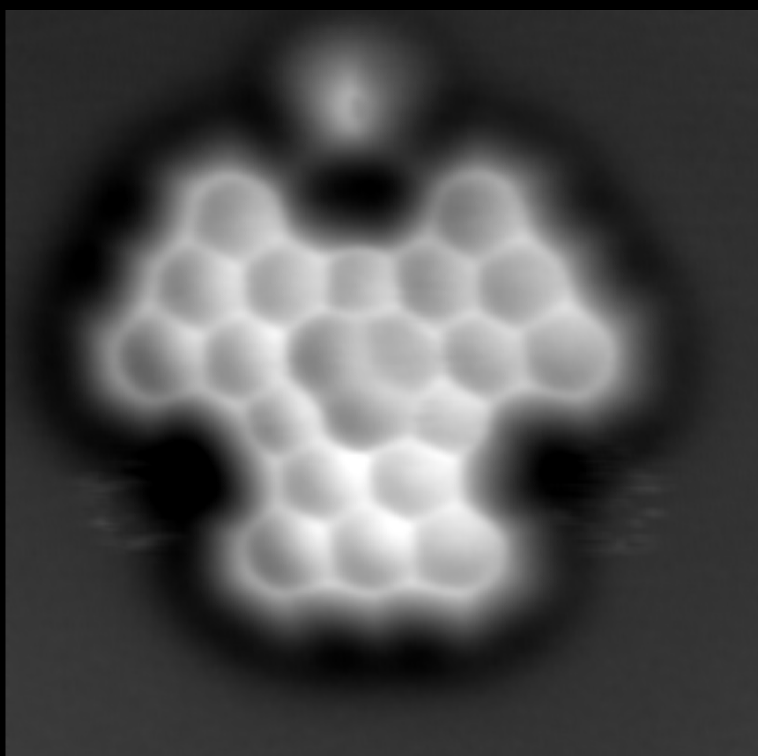
Paramagnetism in triangular pieces of graphene



Nacho Pascual

CIC nanoGUNE, San Sebastian

10th May at El Escorial

ESMolNa 2023

SPRING

H2020 FET-OPEN Project # 863098

FunMolSys

MINISTERIO DE CIENCIA E INNOVACIÓN

AGENCIA ESTATAL DE INVESTIGACIÓN

EXCELENCIA MARÍA DE MAEZTU

PID2019-107338RB-C6

MCIN/AEI/10.13039/501100011033

Organic Synthesis

STM - STS in UHV at 4K

Theory & Simulations

CiQUS

@ Santiago de Compostela

- Manuel Vilas
- Jesus Castro
- Iago Pozo
- Silvia Castro
- Diego Peña

CIC nanoGUNE

nanoscience cooperative research center

@ Donostia San Sebastian

- Jingcheng Li
- Hector Briongos
- Alessio Vegliante
- Fran Romero
- Niklas Friedrich
- Fabian Schulz
- Emilio Artacho
- Unai Uriarte
- Natalia Koval

DIPC

@San Sebastian Donostia

- Sofia Sanz
- Aran G. Lekue
- David Casanova
- Thomas Frederiksen
- Nestor Merino
- Alejandro Berdonces
- Dimas G. de Oteyza

CFM

@San Sebastian Donostia

- Tao Wang
- Martina Corso
- Jan Calupitan
- Daniel Sanchez Portal

SPRING

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FunMolSys

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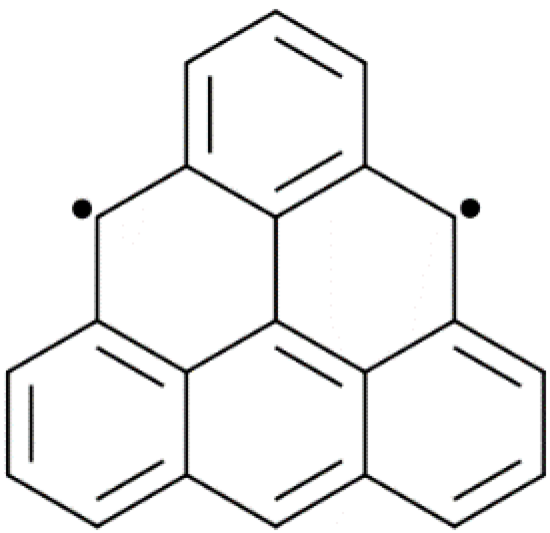
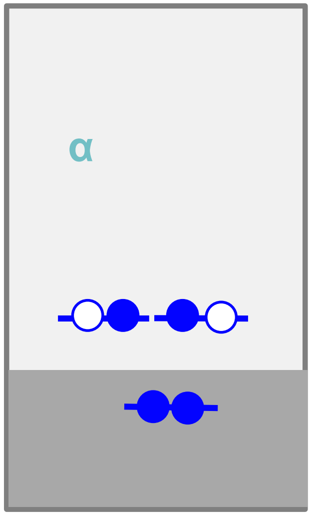
Sources of magnetism in Triangulenes

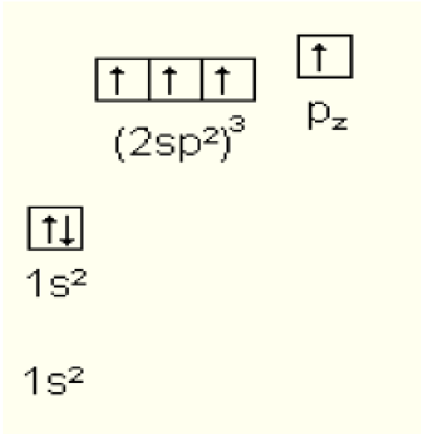
Benzenoid Graph Theory:

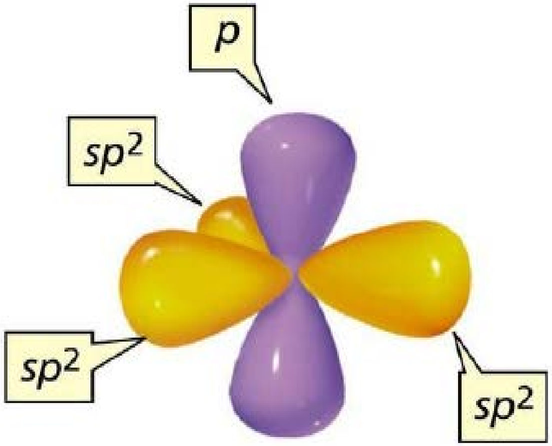
$Nulity$: $\eta = 2\theta - N$



$\eta = 2$ half-filled states







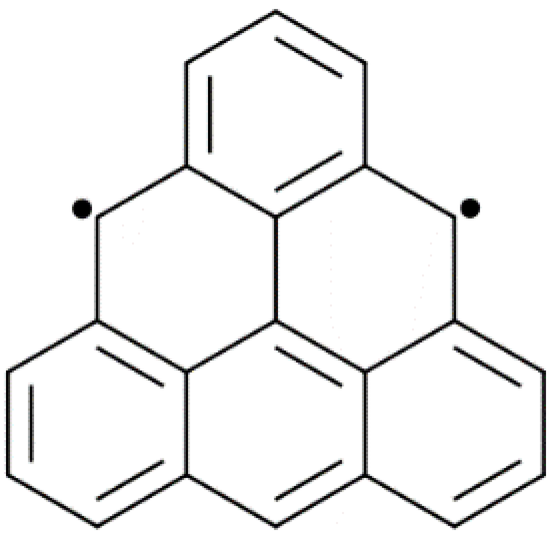
[3]Triangulene: 22 p_z electrons

Sources of magnetism in Triangulenes

Benzenoid Graph Theory:

$Nulity\colon\ \eta = 2\theta - N$

Coulomb Energy



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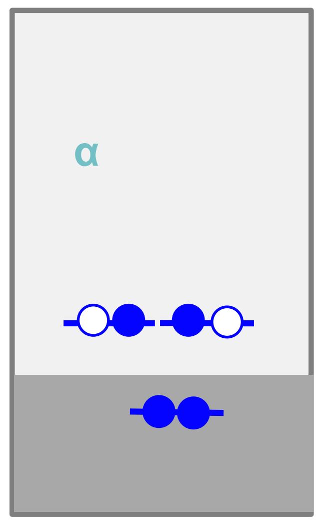
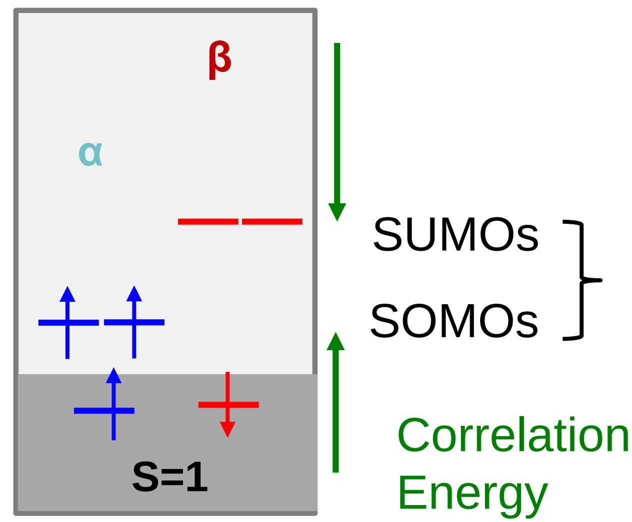


$\eta = 2$ half-filled states



[3]Triangulene: 22 p_z electrons

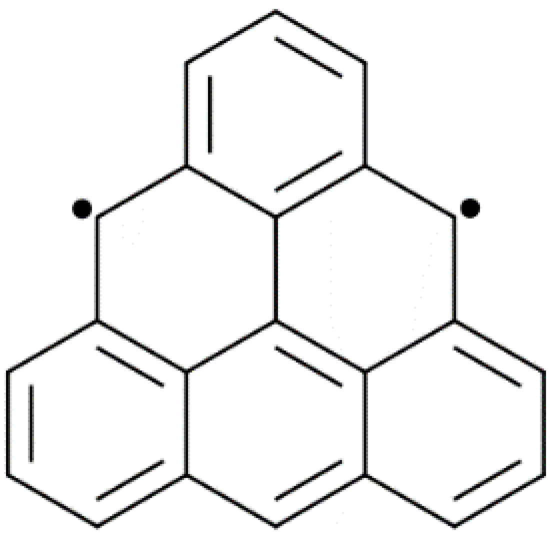
Sources of magnetism: Triangulenes

Benzenoid Graph Theory:

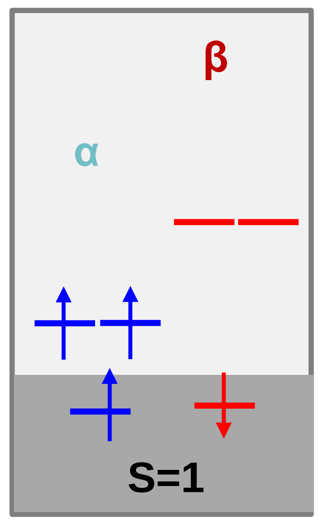
Nulity: $\eta = 2\theta - N$

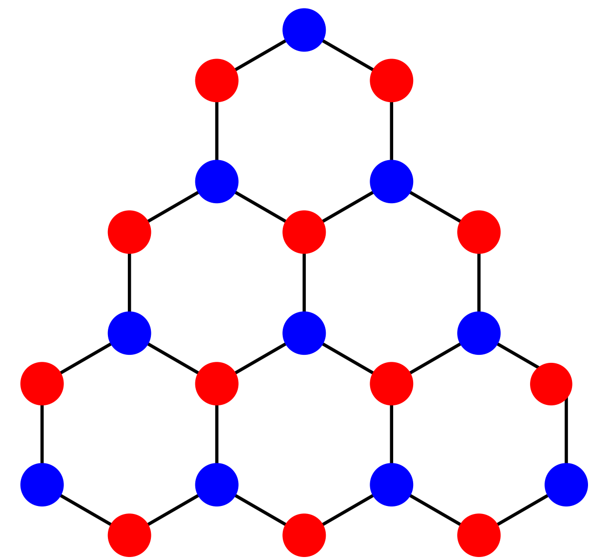
Ovchinnikov's rule

S=1/2(12-10)=1



$\eta = 2$ half-filled states





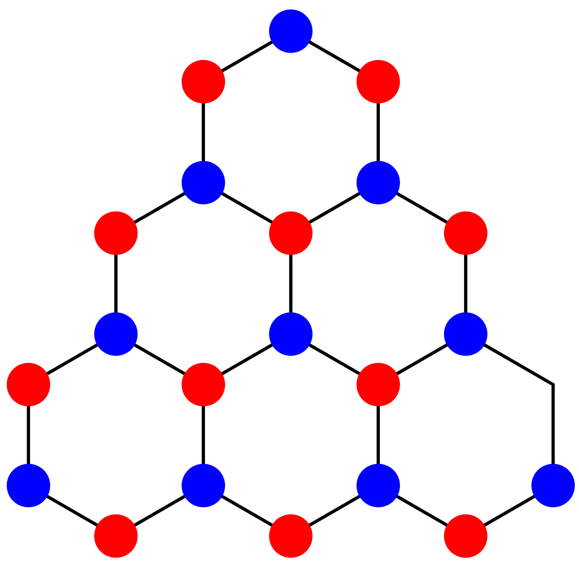
Triangulene: **π frustration causes unpaired electrons**

Intrinsic π-paramagnetism

Delocalized spin clouds

Spin is scales with size

- High Spin Graphene nanostructures



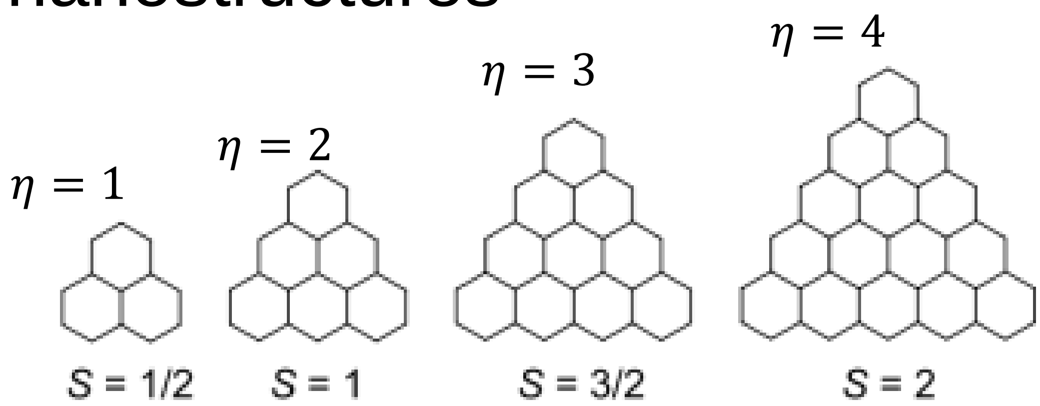
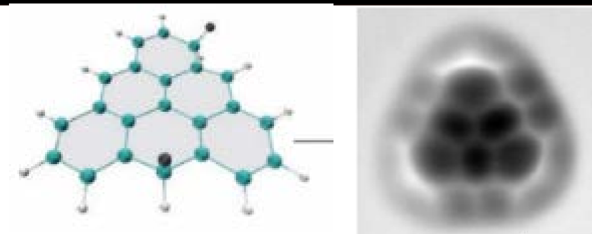


Figure 6. Evolution of the total spin of triangular graphene fragments with size.

O.Yazyev Rep. Prog. Phys. (2010)

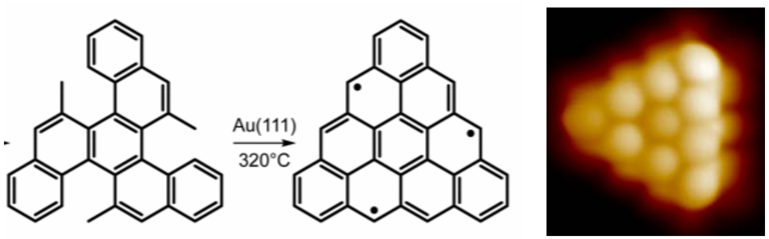
Triangulene: π frustration causes unpaired electrons
Intrinsic π-paramagnetism
Delocalized spin clouds
Spin is scales with size

Synthesis of [n]Triangulene and related



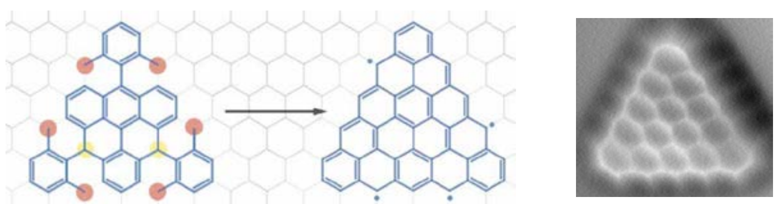
[3]Triangulene
S=1

Gross at al, Nature Nano 305 (2016)



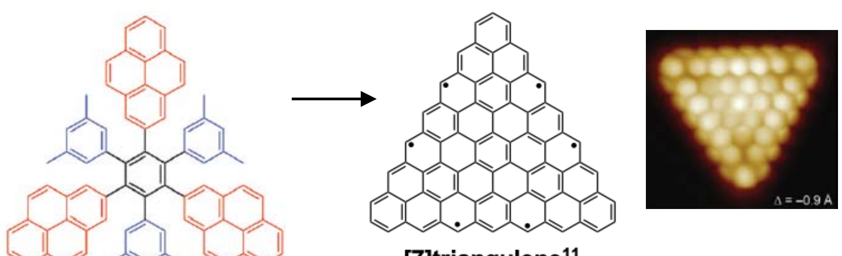
[4]Triangulene
S=3/2

Mishra et al, J. Am. Chem. Soc. 141, 27,10621(2019)



[6]Triangulene
S=5/2

Su at al, Science Advances 5,eaav7717(2019)

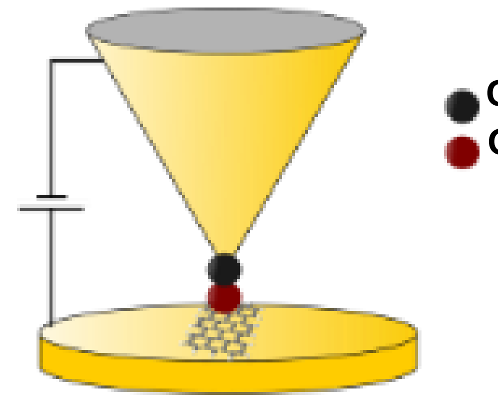


1

[7]triangulene[11]
6 unpaired electrons

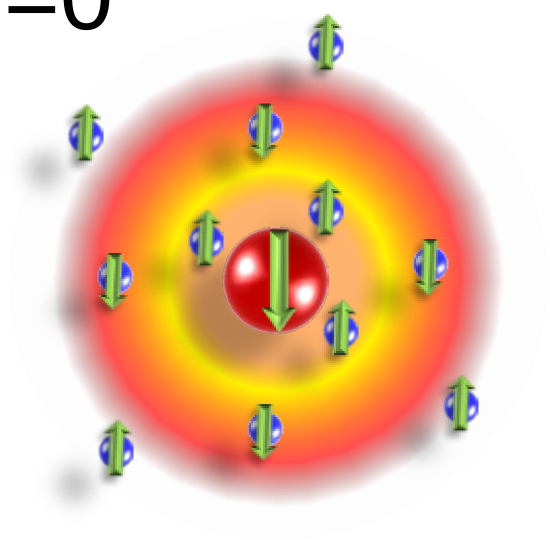
[7]Triangulene
S=3

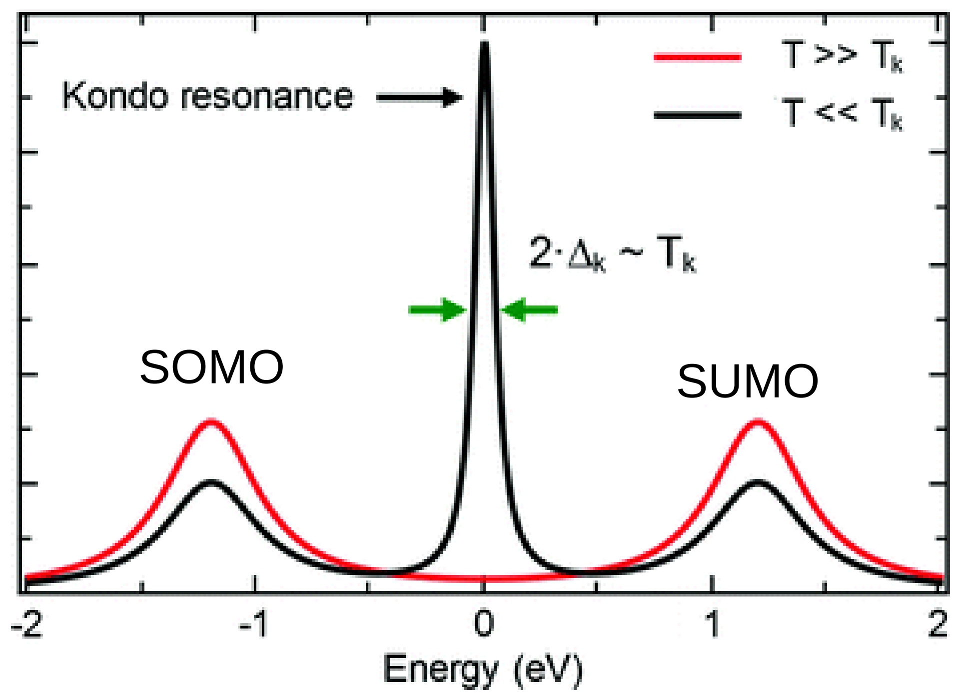
Mishra et al, Nanoscale, 2021, 13, 1624 (2021)



Kondo screening of a SPIN ½

S=0





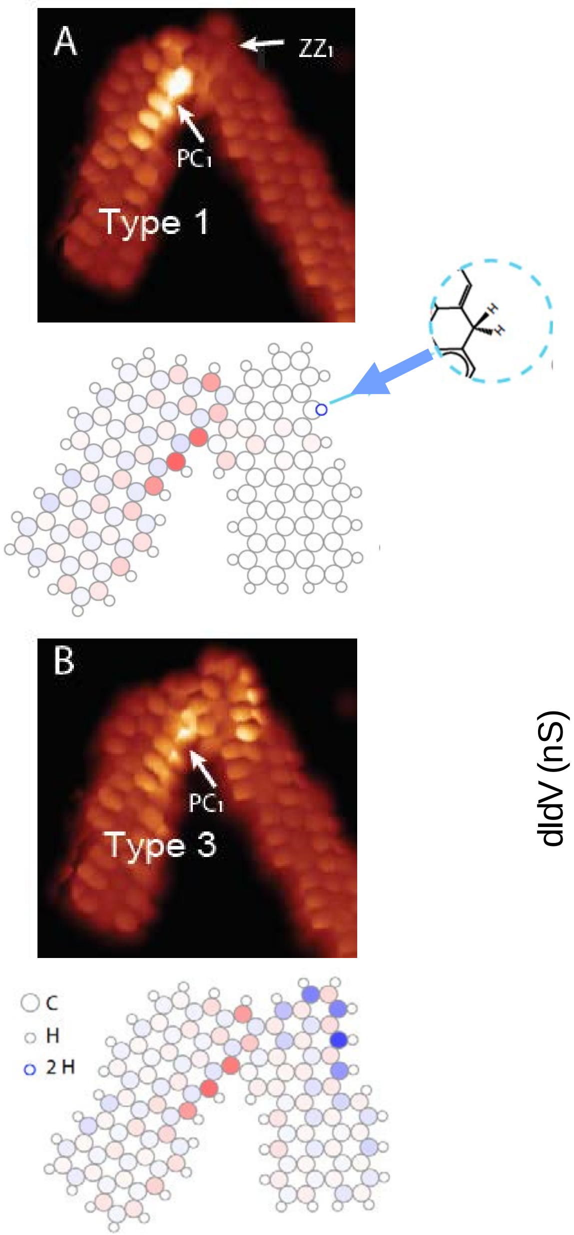
Kondo screening | free magnetic moment

0 K

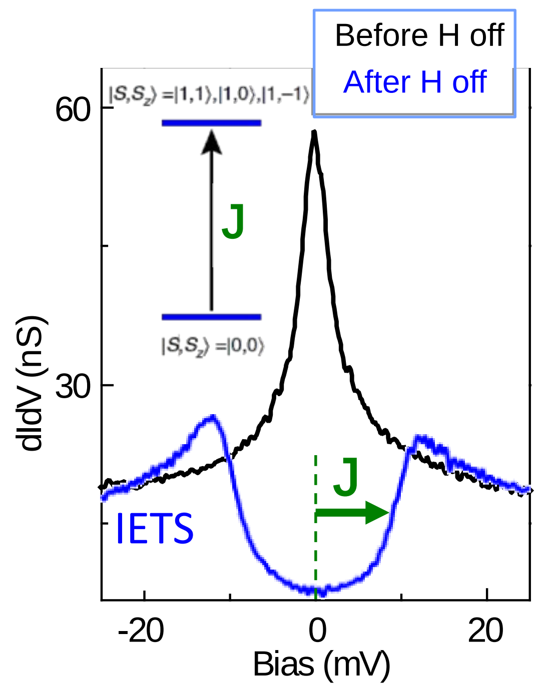
Proofs of The Kondo Effect

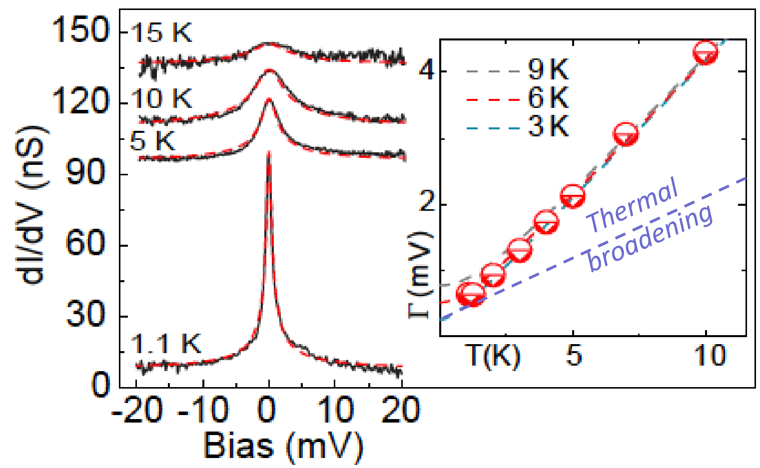
- ❑ Zero bias, narrow resonance with logarithmic-like shape
- ❑ Linewidth increases peculiarly with T
- ❑ Linewidth responds to a magnetic field

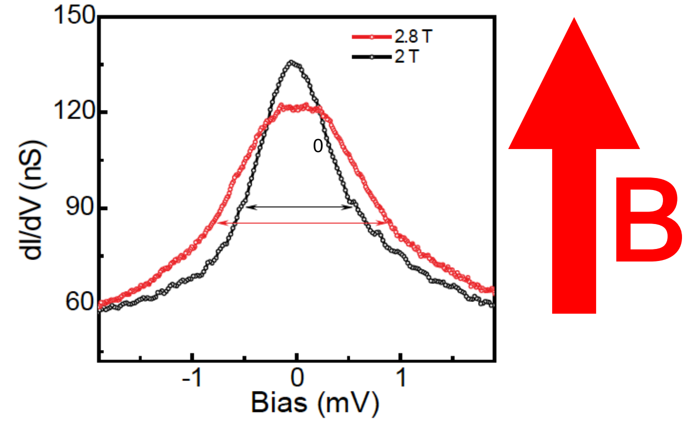
Detecting Spins in graphene junctions



Li et al. Nat Comm 10:200 (2019)

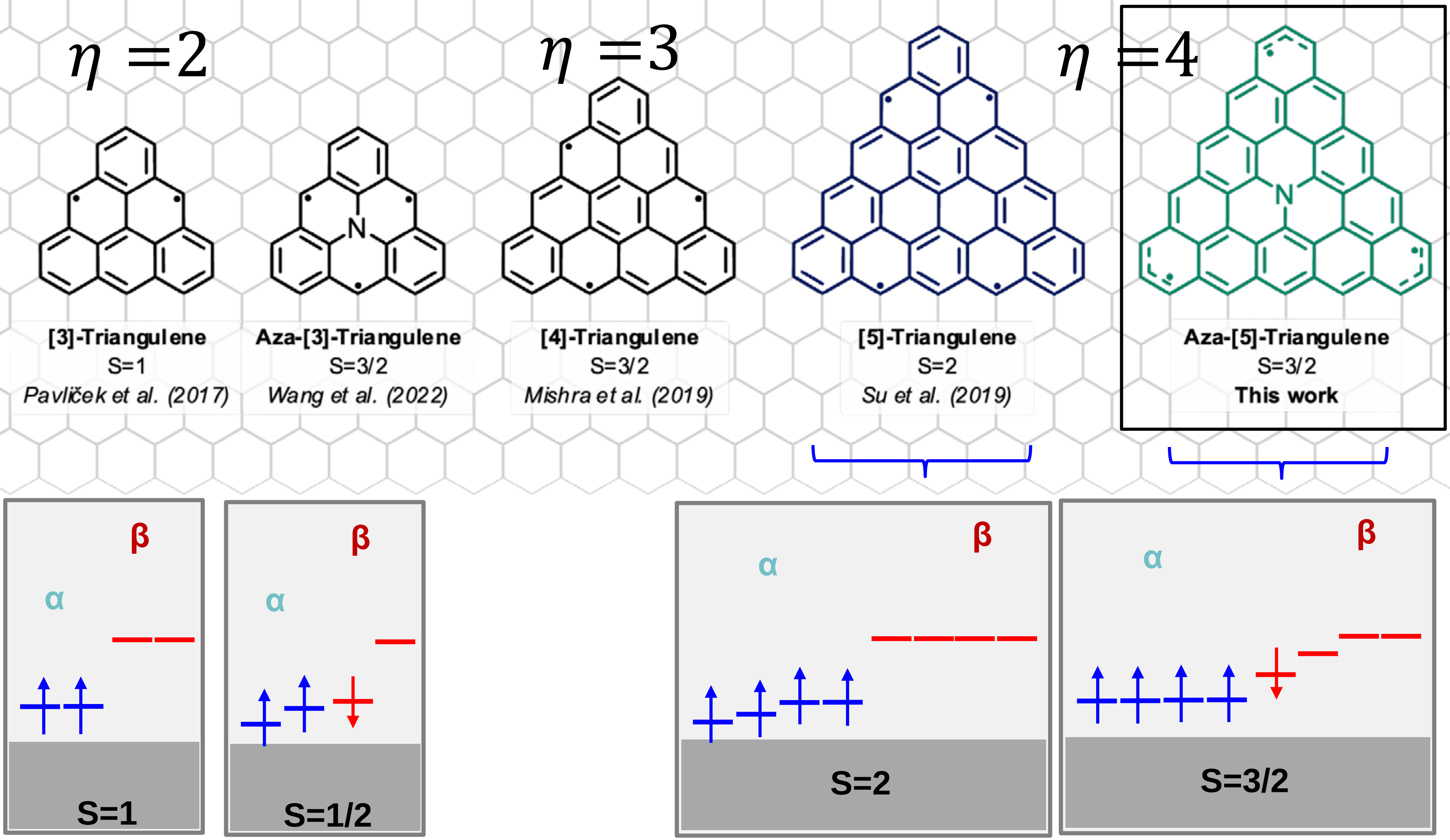






- ❑ Kondo widens with B
- ❑ S=1/2

Aza-[5] Triangulenes



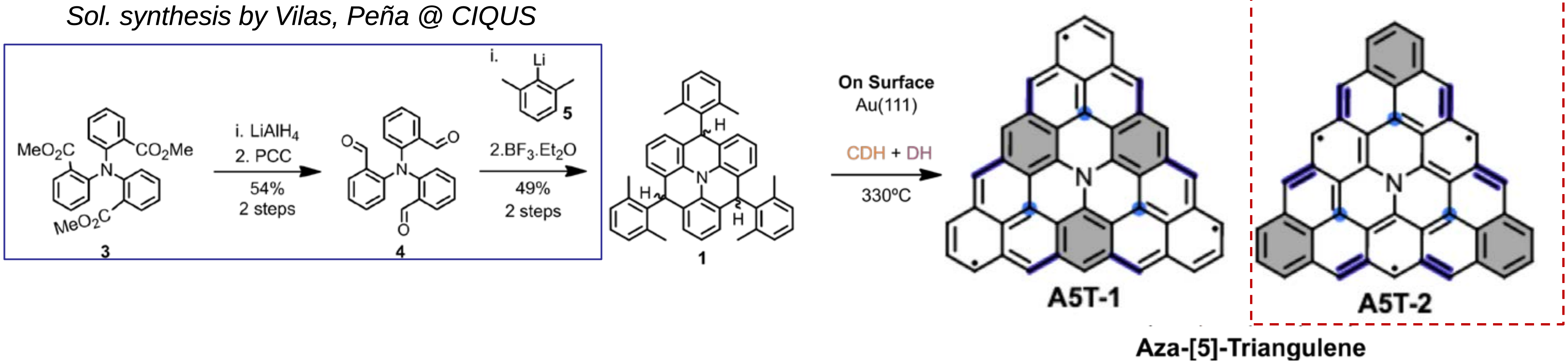
- The Aza group adds one electron

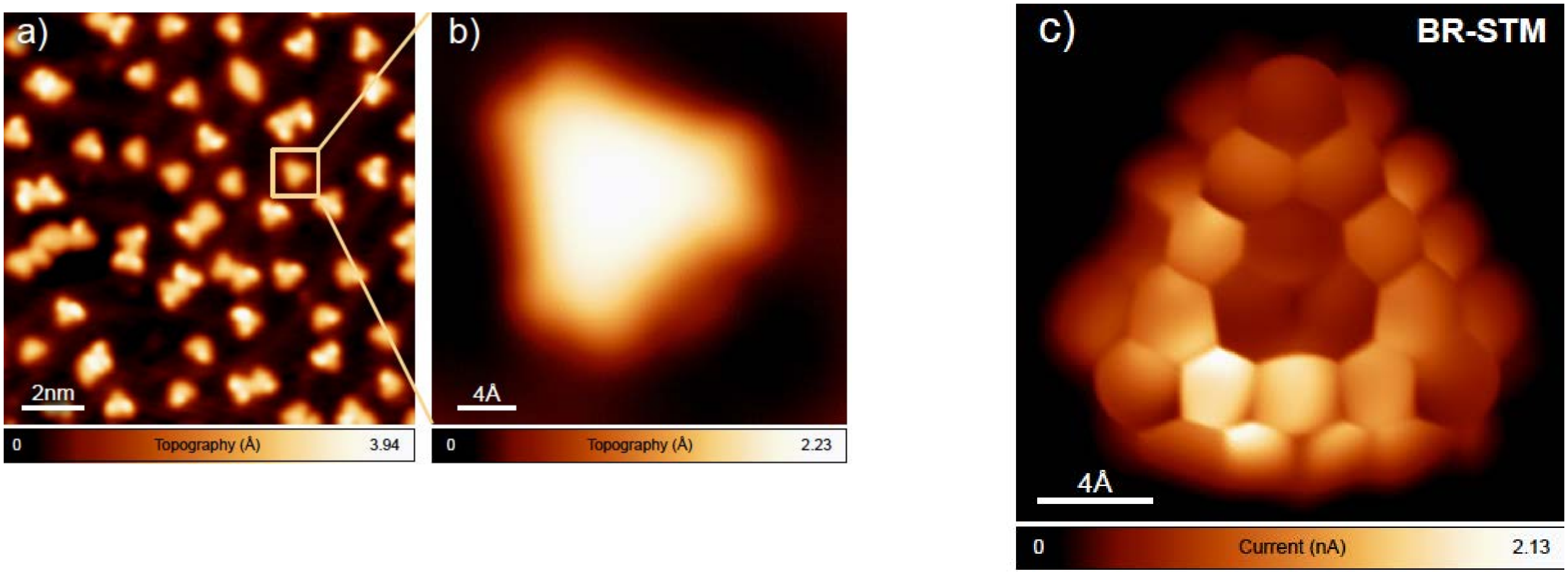
Wang….de Oteyza, JACS 144, 4522 (2022)

DFT results by Uriarte, Koval and Artacho @ nanoGUNE

Sinthesys of Aza-[5] Triangulene

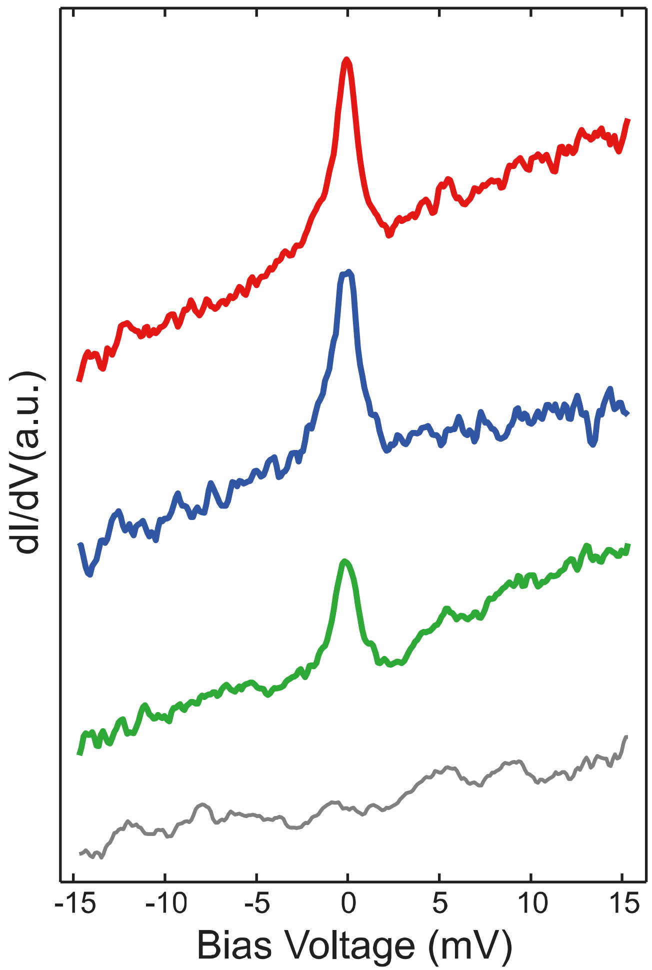
Sol. synthesis by Vilas, Peña @ CIQUS

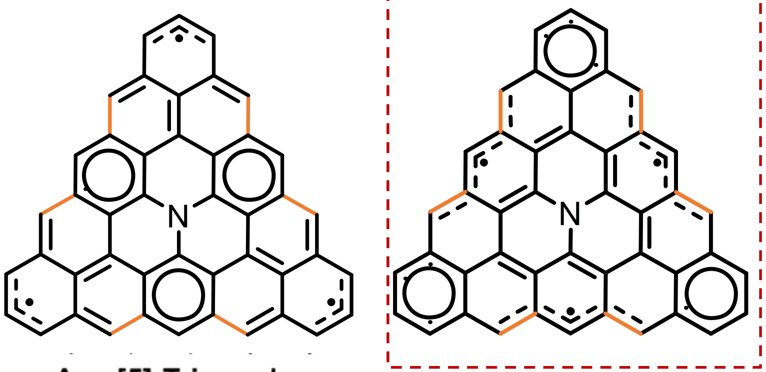




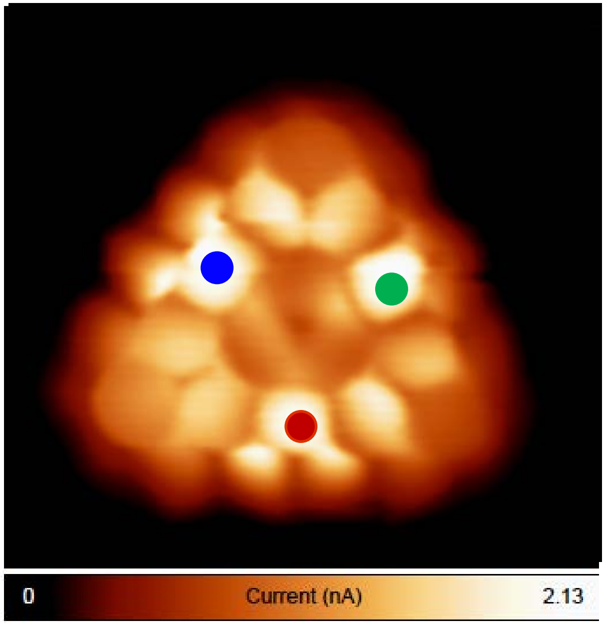
Magnetic state of Aza-[5] Triangulene

1 K @ JT-Specs





Aza-[5]-Triangulene



Magnetic state of Aza-[5] Triangulene

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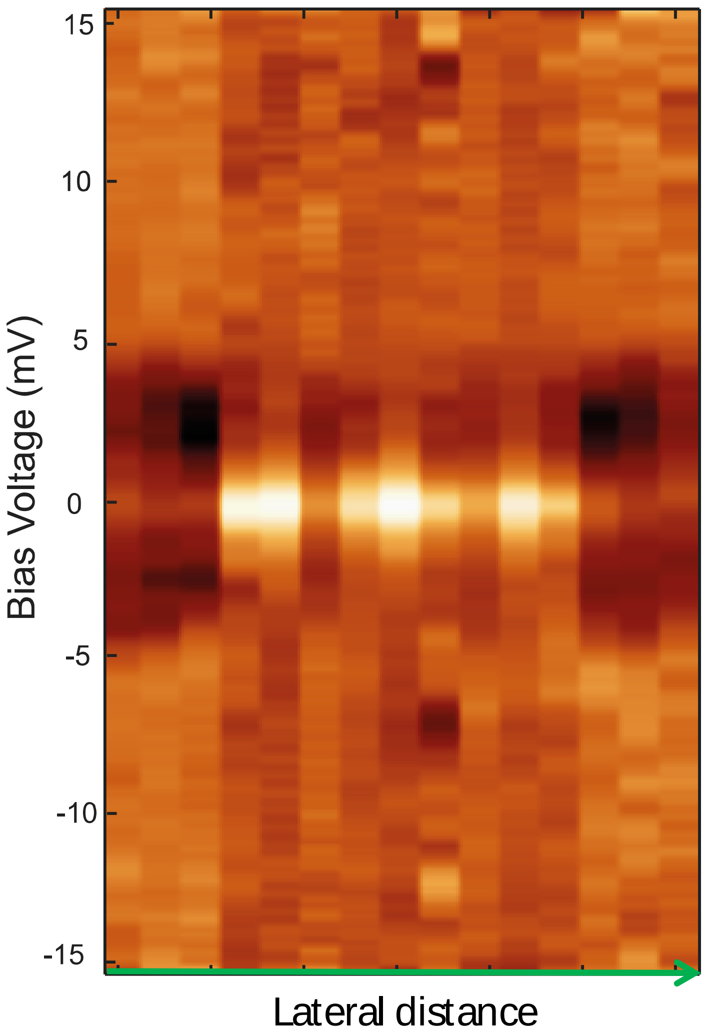
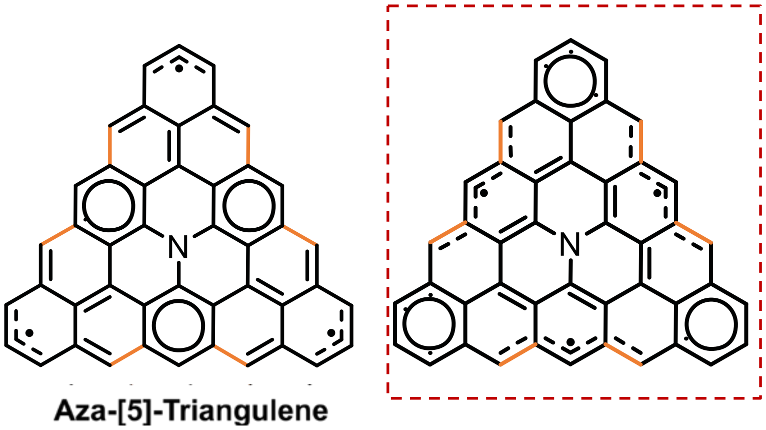
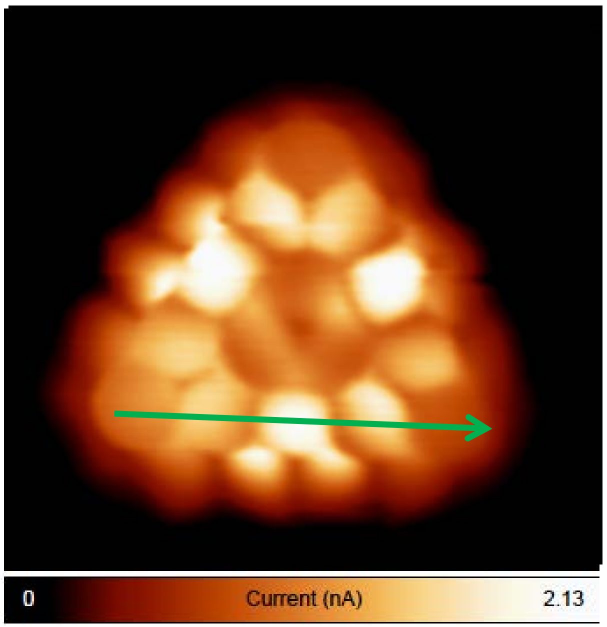
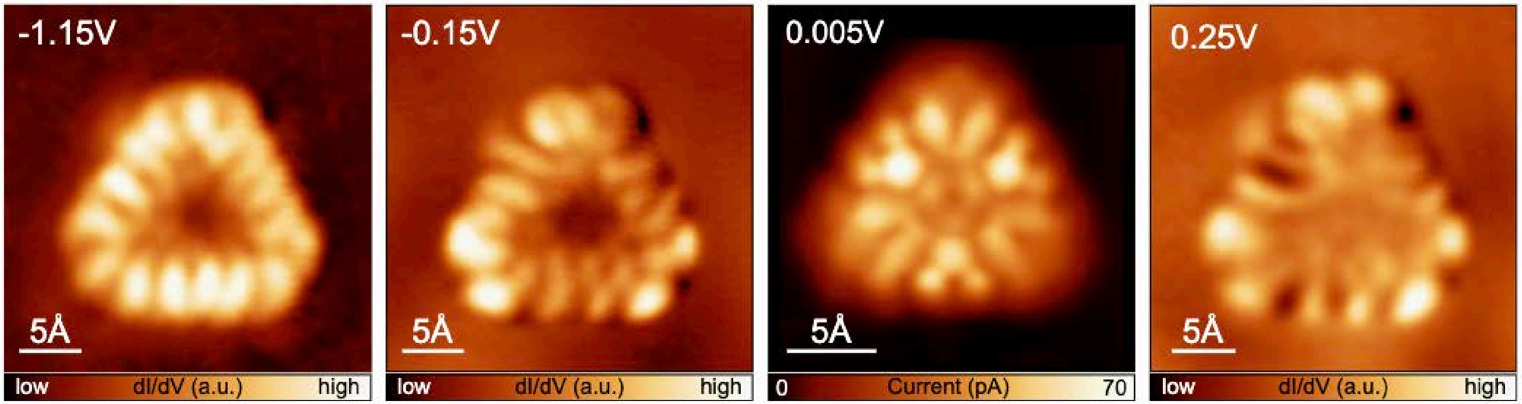
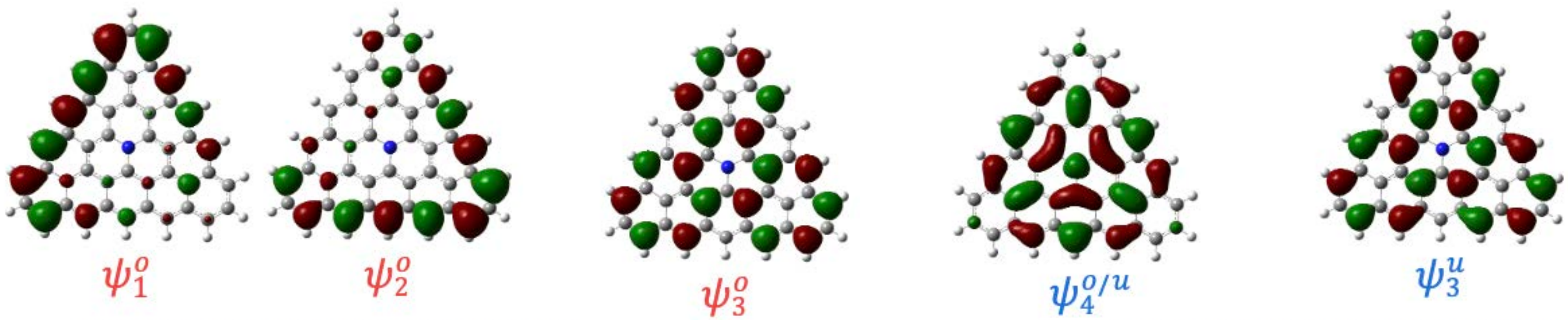


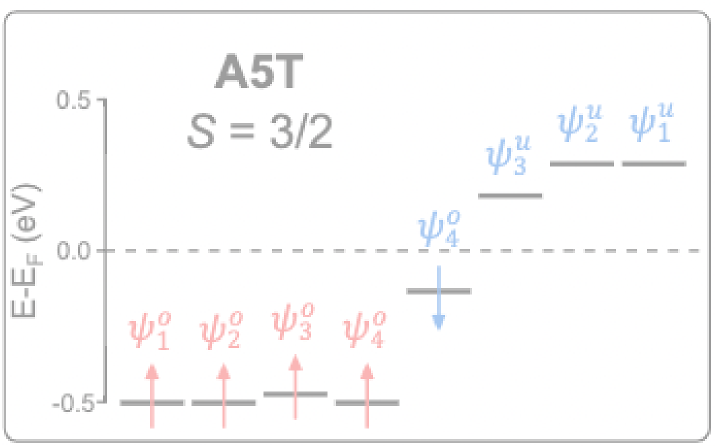




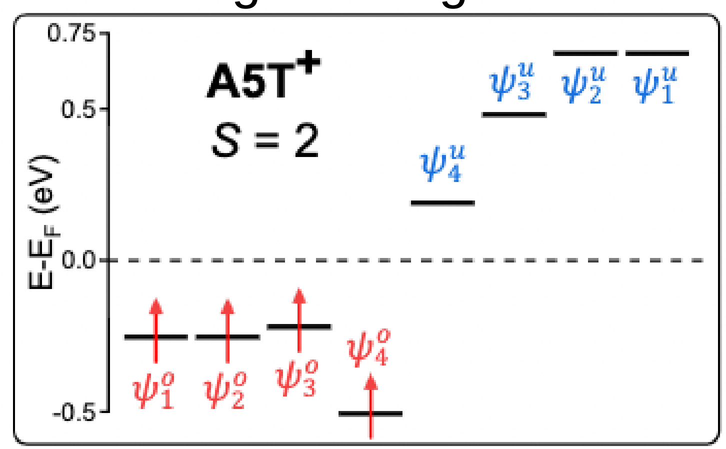
Orbital imaging



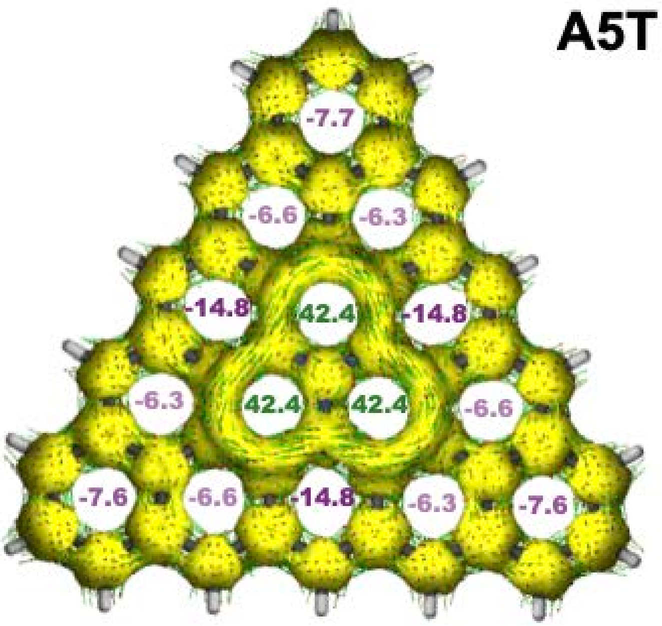




Charged triangulene

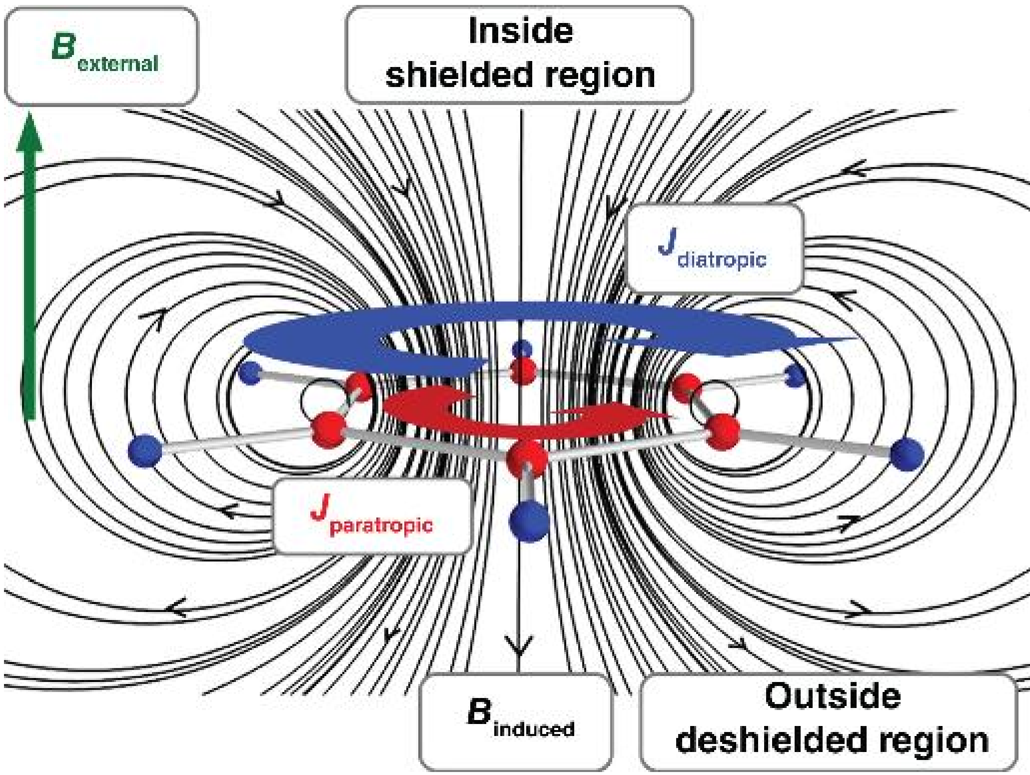


ACID and NICS simulations



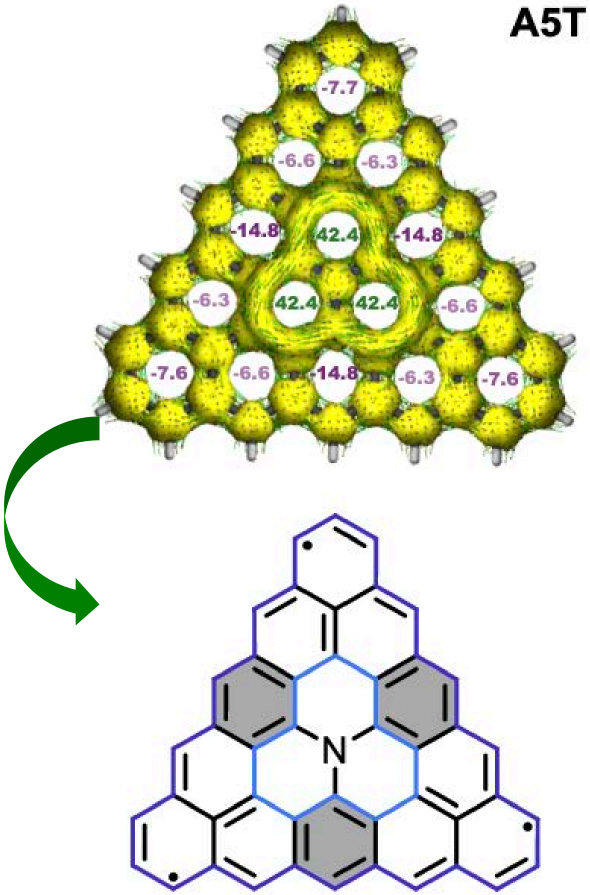
Anisotropic Current Induced Density

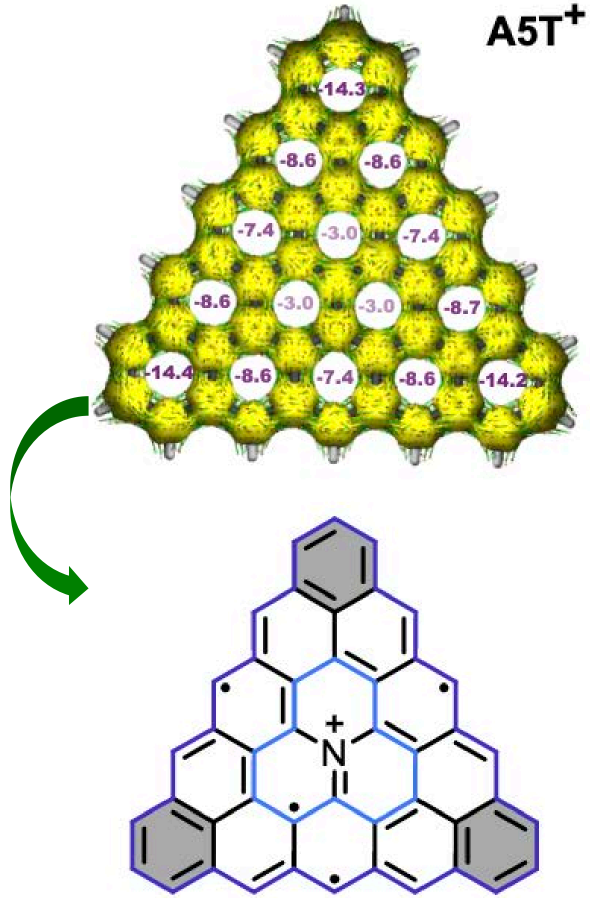
Nuclear Induced Chemical Shifts

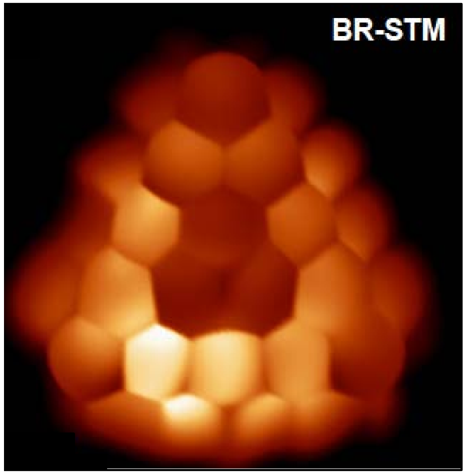


- ❑ Aza-group makes A5T antiaromatic at the center
- ❑ Radicals more at vertexes

ACID and NICS simulations







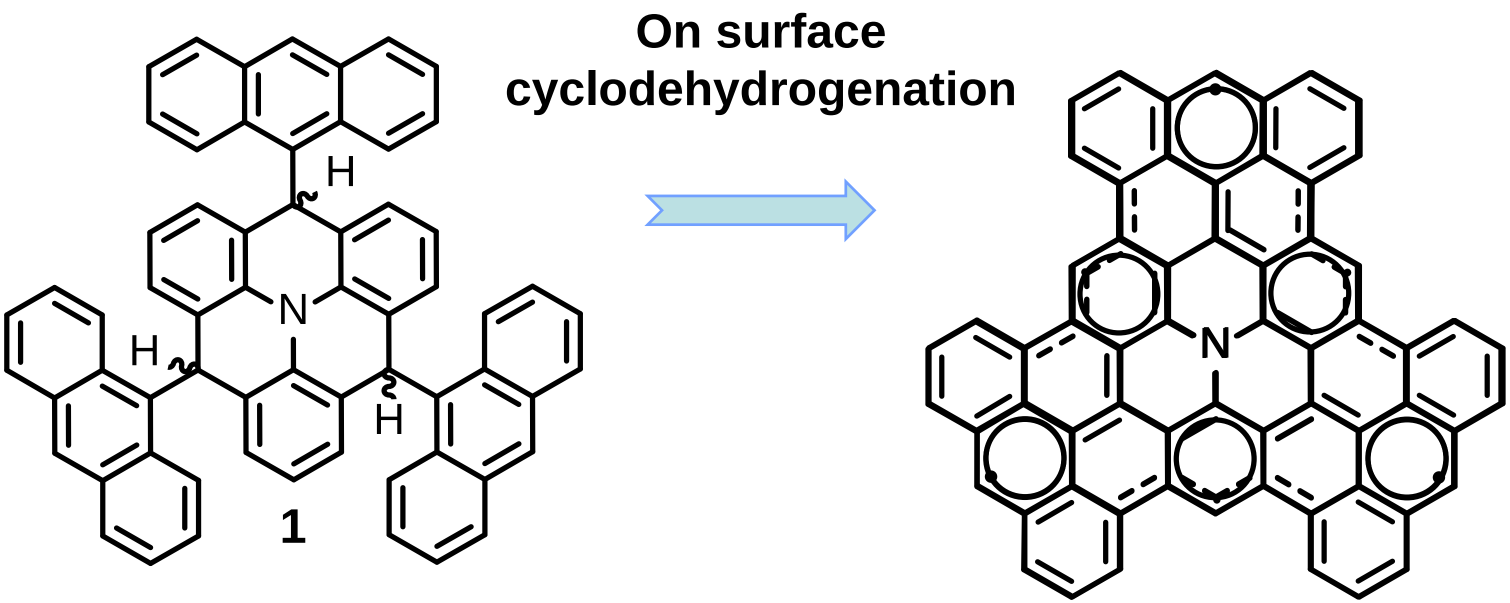
- ❑ Aza-group makes A5T antiaromatic at the center
- ❑ Radicals more at vertexes

- ❑ Cation recovers aromatic character
- ❑ Radicals more at edges

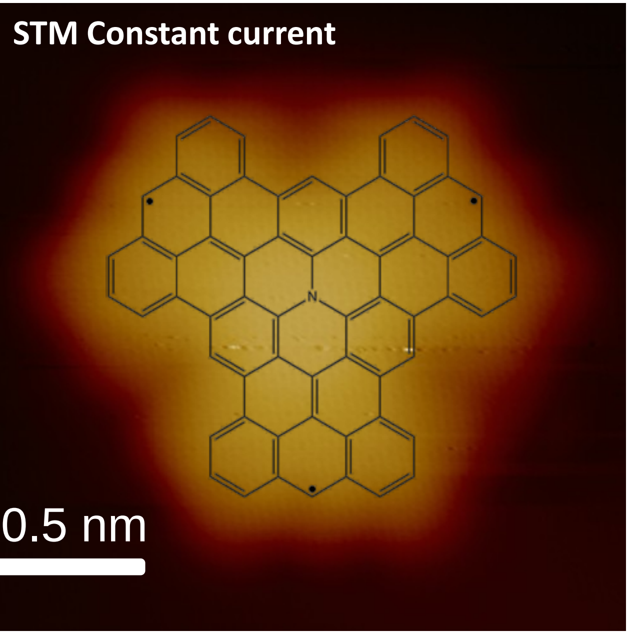
- ❑ **Aromatic pattern by STM reveals cationic state and S=2**

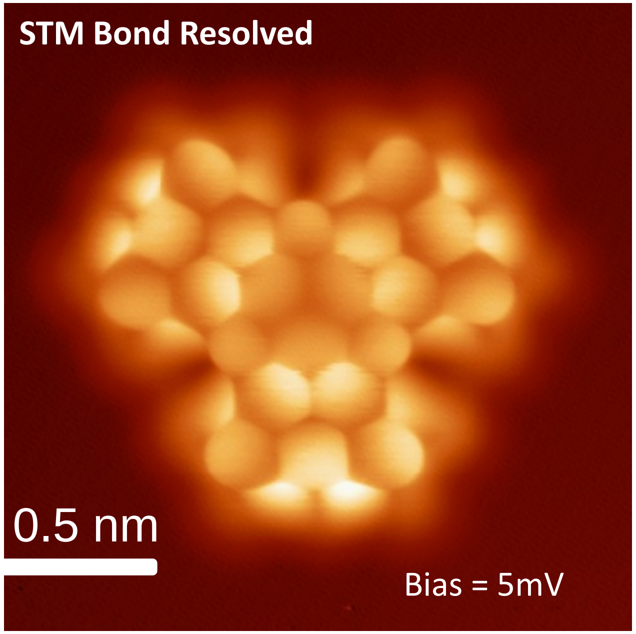
Synthesis and imaging of TATAT

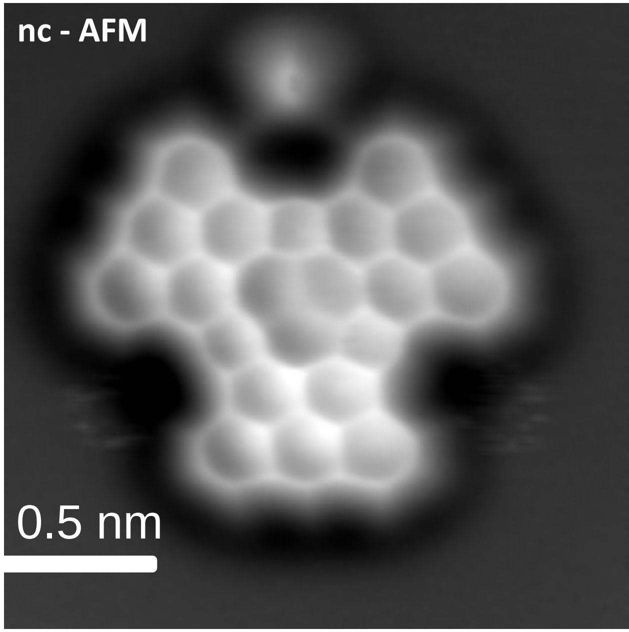
- TATAT - Tri-Anthracene [3] Aza Triangulene
  a larger aza-[3]triangulene



Synthesis and imaging of TATAT

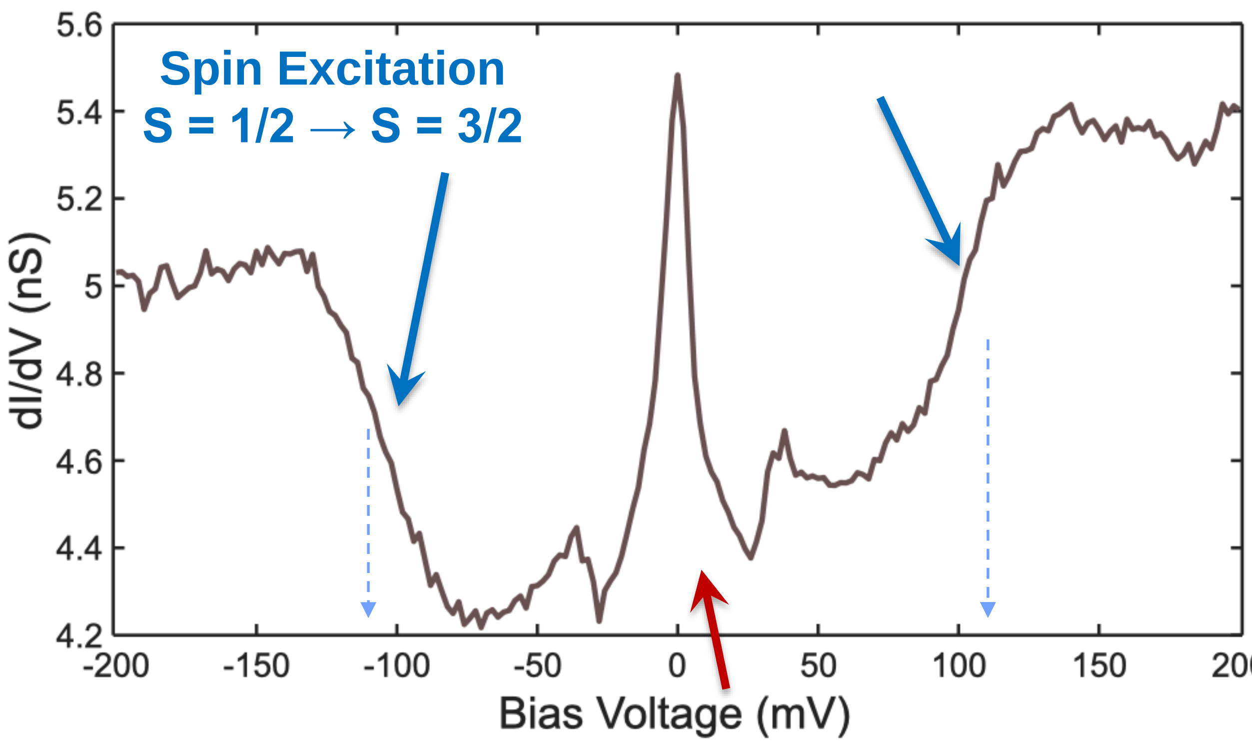


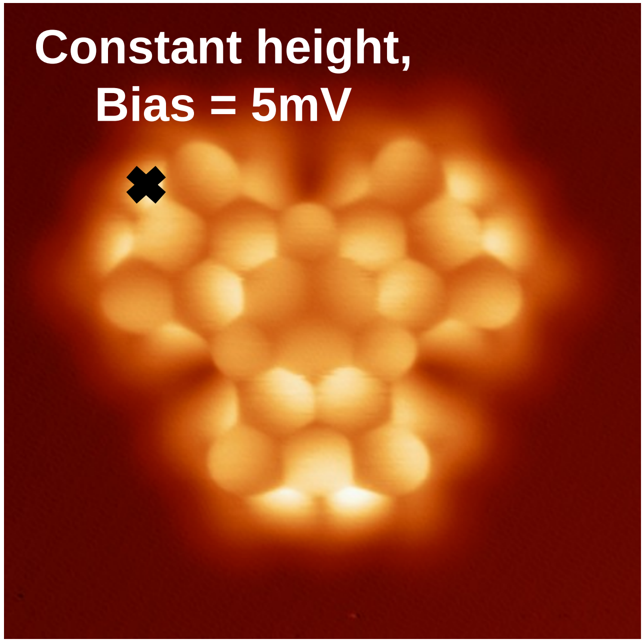




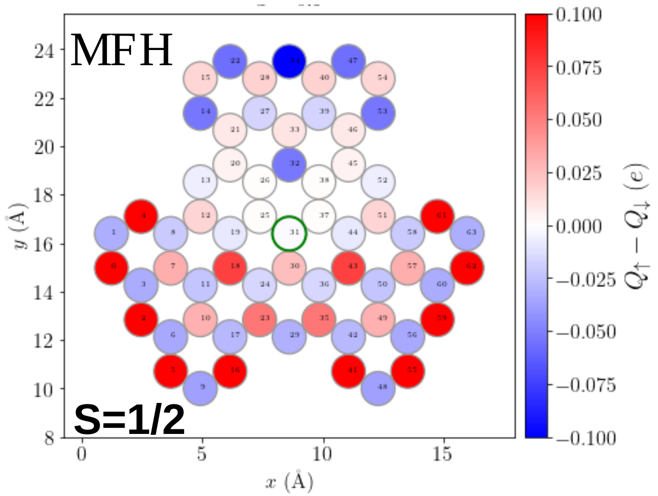
- ❑ Strong current cloud on the zigzags ends
- ❑ Bare bond contrast on the Aza region

Magnetic state of TATAT





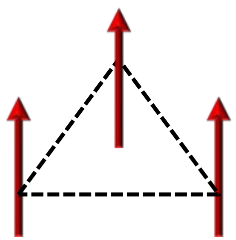
Kondo resonance
S = 1/2



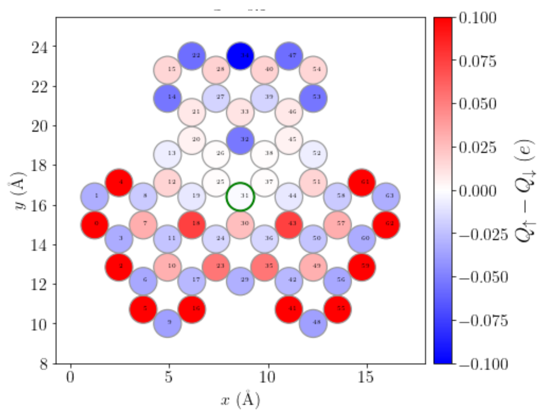
- ❑ Coexistence of S=1/2 Kondo screening with spin excitation
- ❑ Low energy excitation
- ❑ No Charge Transfer for this system!!!

Competing Hybridization and Coulomb

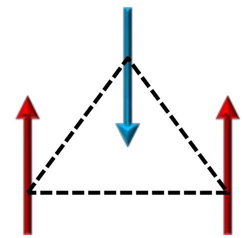
High spin excitation



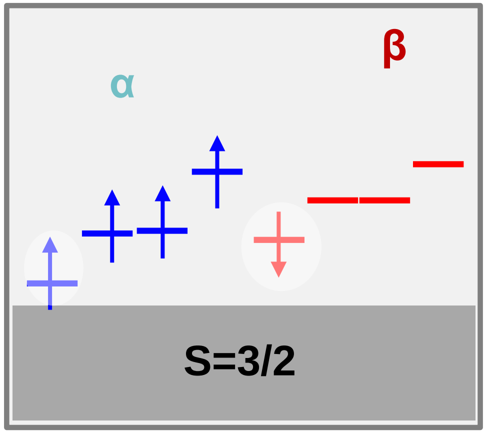
MFH simulations

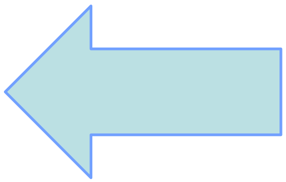


Magnetic frustration in ground state

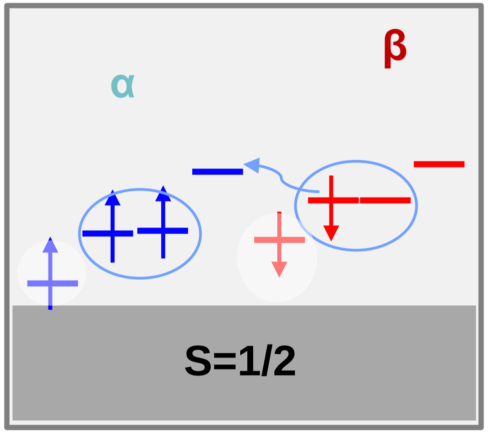


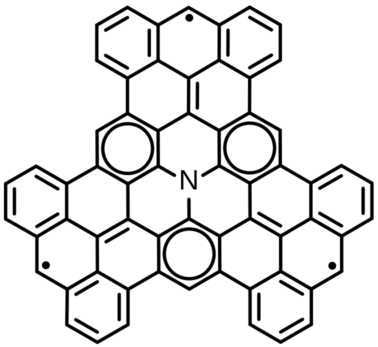
Spin excitation





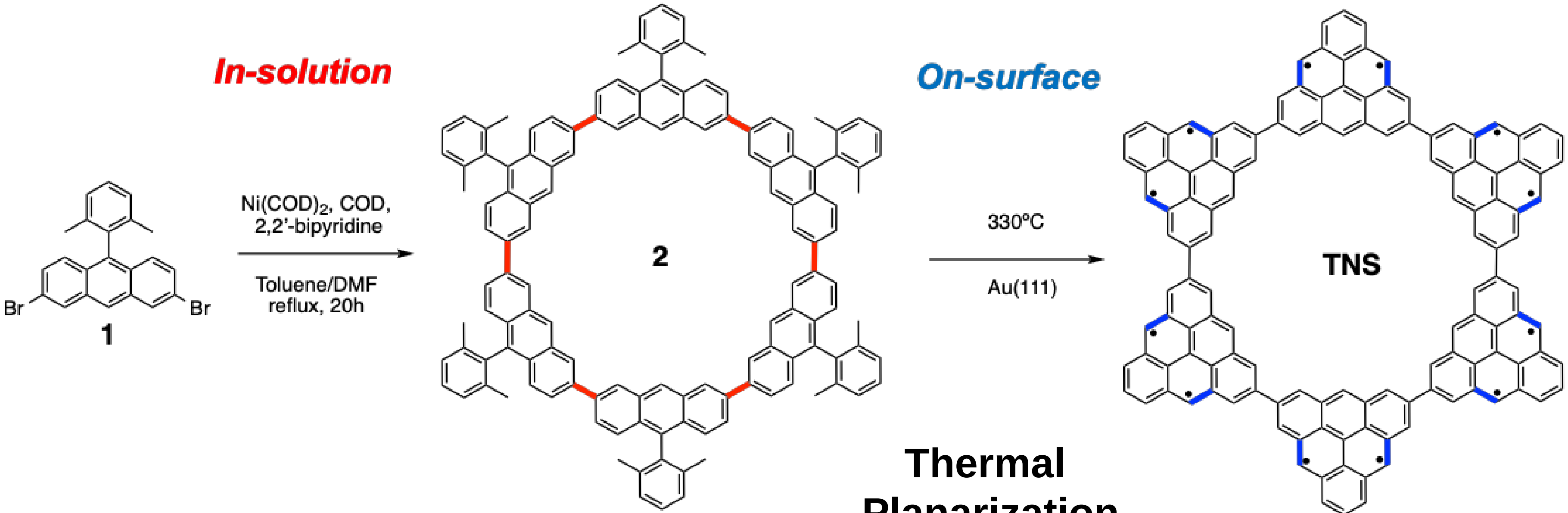
Low energy spin excitation





$\eta = 2$

Synthesis of triangulene-ring

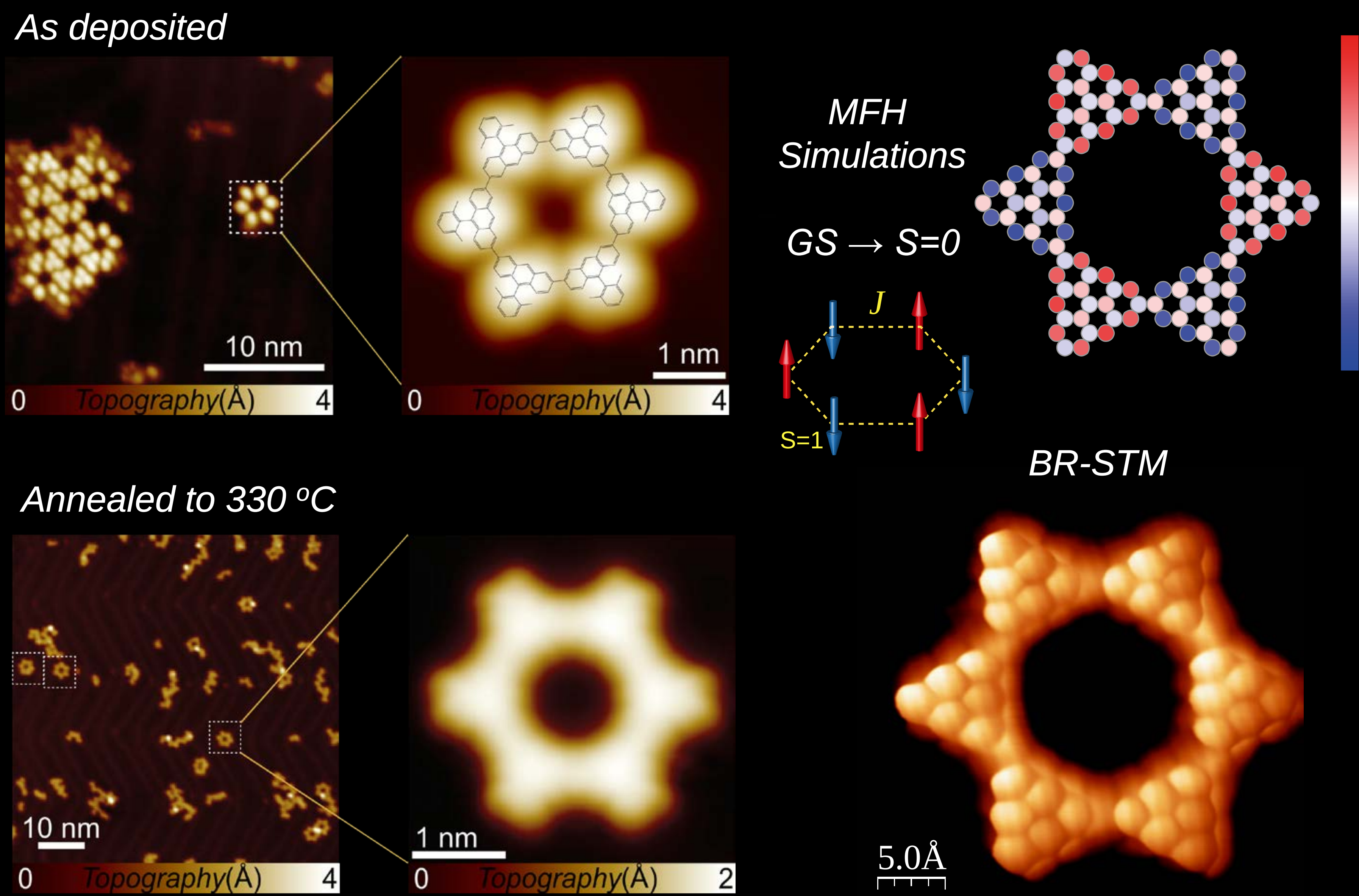


Triangulene-based NanoStar
12 unpaired electrons

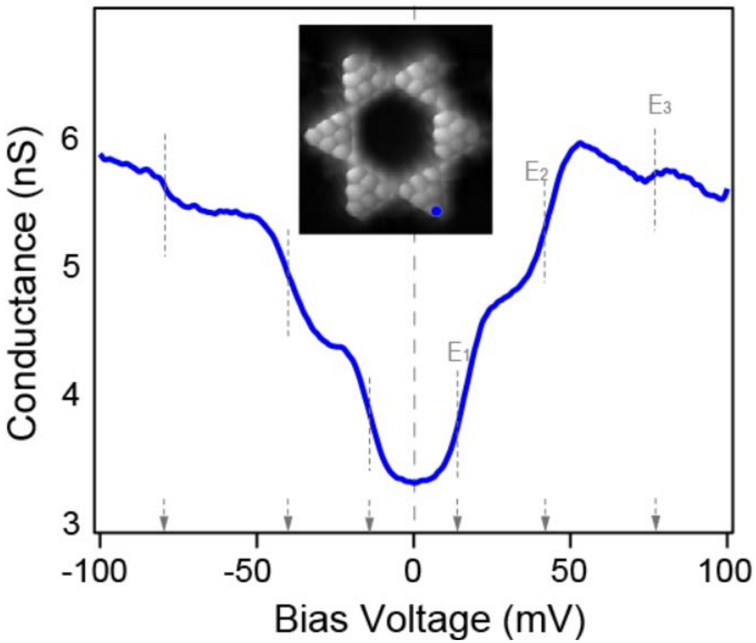
Synthesis by S. Castro & D. Peña (USC)

Hieulle et al. Ang. Chem. 60 (2021) 10.1002/anie.202108301

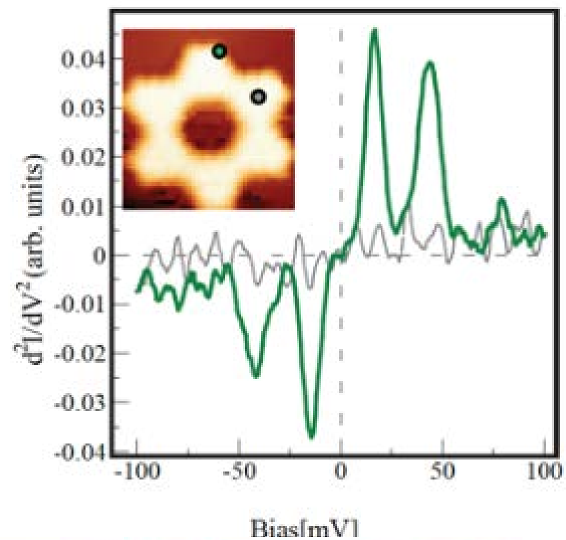
On-Surface Synthesis of Triangulene Star

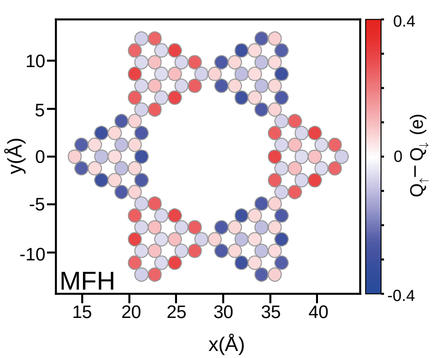


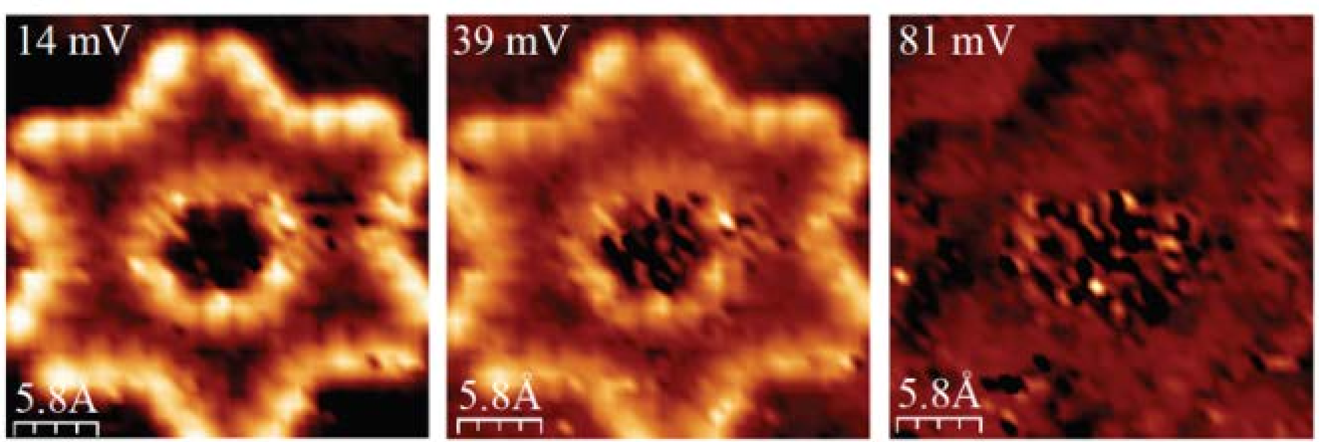
Collective spin excitations in a triangulene ring



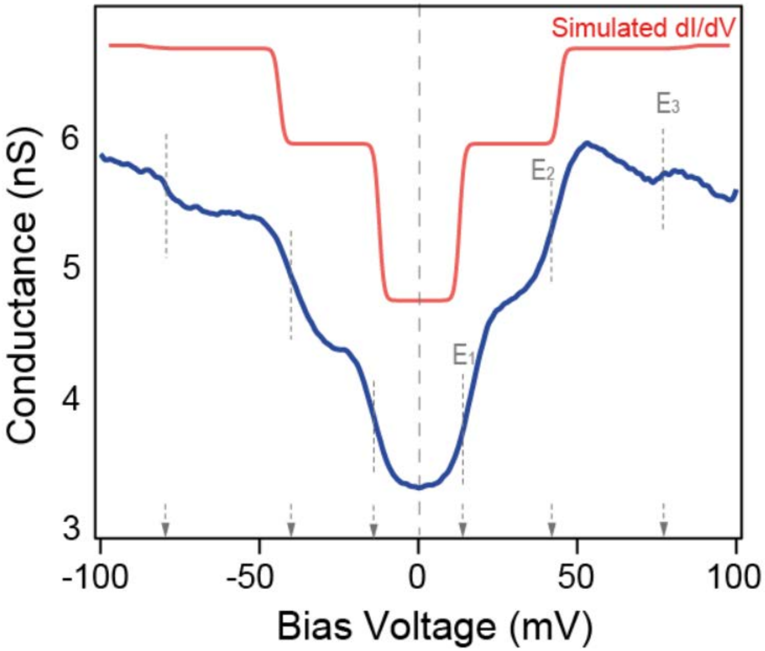
- Spin IETS finds three inelastic steps on the triangulenes

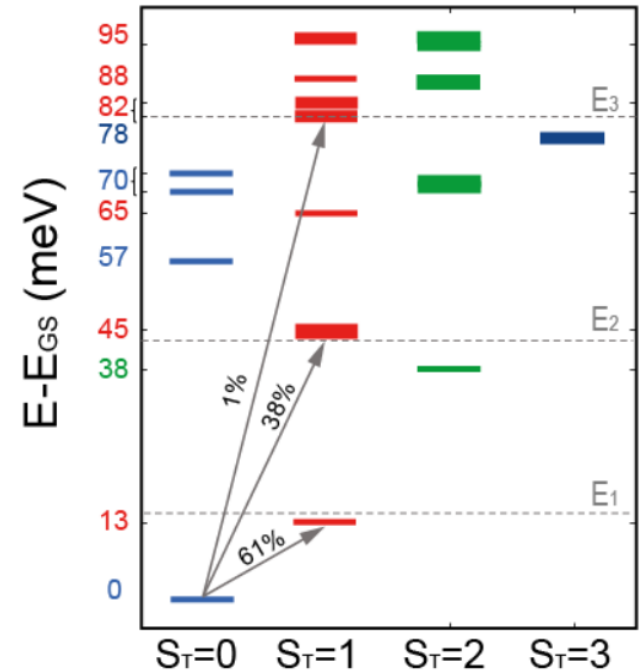






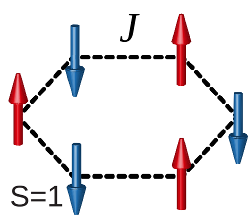
Collective spin excitations in a triangulene ring

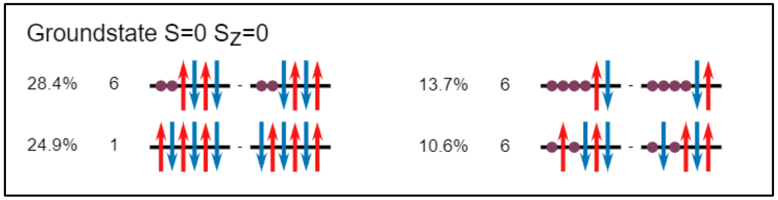




- Heisenberg Hamiltonian for a ring of 6 S=1 Spins

$$H = \sum_{i=1}^{6} J\, S_i \cdot S_{i+1}$$





Superposition of six
$S = 1, Sz = \pm 1, 0,$

- Spin excitations, from S=0 to S=6

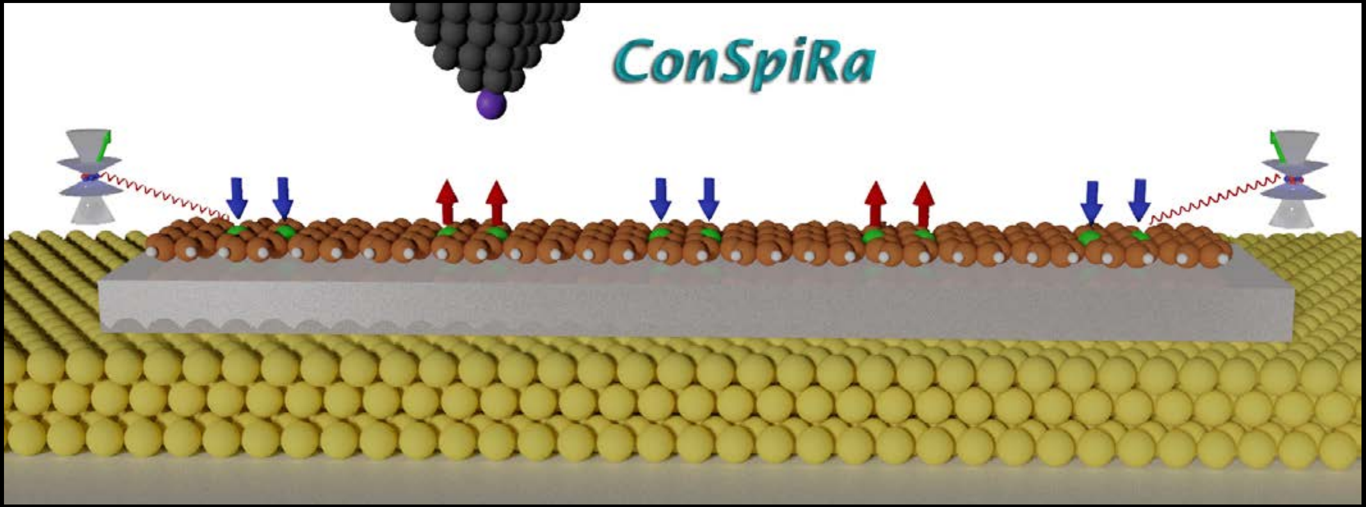
$$\left|M_{mn}^{(i)}\right|^2 = \frac{1}{2}\left|\left\langle m\left|S_+^{(i)}\right|n\right\rangle\right|^2 + \frac{1}{2}\left|\langle m|S_-^{(i)}|n\rangle\right|^2 + \frac{1}{2}\left|\left\langle m\left|S_z^{(i)}\right|n\right\rangle\right|^2$$

M. Ternes (2015) New J. Phys. 17

Summary

- *Triangulenes get magnetic*
- *High Spin detected through their weak Kondo resonance*
- *Charge transfer to/from substrate affects the spin*
- *Doublet – Quadruplet transition detected*
- *Spin collective excitations in a triangulene ring*

Outlook:
Graphene spins in quantum states



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