Recent advances in on-surface synthesis of carbon-based π-magnetic nanomaterials

Ana Sánchez Grande

- Science Lunch, 29/2/2024

Co-funded by the European Union

MINISTRY OF EDUCATION, YOUTH AND SPORTS

FZU Institute of Physics of the Czech Academy of Sciences

Outline

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- **Nanosurf Lab Group**
- **On-Surface Synthesis (OSS) approach**
- **OSS of π-magnetic Nanographenes (0D):**
  - ❑ Sublattice Imbalance
  - ❑ Topological Frustration
  - ❑ Polarization of edge states
  - ❑ Topological defects
- **How to extend π-magnetism to 1D and 2D (our contributions)**
  - ❑ 1D π-conjugated Polymers
  - ❑ 2D Supramolecular organic radical frameworks

Nanosurf Lab group

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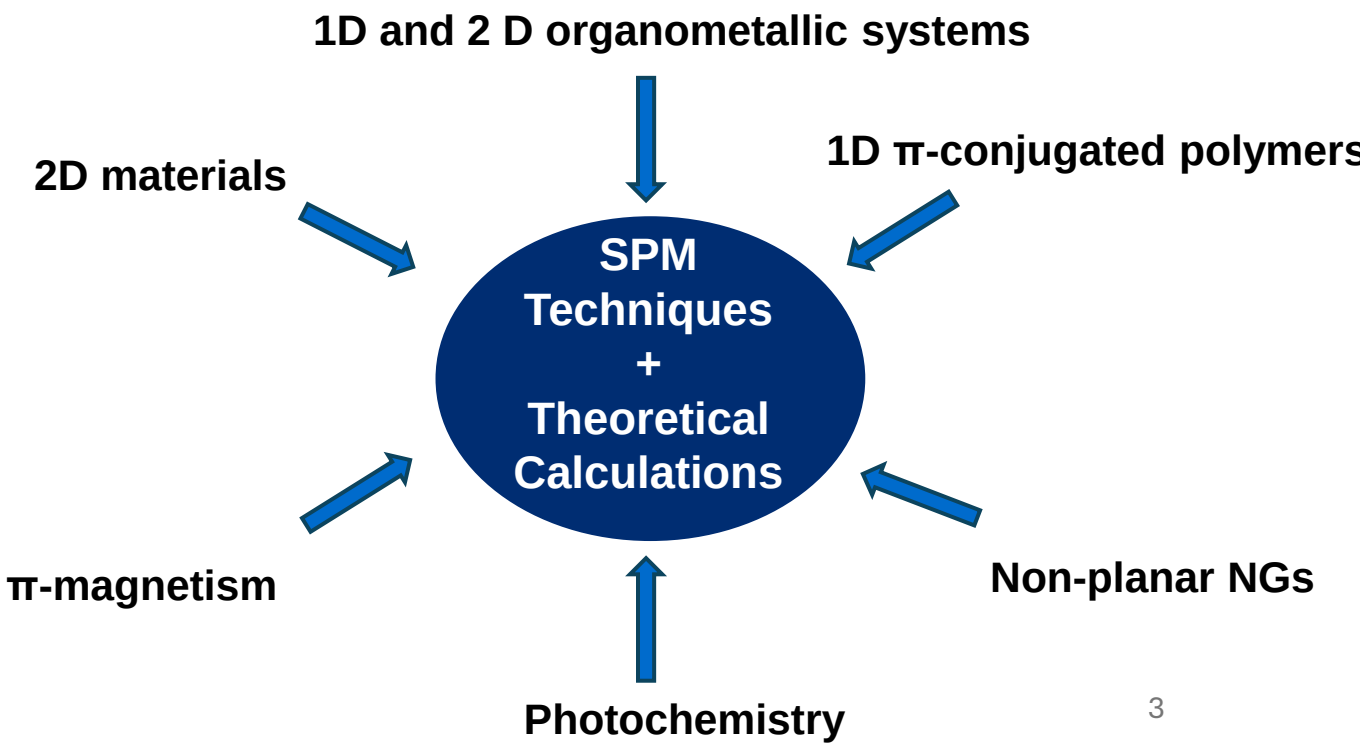
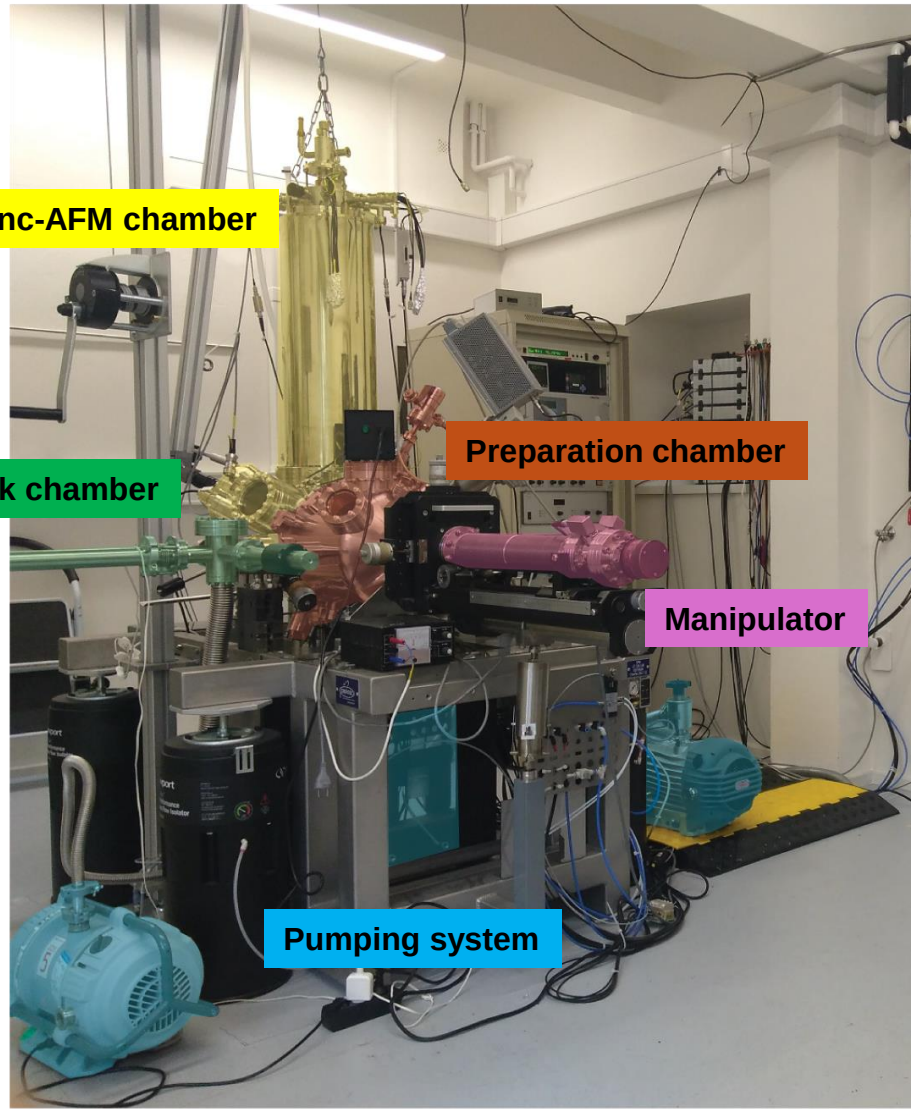
Fyzikální ústav Akademie věd ČR
Cukrovarnicka 10
Prague 6, Czech republic

PI: Ass. Prof. Pavel Jelínek

@nanosurflab



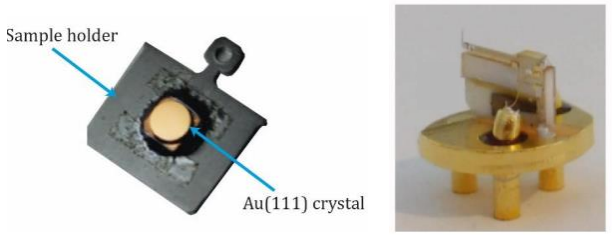
Instruments and techniques

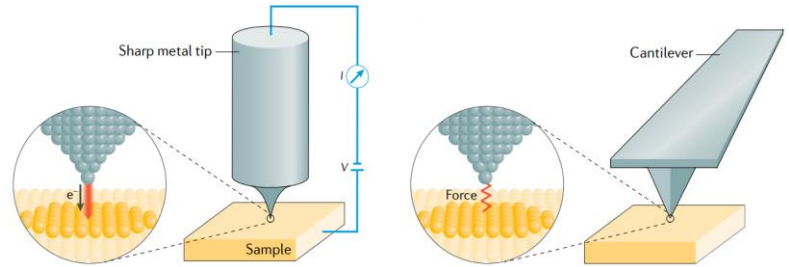


- **LT-SPM by Createc**
  - Base pressure 1.2 x 10^{-10} mbar
  - Temperature 4.3 K
  - UHV conditions

- Techniques: STM/STS/nc-AFM

- Sample Preparation:
  - Temperature range: 77–1500 K
  - UV light exposure





Bian K.; et al., Nat Rev Methods Primers 1, 36 ***(2021)***

STM vs nc-AFM measurements

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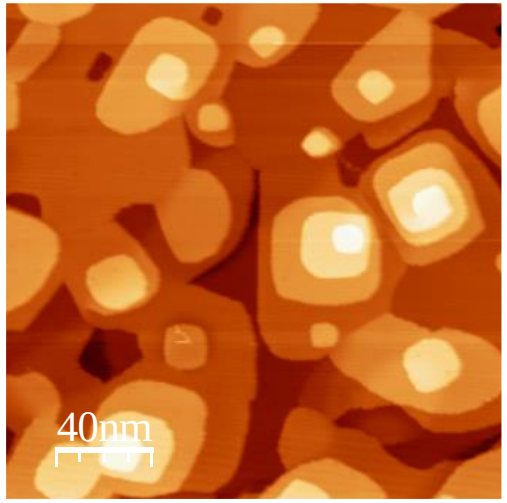
SnSe crystal

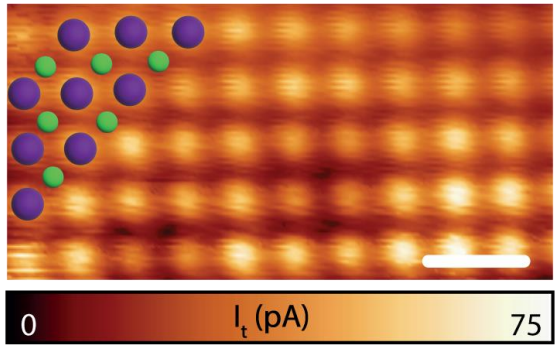
STM

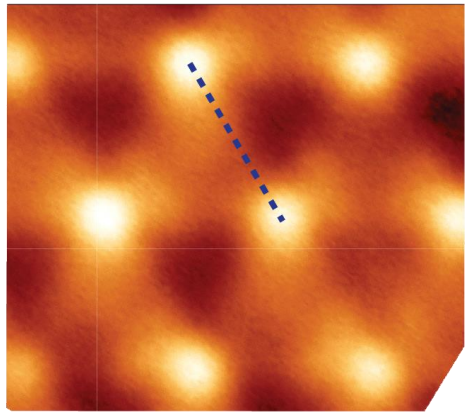
Nc-AFM

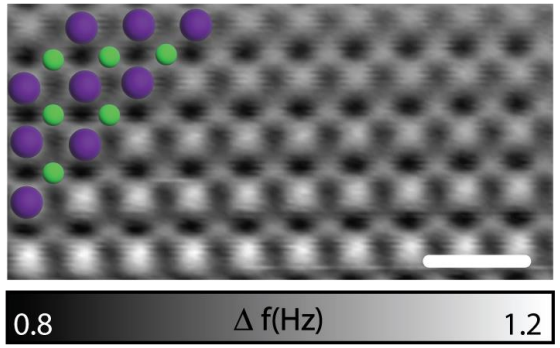
STS

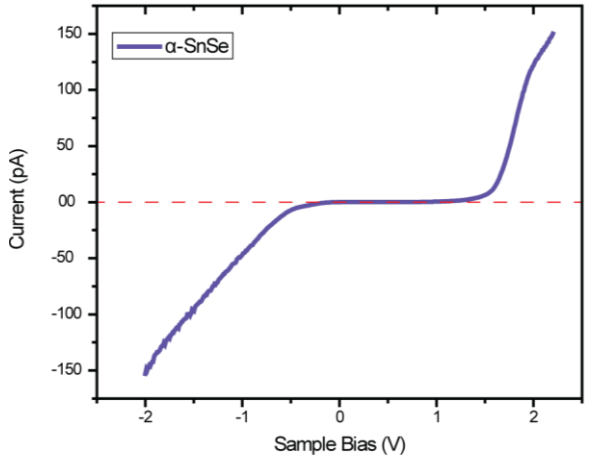
Overview





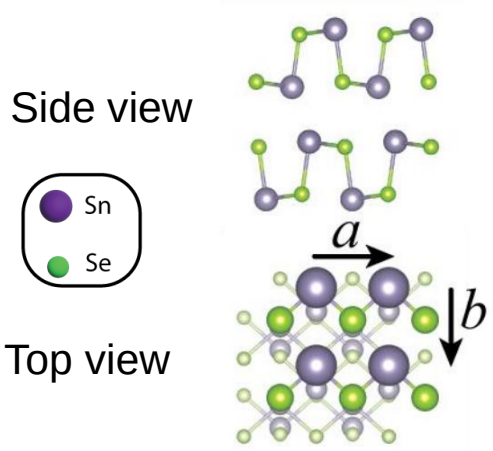


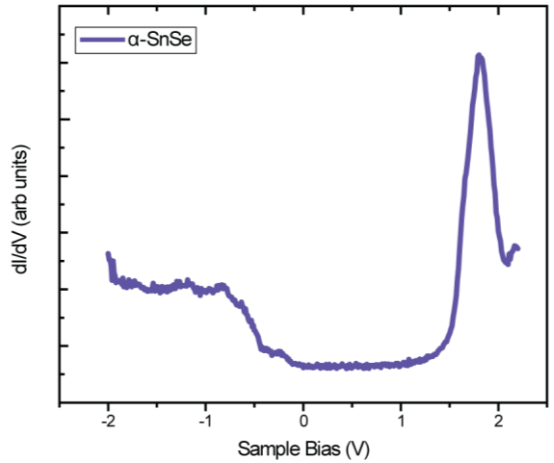




Side view

Top view





Frezza F.; et al., J. Phys.: Condens. Matter 35, 335001 ***(2023)***

Single atom manipulation

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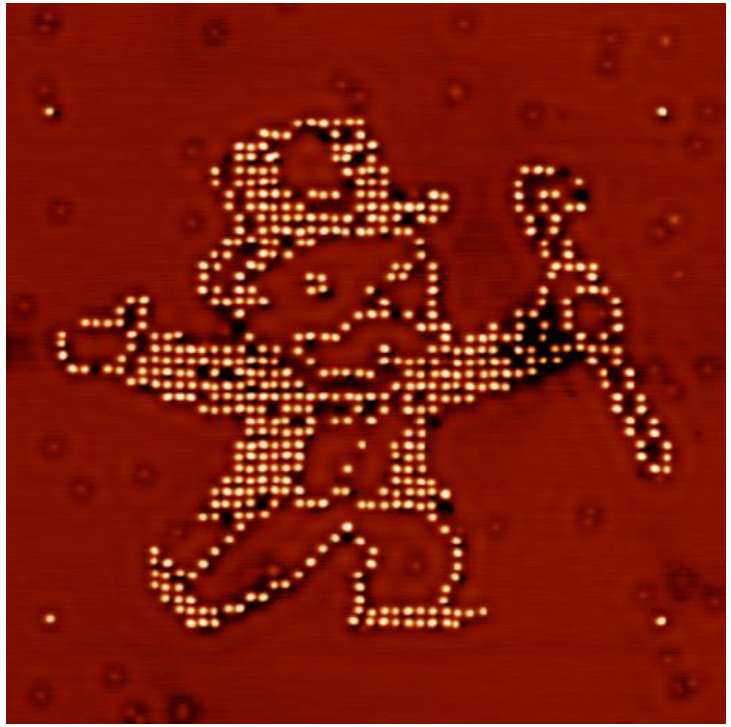

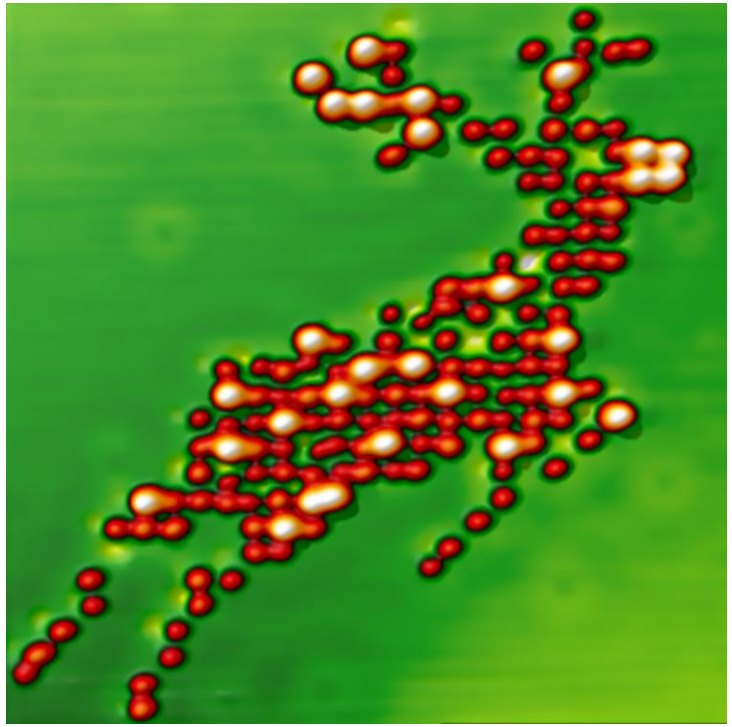

By Oleksandr Stetsovych, PhD

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  - ❑ Topological defects
- How to extend π-magnetism to 1D and 2D (our contributions)
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  - ❑ 2D Supramolecular organic radical frameworks

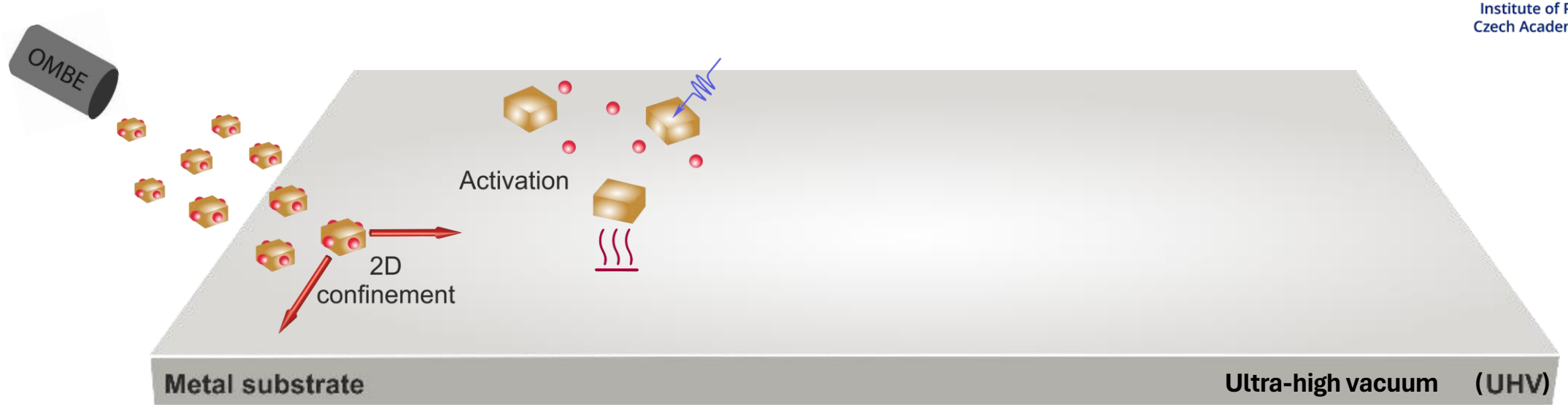
On-Surface Synthesis approach

Ideal conditions for the synthesis of carbon-based nanostructures

- Inert vacuum environment
- Stabilizing effect of the supporting substrate
- Catalytic role of the metal substrate

Pioneering work exploiting Ulmann-like reaction coupling by the group of Leonhard Grill
*Grill L.; et al., Nat Nanotechnol 2, 687–691 (**2007**)*

On-Surface Synthesis approach



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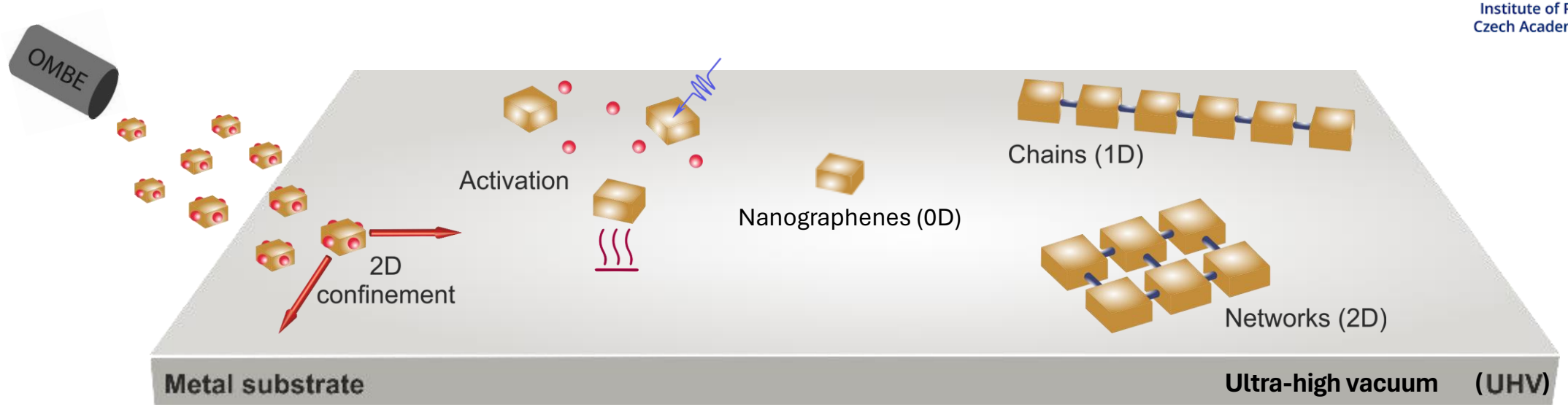

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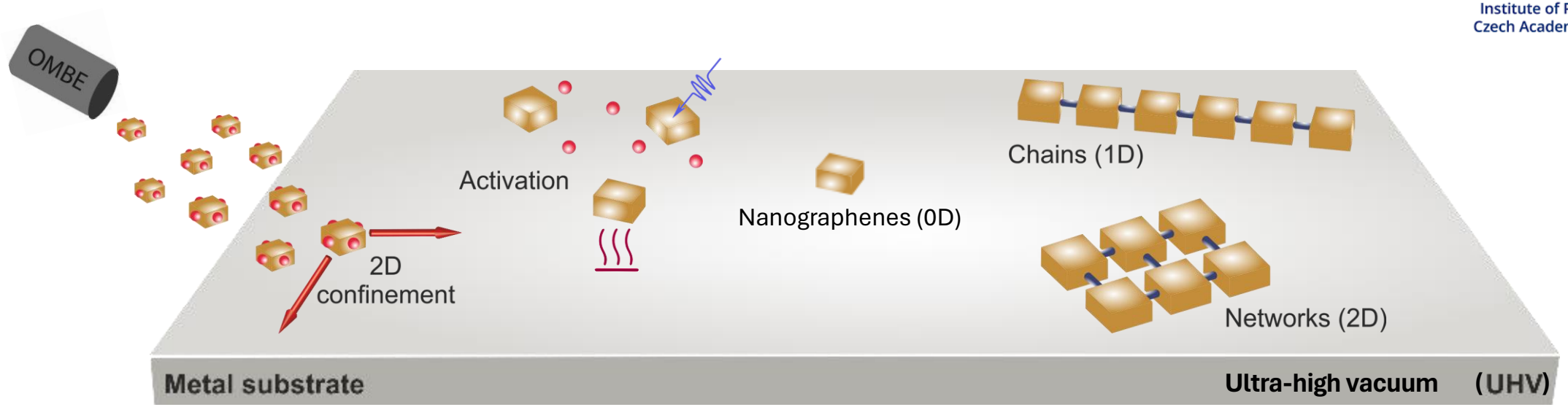
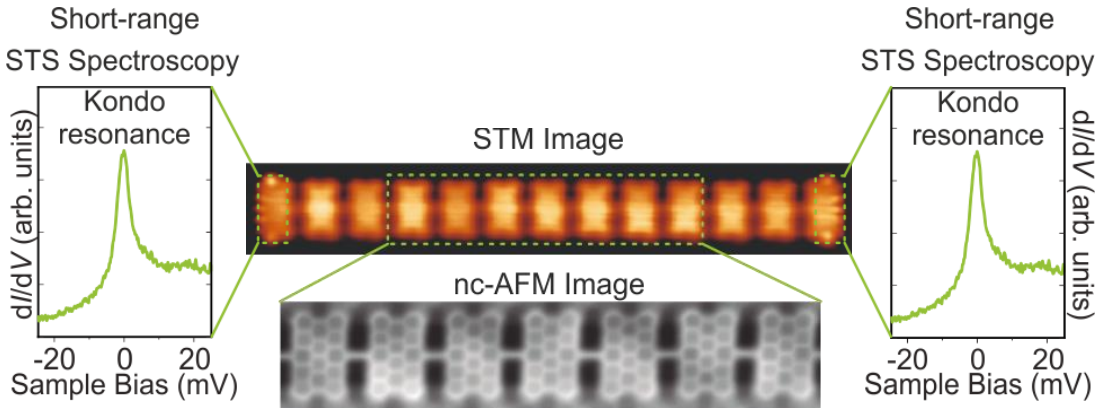
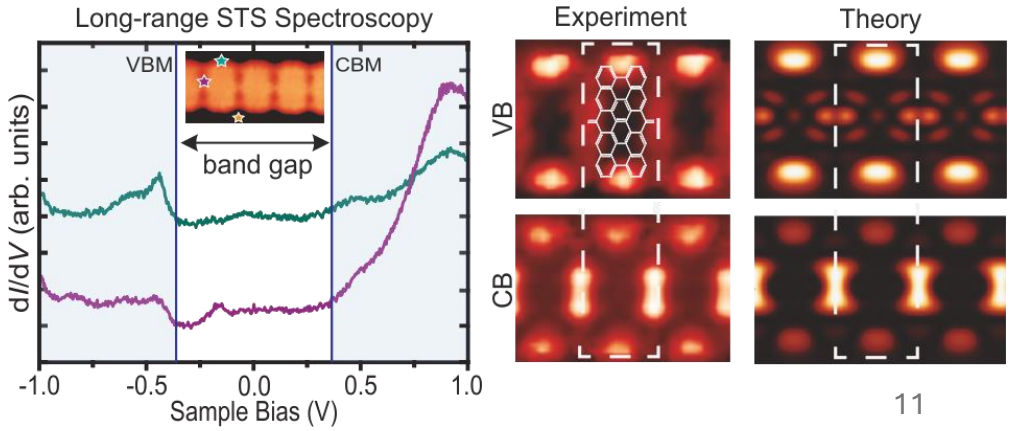


Scanning probe techniques: simultaneous structural and electronic characterization



Sánchez-Grande, A; et al. ACIE, 59 ***(2020)***



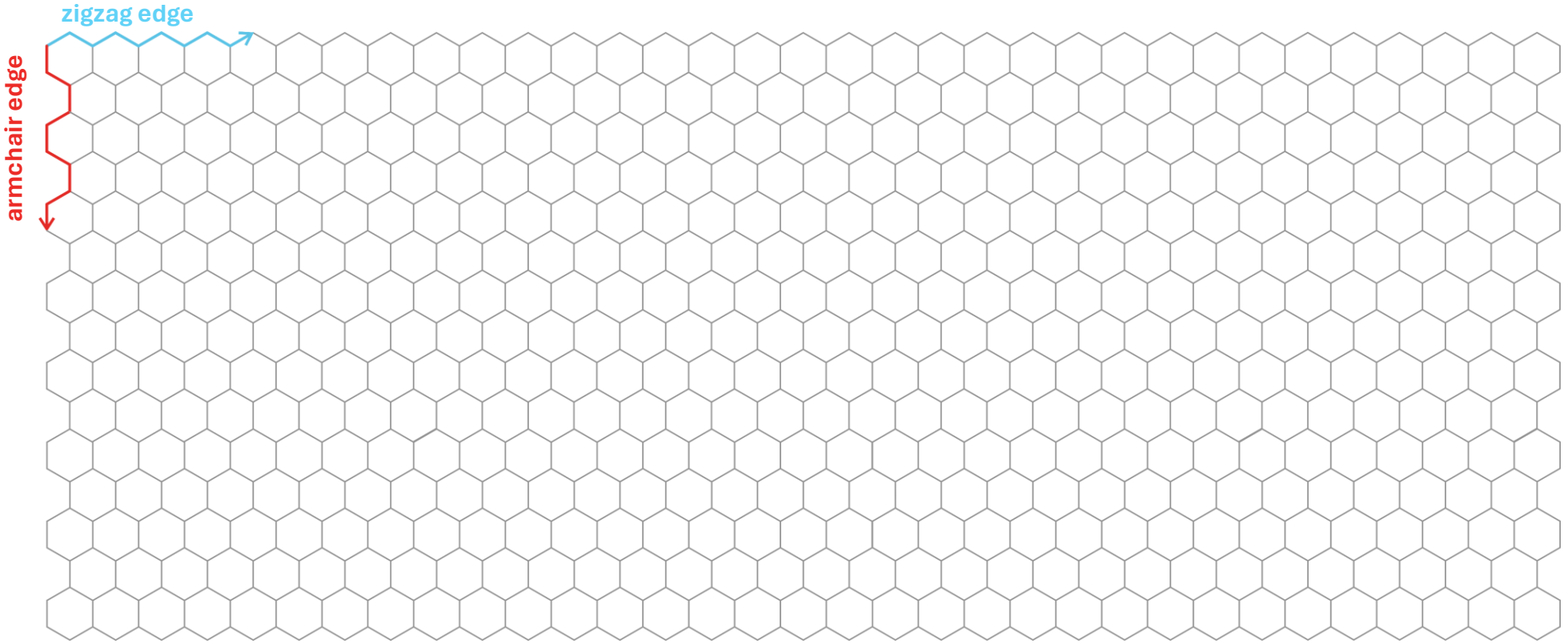
On-Surface Synthesis approach

Main Advantage: Overcomming limitations instrinsic to conventional solution synthesis.

DISRUPTIVE NANOGRAPHENE & POLYMER SCIENCE (organic chemistry + **on-surface synthesis**)

Unprecedented tailor-made nanomaterials **Unique properties at the nanoscale** **Novel chemical reactions**

► **Low bandgap** ► **π-magnetism**



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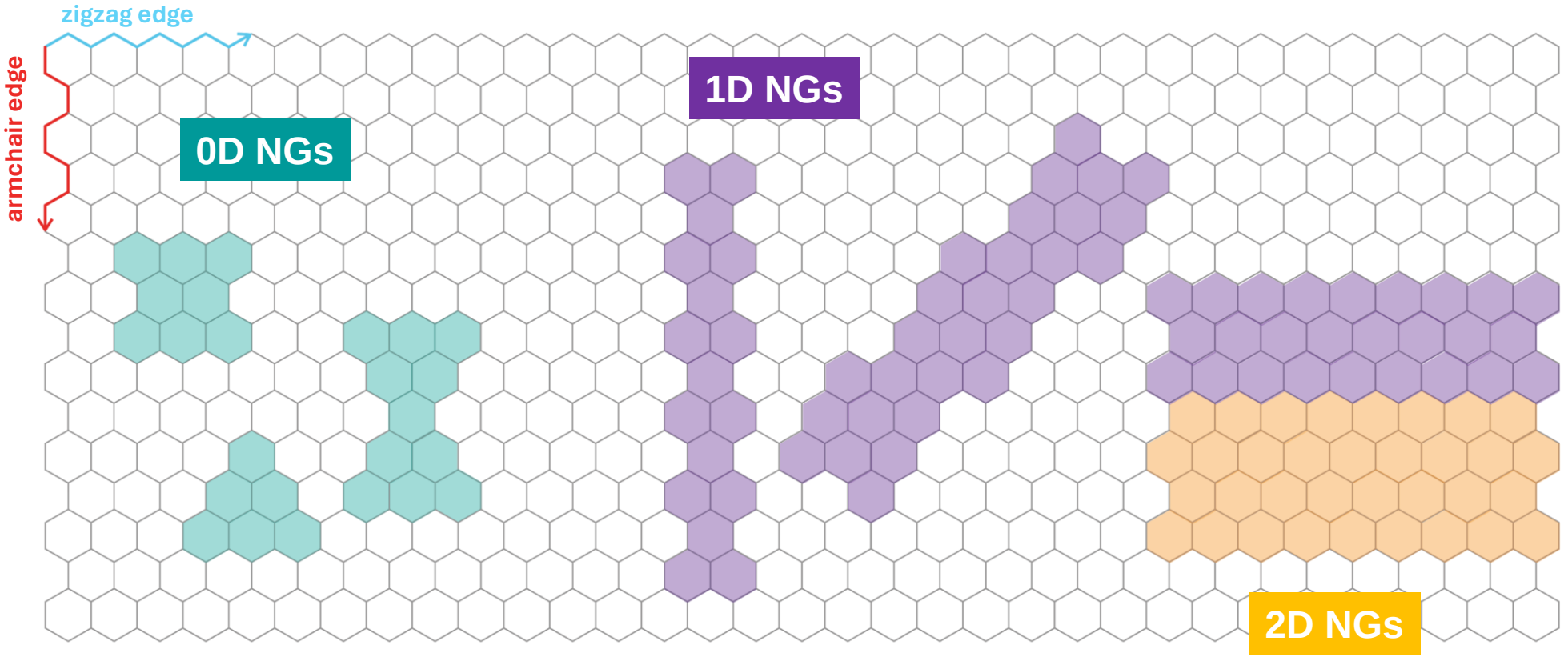

Dimas G de Oteyza and Thomas Frederiksen, J. Phys.: Condens. Matter 34 443001 ***(2022)***

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Sublattice Imbalance

If the two sublattices have different number of atoms, they cannot bind pairwise, presenting **π-radicals**

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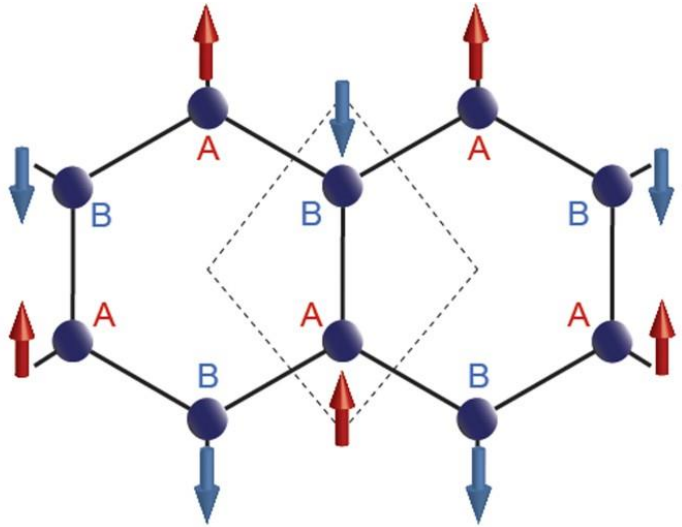
Bipartite system

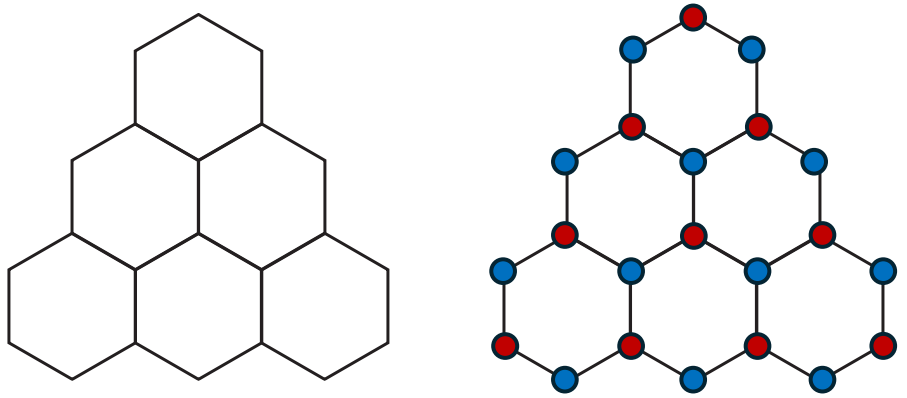


Lieb's Theorem

$$S = \frac{1}{2}|N_A - N_B|$$

*Lieb E. H., Phys. Rev. Lett. 62, 1927 (**1989**)*
*Dutta S. and Wakabayashi K., Sci Rep 5, 11744 (**2015**)*

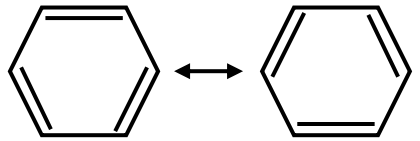
Triangulenes



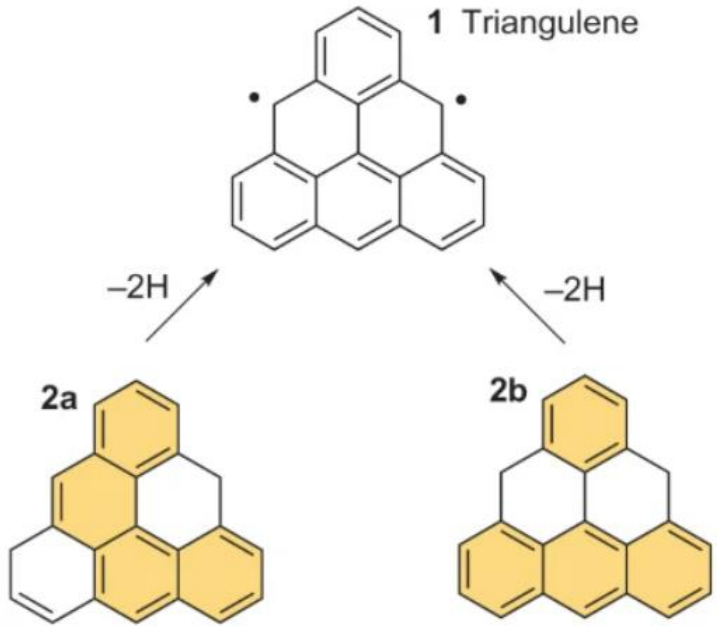
$N_A = 12$
$N_B = 10$
$S = 1$

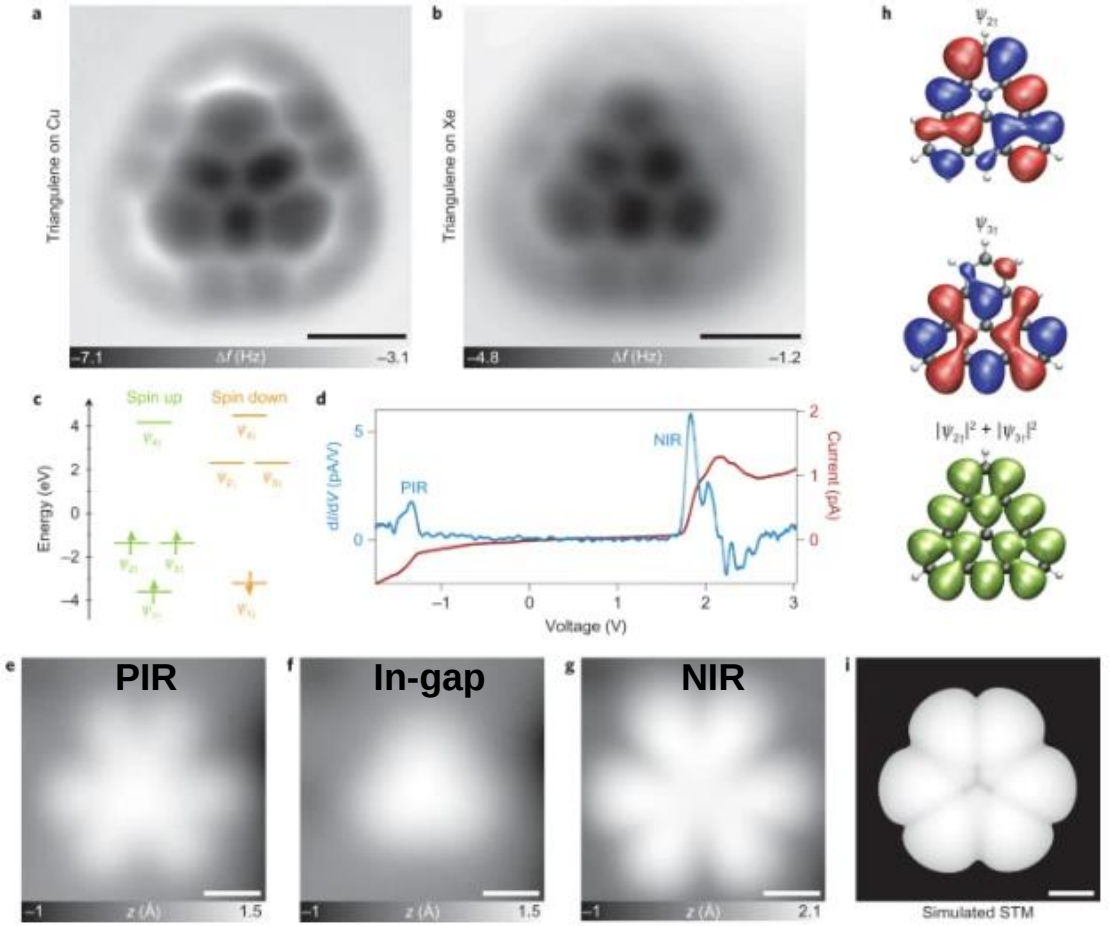
Non-Kekule structure

*Clar E. And Stewart D. G., J. Am. Chem. Soc., 75, 11, 2667–2672 (**1953**)*



Triangulene molecule





*Pavliček N.; et al., Nat Nanotechnol 12, 308–311 (**2017**)*

- **Indirect demonstration of its magnetism** by the characterization of the singly occupied molecular orbitals: the frontier orbitals are two degenerate orbitals (ψ_2 and ψ_3), an occupied pair (spin up) and an unoccupied pair (spin down)

Larger members of triangulene family

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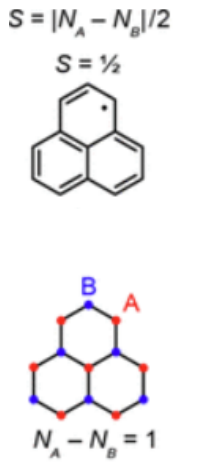
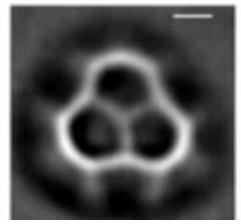
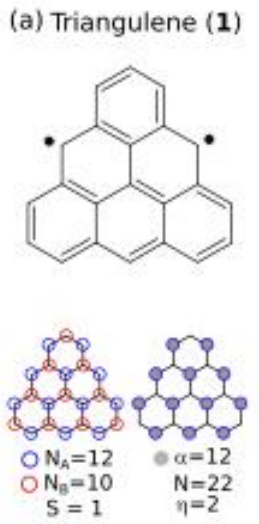
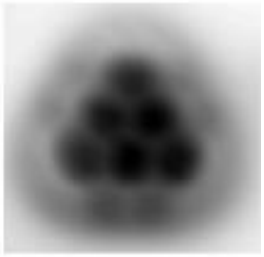


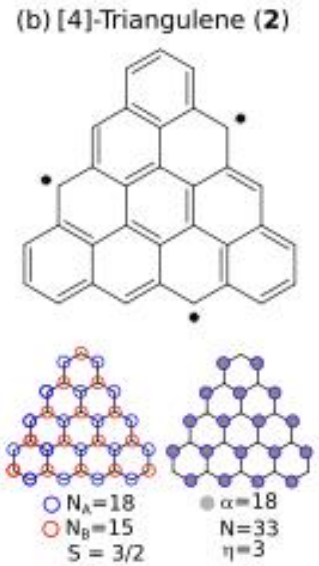


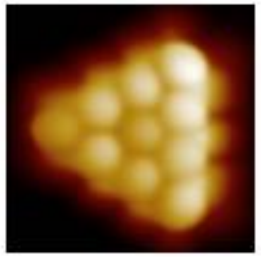
*Turco E.; et al., J. Am. Chem. Soc. Au **3**, 5, 1358–1364 (**2023**)*



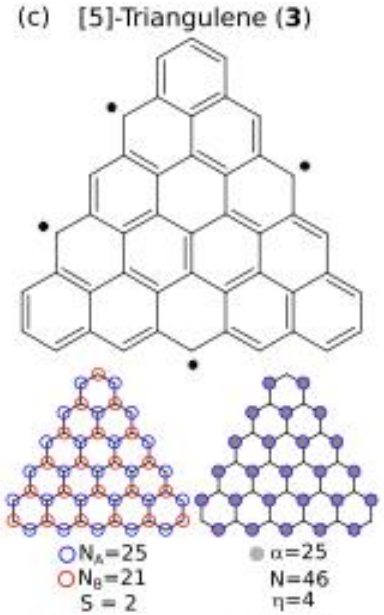


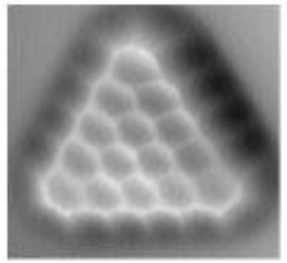
*Pavliček N.; et al., Nat Nanotechnol 12, 308–311 (**2017**)*



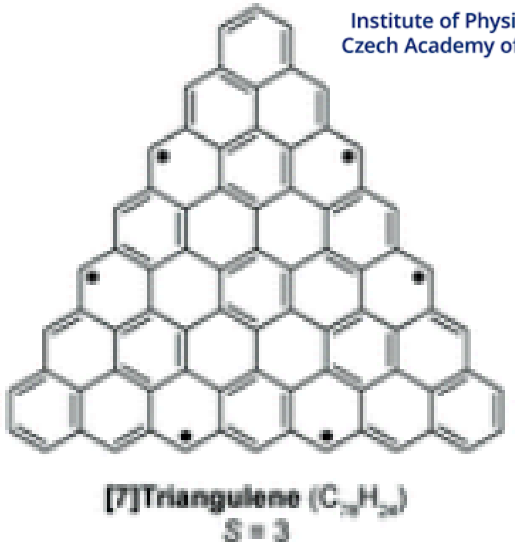


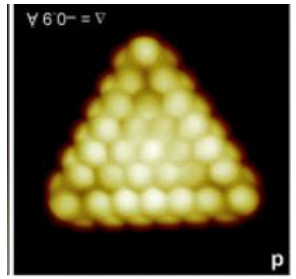
*Mishra S.; et al., J. Am. Chem. Soc. 141, 10621–5 (**2019**)*





*Su J.; et al., Sci. Adv. **5** eaav7717 (**2019**)*





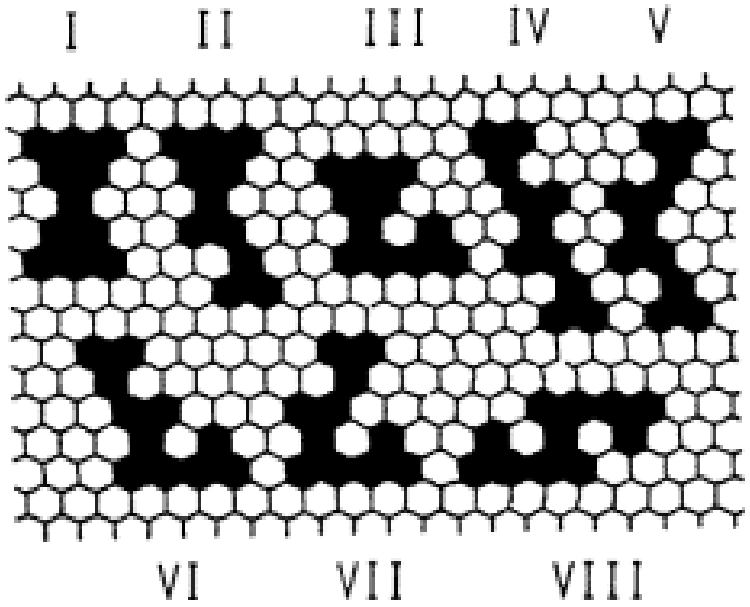
*Mishra S.; et al., Nanoscale 13, 1624-1628 (**2021**)*

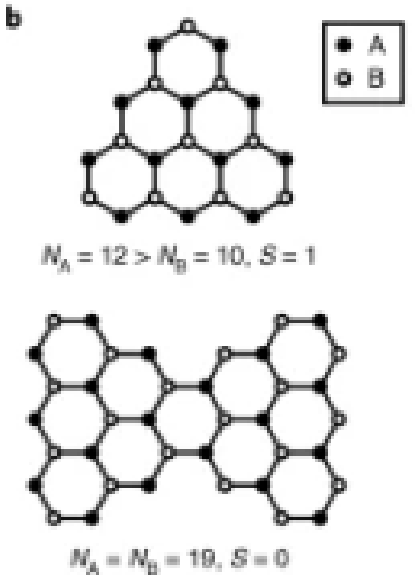
- As the size is increased, the sublattice imbalance becomes greater and the **high-spin ground states** are generated

Topological frustration

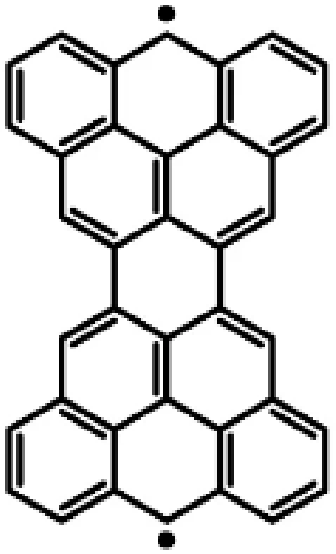
Benzenoid carbon NGs that even showing sublattice balance, they present non-Kekule structures.

Smallest NGs comprising eleven hexagons exhibiting topological frustration





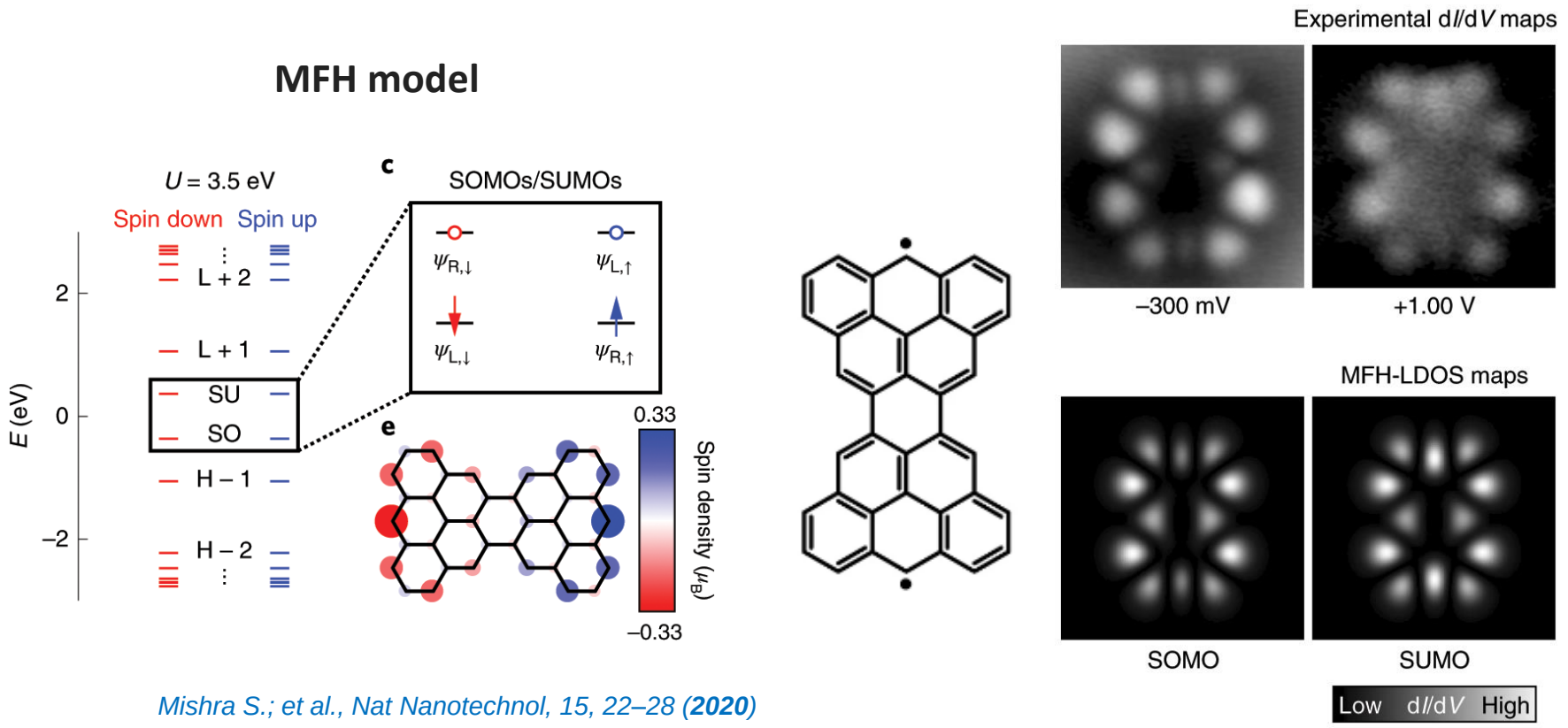
Clar's Goblet

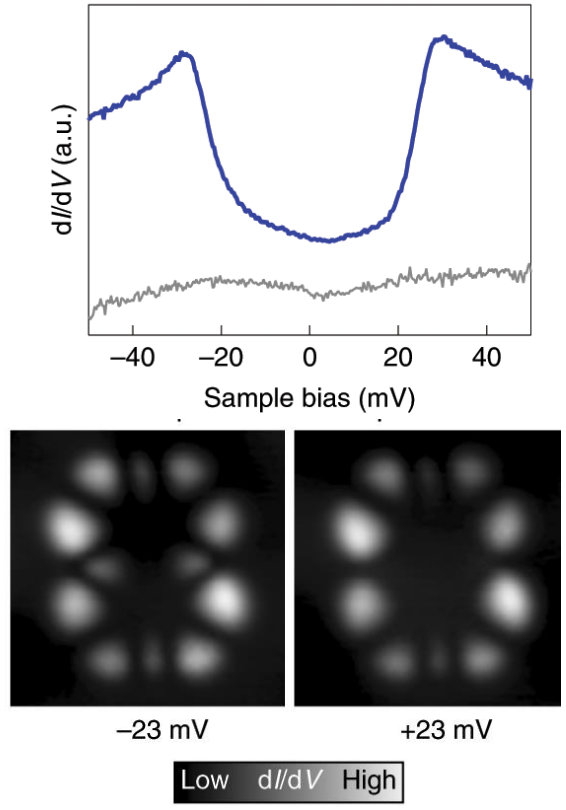


*Cyvin S. J., et al., Journal of Math Chem, 4, 47-54 (**1990**)*

Theory predicts a **singlet open-shell ground state**, where the two unpaired electrons are antiferromagnetically coupled

Topological frustration



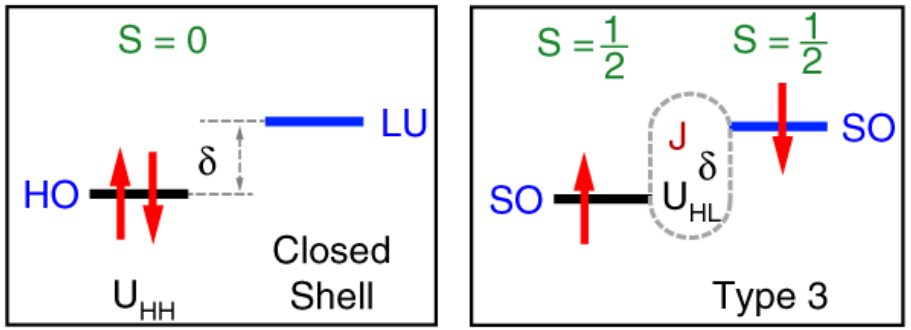


*Mishra S.; et al., Nat Nanotechnol, 15, 22–28 (**2020**)*

- The MFH solution predicts an **antiferromagnetic (open-shell singlet) ground state**.
- The spin-polarized wave functions of the singly occupied molecular orbitals (SOMOs) and singly unoccupied molecular orbitals (SUMOs) are spatially separated and sublattice-polarized
- Low-energy **STS reveal evidence of magnetism** in the form of steps located at ± 23 mV

Polarization of edge states

Low energy states can present spin polarization triggered **by effective Coulomb repulsion in double occupied molecular orbitals** (e-e interaction).

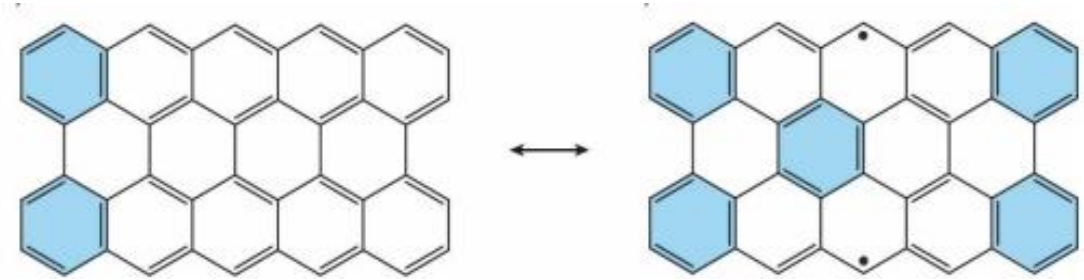


*Li J.; et al., Nat Comm, 10, 200 (**2019**)*

Size-dependance spin-polarization due to the important influence of the electronic HOMO-LUMO gap

- Extended Clar´s rule, together with the degeneracy of a NG, gives a simple and intuitive explanation about the nature of the ground state of NGs.
- The stabilization energy of **three new Clar** sextets compensates the energetic cost of forming **a pair of π-radicals**.

2 Clar sextets *vs* 5 Clar sextets

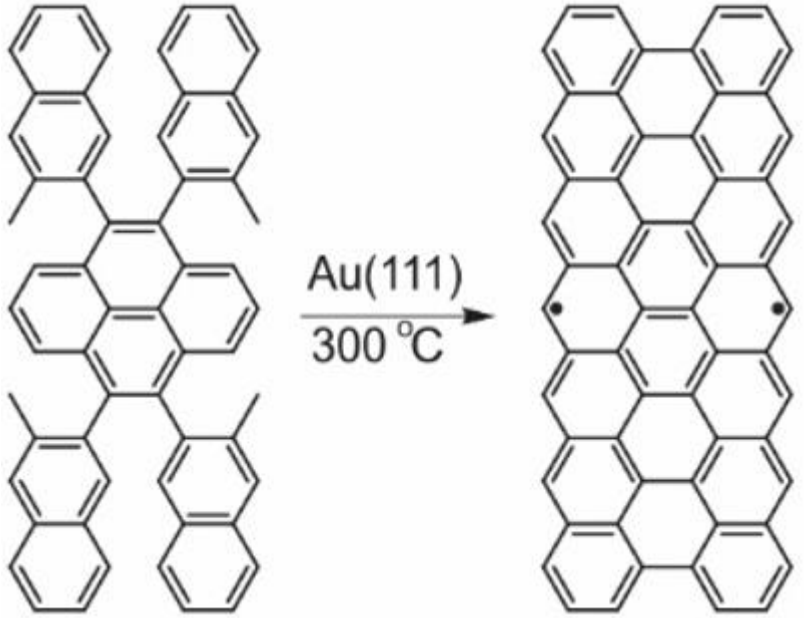


OSS of *peri*-acenes

Peri-pentacene

*Sánchez-Grande, A; et al. J. Phys. Chem. Lett,12 (1), 330-336 (**2020**)*

Peri-heptacene



*Biswas, K. et al. Angew. Chem.Int. Ed. 61 (23), e202114983 (**2022**)*

- Thermal activation on Au(111) towards the synthesis of peri-acenes

Peri-acenes family

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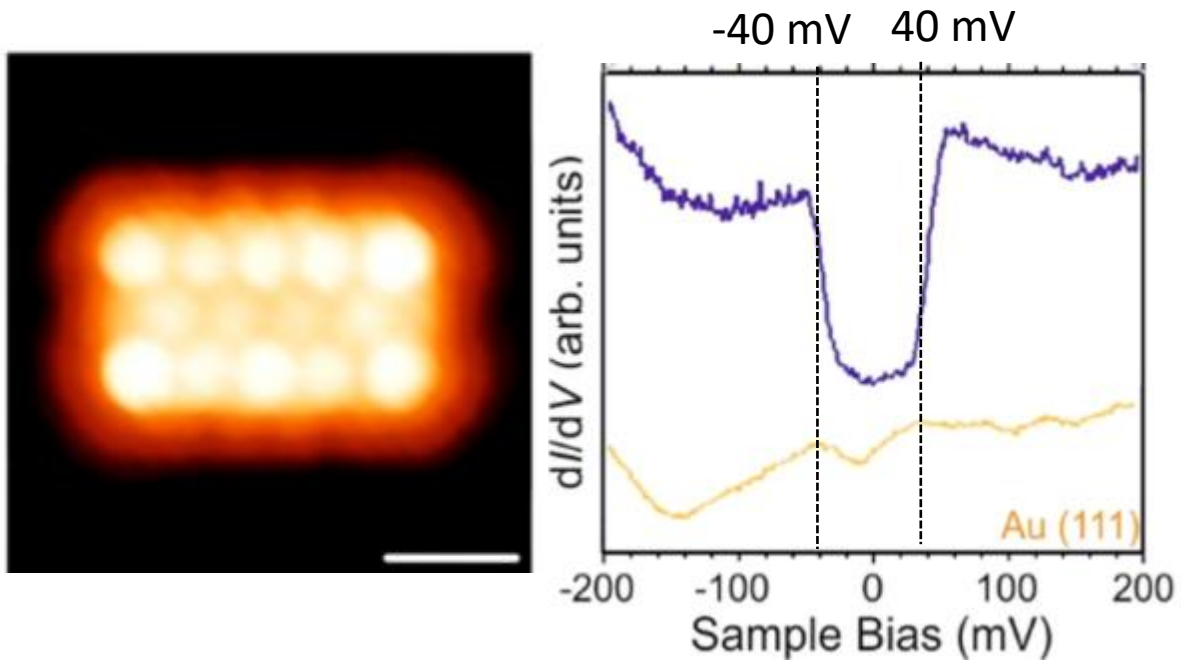
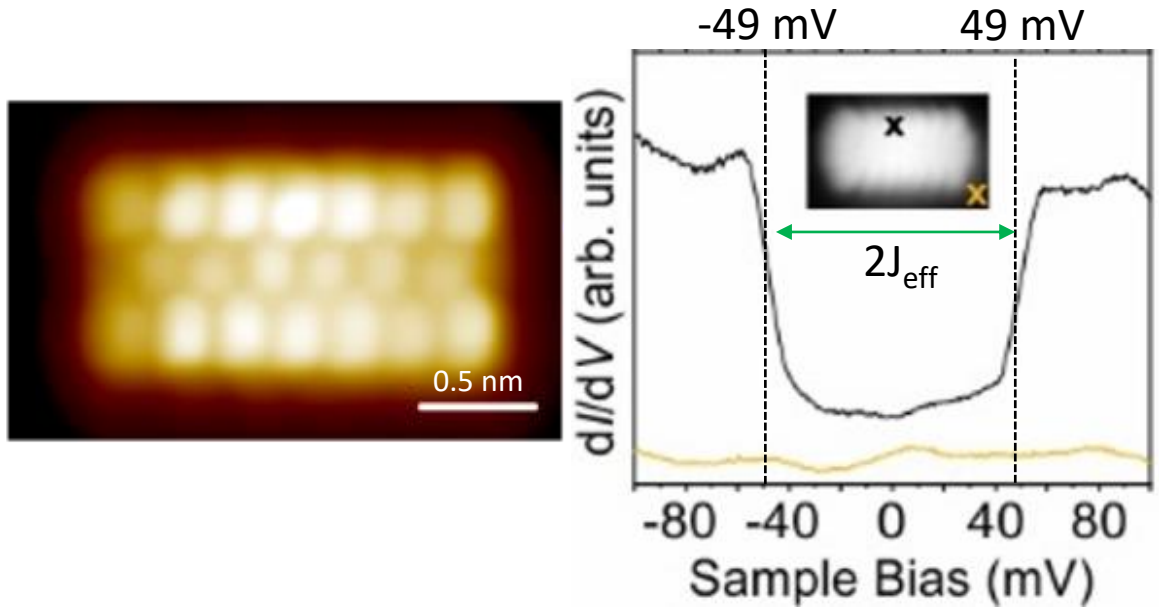
Peri-pentacene



*Sánchez-Grande, A; et al. J. Phys. Chem. Lett,12 (1), 330-336 (**2020**)*

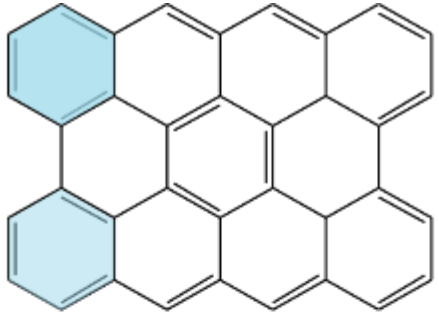
Peri-heptacene



*Biswas, K. et al. Angew. Chem.Int. Ed. 61 (23), e202114983 (**2022**)*

- STS measurements confirm the **open-shell singlet ground state (S = 0)** of peripentacene and periheptacene on Au111.

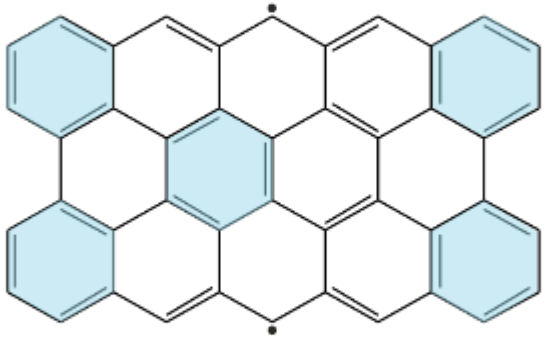
Peri-acenes family



Controversial ground state

Mishra, S.; et al., ACS Nano 12, 11917−11927 ***(2018)***

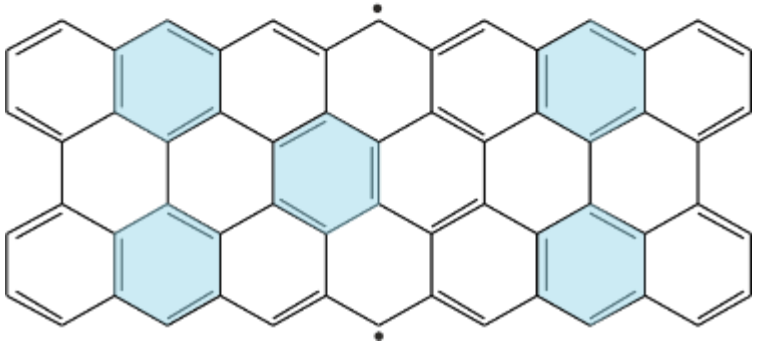
J_{eff} = 40 meV



Open-shell ground state

*Sánchez-Grande, A; et al. J. Phys. Chem. Lett,12 (1), 330-336 (****2020****)*

J_{eff} = 49 meV

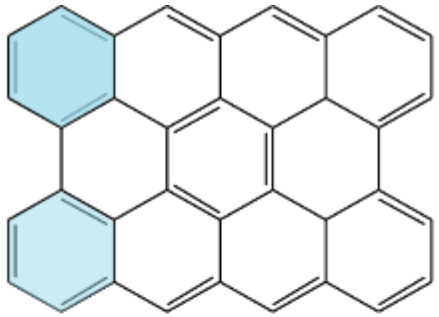


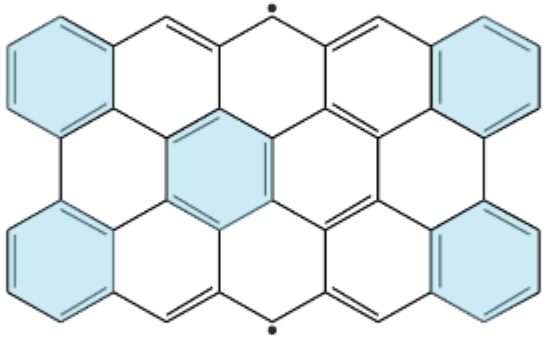
Open-shell ground state

*Biswas, K. et al. Angew. Chem.Int. Ed. 61 (23), e202114983 (****2022****)*

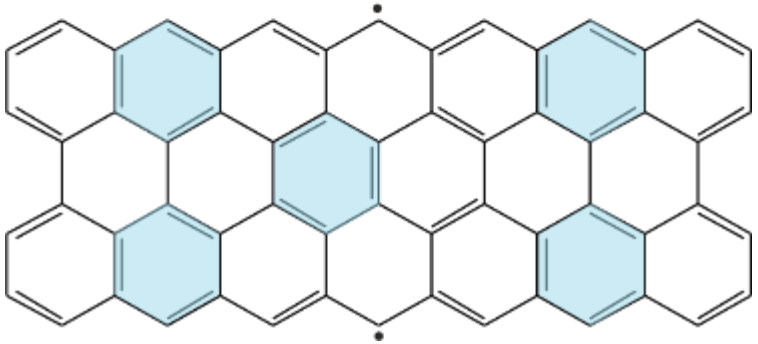
- The ground state structure of different periacenes have been elucidated by STM/STS on the Au111 surface.

Peri-acenes family



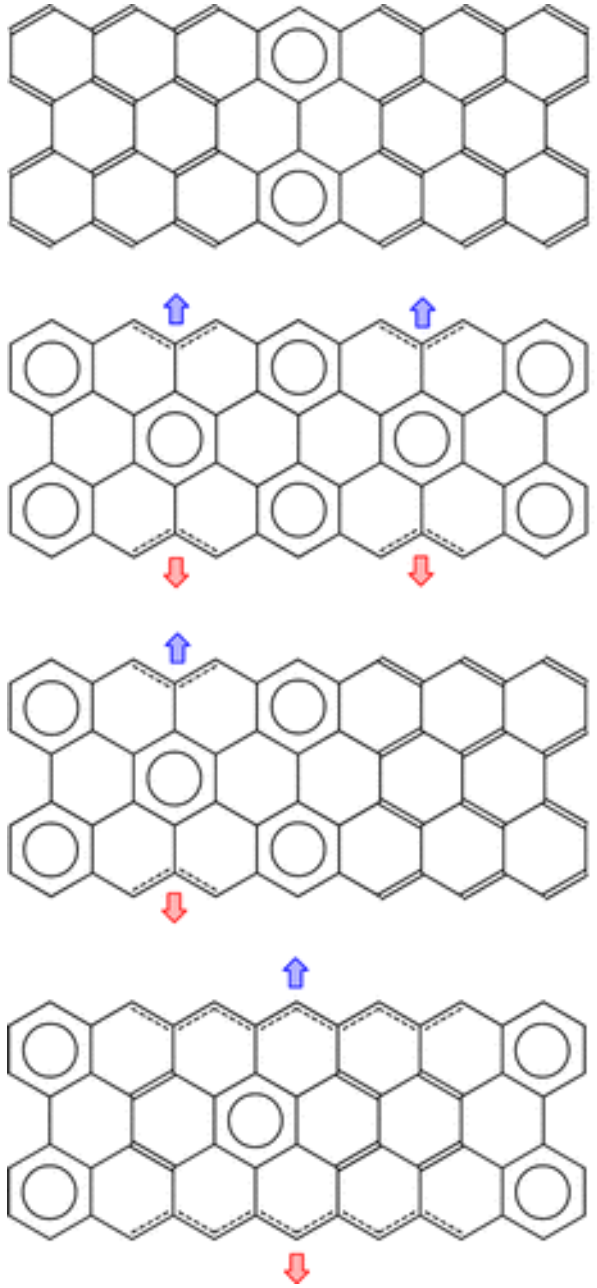


J_{eff} = 40 meV



J_{eff} = 49 meV

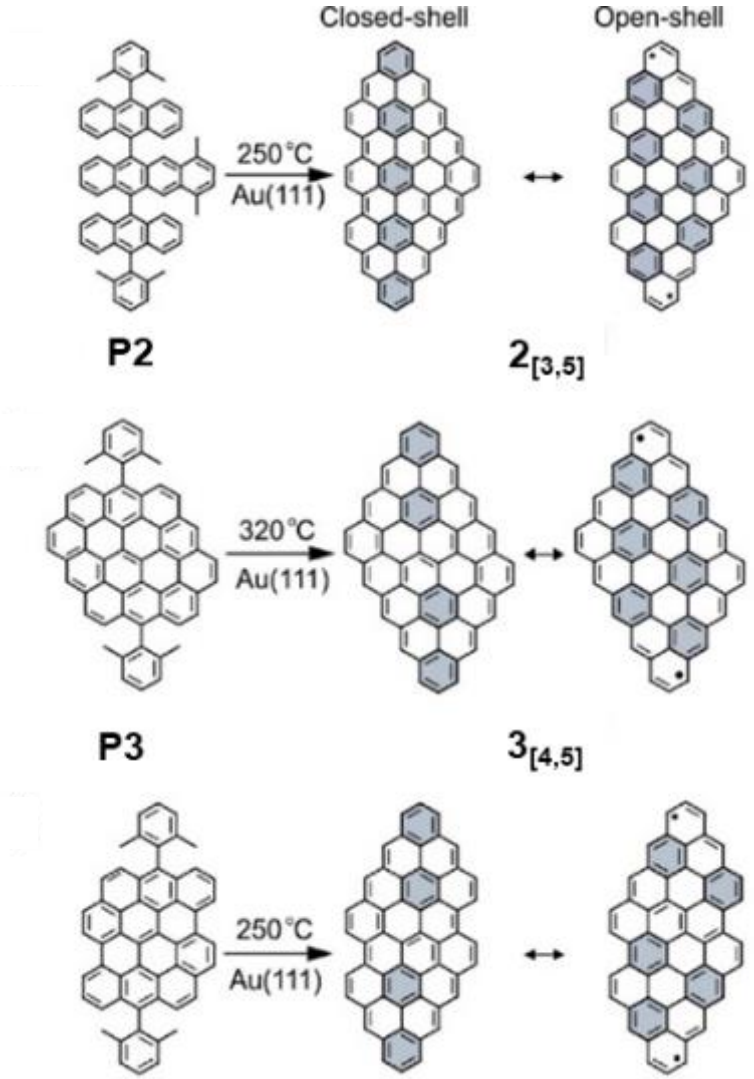
Clar sextets migration

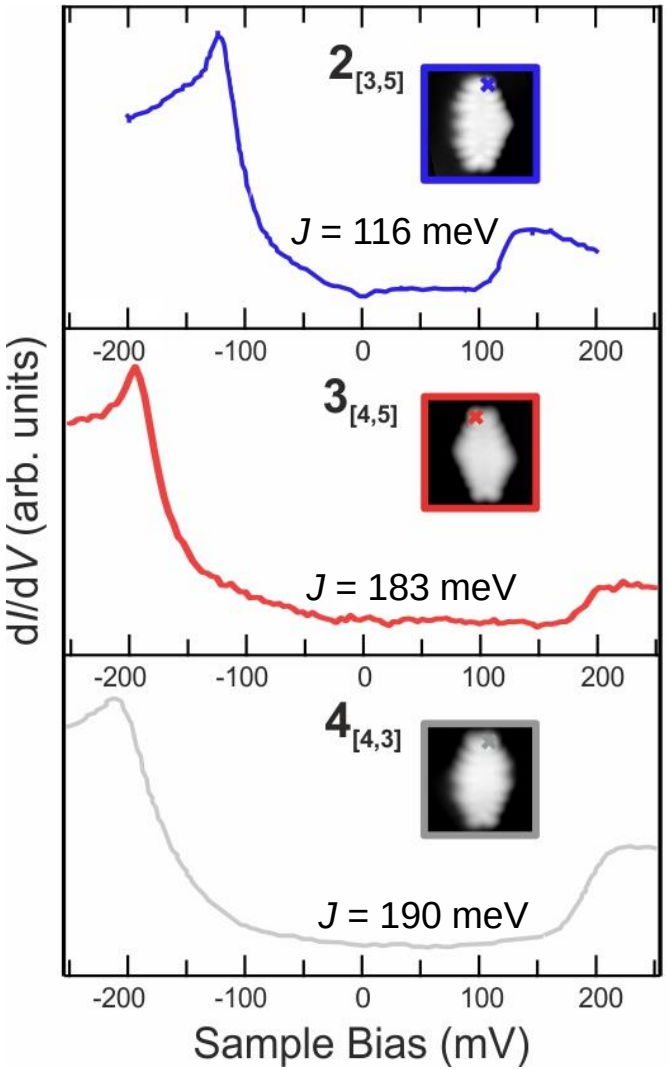


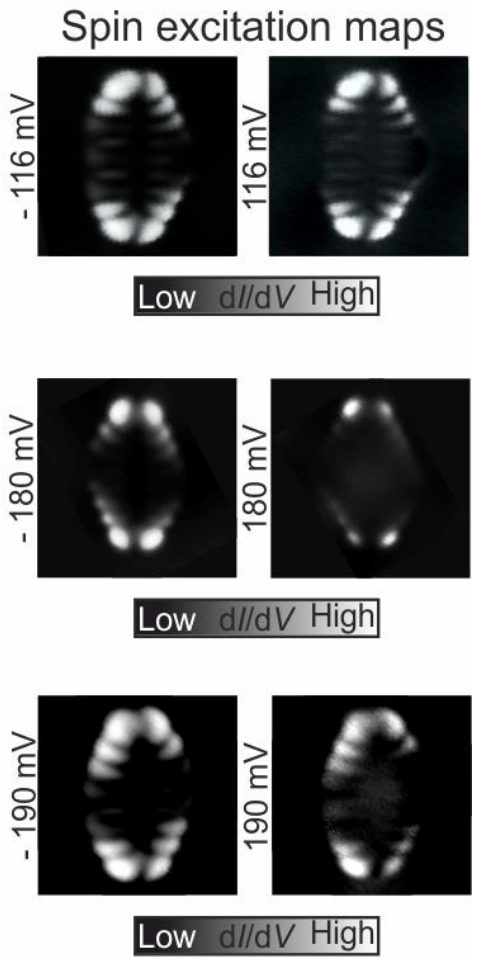
- Counting rules are only a guidance

*Trinquier G and Malrieu J-P., J. Phys. Chem. A, 122, 4, 1088–1103 (**2018**)*

Rhombene-like NGs



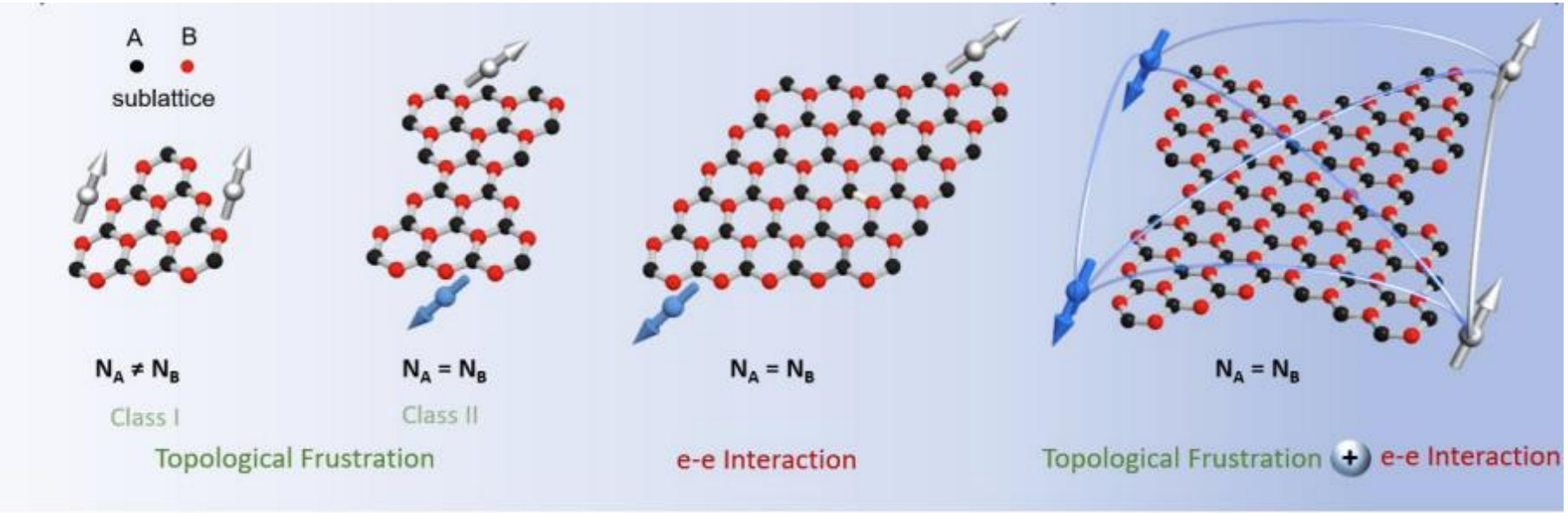




*Biswas, K.; et al. J. Am. Chem. Soc. 145(5), 2968-2974 (**2023**)*

- On-surface synthesis of selected rhombene-like nanographenes with majority zigzag peripheries, where the role of electronic correlations above a critical system size makes feasible that Coulomb repulsion overcomes the hybridization energy of the frontier states, giving rise to **giant magnetic exchange couplings**.

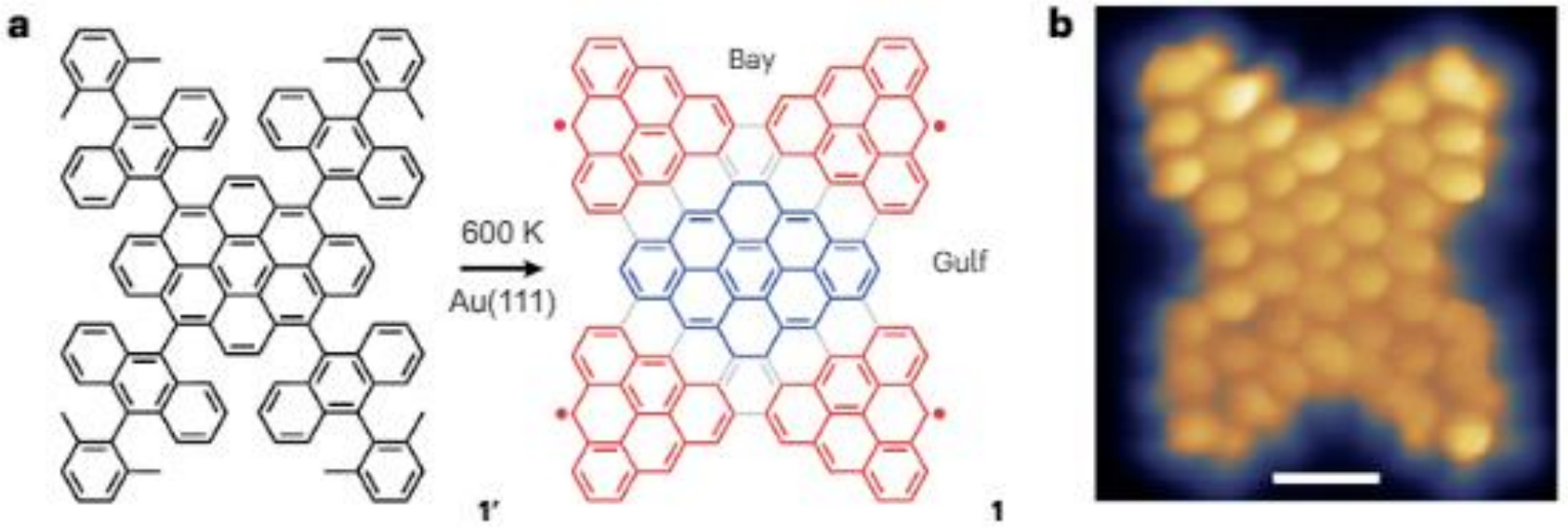
New generation of π-magnetic NGs



*Song S., Nat. Chem. (**2024**). DOI: 10.1038/s41557-024-01453-9aria*

- Polyradical nanographene featuring multiple strongly entangled many-body quantum spins arising from **the interplay of strong e–e correlation and topological frustration**.

New generation of π-magnetic NGs

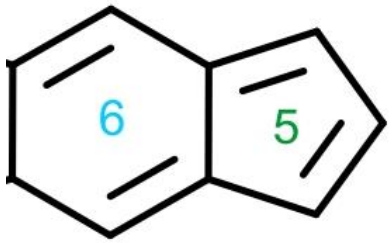


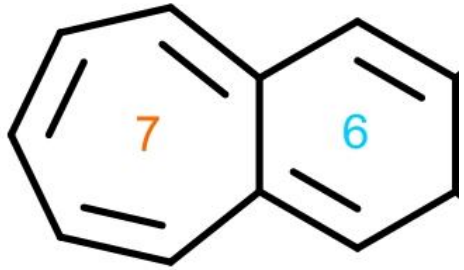
*Song S., Nat. Chem. (**2024**). DOI: 10.1038/s41557-024-01453-9aria*

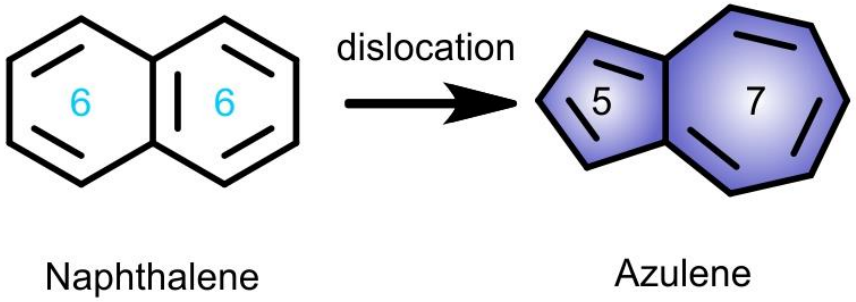
- This system presents a **topologically frustrated** butterfly geometry suggesting the presence of two radicals. Additionally, this design creates a sufficiently large-sized, fully fused, open-shell nanographene to trigger spin-symmetry breaking of occupied frontier orbitals through **strong e–e interaction** that dominates over the hybridization energy, yielding two more radicals.

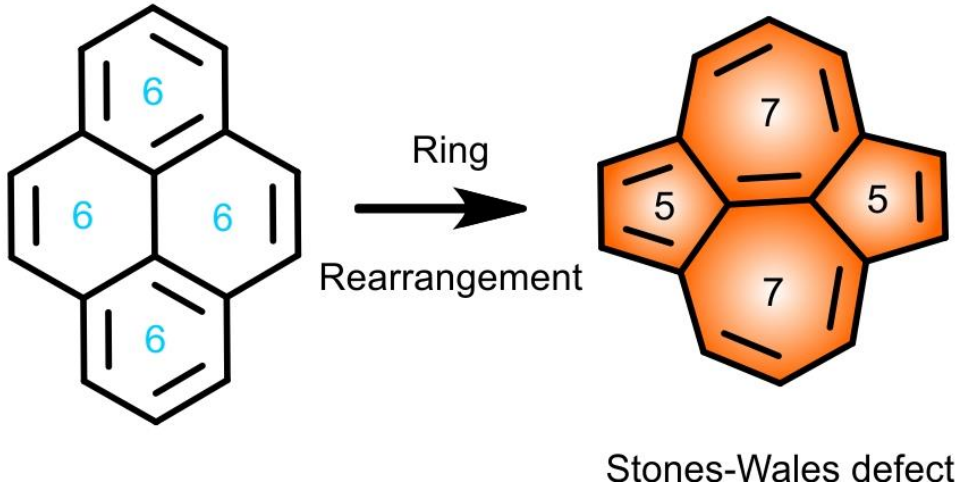
Topological defects

Introducing non-benzenoid units:





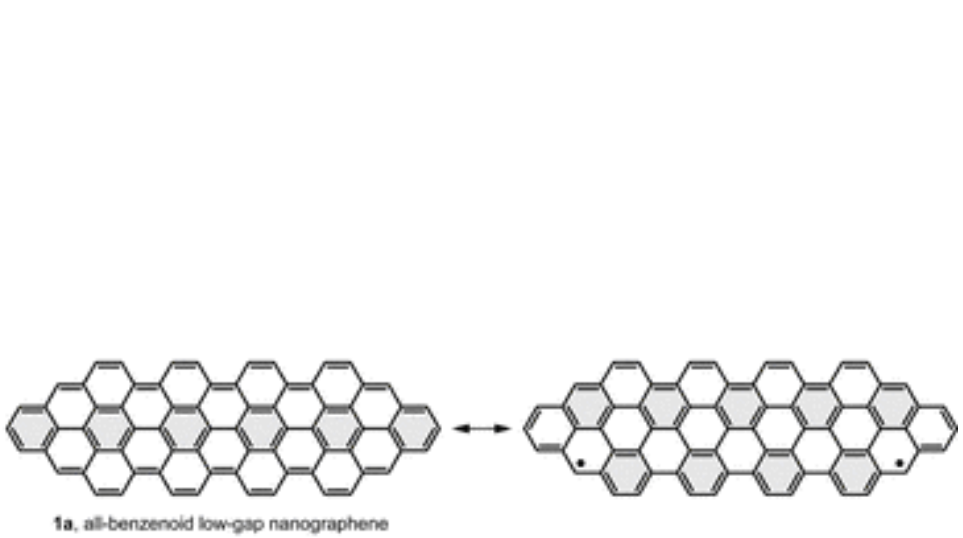


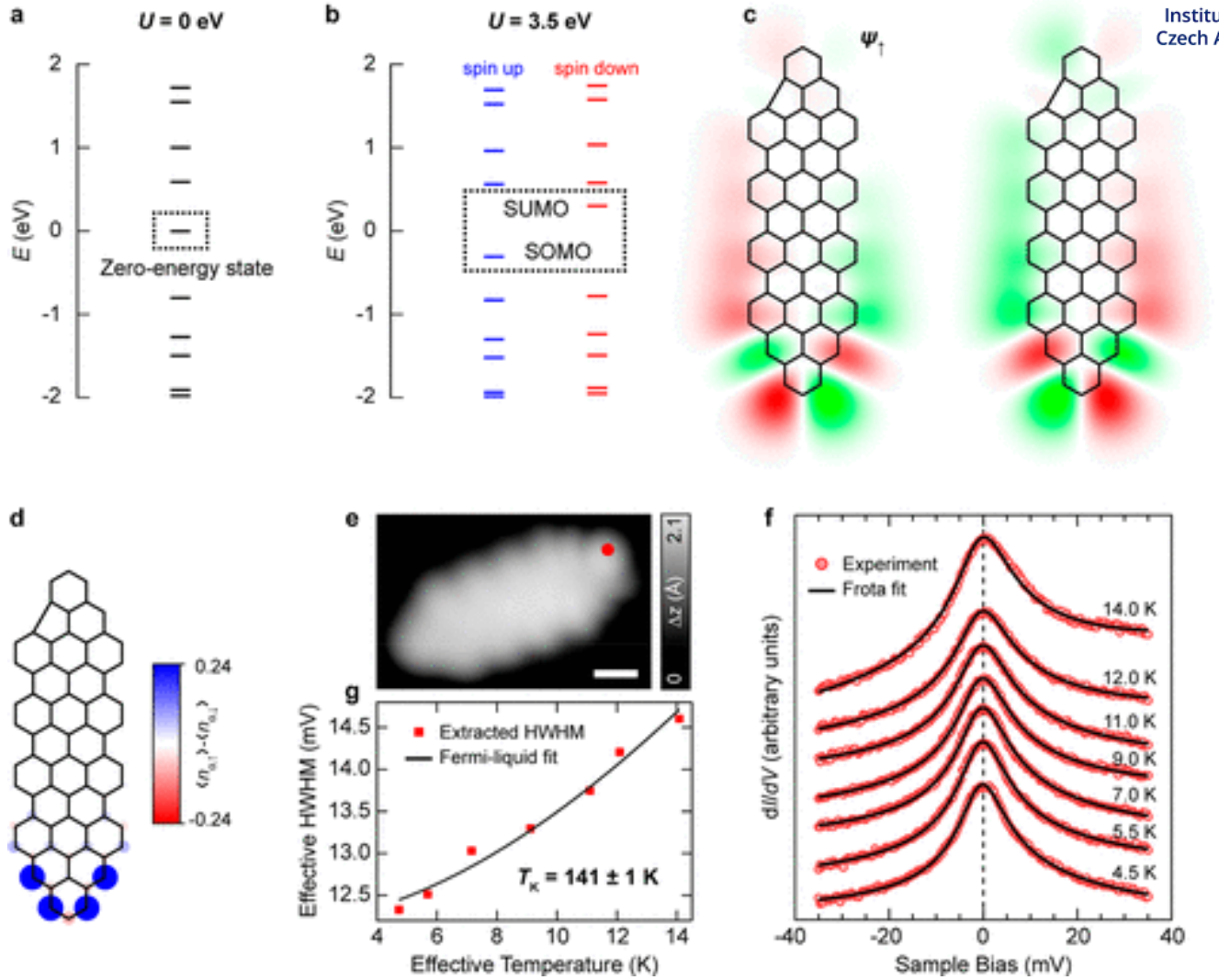


- Non-benzenoid moieties greatly change electronic properties (e.g. charge transfer, shifting HOMO-LUMO gap…).
- Inducing magnetism by **removing/adding p_z orbitals** and creating open-shell radical character.

Defect induced magnetism

By **removing p_z electron** by creating a carbon vacancy





*Mishra S.; et al., J. Am. Chem. Soc. 2020, **142**, 3, 1147–1152*

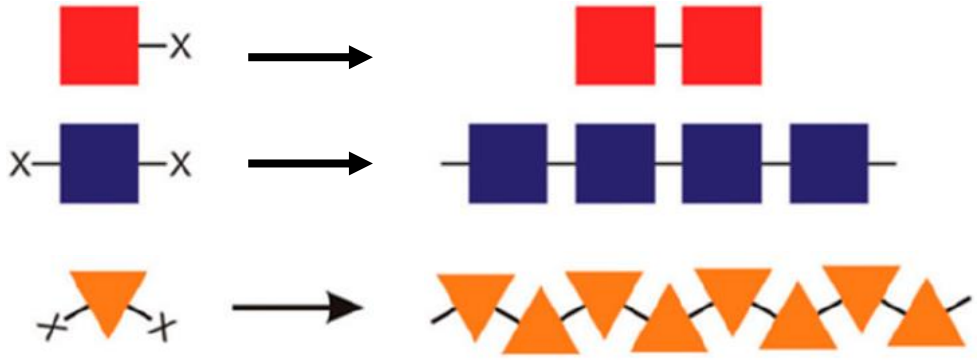
- The presence of this topological defect renders a non-Kekulé system with $S = 1/2$

Outline

- Nanosurf Lab Group
- On-Surface Synthesis (OSS) approach
- OSS of π-magnetic Nanographenes (0D):
  - ❑ Sublattice Imbalance
  - ❑ Topological Frustration
  - ❑ Polarization of edge states
  - ❑ Topological defects
- **How to extend π-magnetism to 1D and 2D (our contributions)**
  - ❑ 1D π-conjugated Polymers
  - ❑ 2D Supramolecular organic radical frameworks

1D π-conjugated polymers

Π-Conjugated polymers are organic macromolecules made up from building blocks with conjugated π-electrons that can be easily delocalized along the molecular backbone due to **p-orbitals overlapping**.



*Clair S. and de Oteyza D. G., Chem. Rev., 119, 7, 4717–4776 (**2019**)*

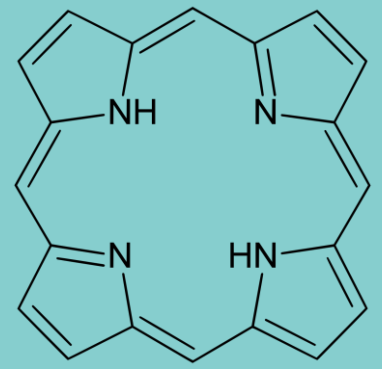
The importance of the building blocks

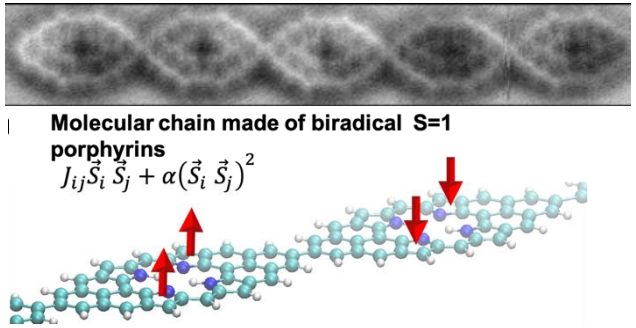
- Tunability of their properties depending on their π-extended conjugation along the molecular backbone.
- The periodicity and the functionalities can be directly modulated by the precursor design.
- Building blocks with an intrinsic magnetic momentum can be employed.

1D π-conjugated polymers

Classification based on the building blocks

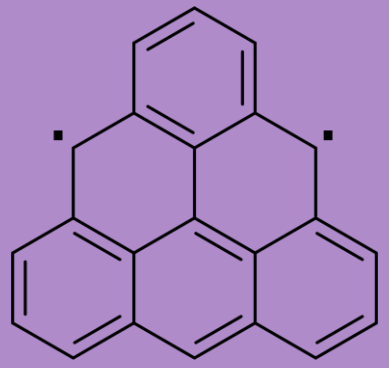
Porphyrinoid polymers

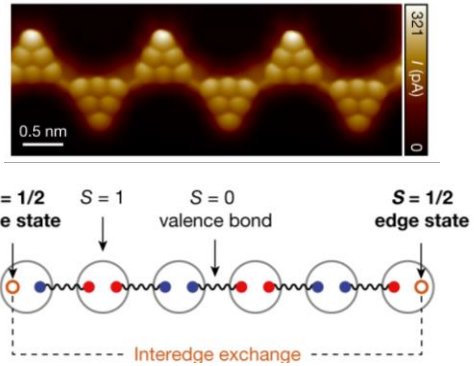




*Zhao Y.; et al., Nat Chem 15, 53–60 (**2023**)*

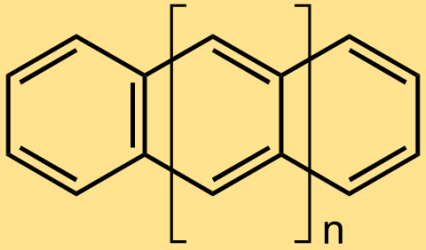
Triangulene polymers

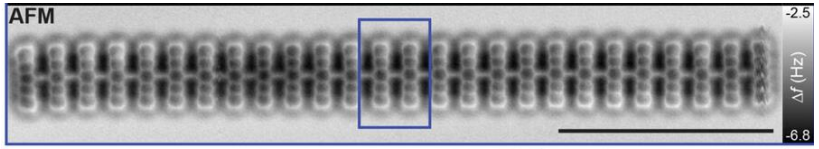


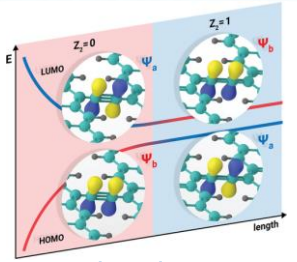


*Mishra S.; et al., Nature 598, 287–292 (**2021**)*

Acene polymers

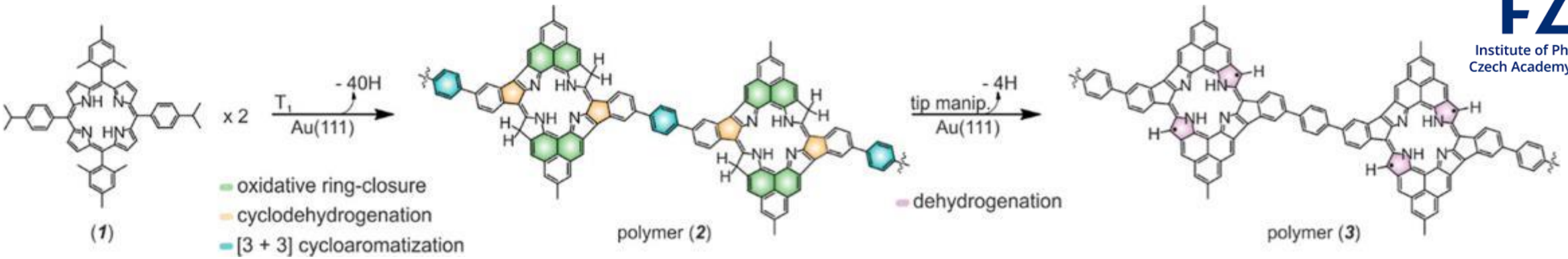


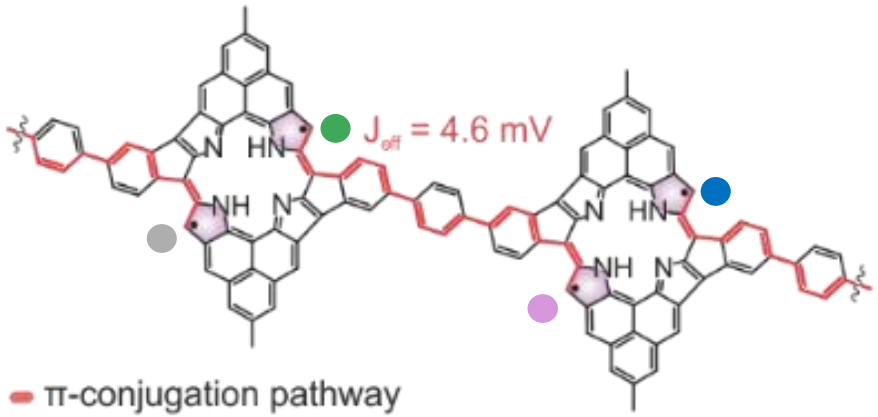


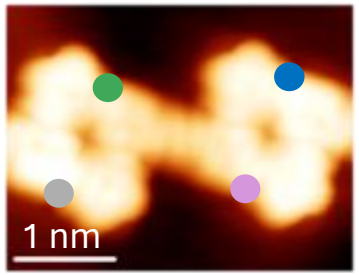


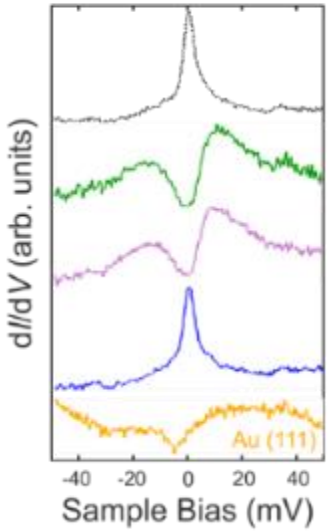
*González-Herrero H.; et al., Adv. Mater., 33, 2104495 (**2021**)*

Porphyrinoid polymers

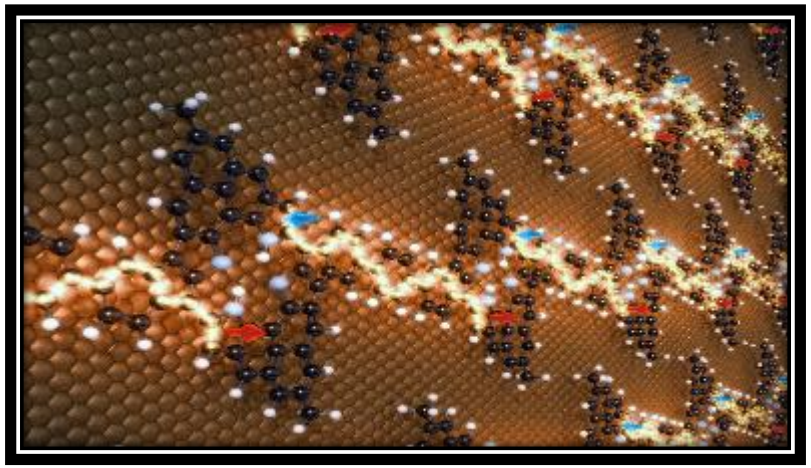








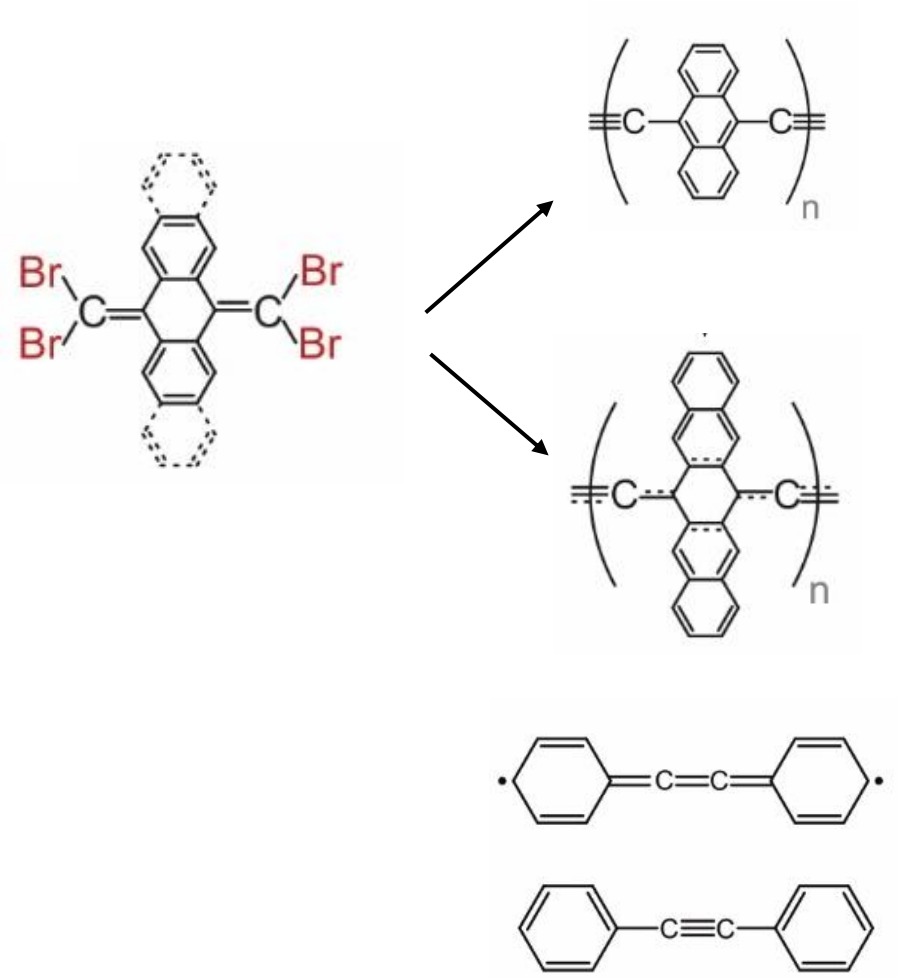
- Antiferromagnetic coupling with an **experimental exchange-coupling strength of 4.6 mV**, between the two closer spins from adjacent porphyrinoid units.

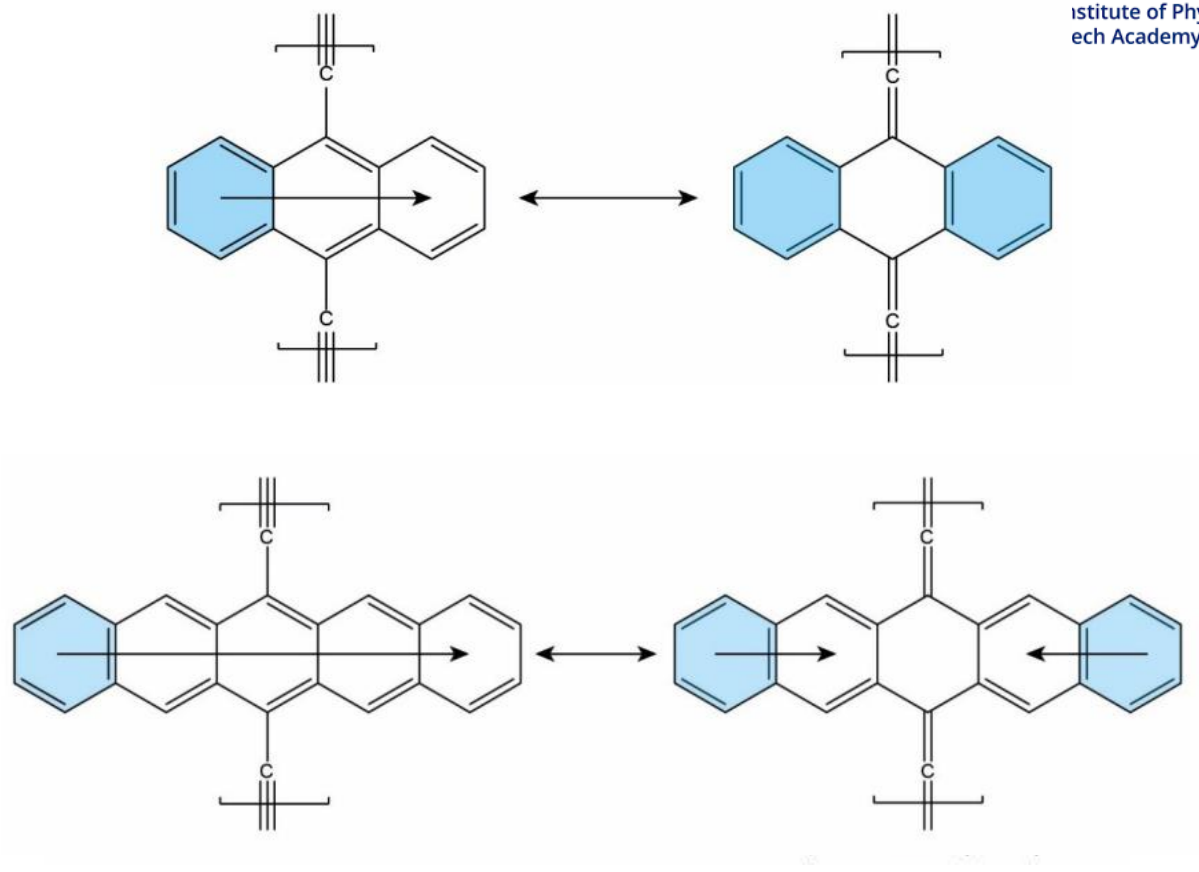


- **Relevance of the π-conjugation in the correlations between spins,** representing a profitable step towards the on-surface synthesis of covalently-linked 1D magnetic polymers.

*Biswas K.; et al., J. Am. Chem. Soc.,144, 28, 12725–12731 (**2022**)*

Acene polymers

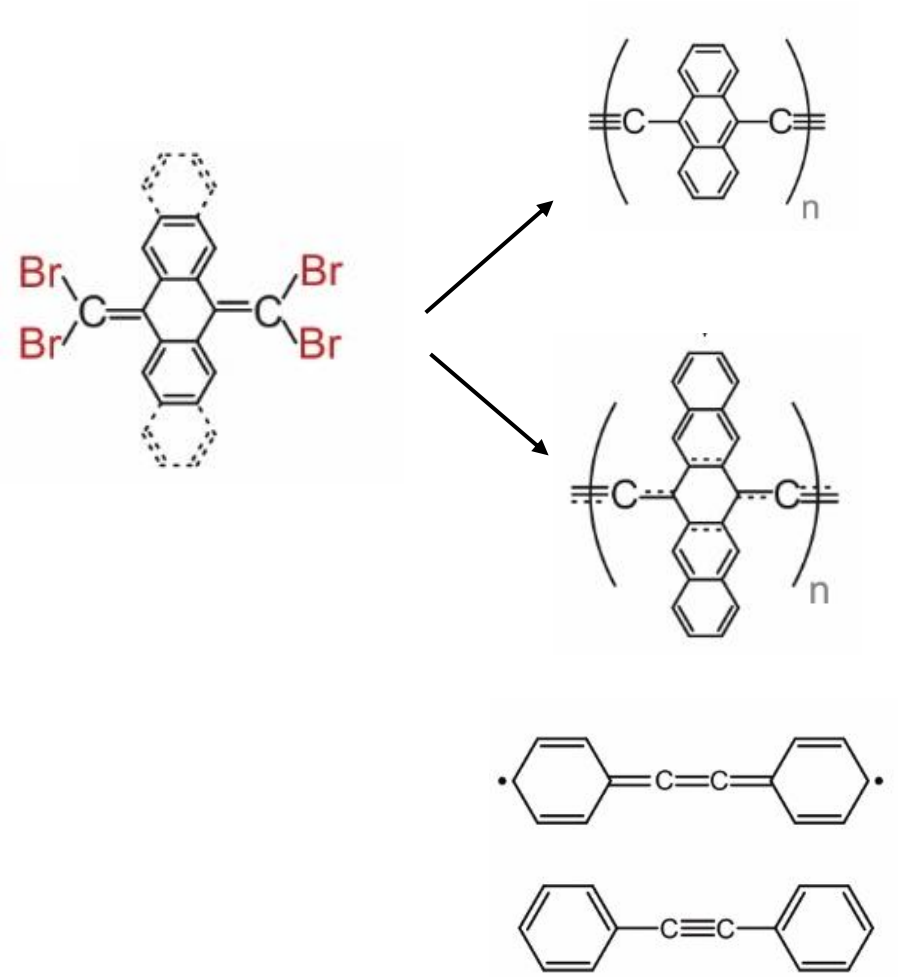


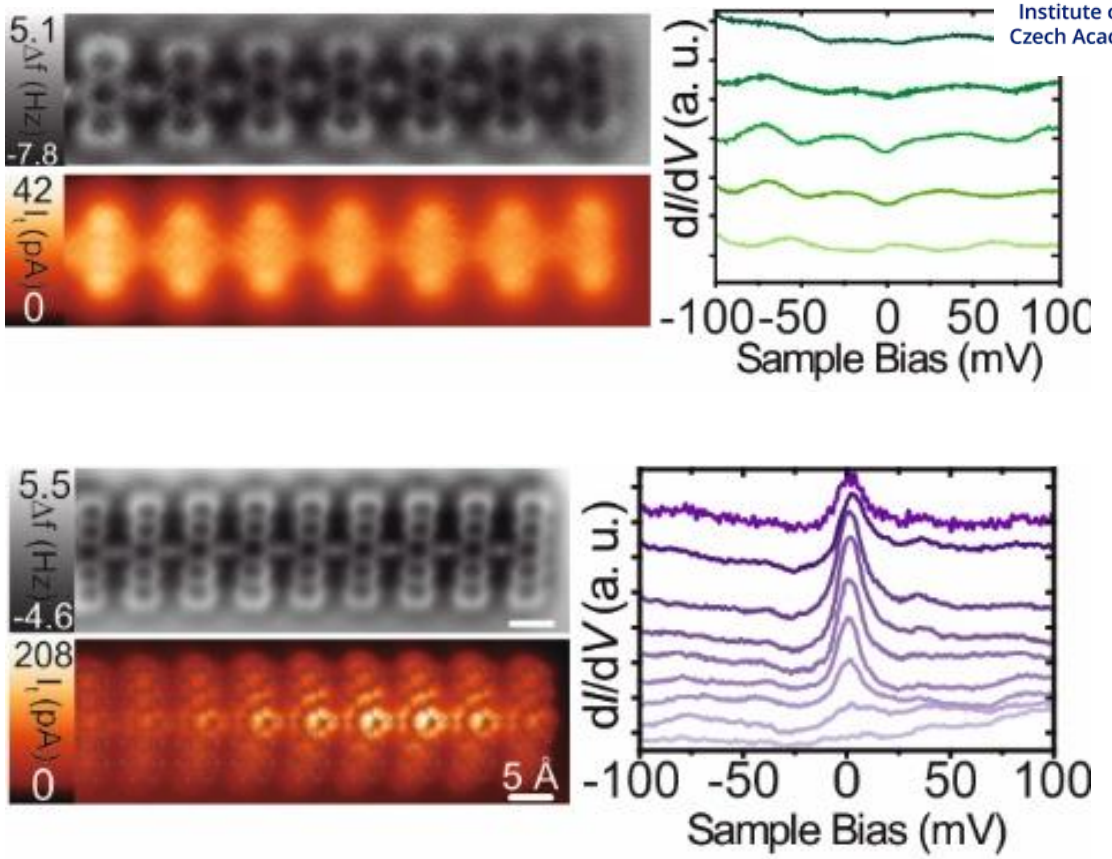


Cirera B.; et al., Nat Nanotechnol 15, 421–423 (**2020**)

- On-surface synthesis of acene-based polymers on Au(111).
- **Parallelism between the emergence of topological edge states and the chemical form** (aromatic/ethynylene vs quinoid/cumulene).
- The resonant form is controlled by the size of the building blocks.

Acene polymers





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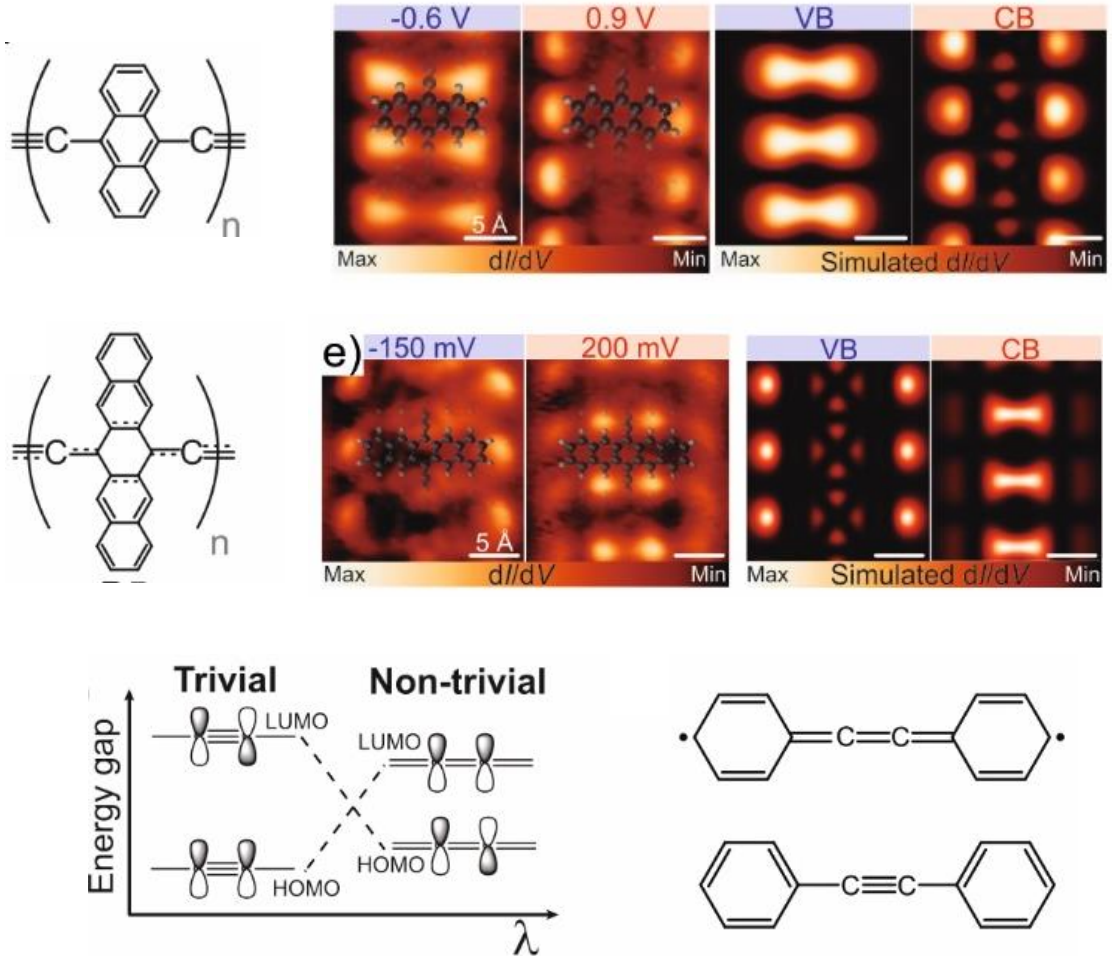

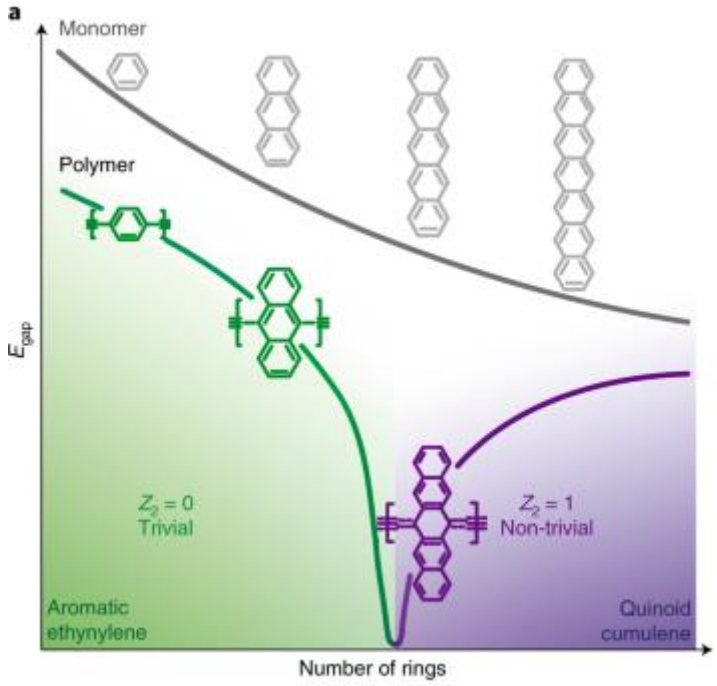

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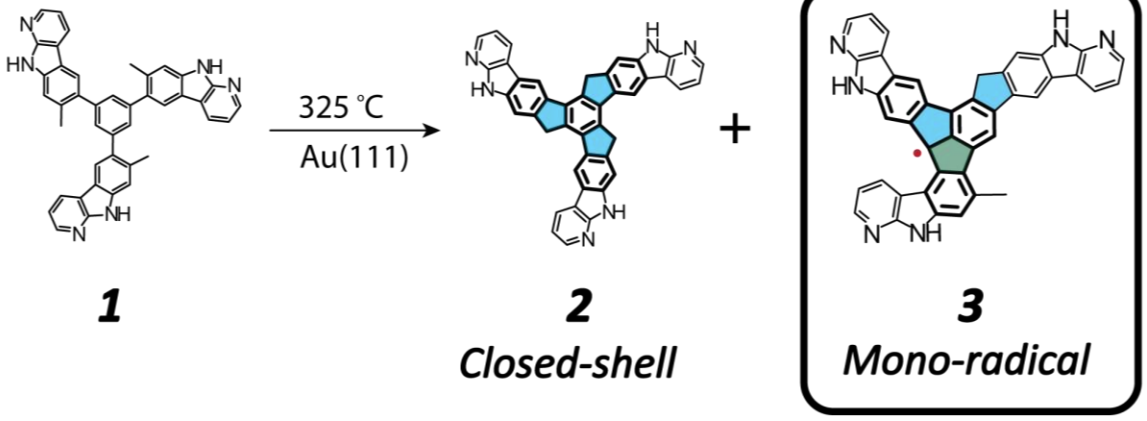
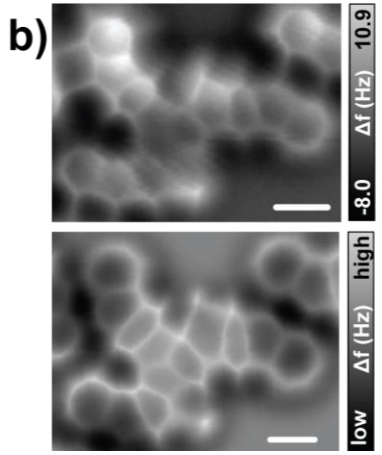
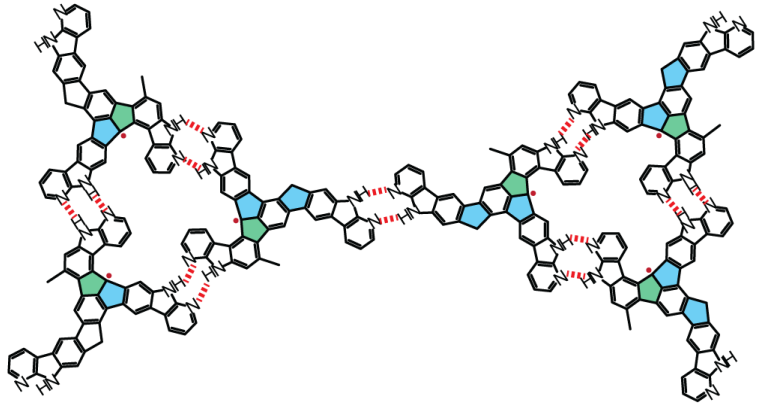
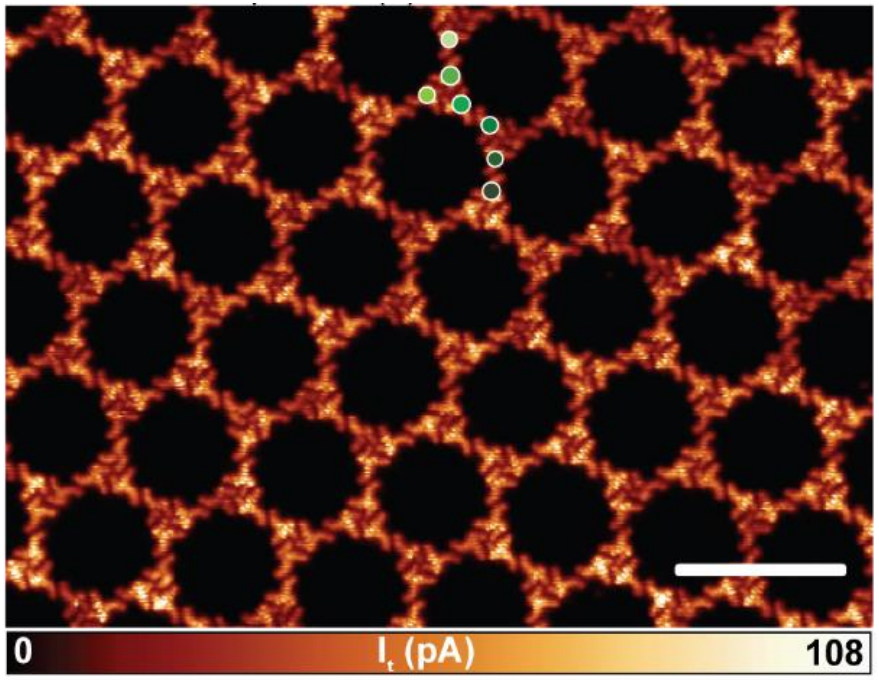
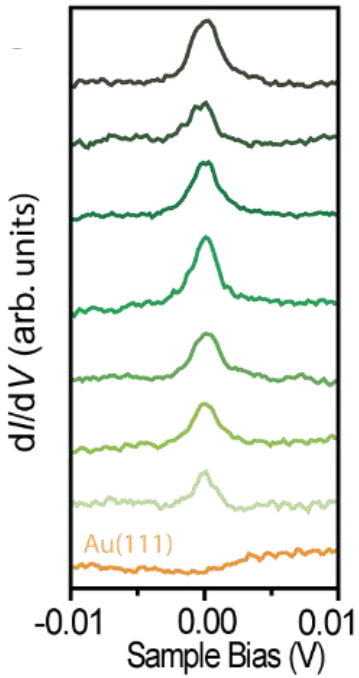
Supramolecular radical frameworks

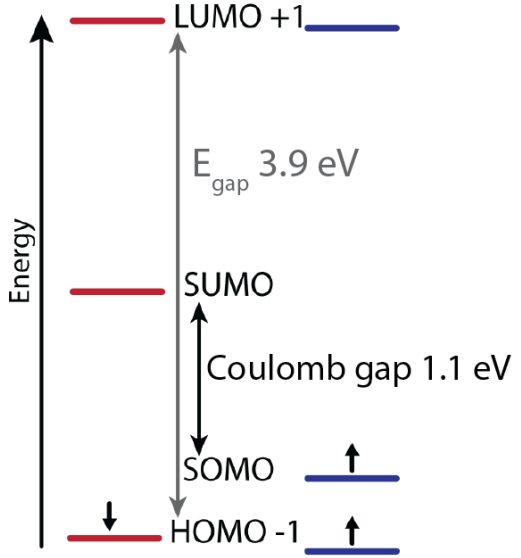


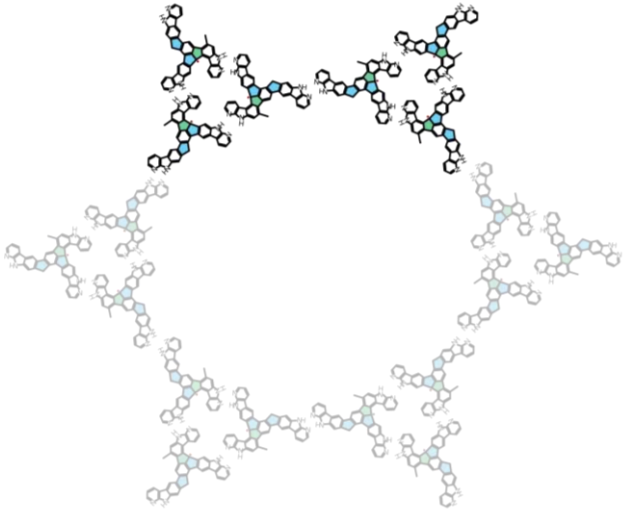












*Frezza F.; et al., J. Am. Chem. Soc., 146, 5, 3531–3538 (**2024**)*

- The combination of supramolecular chemistry, π-magnetism, and on-surface synthesis, results in the synthesis of a **supramolecular radical framework on Au(111) made up of monoradical building blocks**.

Conclusions

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- Great advances have been made in π-magnetism thanks to the on-surface synthesis approach, reporting impressive progress in short time.
- SPM techniques allow precise determination of the chemical structures and the study of the electronic and magnetic properties at the single molecule level.
- There is a substantial progress in our capabilities to realize localized electron spin states and to control electron spin interactions at the atomic scale.
- The important relevance of the field with worldwide groups working on it.

nanoSURF

Conclusions

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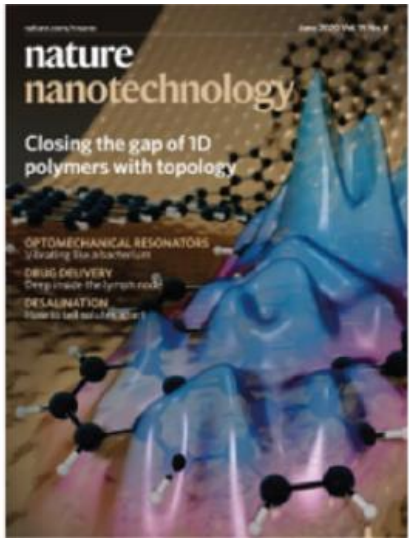

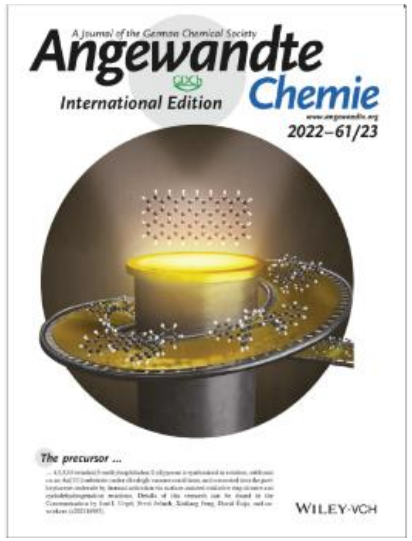

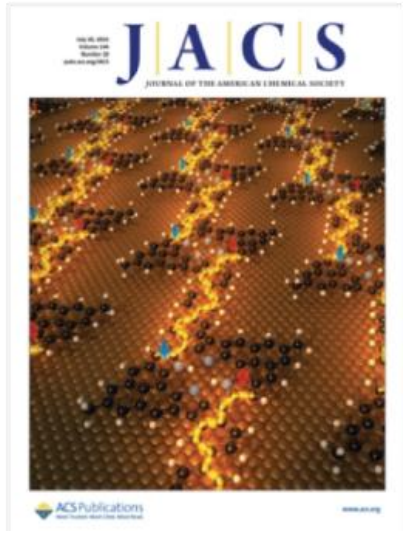

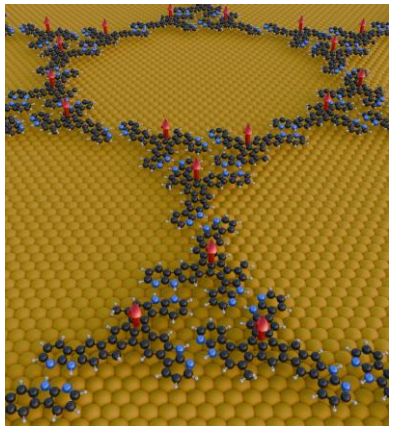

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Thank you

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