functional group in odd member rings





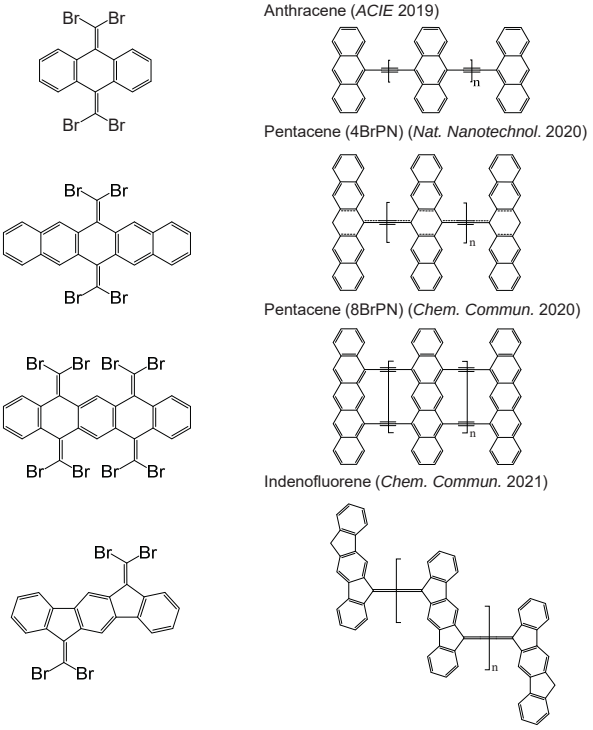
C. Martín-Fuentes et al, Chem. Commun. 2022

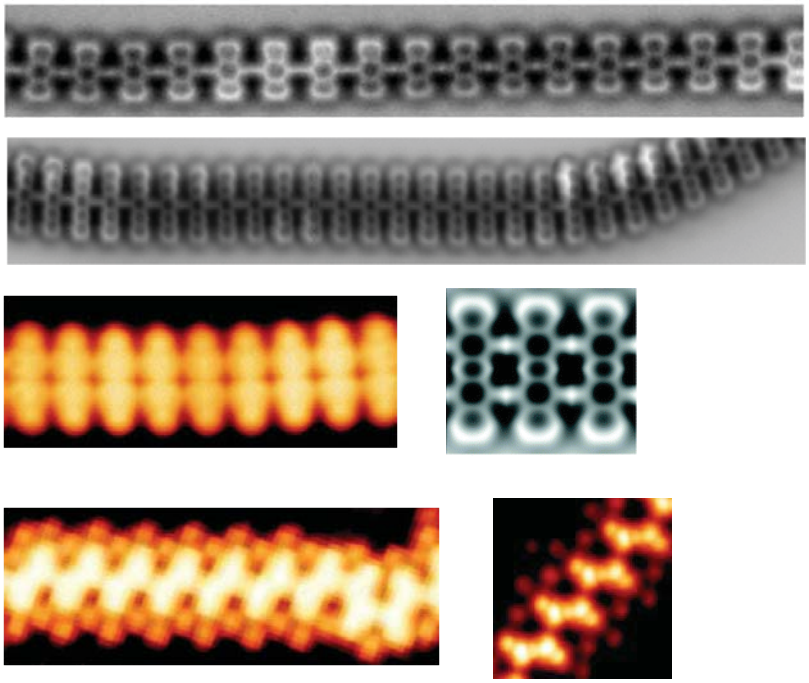
institute IMdea nanoscience

PART V: $A \times B \overset{?}{=} B \times A$

The role of substrate temperature!

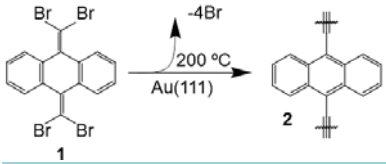
The role of substrate temperature

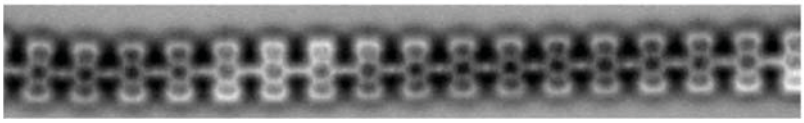


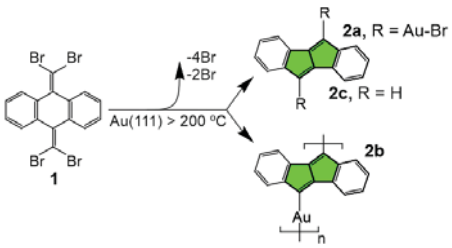


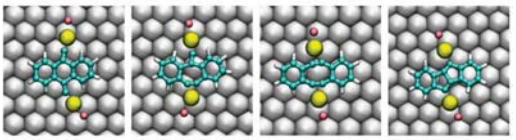
www.nanoscience.imdea.org

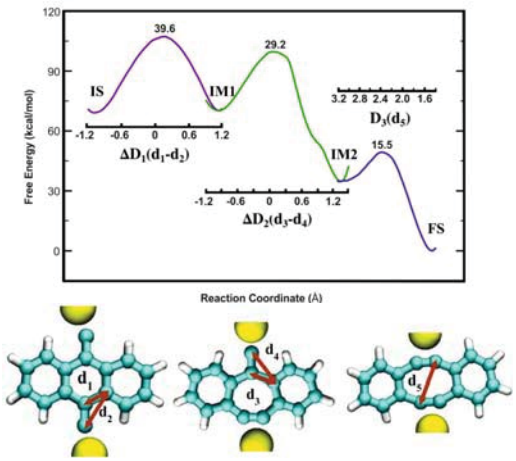
The role of substrate temperature

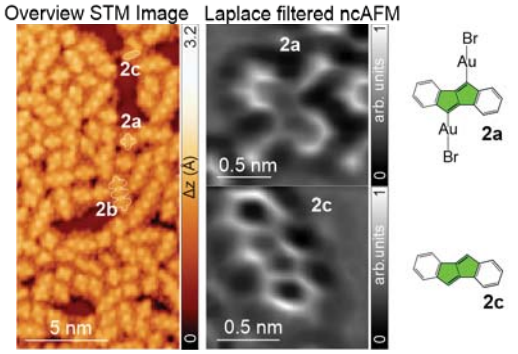




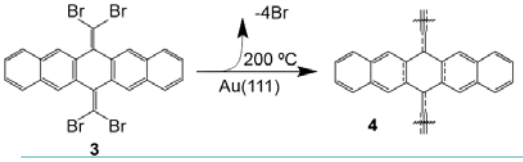


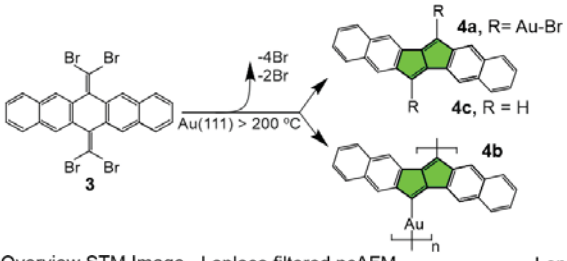


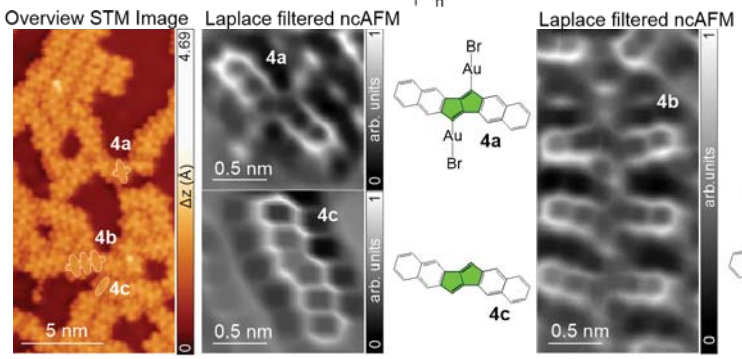


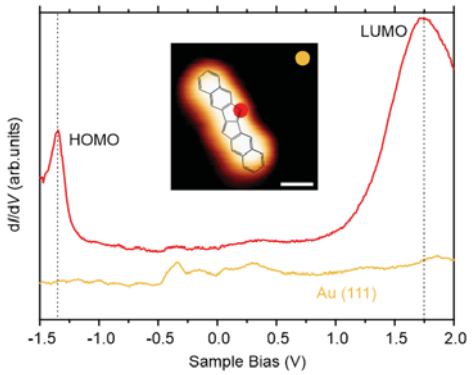


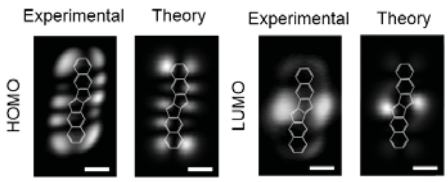
The role of substrate temperature





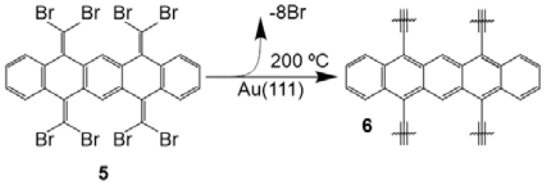


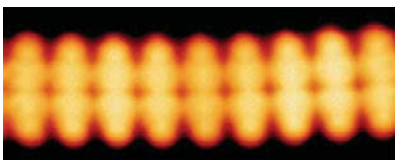


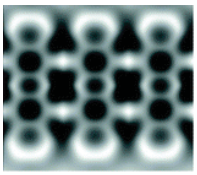


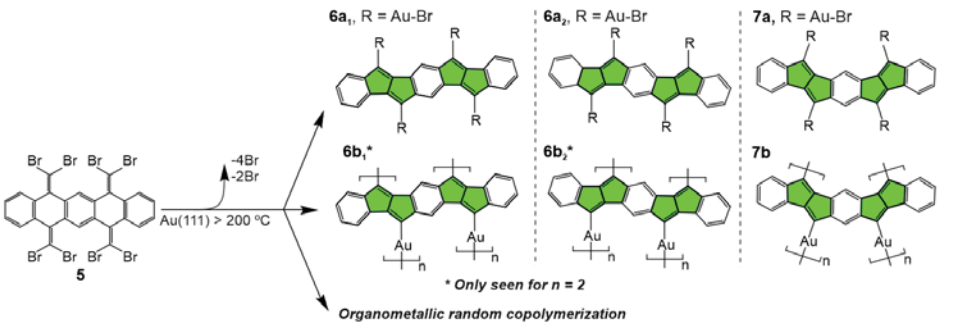
www.nanoscience.imdea.org

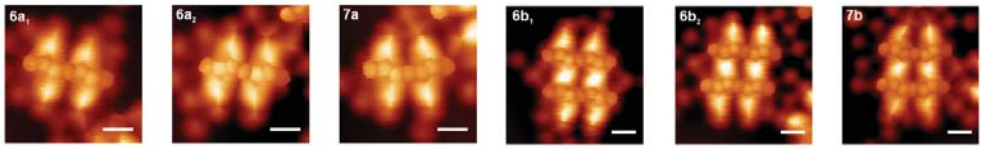
The role of substrate temperature

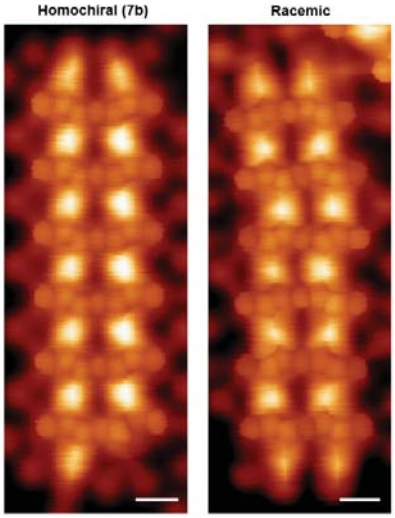




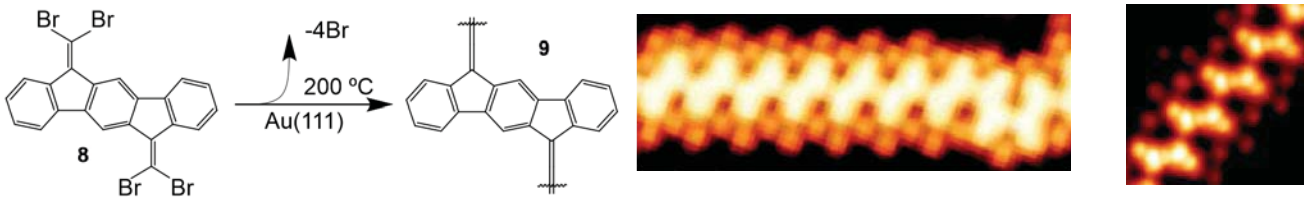


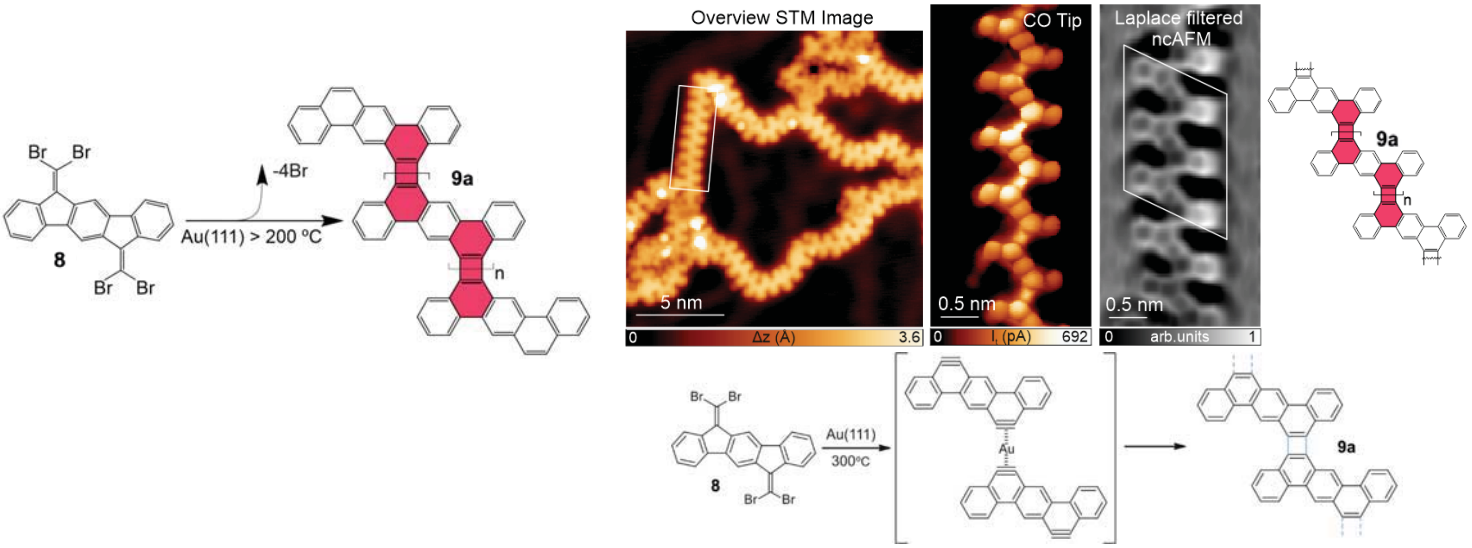






The role of substrate temperature



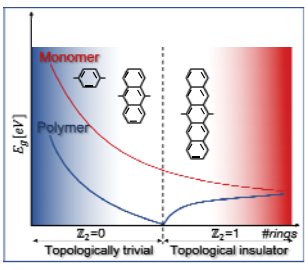


institute IMdea nanoscience

www.nanoscience.imdea.org

Conclusions

- Emergence of π-magnetism of nanographenes: Giant Magnetic Exchange Coupling
- $=CBr_2$ termini allows homocoupling and formation of atomistically precise π-conjugated 1D polymers (all-carbon or heteroatomic)



- Topology matters: New paradigm to lower, even quench the bandgap!!!
- Vibrations play a role in chemical reactions on surfaces (Beyond TST)
- Substrate (and its temperature) can be non-innocent and drive distinct reactions

www.nanoscience.imdea.org

Acknowledgements

IMDEA Madrid

- Borja Cirera
- Ana Sánchez Grande
- Cristina Martín-Fuentes
- Kalyan Biswas
- Ana Barragán
- Elena Pérez
- Koen Lauwaet
- José María Gallego
- José I. Urgel
- Rodolfo Miranda

UCM, Madrid

- Eider Rodríguez
- José Santos
- Nazario Martín

TU Dresden

- Ji Ma
- Xinliang Feng

Czech Academy of Sciences, Prague

- Shayan Edalatmanesh
- Jesús I Mendieta-Moreno
- Adam Matěj
- Pavel Jelínek

Linköping University

- Jonas Björk

Regional Centre of Advanced Technologies, Olomouc

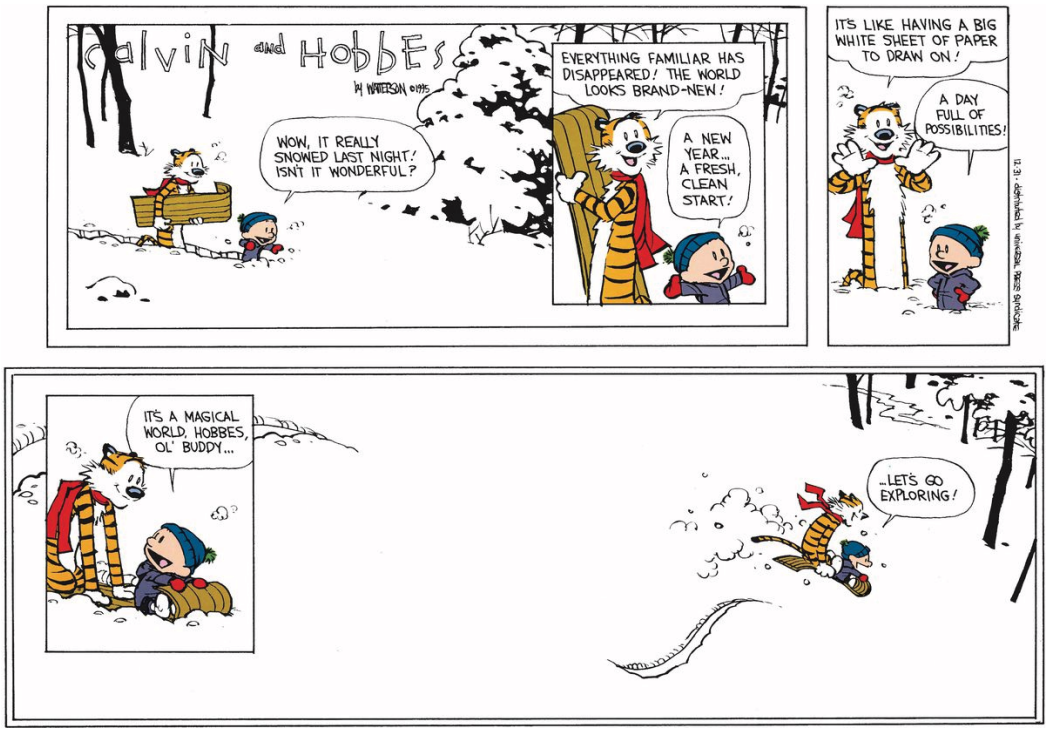
- Benjamín Mallada
- Bruno de la Torre

EMPA

- Shantanu Mishra
- Oliver Gröning
- Roman Fasel

www.nanoscience.imdea.org

TAKE-HOME MESSAGE



On-surface synthesis is a brand new world for designing low dimensional materials to explore the roots of physics and chemistry!

OUTLINE

1.- The group

2.- On-surface synthesis.

3.- Emergence of π-magnetism in nanographenes.

4.- Topology and magnetism in π-conjugated 1D polymers.

5.- Conclusions and outlook

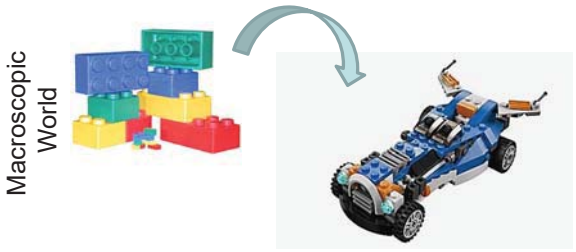
institute IMdea nanoscience

BONUS TRACK

www.nanoscience.imdea.org

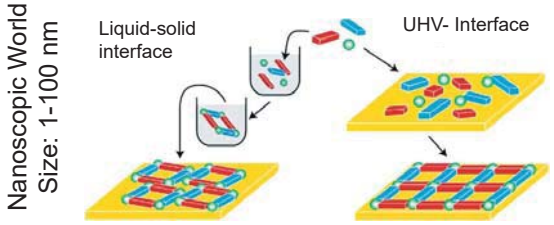
ON-SURFACE CHEMISTRY: Supramolecular chemistry

Bottom–up approach



Self-assembly

Building blocks: molecules and atoms

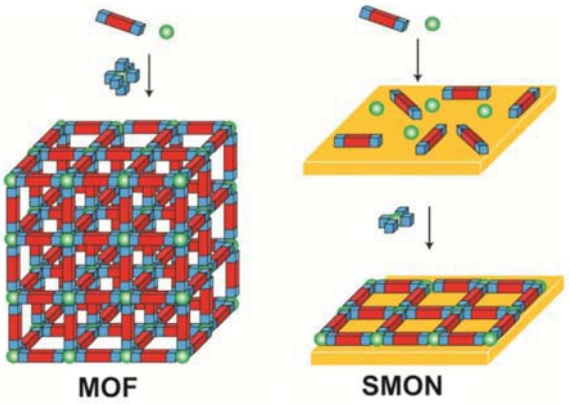


Top Curr Chem (2009) 287: 1–44

institute imdea nanoscience

ON-SURFACE CHEMISTRY: Supramolecular chemistry

Surface metal-organic networks (SMONs)



Focused on:

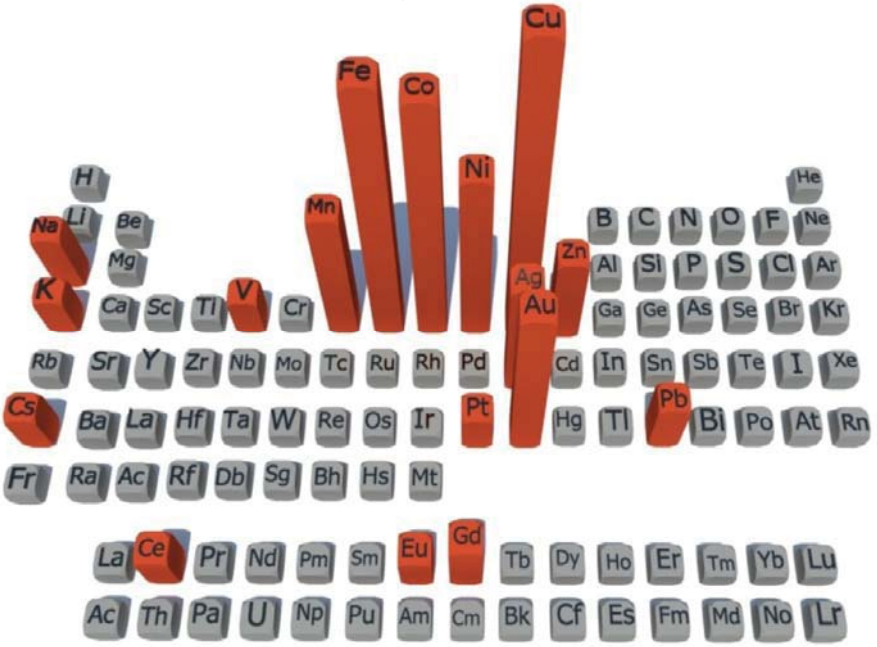
- Design
- Catalytic properties
- Magnetic properties
- Information storage
- Quantum information
- Topologically non trivial matter

Prog. Surf. Sci. 91, 101, 2016

www.nanoscience.imdea.org

ON-SURFACE CHEMISTRY: Supramolecular chemistry

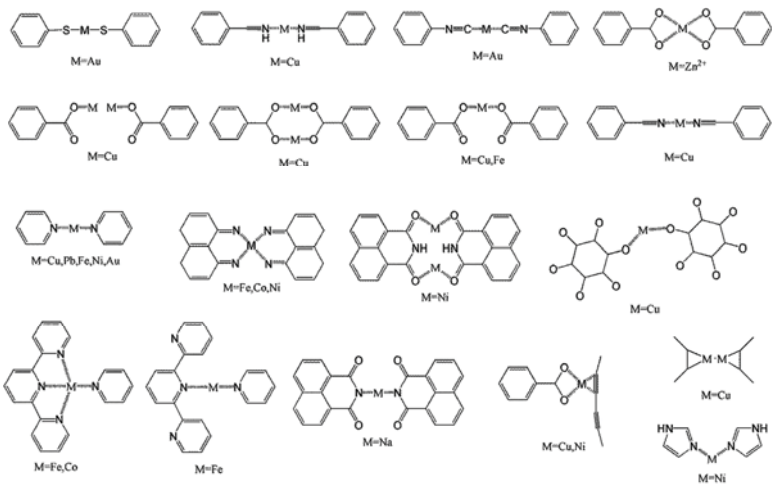
Surface metal-organic networks (SMONs)



institute IMdea nanoscience

ON-SURFACE CHEMISTRY: Supramolecular chemistry

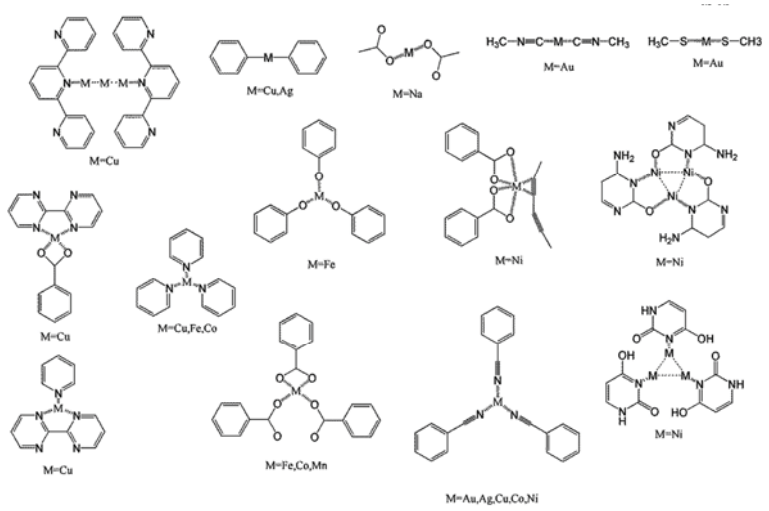
Surface metal-organic networks (SMONs)



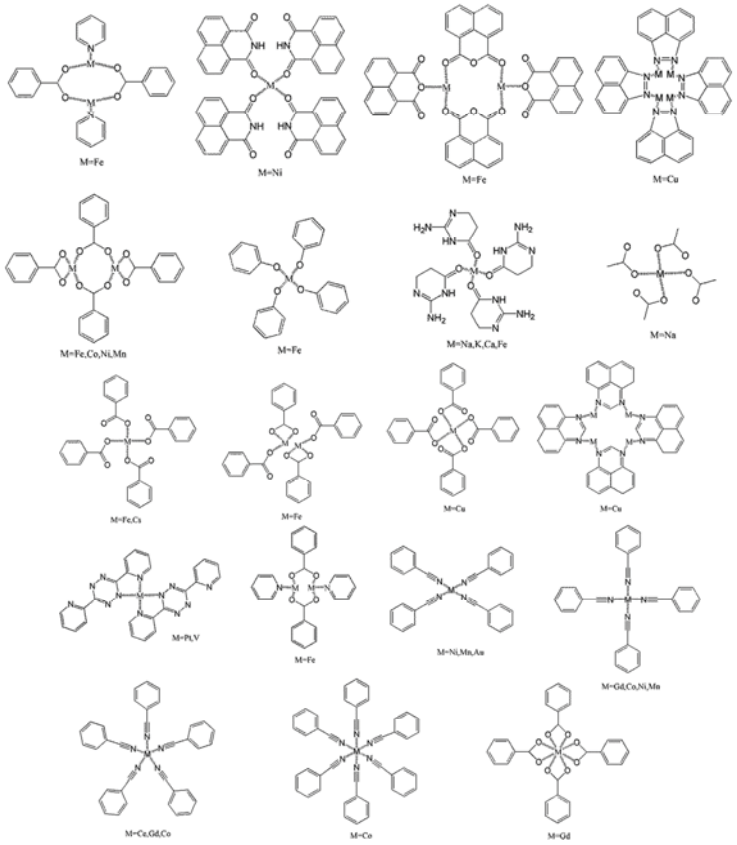
www.nanoscience.imdea.org

ON-SURFACE CHEMISTRY: Supramolecular chemistry

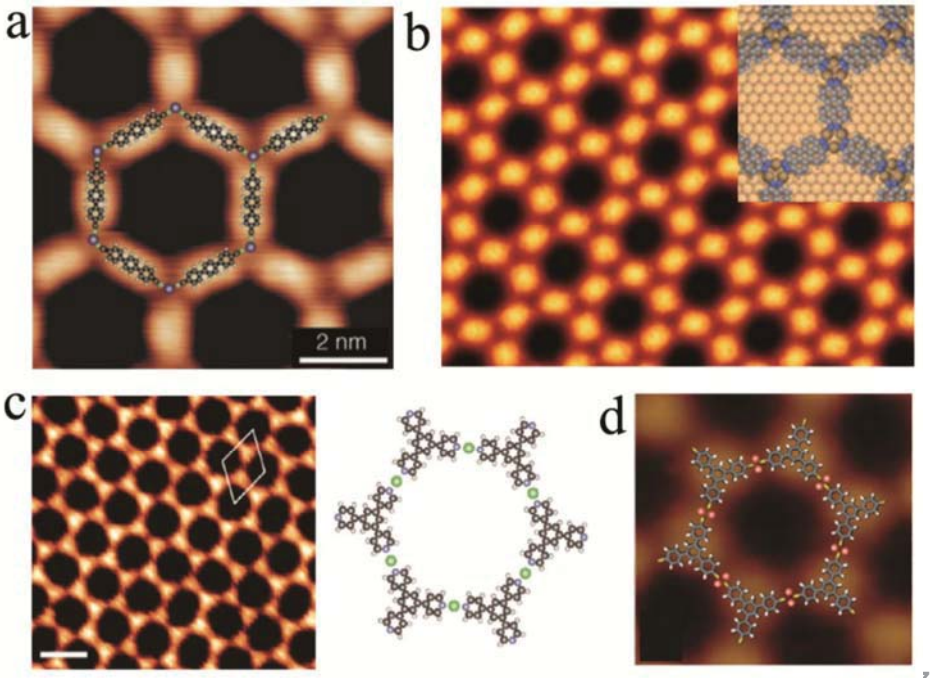
Surface metal-organic networks (SMONs)



institute IMdea nanoscience
www.nanoscience.imdea.org

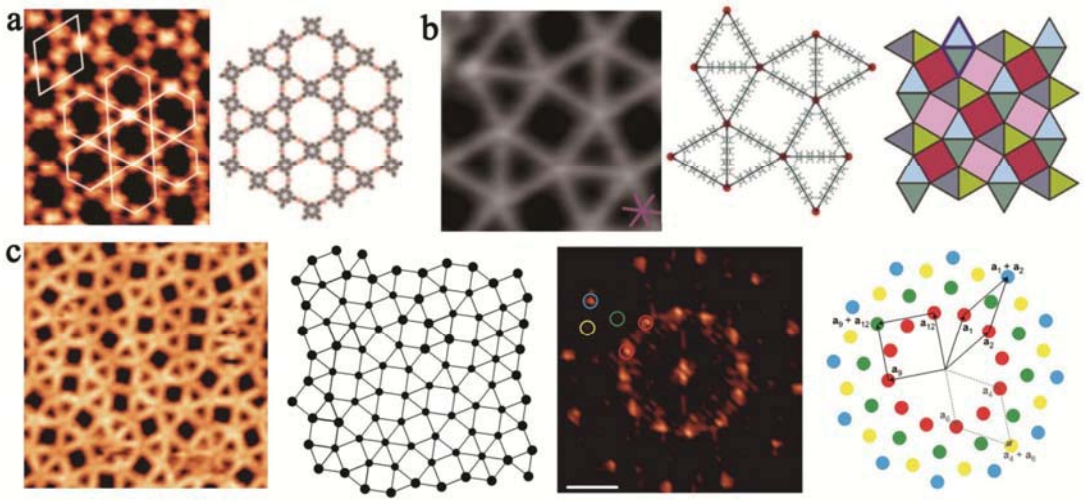


Seminal examples of surface metal-organic networks (SMONs)



institute IMdea nanoscience
ON-SURFACE CHEMISTRY: Supramolecular chemistry

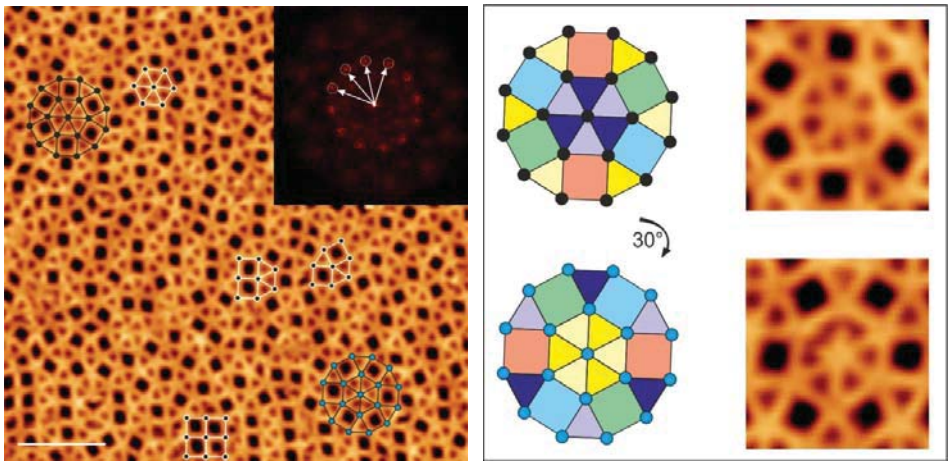
Seminal examples of surface metal-organic networks (SMONs)



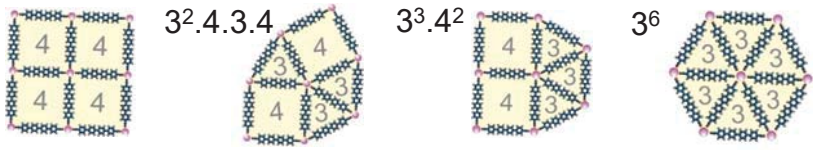
ON-SURFACE CHEMISTRY: Supramolecular chemistry

Random-Tiling dd-Quasicrystal

Eu : qdc ratio (2 : 5.1)



4^4 $3^2.4.3.4$ $3^3.4^2$ 3^6



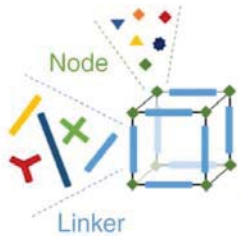
- Complex open network structure with linkers in 6 orientations.
- Expression of dodecagonal motifs without translational symmetry and self-similarity.

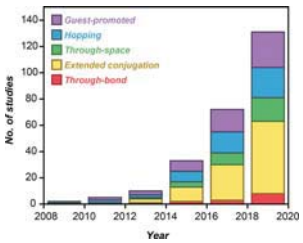
Nature Chemistry 2016, vol. 8, 657-662

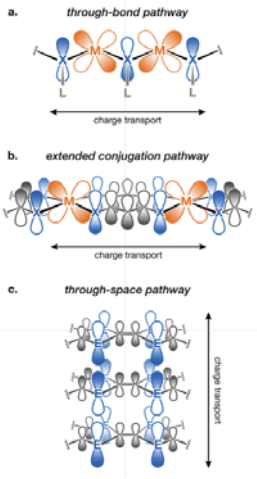
www.nanoscience.imdea.org

Electrically conducting MOFs

- 2009- Born of a new field: Electrically conducting MOFs



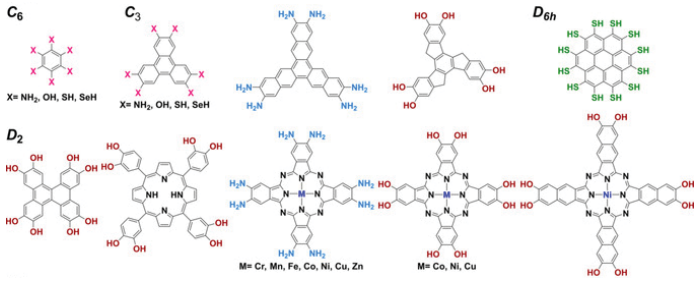




π-d conjugation plays a major role as a mechanism to enhance conductivity

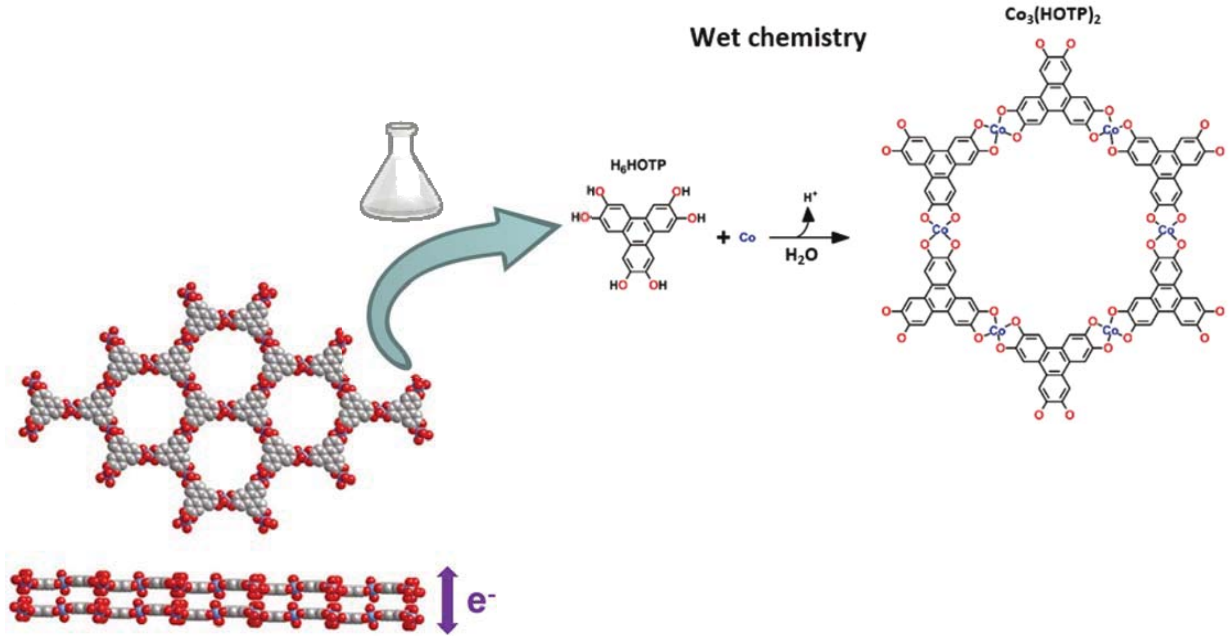
2D Electrically conducting MOFs

- Trully 2D MOFs are pursued by surface science techniques.
- Beyond high conductivity, predictions include complex quantum phases of matter:
  Ferromagnetism, Antiferromagnetism, Quantum spin liquids,…
  Superconductivity, Topological non-trivial insulators, 2D Weyl semimetals, …
- Race for designing such materials on surfaces
- Inspiration from inorganic and material chemistry

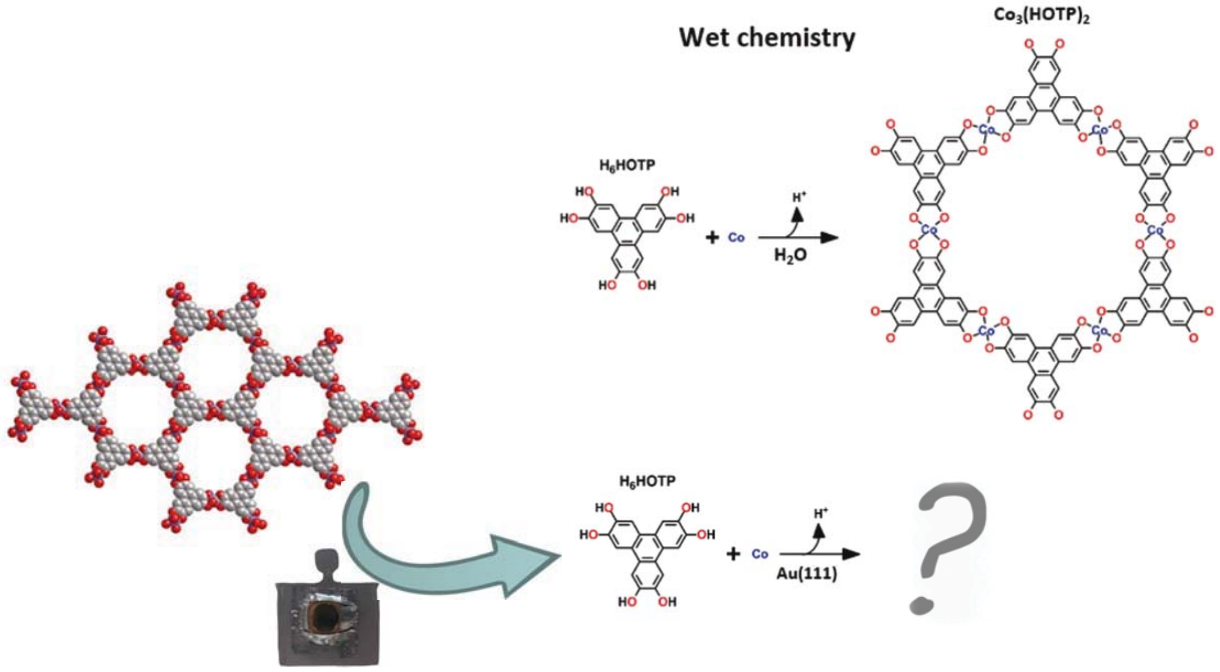


www.nanoscience.imdea.org

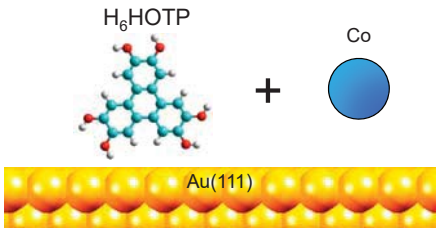
2D Electrically conducting MOFs



2D Electrically conducting MOFs

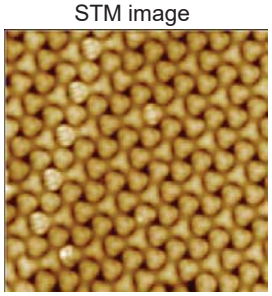


Co-HOTP network on Au(111)



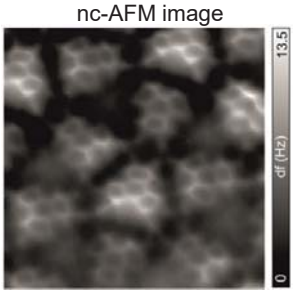
- Co-O coordination: 3-fold
- Two distinct molecular coordination: 4-fold and 6-fold

STM image



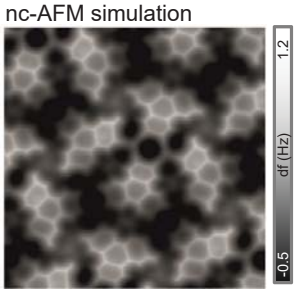
V_b = 20 mV, I = 120 pA,
T = 4 K, 11.7 nm x 11.7 nm

nc-AFM image

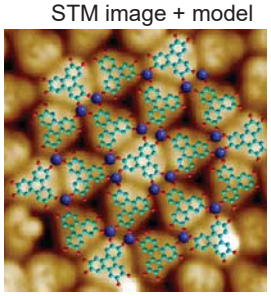


Open feedback: V_b = 5mV, I_t = 150 pA,
Z_{offset} = 150 pm,T = 4 K, 3.2 nm x 3.2 nm

nc-AFM simulation



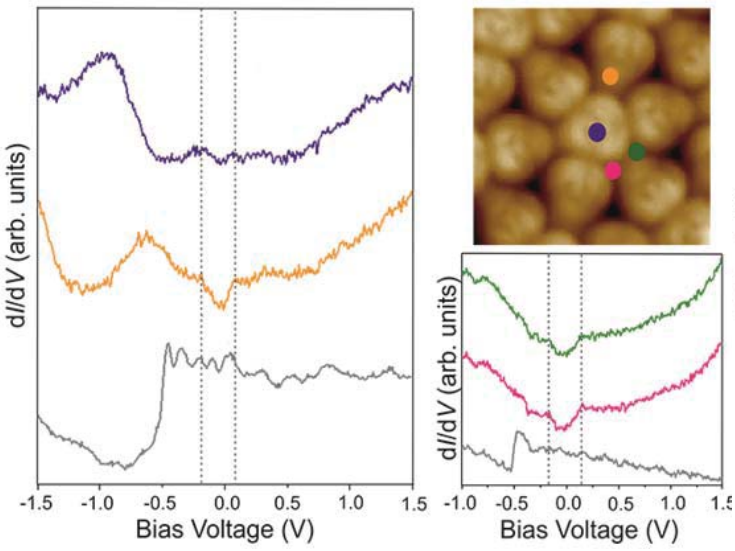
STM image + model



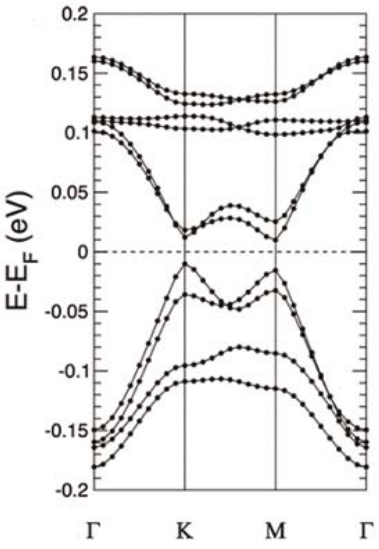
V_b = 20 mV, I = 100 pA,
T = 4 K, 4 nm x 4 nm

Electronic properties of Co-HOTP network

STS



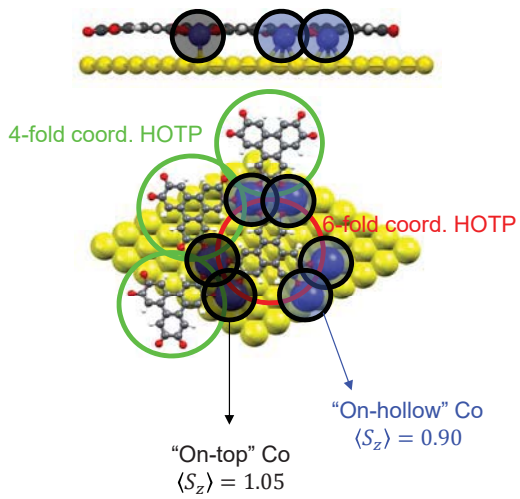
DFT+U



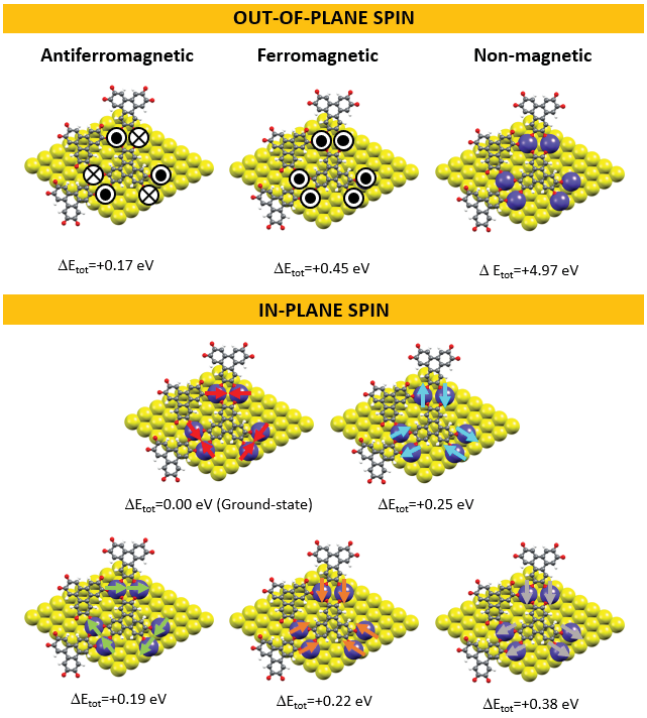
www.nanoscience.imdea.org

Magnetic properties of Co-HOTP network

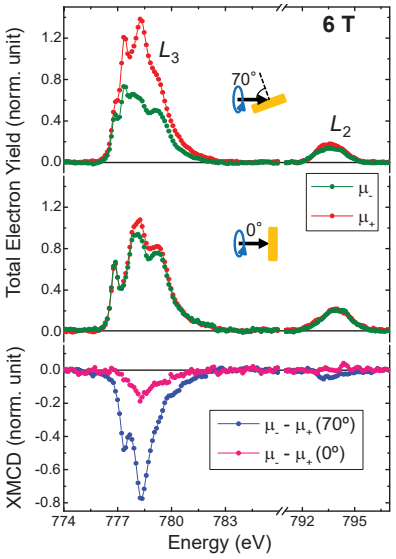
DFT+U



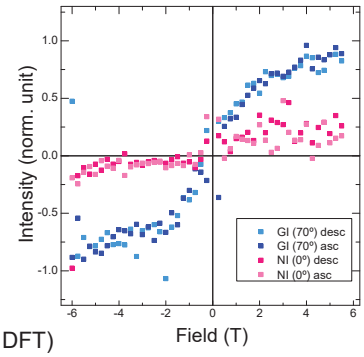
In-plane antiferromagnetic

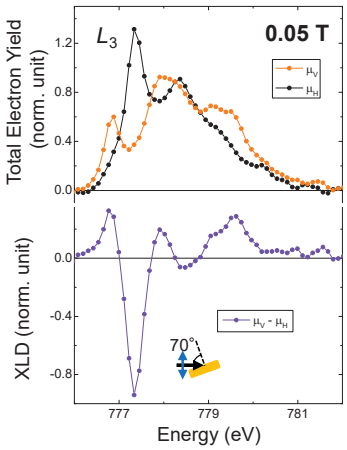


Magnetic properties of Co-HOTP network



- Strong in-plane magnetic anisotropy
  - Large unquenched orbital moment
  - Large orbital to effective spin moment
- Strong charge anisotropy
- Magnetization curves compatible with antiferromagnetism





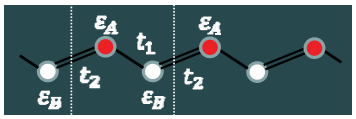
Magnetic moments (n_H=2.74, DFT)

Incidence angle (º)	$\langle S_{eff} \rangle$ ($\hbar$)	$\langle L_z \rangle$ ($\hbar$)	$m_{S_{eff}}$ (μ_B)	m_L (μ_B)	$\langle L_z \rangle / 2\langle S_{eff} \rangle$
70	0.61 (6)	0.98 (10)	1.22 (12)	0.98 (10)	0.80(11)
0	0.14 (1)	0.19 (2)	0.28 (3)	0.19 (2)	0.68(10)

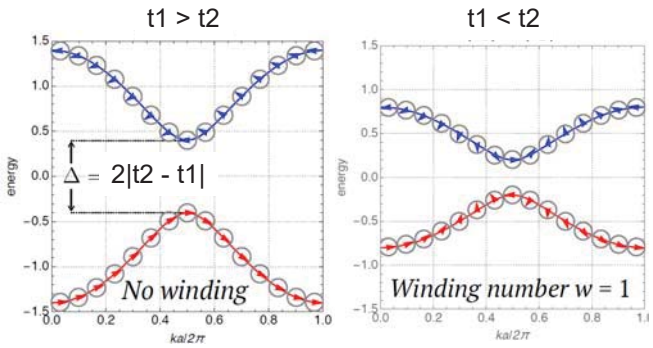
SUPPLEMENTARY MATERIAL

Fundaments: Topological analysis

- The two sublattices define a pseudospin



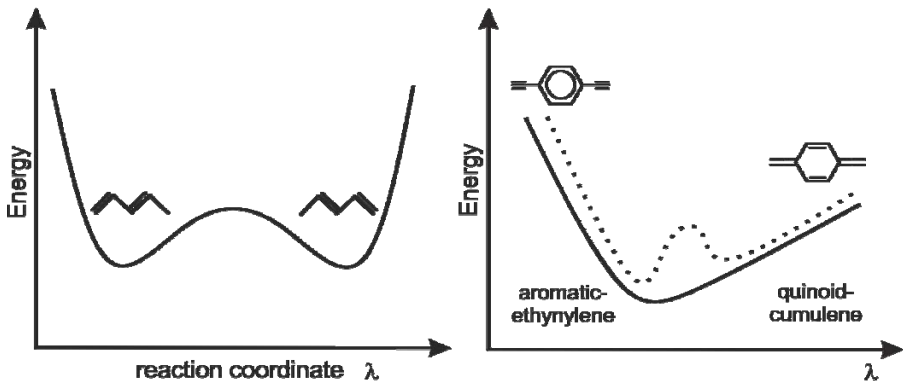
$$\langle x_n|\Psi_k\rangle = \begin{pmatrix} \psi_k^A \\ \psi_k^B \end{pmatrix} e^{ikx_n}$$



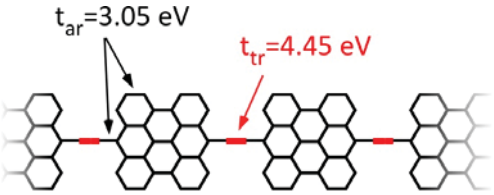
Trivial Non-trivial

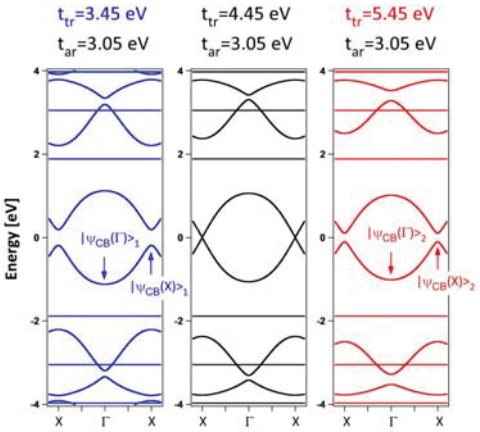
www.nanoscience.imdea.org

Tunability of π-conjugation



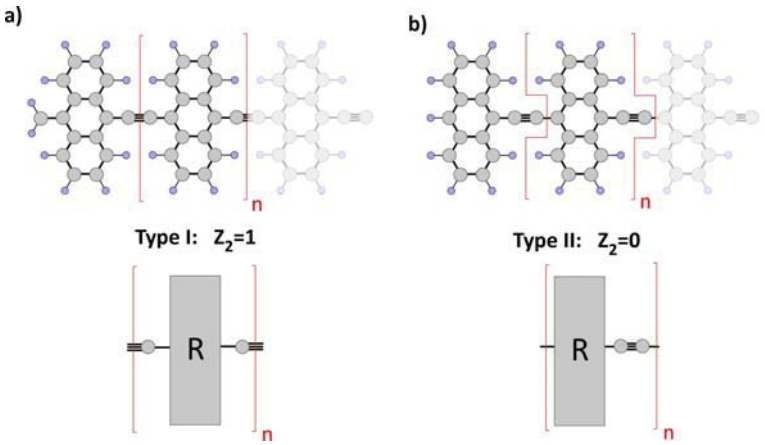
Tight binding modelling





institute IMdea nanoscience

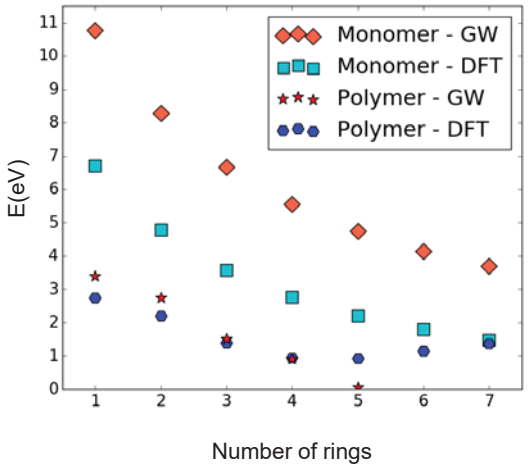
Zak Phase: Unit Cell



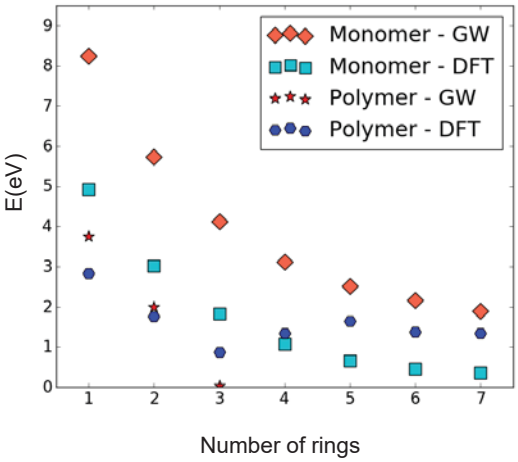
www.nanoscience.imdea.org

RENORMALIZATION OF BANDGAP

Acene family

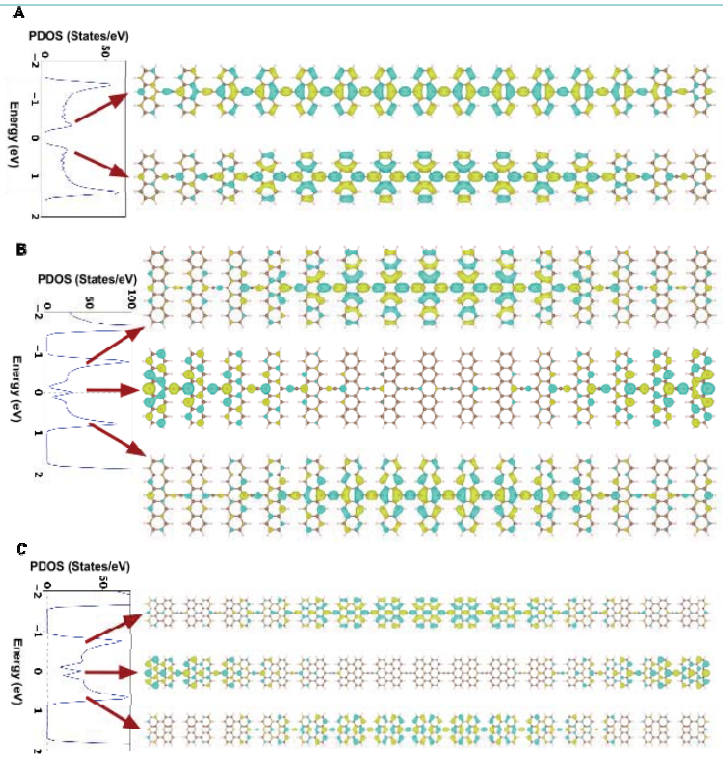


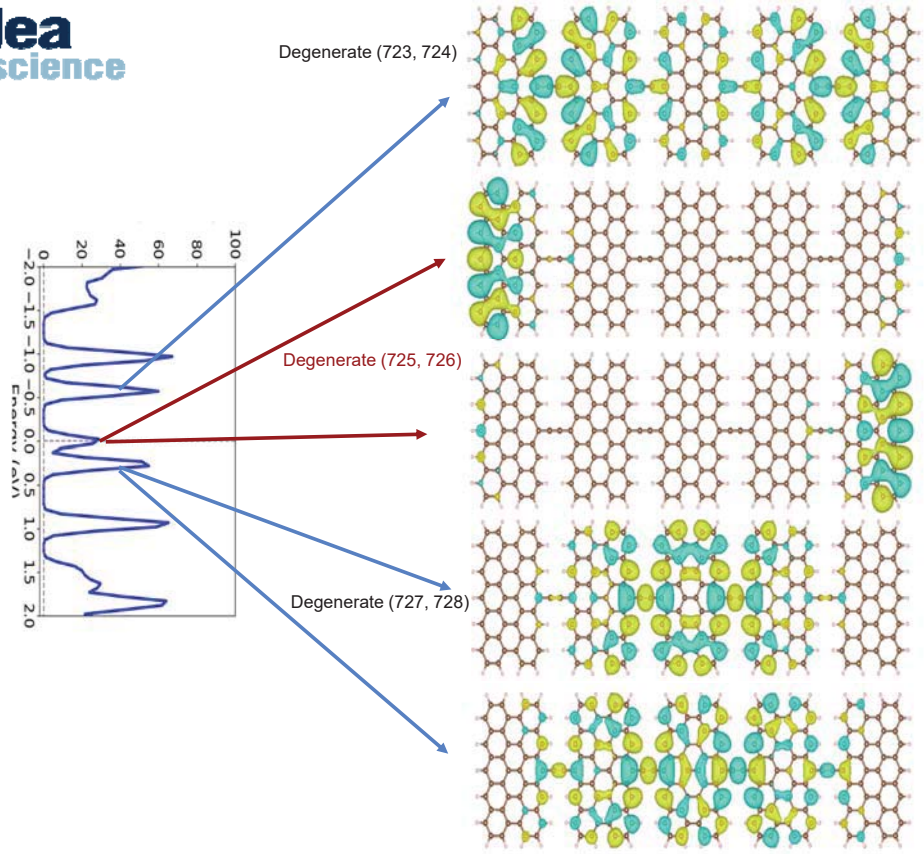
Fused-acene family



www.nanoscience.imdea.org

DFT Edge state and frontier orbitals

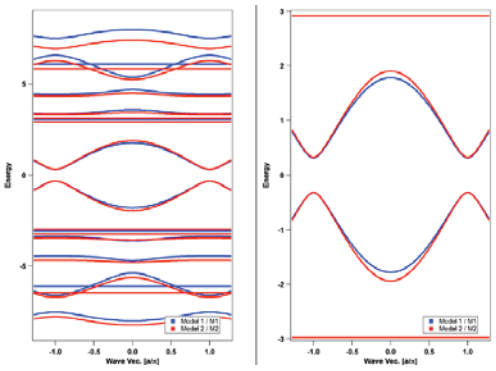




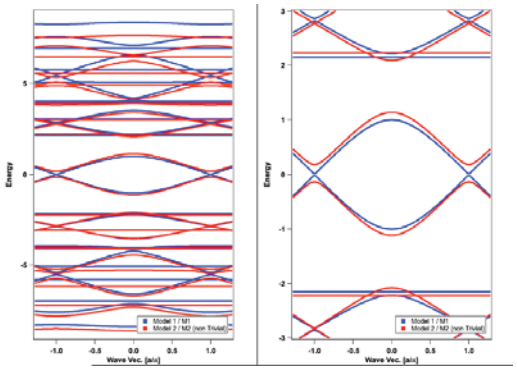
institute IMdea nanoscience

Refined tight binding

Anthracene polymers



Pentacene polymers

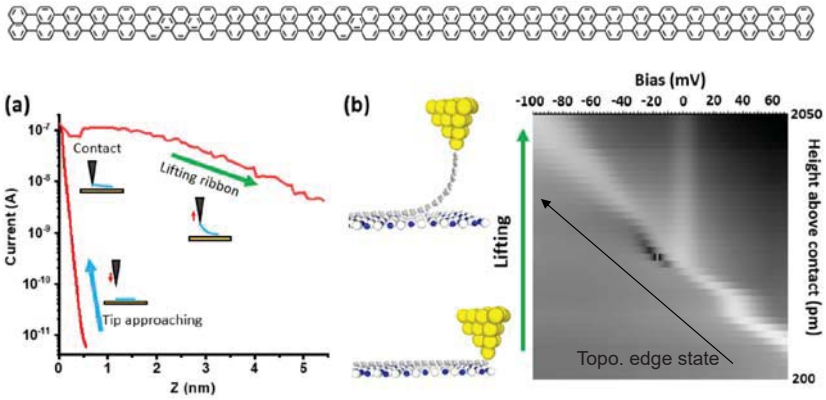


www.nanoscience.imdea.org

ACSNANO
www.acsnano.org

Probing the Magnetism of Topological End States in 5-Armchair Graphene Nanoribbons

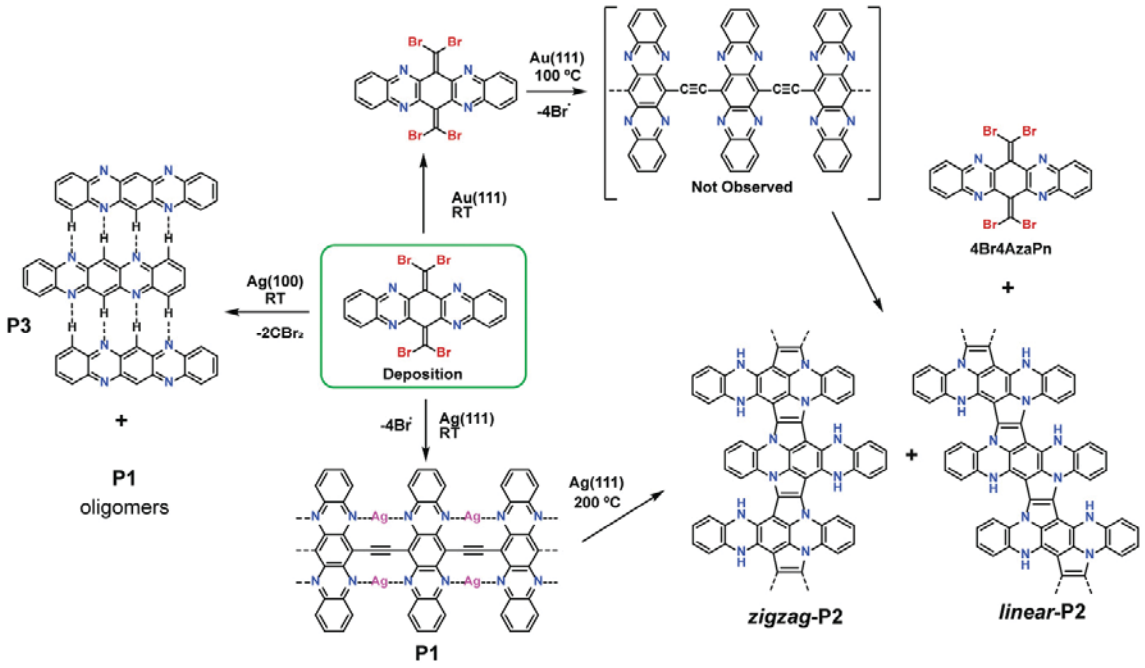
James Lawrence,† Pedro Brandimarte,‡ Alejandro Berdonces-Layunta, Mohammed S. G. Mohammed, Abhishek Grewal, Christopher C. Leon, Daniel Sánchez-Portal,* and Dimas G. de Oteyza*



PART IV: Can we design heteroatomic π-conjugation polymers?

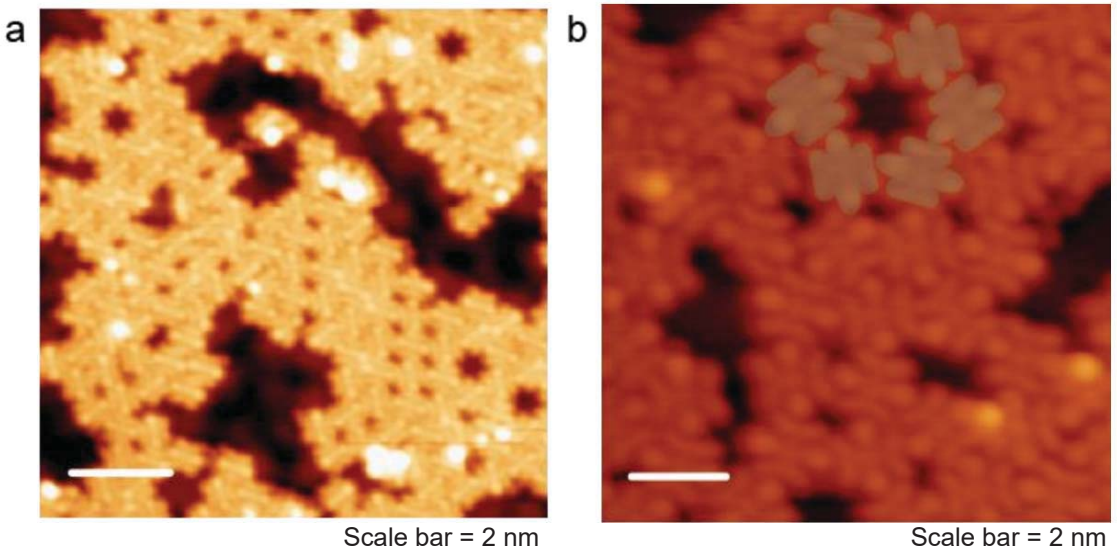
A. Sánchez-Grande., Advanced Science, 2022

N-contanining π-conjugated polymers



www.nanoscience.imdea.org

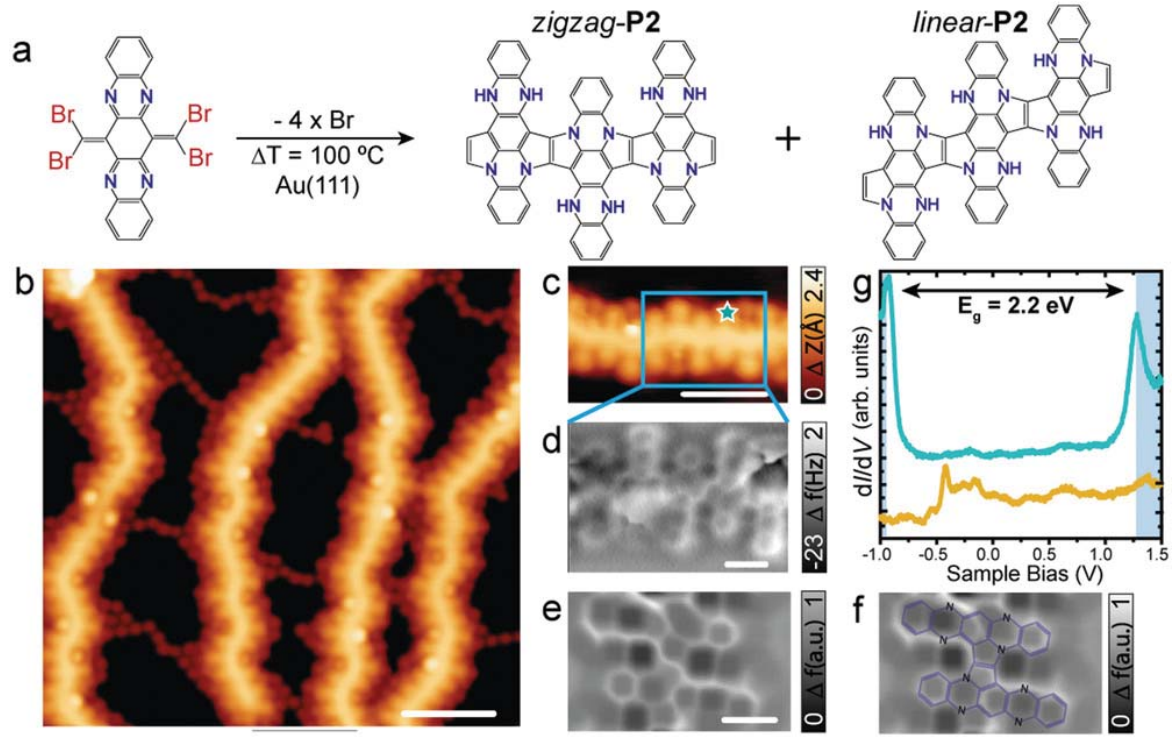
On Au(111) at rt : Self-assembly



Scale bar = 2 nm

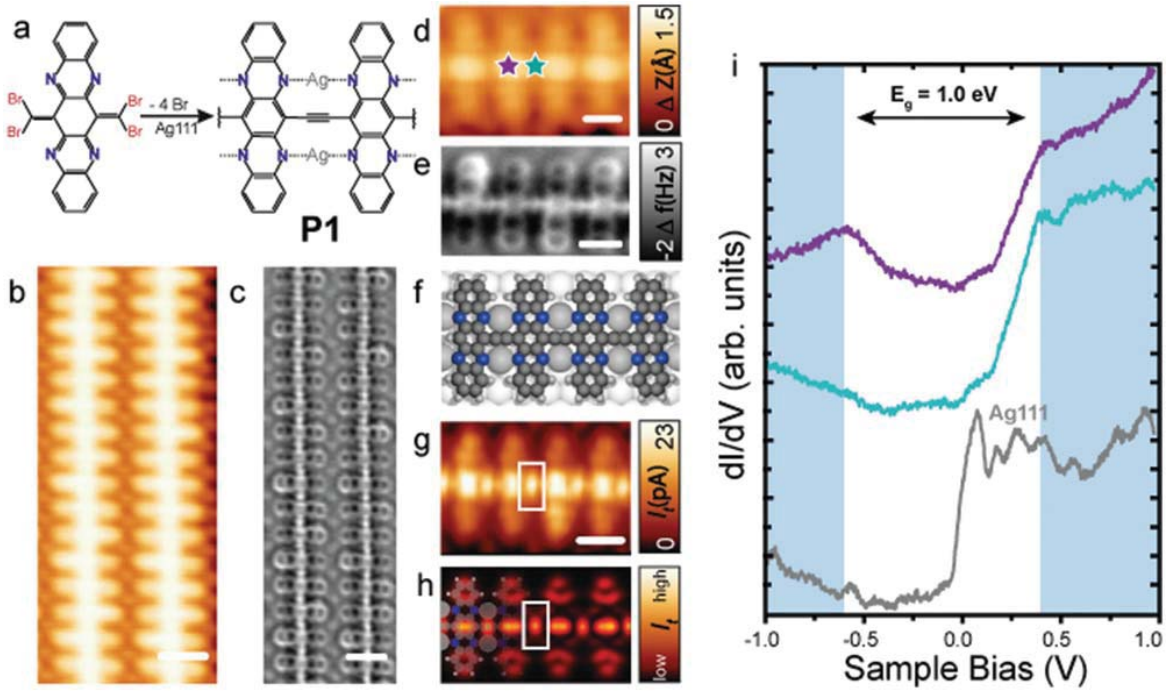
Scale bar = 2 nm

On Au(111) at 100ºC : Synthesis of P2

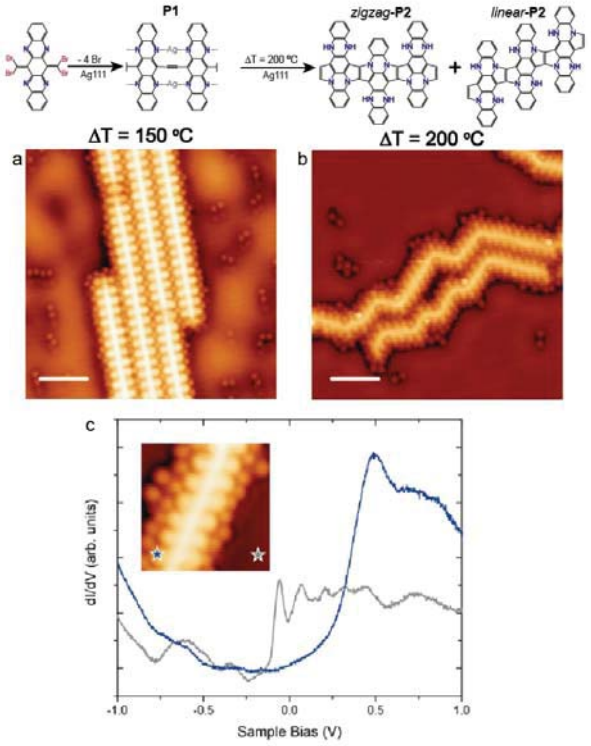


www.nanoscience.imdea.org

On Ag(111) at rt: Synthesis of P1

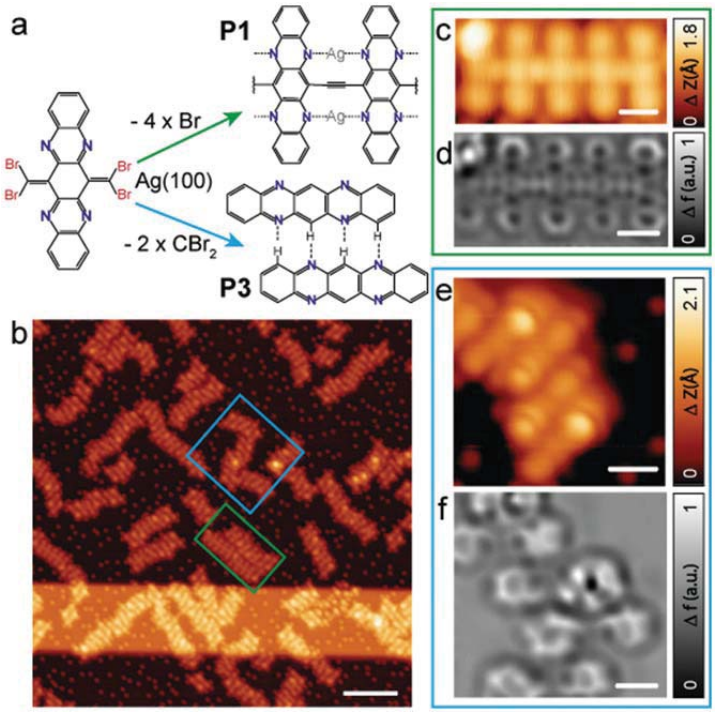


On Ag(111) at 200 ºC : Synthesis of P2



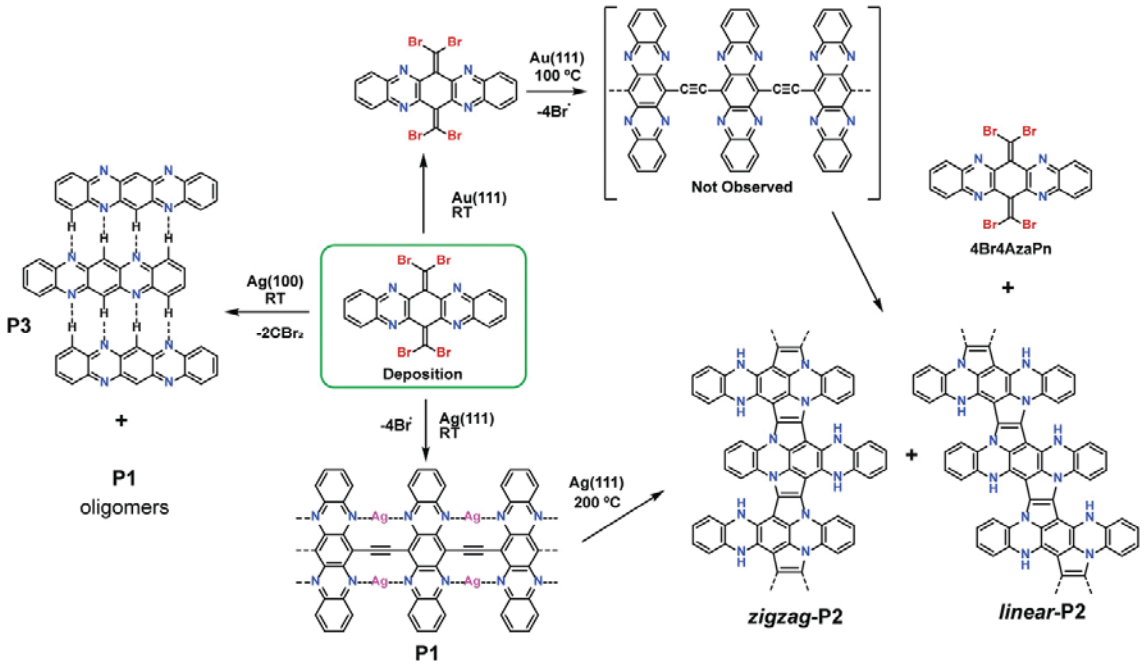
institute IMdea nanoscience

On Ag(100) at rt : Synthesis of P1 and P3



www.nanoscience.imdea.org

The role of coordination



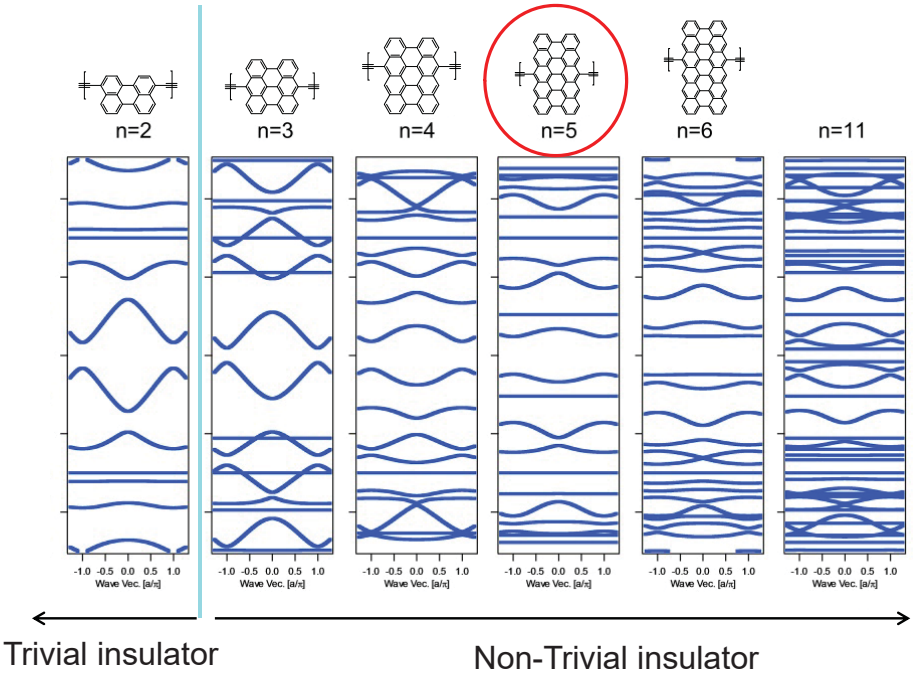
institute IMdea nanoscience

Can we increase the bandgap to protect the topological states?

A. Sánchez-Grande, Angew. Chem. Int. Ed., 2020, 59, 17594

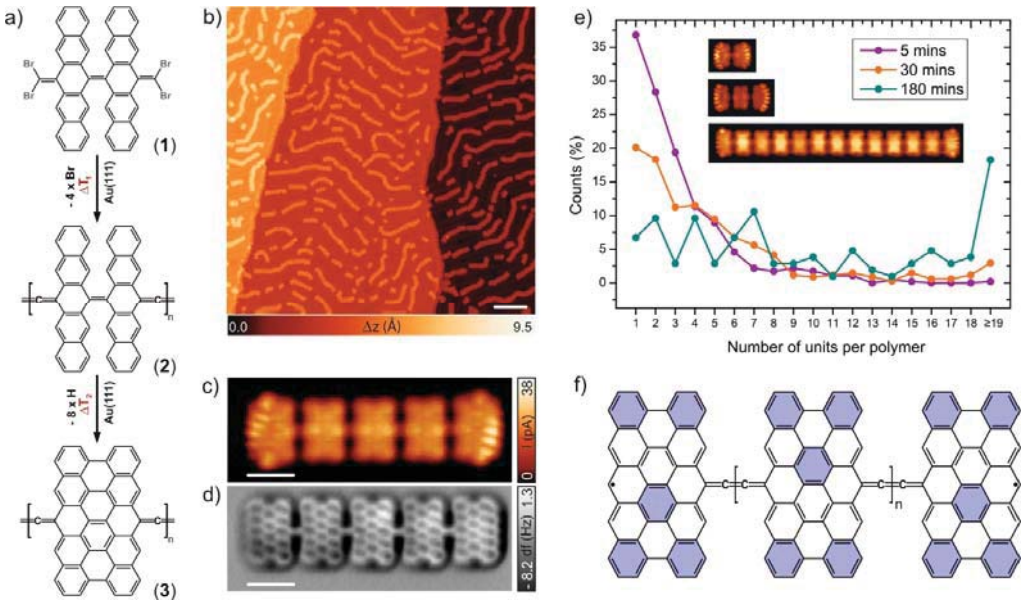
www.nanoscience.imdea.org

Peripentacene polymers

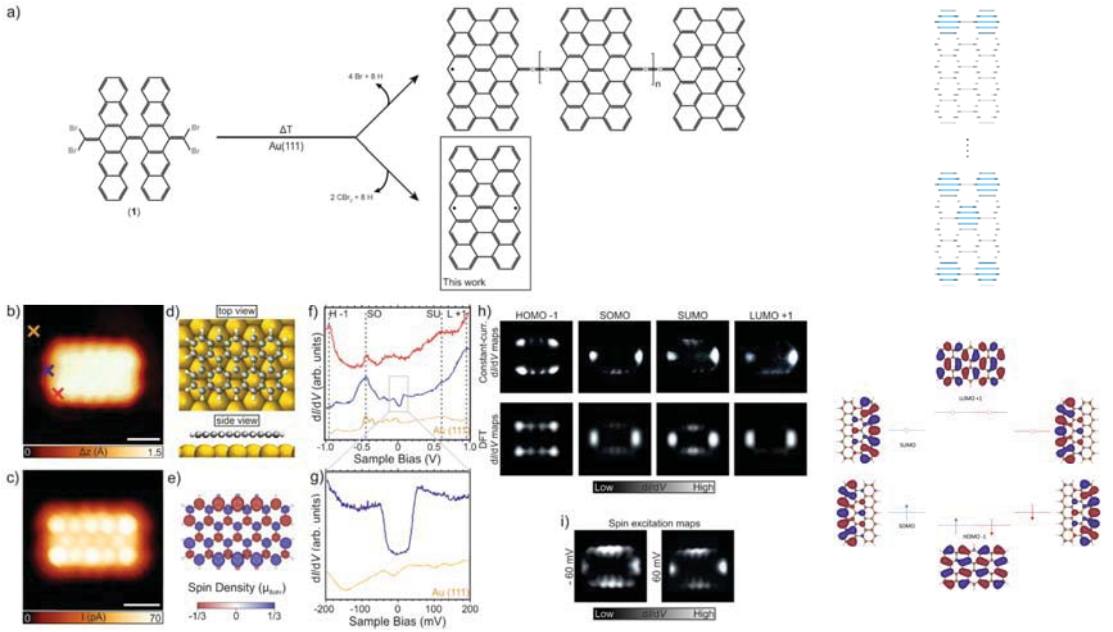


www.nanoscience.imdea.org

Peripentacene polymers: Synthesis



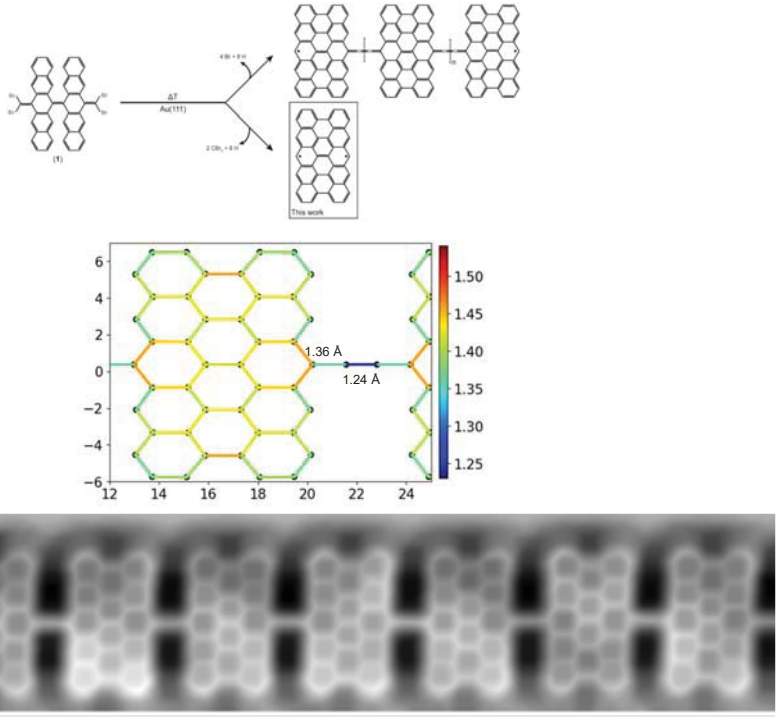
Serendipity: Peripentacene monomer



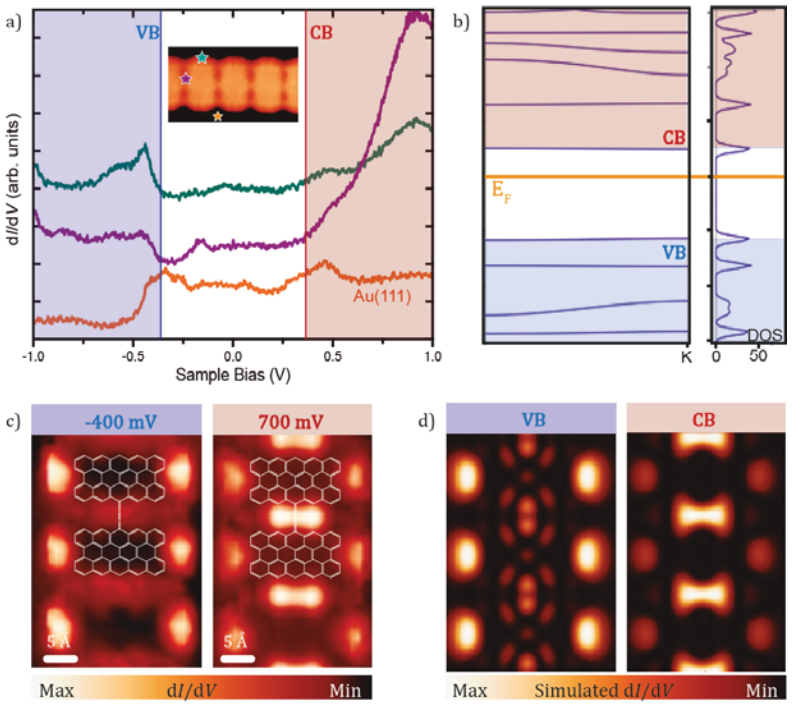
- Open shell character first detected in the acene/periacene family: J = 40.5 meV

www.nanoscience.imdea.org

Peripentacene polymers: Resonant form

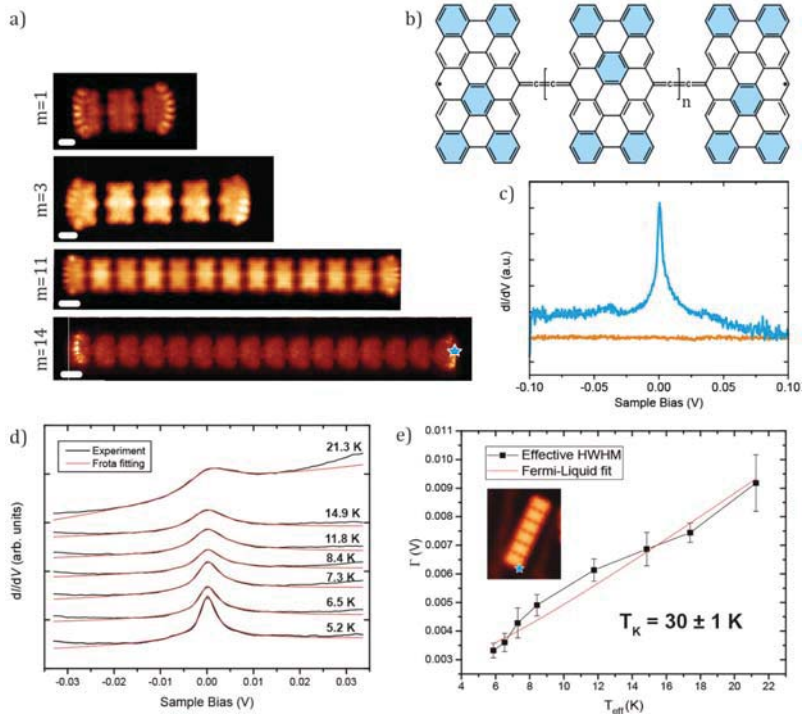


Peripentacene polymers: Low bandgap



institute IMdea nanoscience

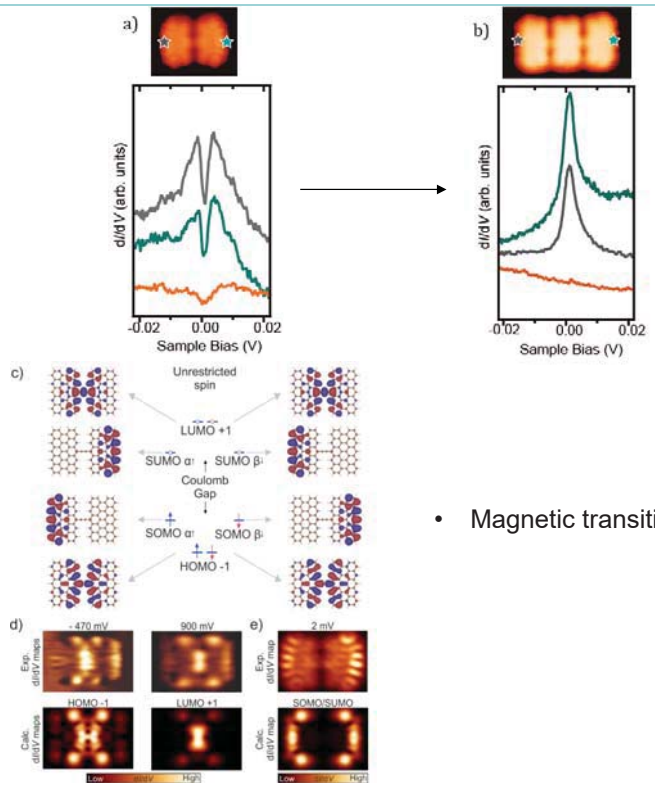
Zero bias resonance at edges



♦ Diradical organic 1D π-conjugated polymers

www.nanoscience.imdea.org

Magnetic transition with length



- Magnetic transition from dimer to trimer