Emerging Electronic and Magnetic Properties due to Molecule-Metal Electronic Coupling in Self-Assembly Two-Dimensional Organic Systems on Metal Surfaces

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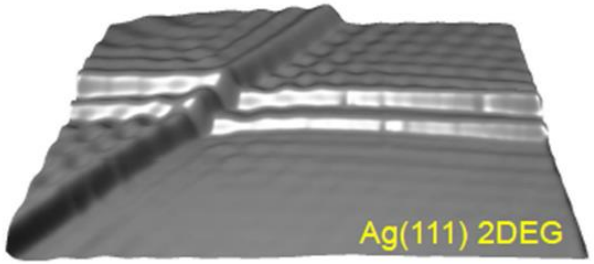
Content

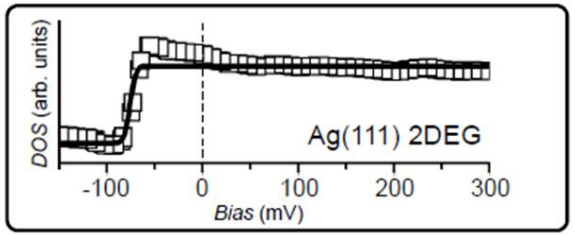
Part 1 Introduction

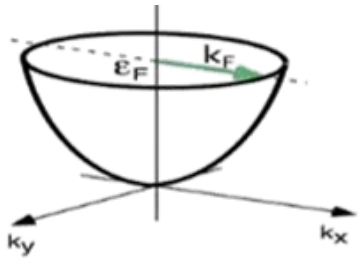
- Electronic and magnetic properties driven by molecule-metal electronic coupling
- Band structure of Quantum dots(QDs) array in supramolecular structure
- Kondo effect in Supramolecular structure built by organic radicals
- Experimental techniques

Electronic and magnetic properties driven by molecule-metal electronic coupling

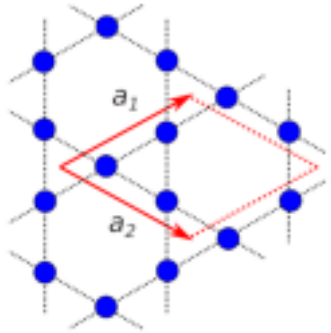
Surface state on metal surface

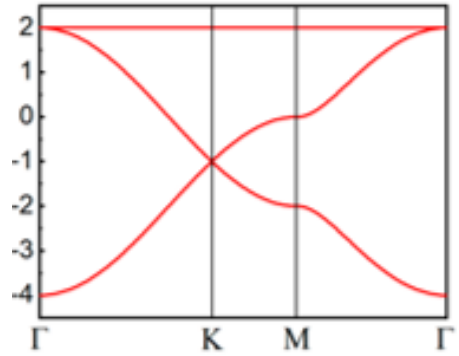




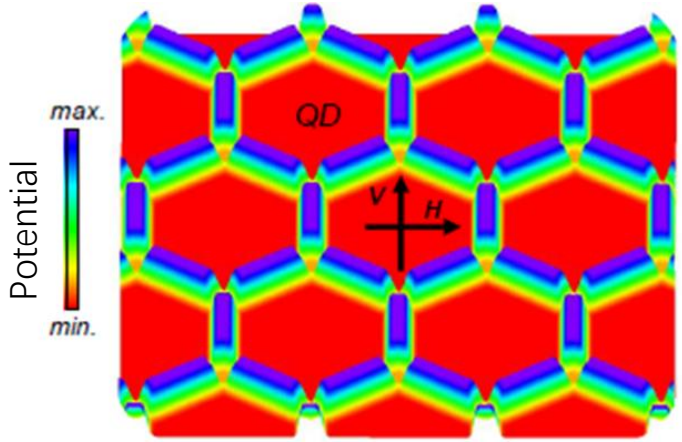


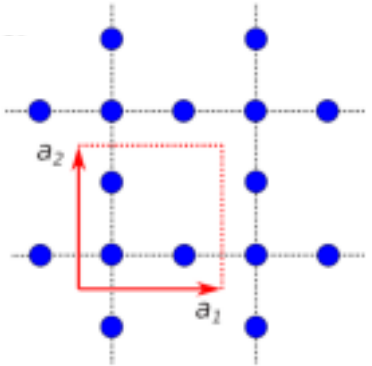
Band structure

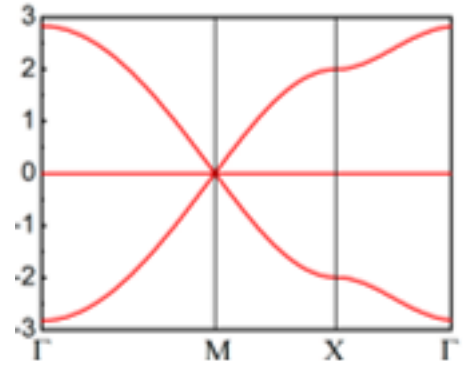




QDs realized by surface state confinement





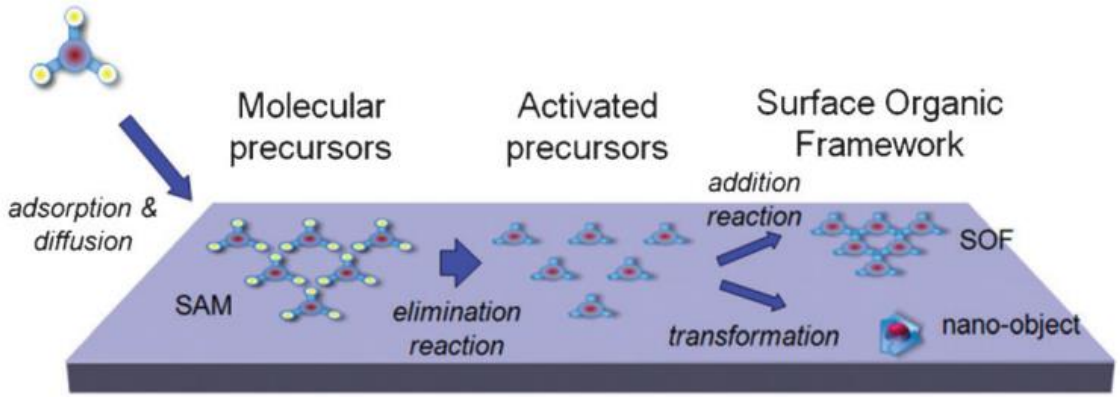


Adv. phys. x. 4, 1(2019)

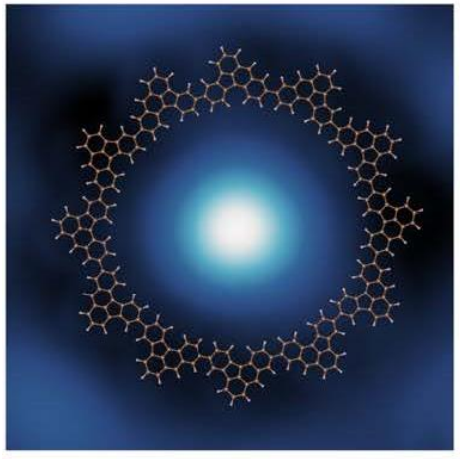
Nat Nanotechnol 2, 99 (2007)

Electronic and magnetic properties driven by molecule-metal electronic coupling

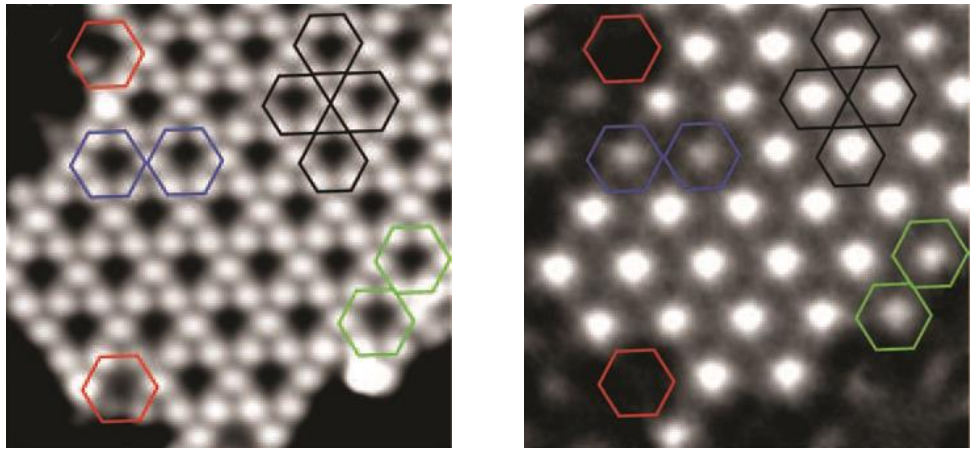
- 1 Supramolecular structure

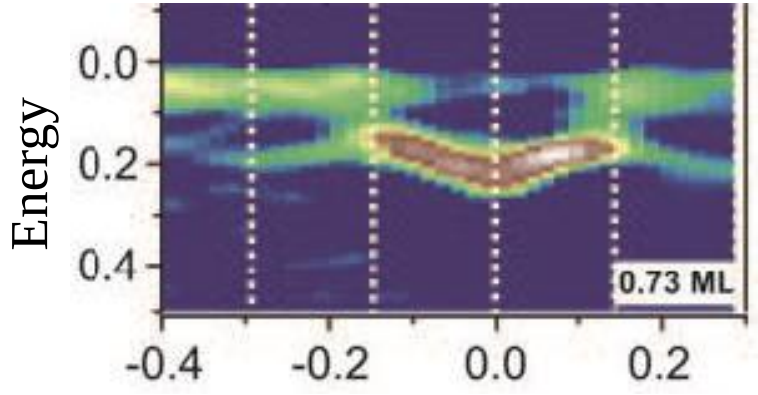


- 2 Surface state confinement



- 3 Electronic band structure realized by QDs lattice





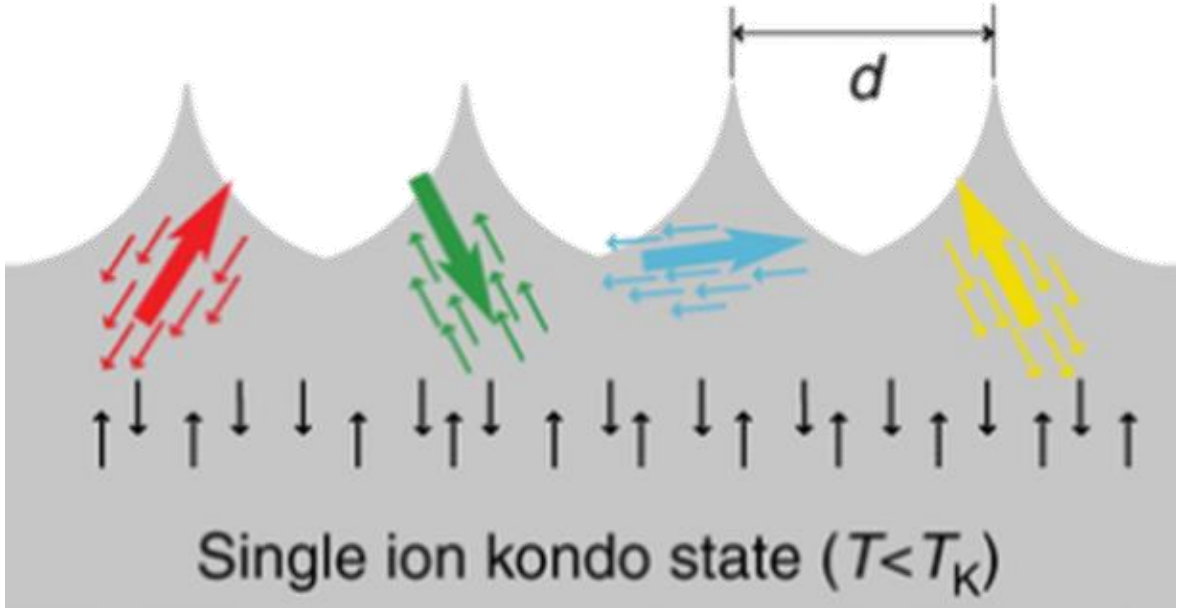
Science, 325(5938), 300-303. (2009)

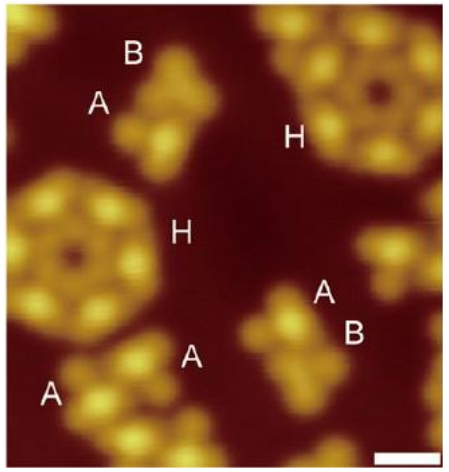
Nat Commun, vol. 12, no. 1, p. 5895 (2021)

Chem. Soc. Rev. 40, 4578-4590 (2011)

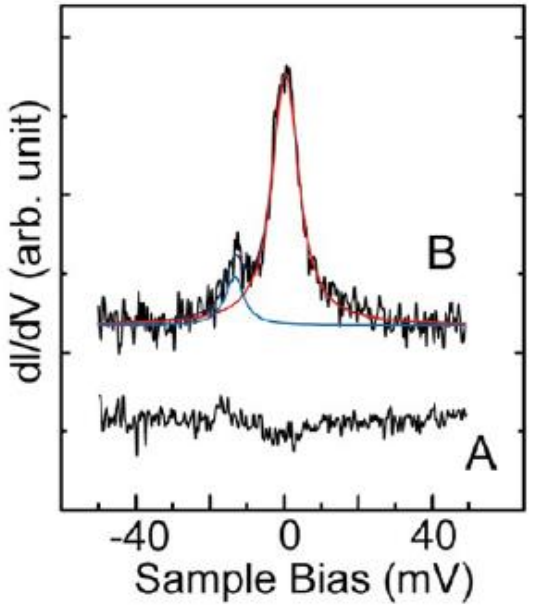
Electronic and magnetic properties driven by molecule-metal electronic coupling

Kondo effect





- Organic radical



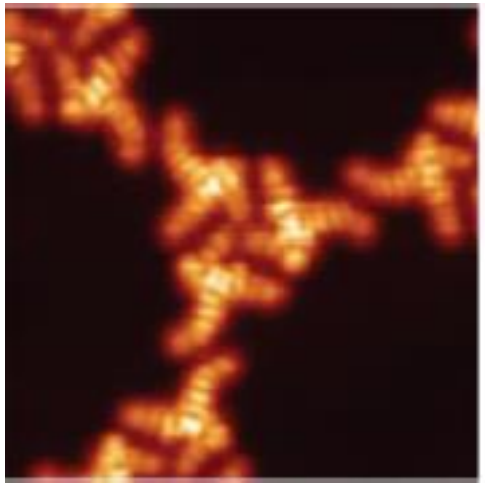
- Experimental detection of the Kondo effect

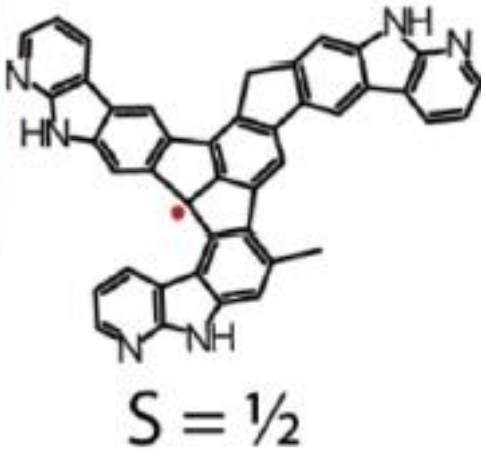
Nat Commun 10, 2211 (2019)

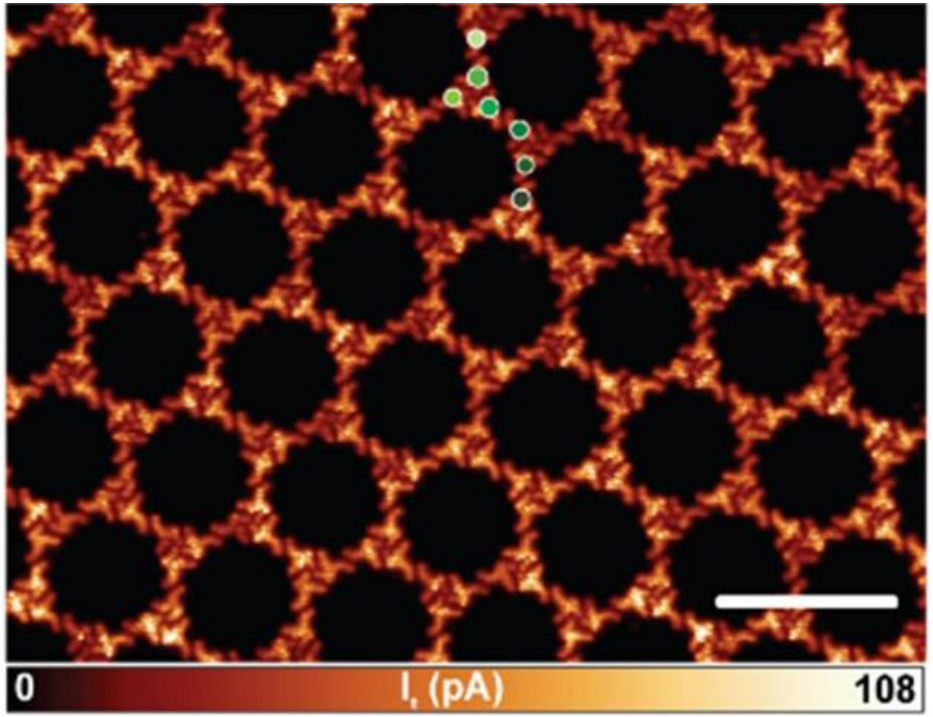
J. Am. Chem. Soc., 135(2), 651-658 (2013)

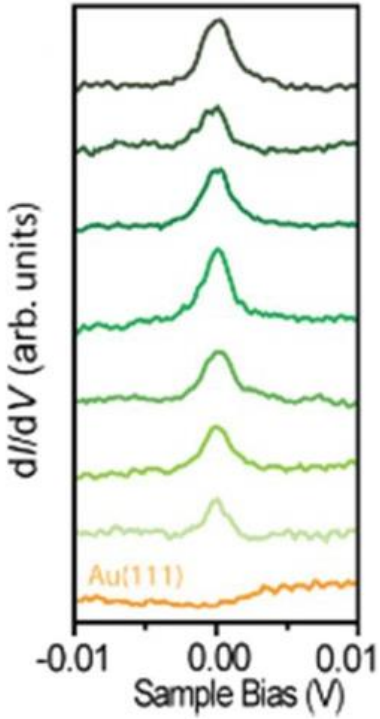
Electronic and magnetic properties driven by molecule-metal electronic coupling

- Supramolecular structure built by organic radicals
- The nano-system of 2D supramolecular structures is also a good platform to realize organic radical lattice.



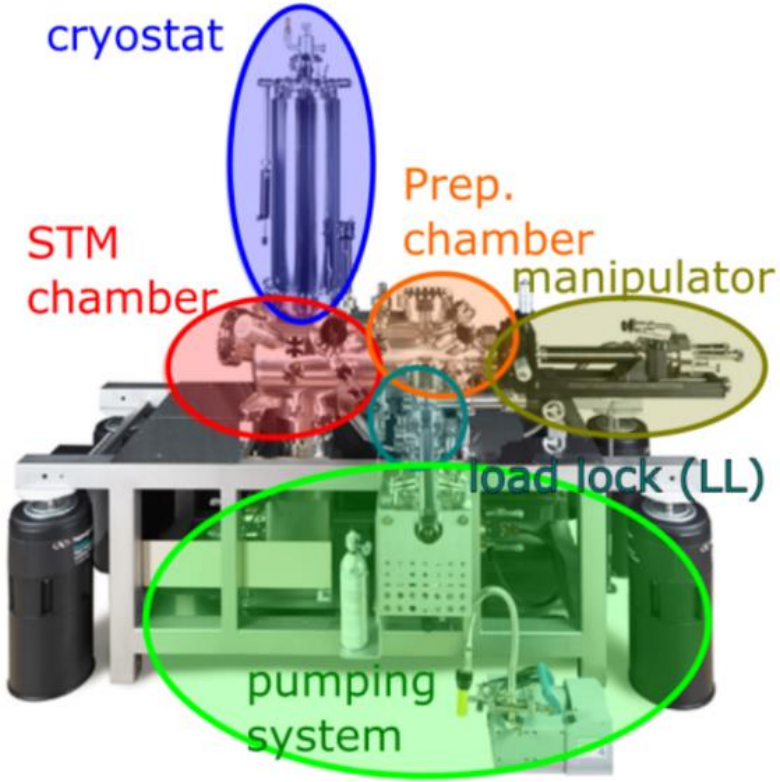


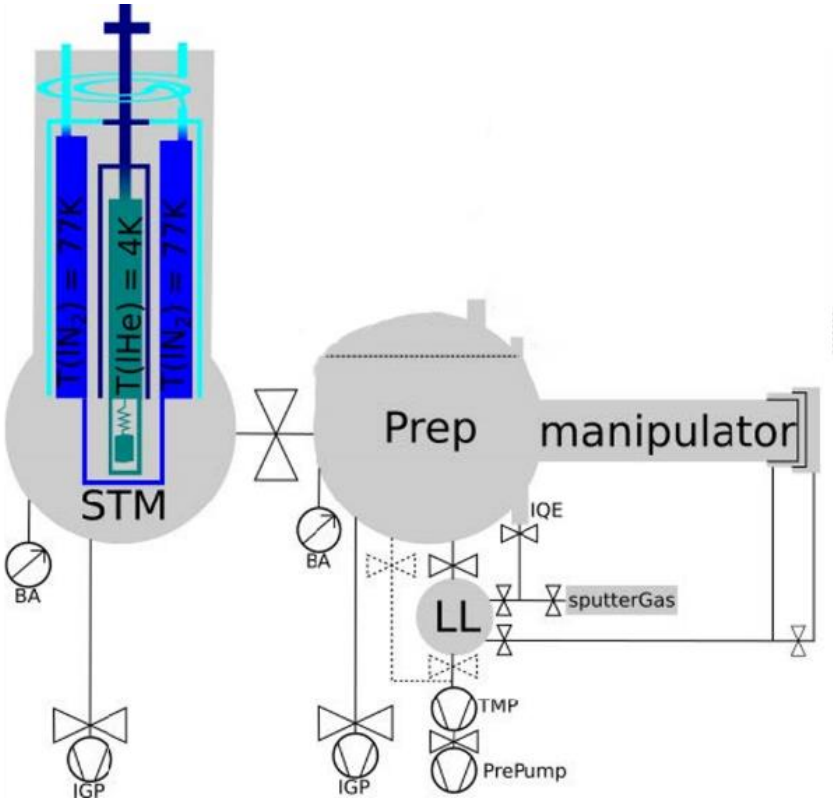


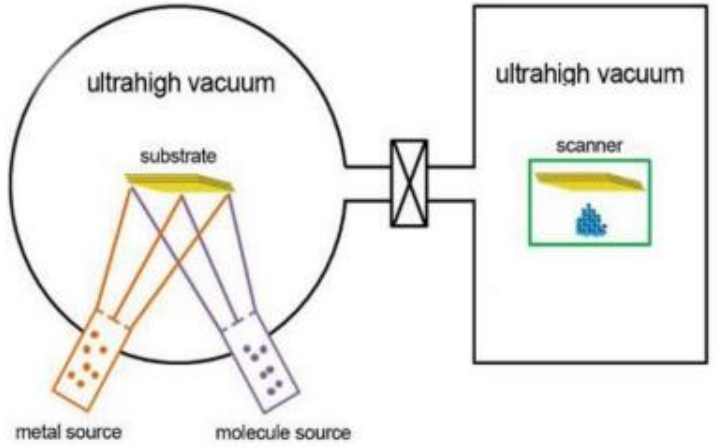


J Am Chem Soc, 146(5), 3531-3538 (2024)

Experimental techniques







- Ultra-High Vacuum

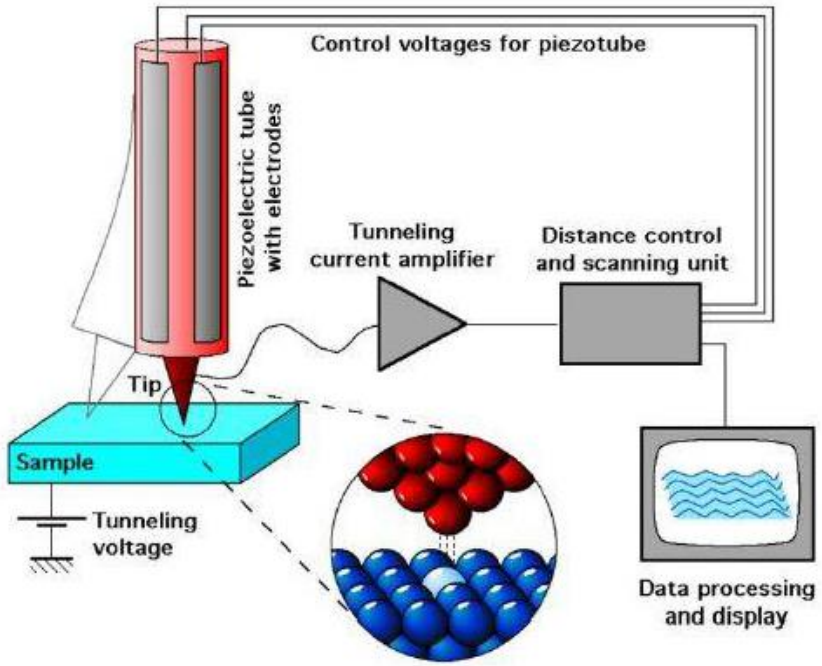
  P ~ 1E-10 mbar

- Low temperature

  T = 5.3K

- Various chambers

Experimental techniques



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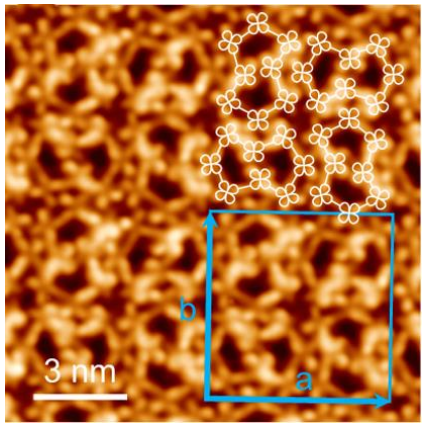
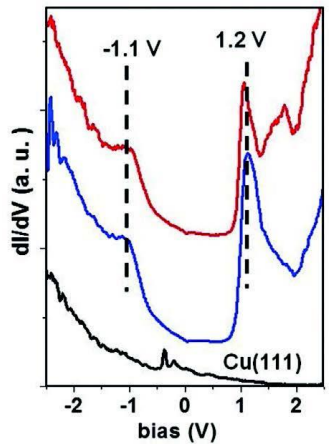
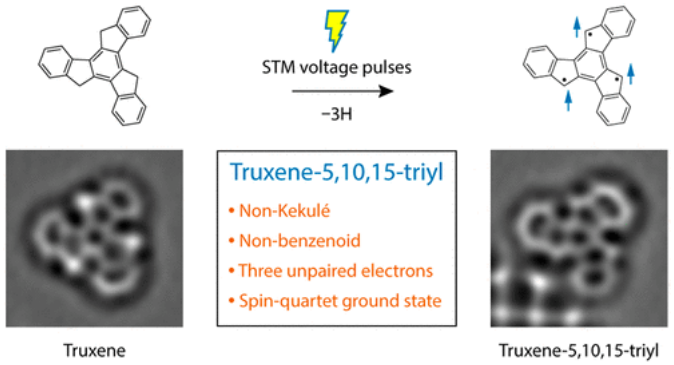


STS



Tip manipulation



Scanning Tunneling Microscopy

$$I \propto \int_0^{eV} \rho_s(E) e^{-2w\sqrt{2(\Phi - E) + eV}}\, dE$$

Prog Surf Sci 92, 83-115 (2017)

ACS nano, vol. 16, no. 2, pp. 3264-3271 (2022)

Commun. Chem., vol. 5, no. 1, p. 174 (2022)

Angew. Chem., vol. 132, no. 7, pp. 2691-2695 (2020)

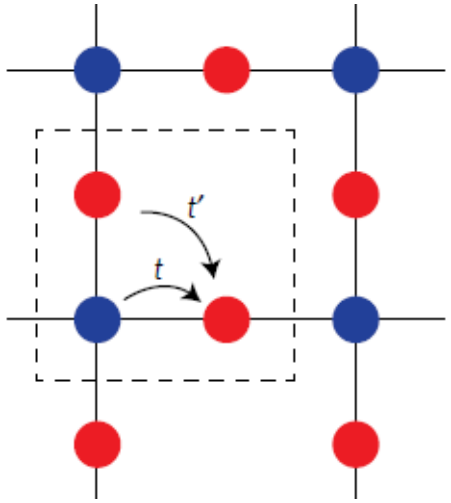
Part 2 Isolated flat band in artificially designed Lieb lattice based on macrocycle supramolecular crystal

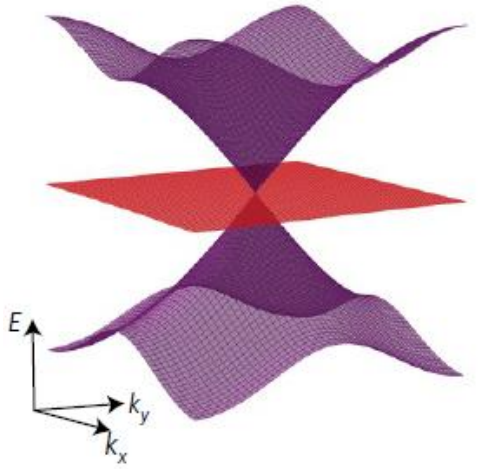
- Design of a Lieb lattice exhibiting an isolated flat band
- Self-assembled synthesis of the macrocycle array confining surface state
- Electronic properties of the QD array

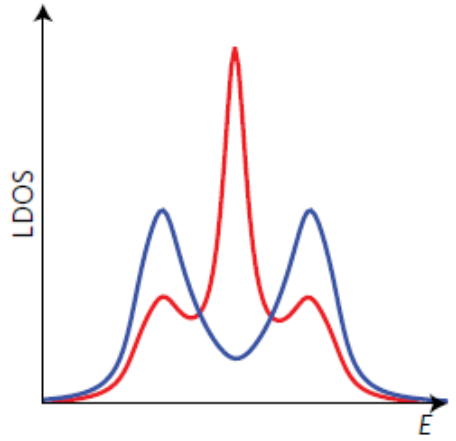
Background: Lieb Lattice

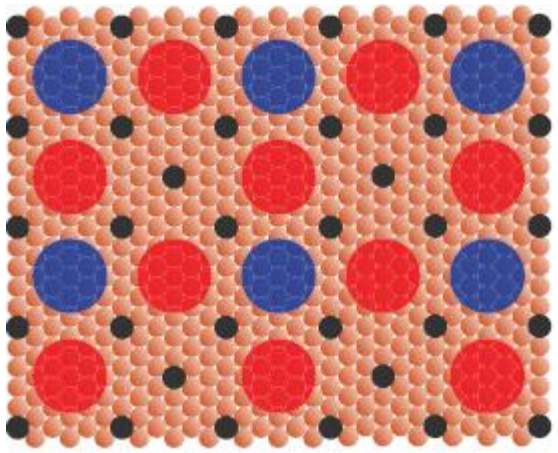
Flat band:

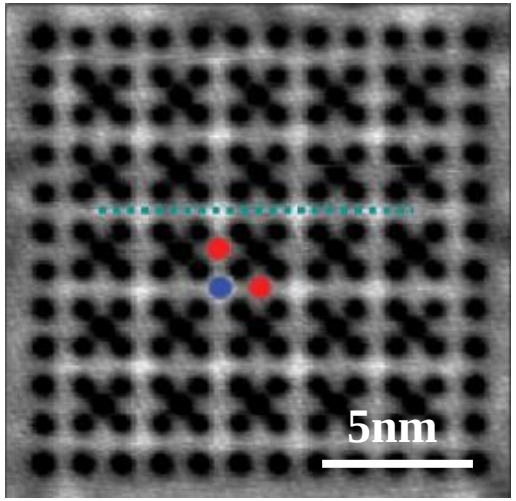
- Magnetic order
- Fractional quantum (spin) Hall effect
- Quantum anomalous Hall effect
- Raise the critical temperature of superconductors

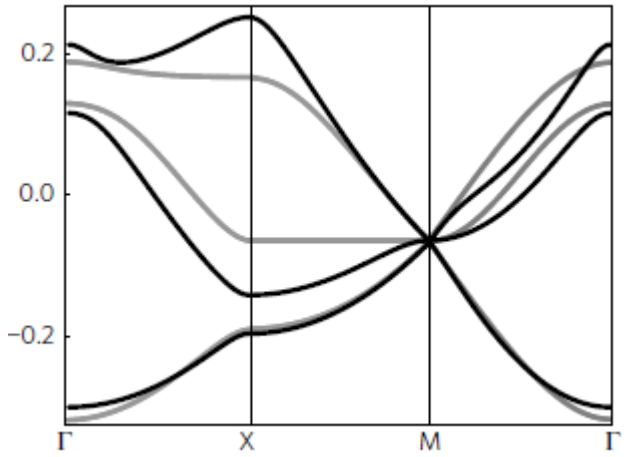


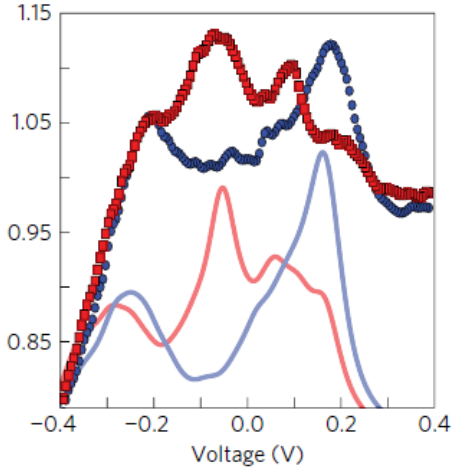








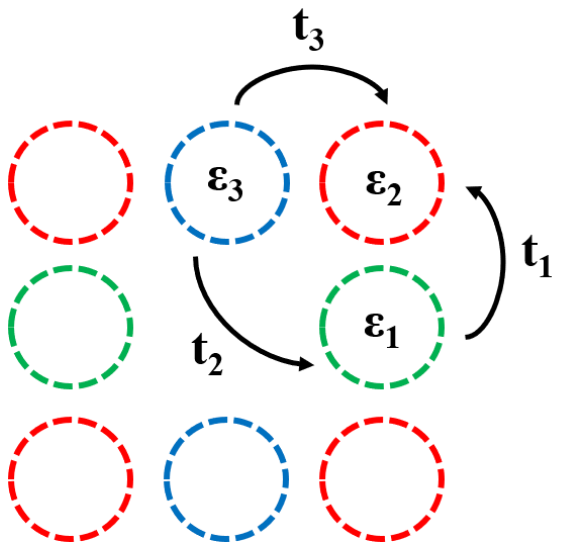




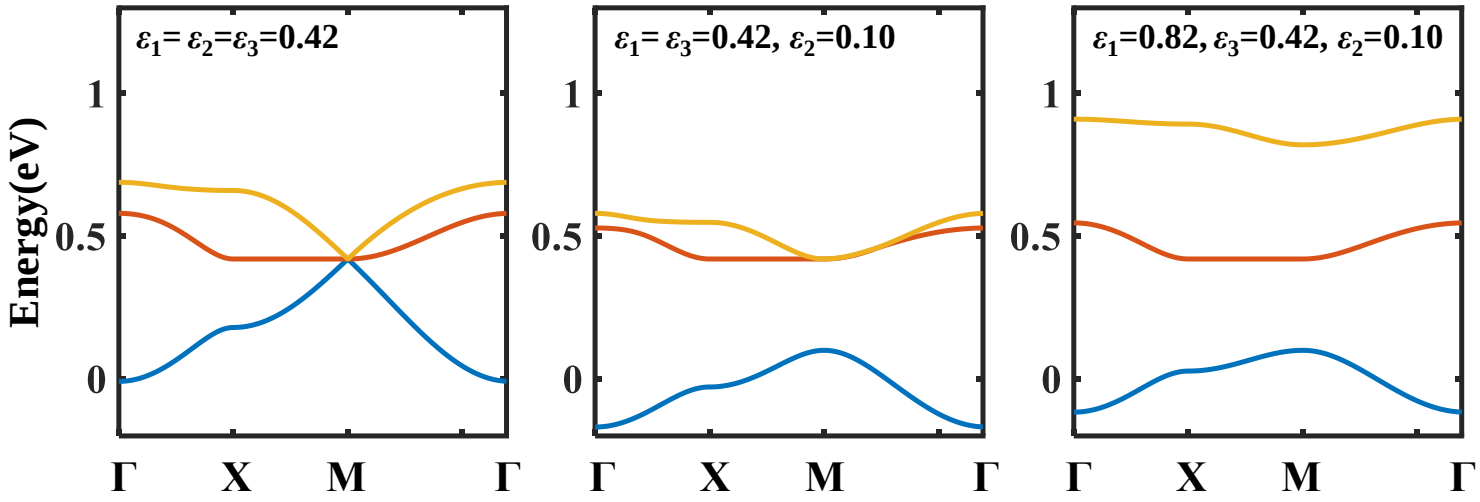
Nat Phys 13, 672-676 (2017)

Design of a Lieb lattice exhibiting an isolated flat band

Tight-binding model

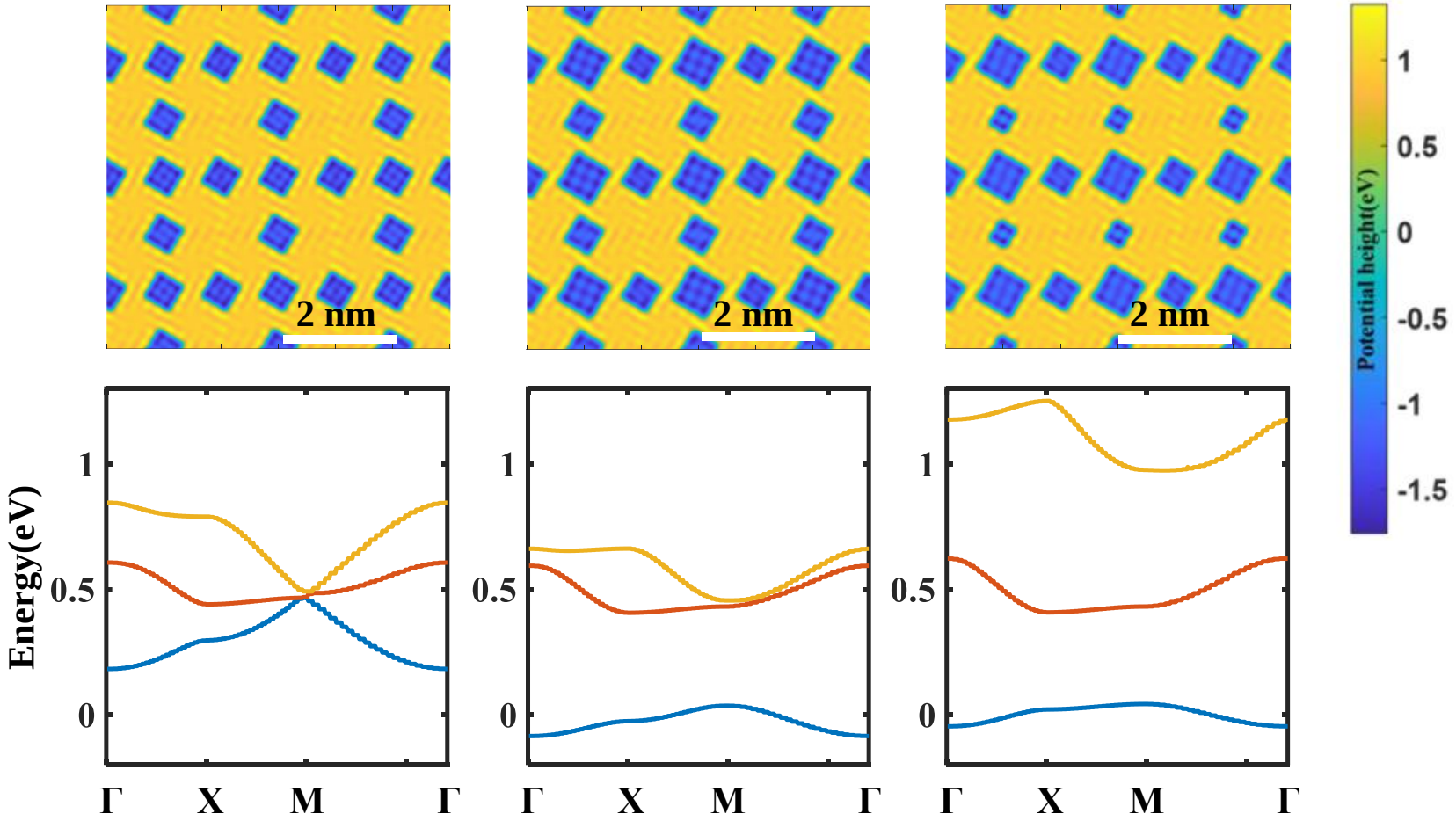


$t_1 = t_3 = 0.12$, $t_2 = 0.04$

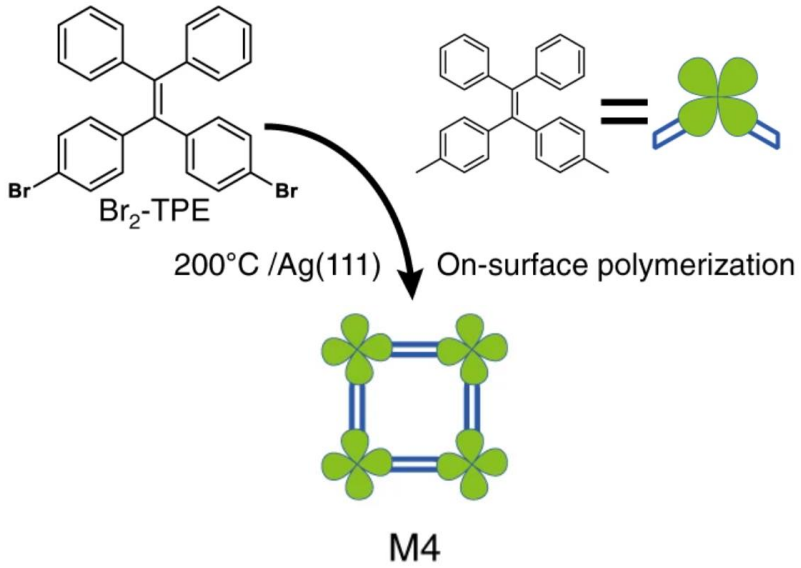


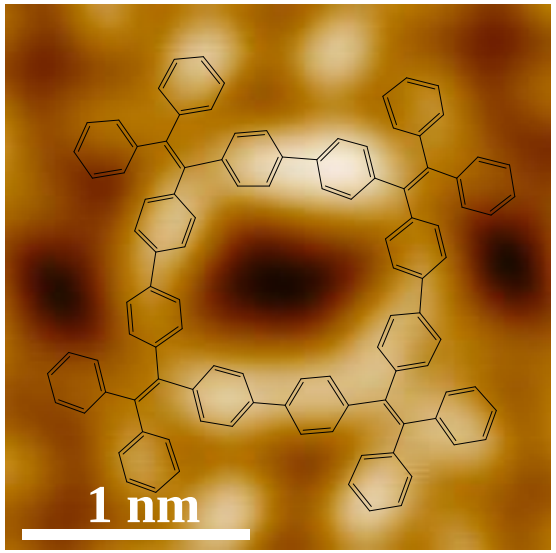
Design of a Lieb lattice exhibiting an isolated flat band

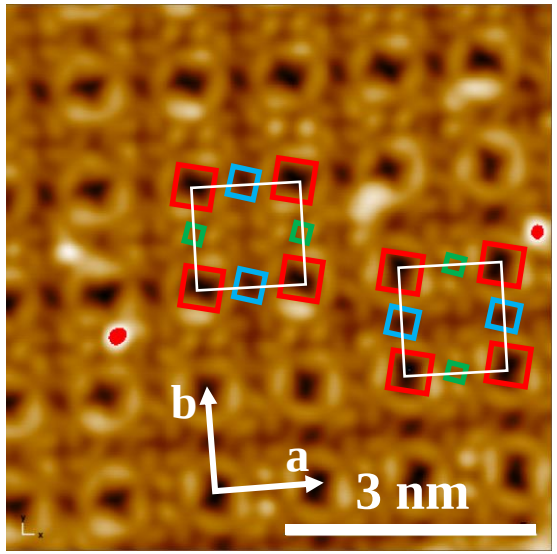
Plane-wave calculation



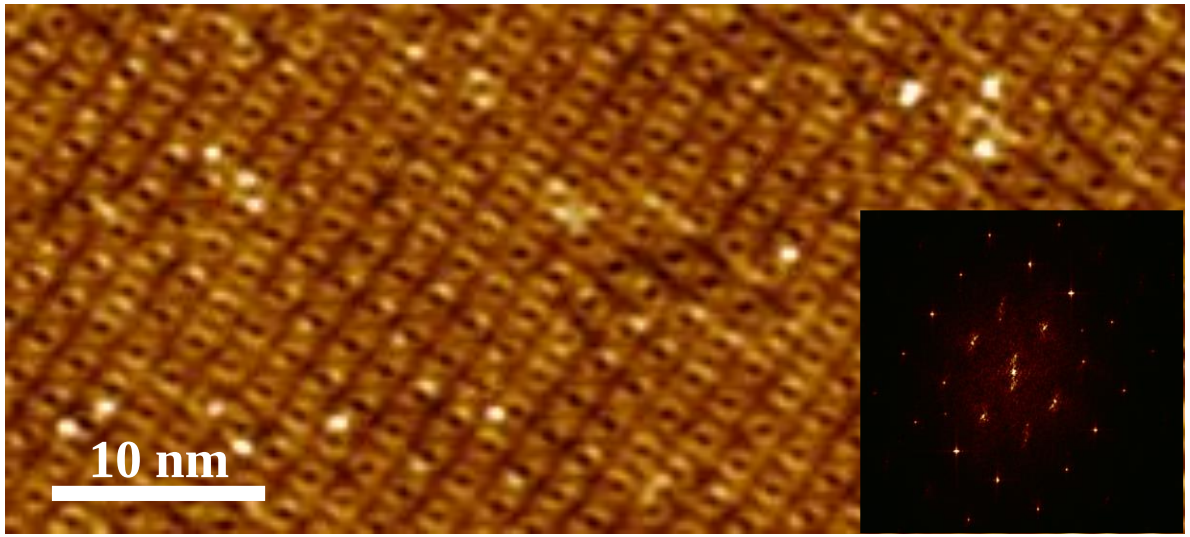
TPE-based macrocycles array







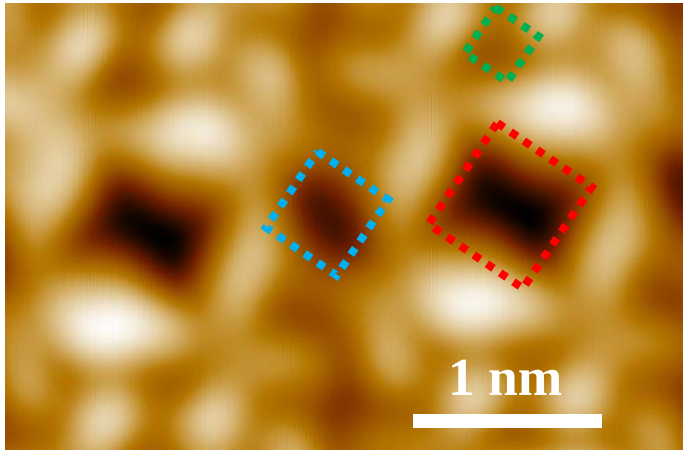
- Square-shape with four-fold symmetry
- Lattice constants:
  a = 2.01 ± 0.02nm
  b = 2.06 ± 0.03nm
- Lieb lattice (Arrangement of nanocavities)
- Nearly defect-free
- High crystallinity

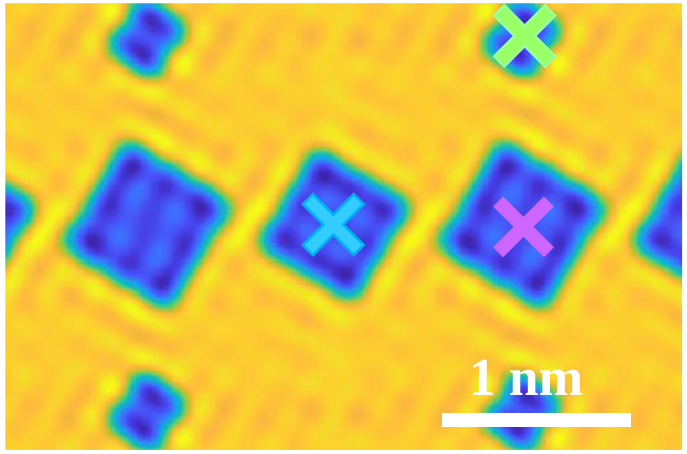


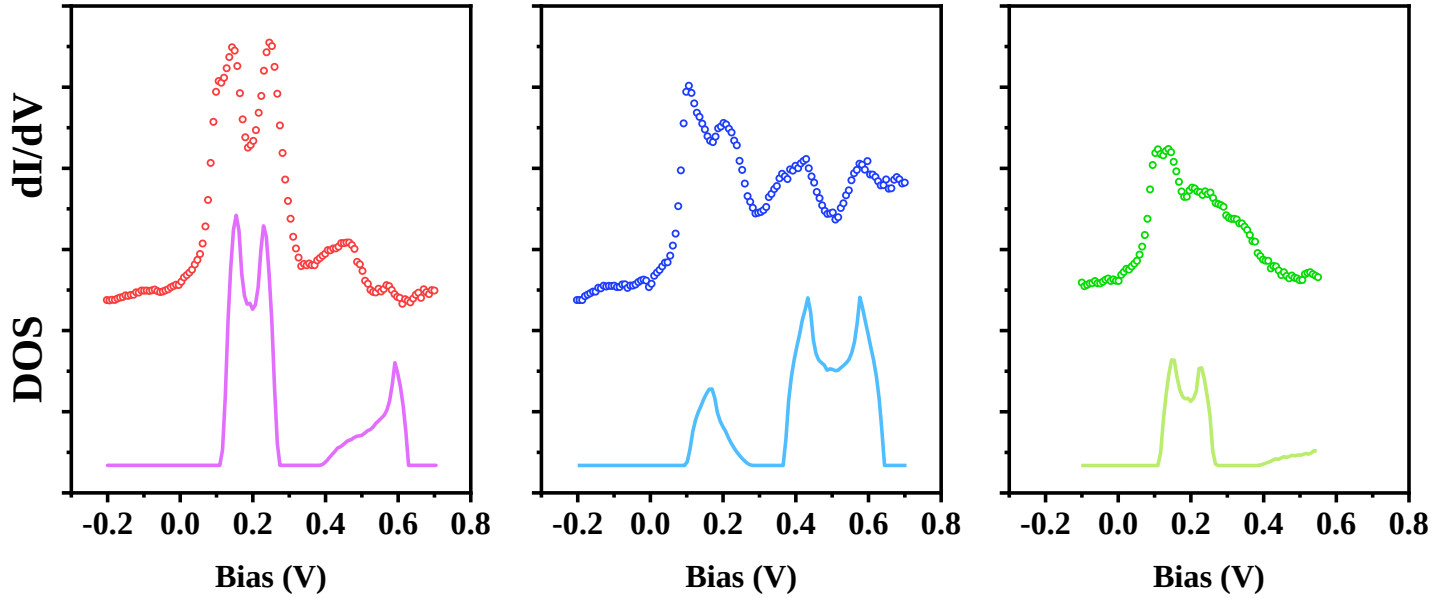
Commun. Chem., 5(1), 174. (2022)

Electronic properties of the QD array

- Corner site(red):
  Prominent peaks at 0.15V, 0.25V
  Weak peaks at 0.46V, 0.60V
- Horizontal edge site(blue):
  Peaks at 0.11V, 0.21V, 0.43V, 0.57V
- Vertical edge site(green):
  Peak at 0.12V,
  Downhill slope from 0.18 to 0.45 V
- Plane-wave calculated DOS agrees well with our *dI/dV* spectra



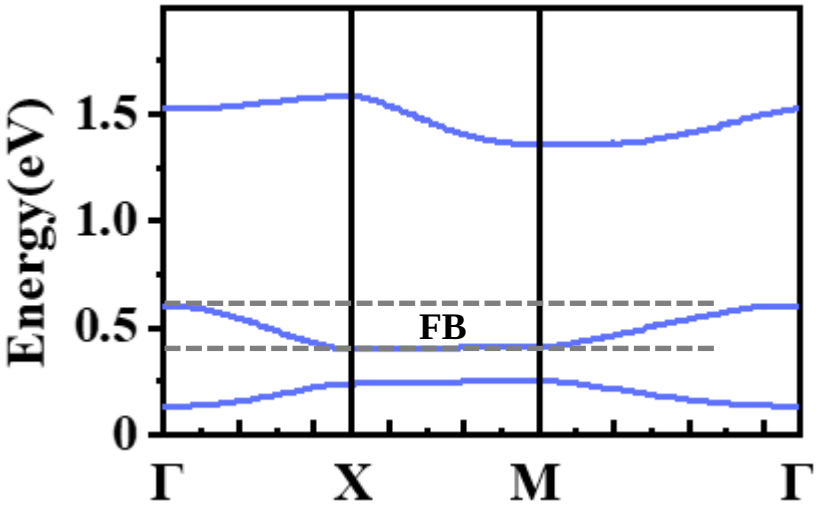


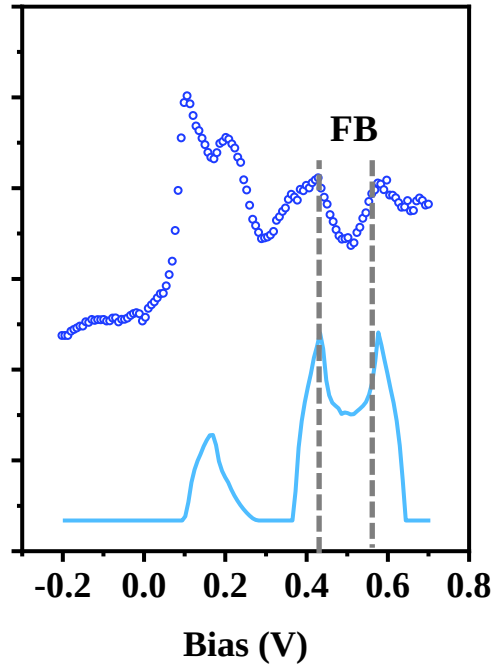


Electronic properties of the QD array

Isolated Flat band

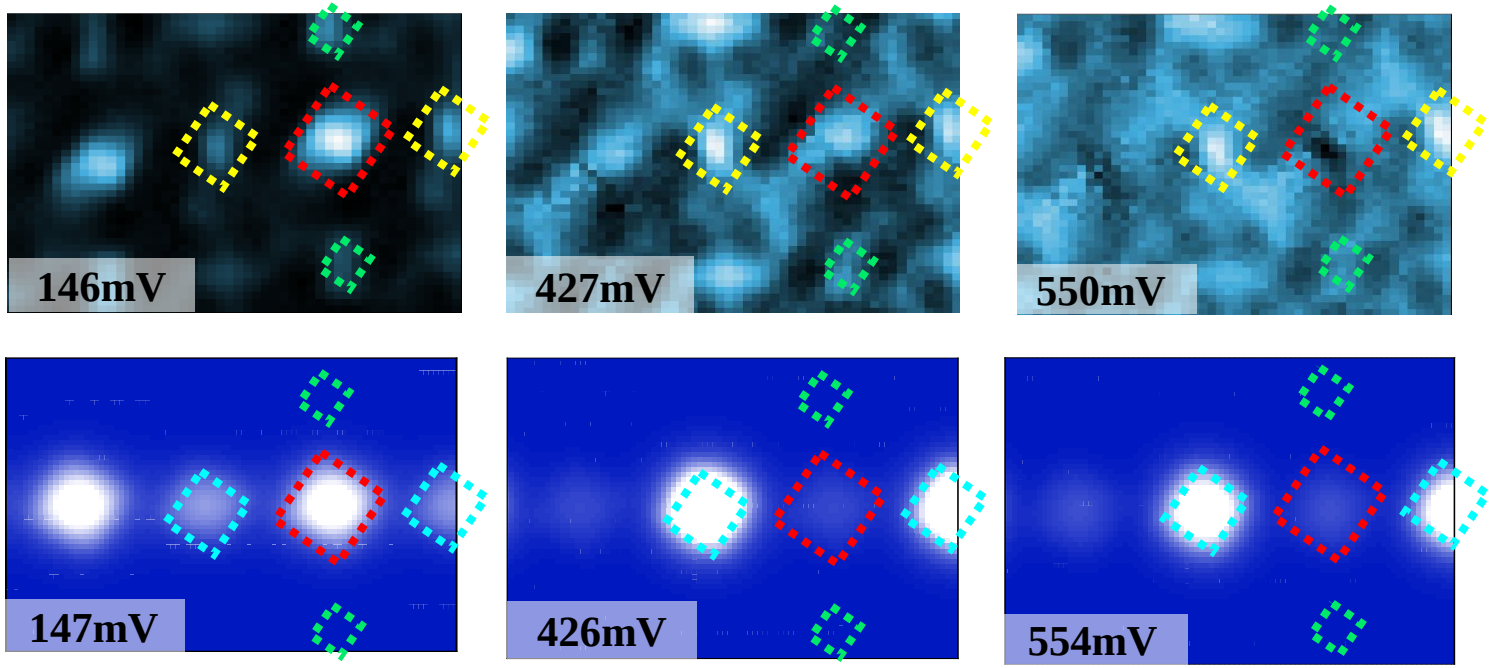
- Nearly perfectly flat from X to M
- Bending near the Γ point is due to the next-nearest-neighbour interaction
- Bandwidth of 0.2 eV





Spatial distribution of the bands

- First band: the state intensity is strongest at the corner site
- Second band (FB): the state intensity at the horizontal edge site surpasses the intensity at the corner sites



Conclusion

Achievement

- Realization of an artificial Lieb lattice featuring an **isolated flat band**

Platform

- 2D supramolecular crystal of square-shaped macrocycles self-assembled on an Ag(111) surface
- Quantum dots arranged in a Lieb lattice with varying energy levels

Superiority of isolated flat band

- Enhance Coulomb interaction
- The band isolation is required to observe an anomalous Hall effect in a flat band

Physical Review B, 82(7), 075104. (2010)

Part 3 Tip-manipulated radical in monomers exhibiting Kondo resonance

- Structure of 2D Ni-TPM MOF
- Tip-induced organic radical in the 2D MOF
- Temperature dependence of the Kondo resonance
- Kondo screening mechanism through Ni channel

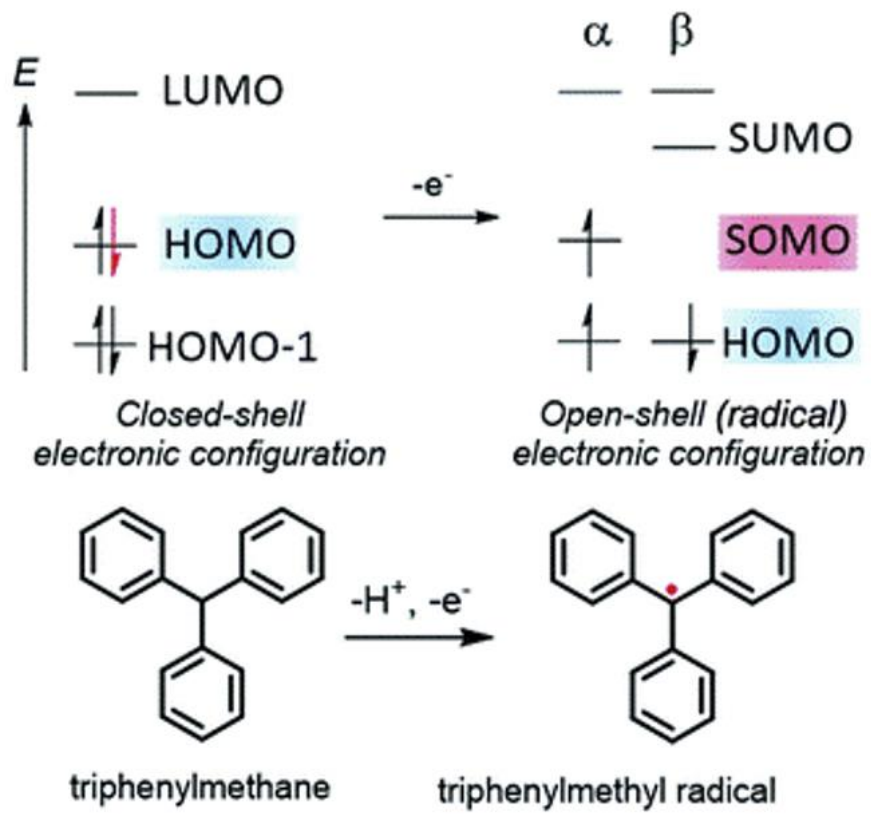
Background: Molecular spintronics

Organic radical:

- Electronic and spin properties
- Generating SUMO-SOMO gap
- Highly reactive, difficult to isolate

Compare with Fe, Cu, Ni i.e.

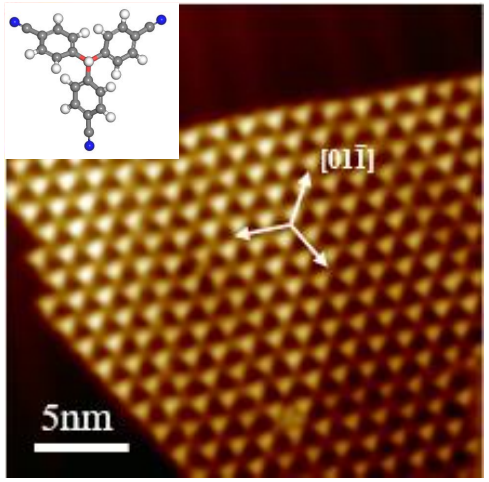
- Weaker spin-orbit coupling
- Hyperfine interactions
- Longer spin coherence length

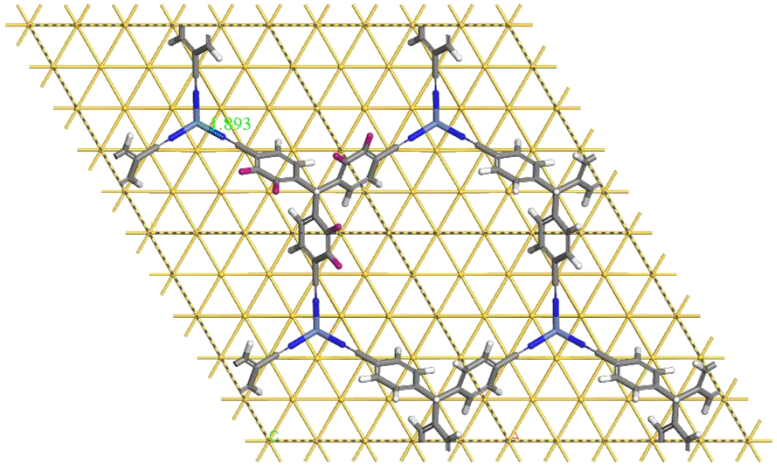


Chem. Sci, 13, 9833-9847 (2022)

Structure of 2D Ni-TPM MOF

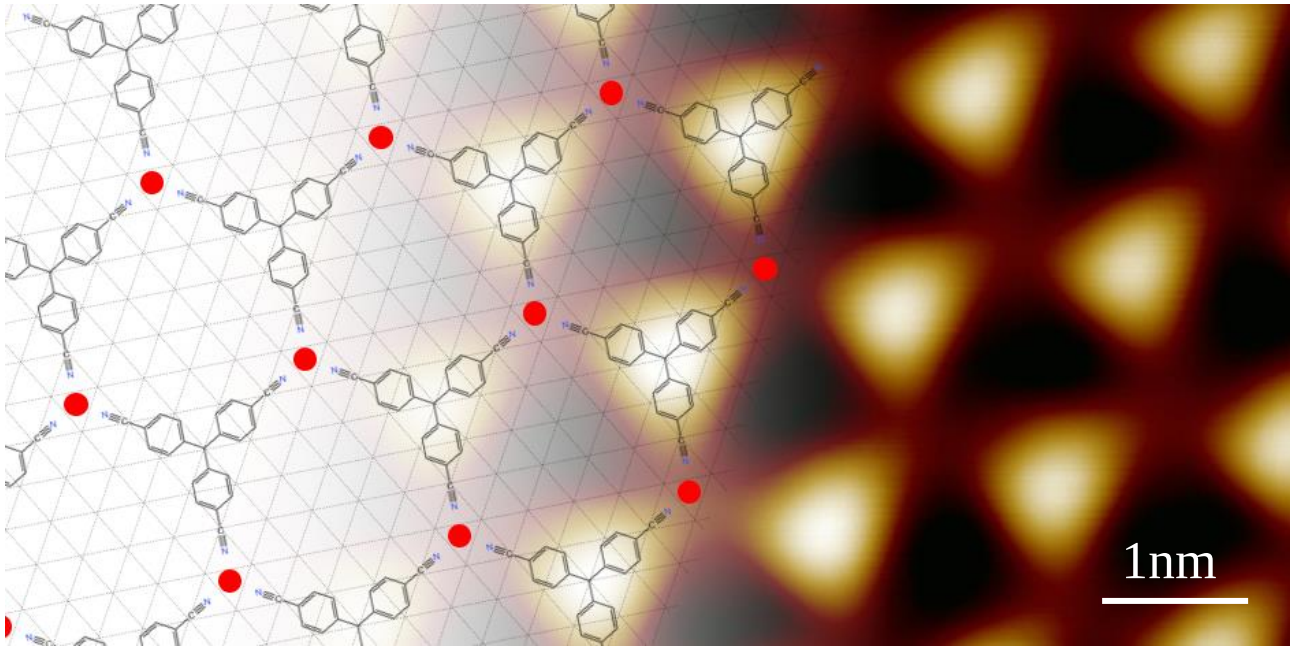
- 4-[bis(4-cyanophenyl)methyl]benzene-1-carbonitrile(TPM)
- Nickel(Ni) atom
- Au (111) substrate



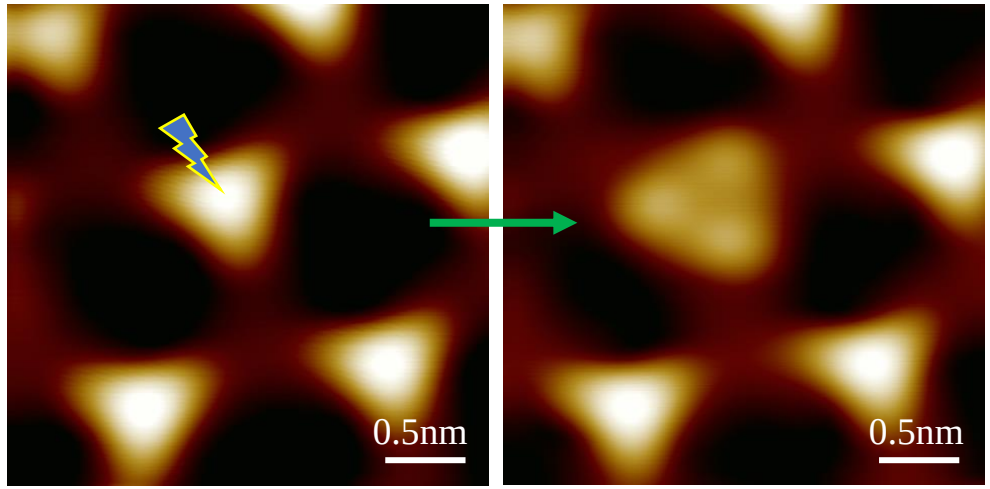


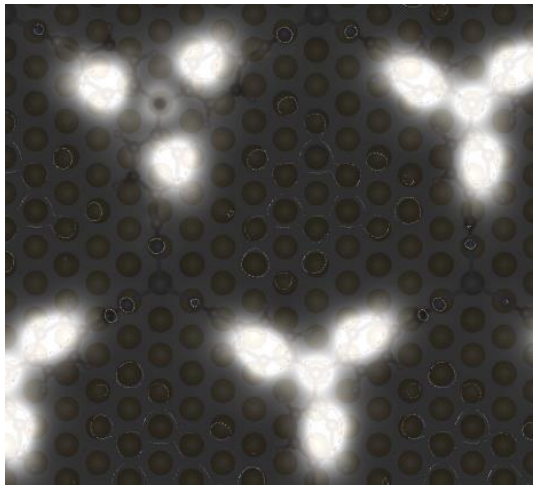
- Lattice constant and orientation:
  a = 1.43 ± 0.03nm along [01-1] direction
  a = 5*a0 (a0 is the Au(111) lattice constant)

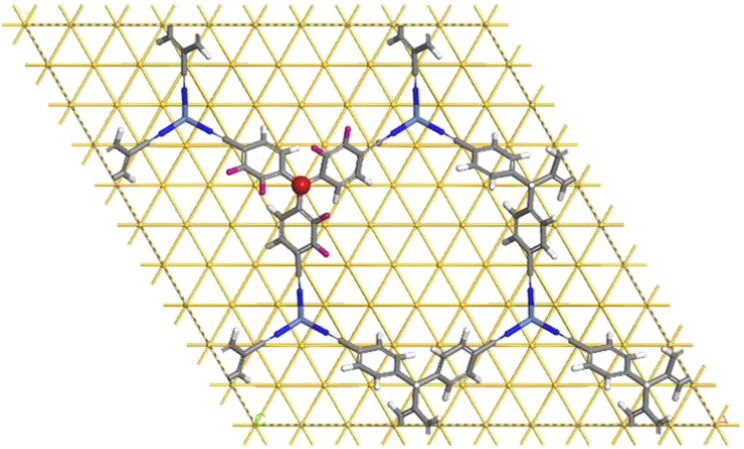
- DFT calculation:
  1. TPM molecules absorbed above the Au atom
  2. Propeller conformation, with the benzene rings tilted out of the plane

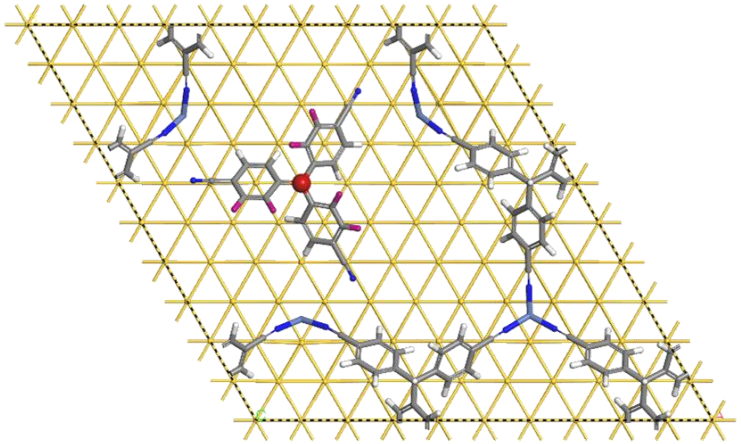


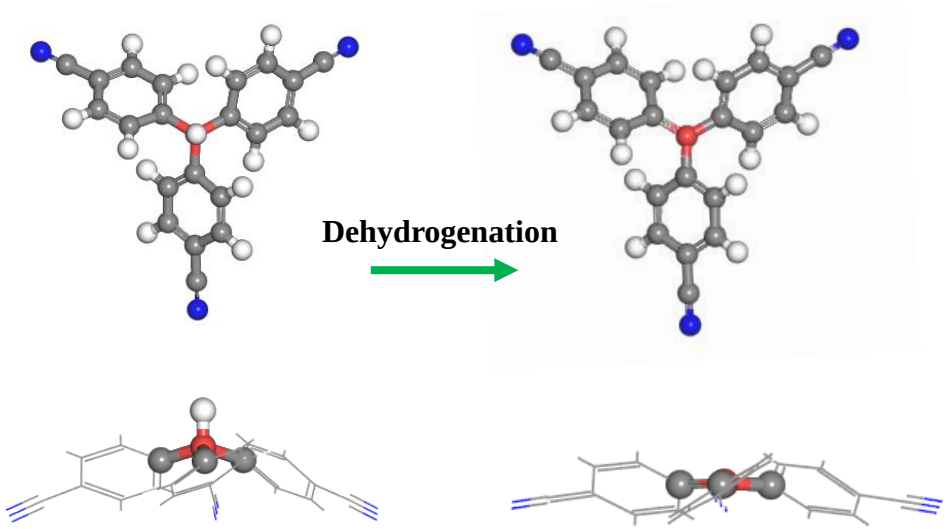
Tip-induced organic radical in the 2D MOF











- **Tip manipulation**

  1. Move the tip to the center of the TPM molecules

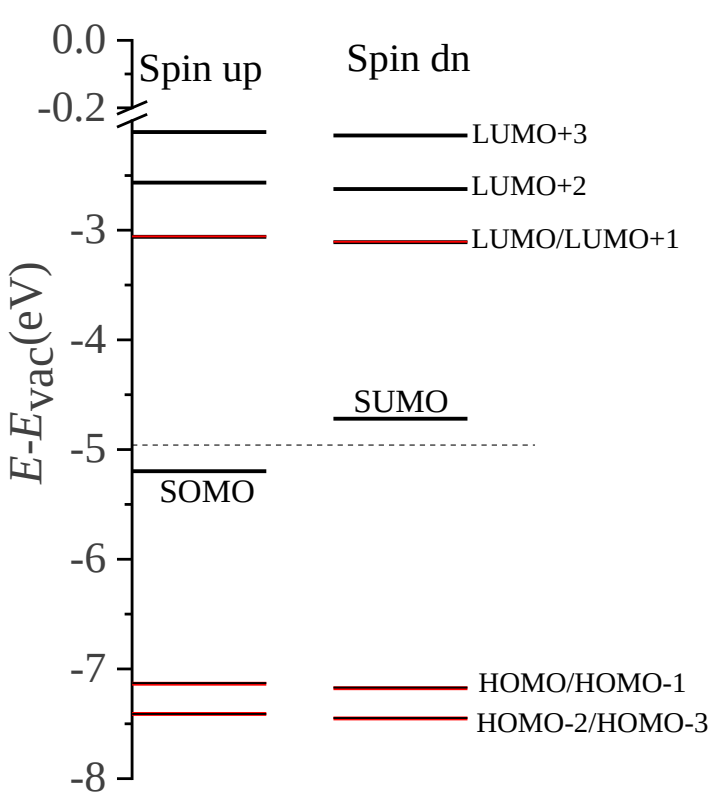
  2. Set bias voltage at 3.5~4.0V and *I* = 300pA

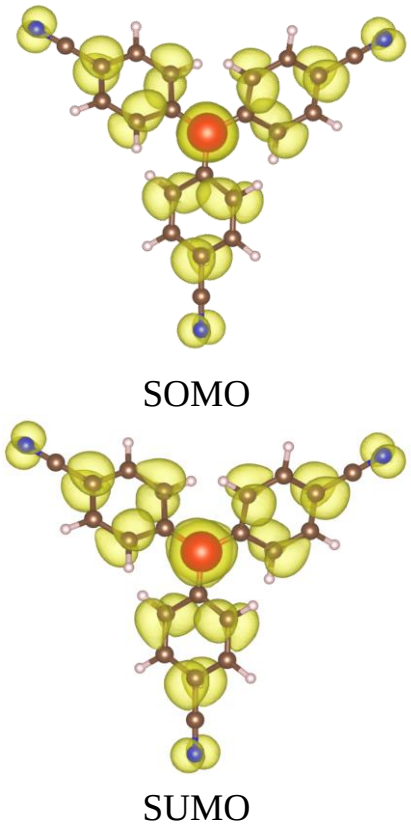
  3. Wait until the tunnel current suddenly drops.

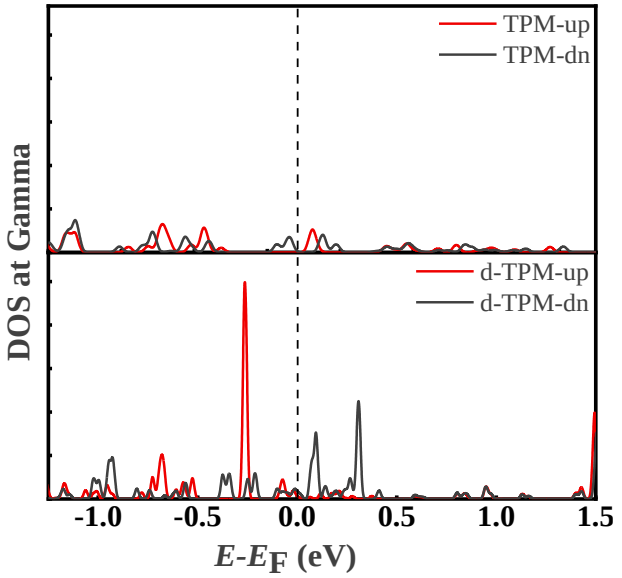
	$E_{relative}$(eV/super cell)
1	0
2	1.021

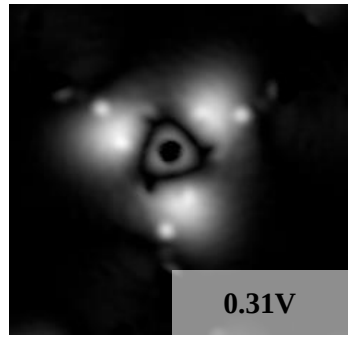
Tip-induced organic radical in the 2D MOF

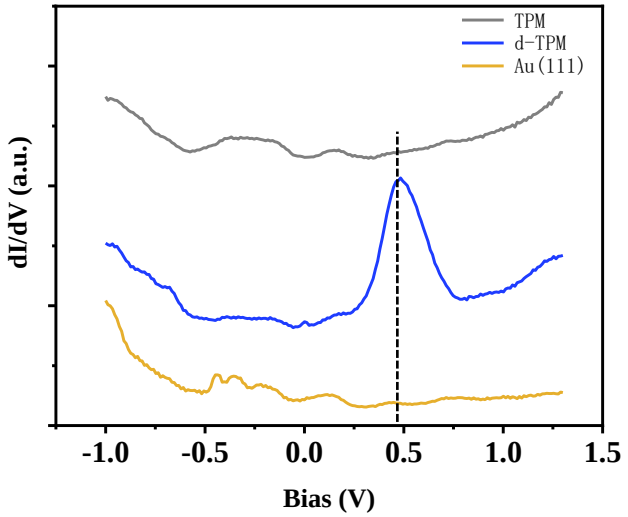
- **DFT: Presence of the SUMO-SOMO**
- **Experiment: Observation of SUMO state**

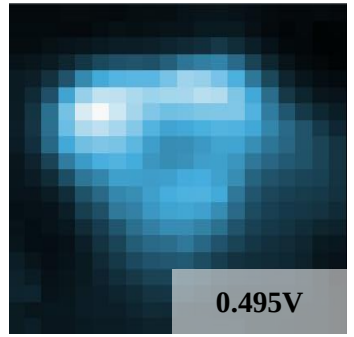






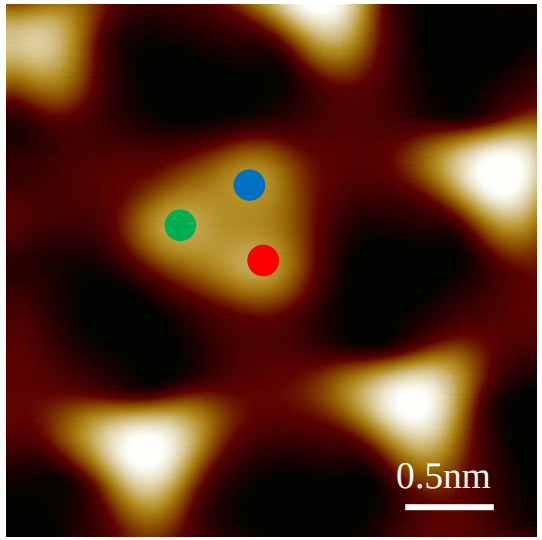


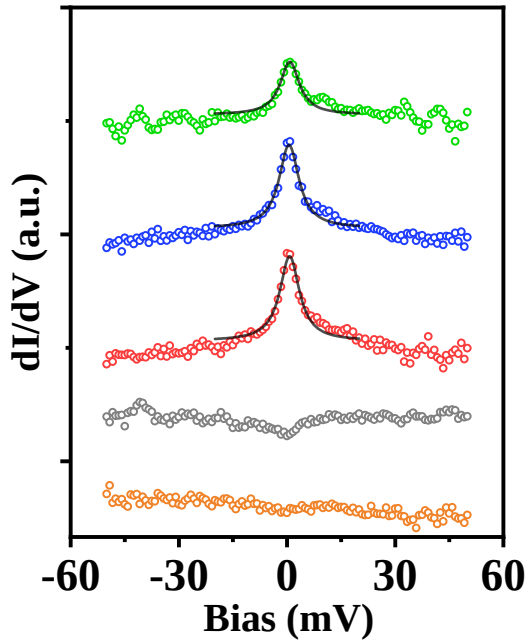


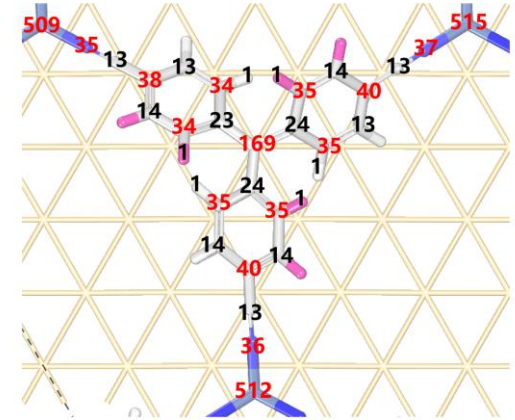


Tip-induced organic radical in the 2D MOF

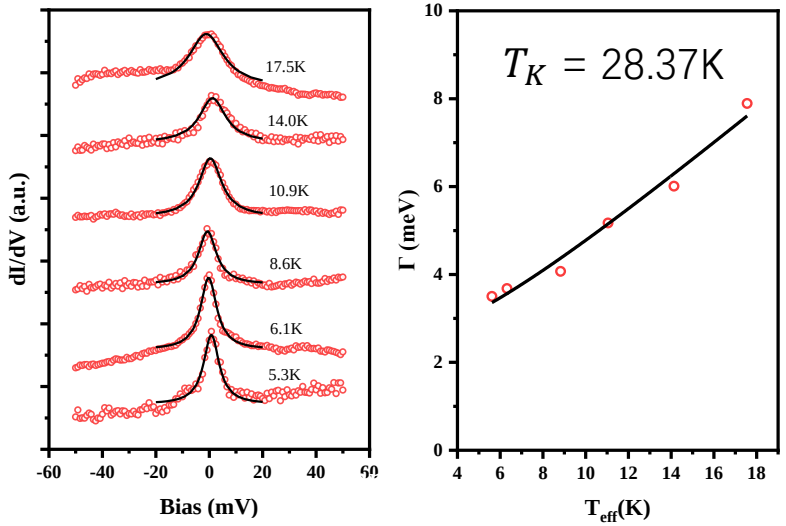
- Kondo resonance



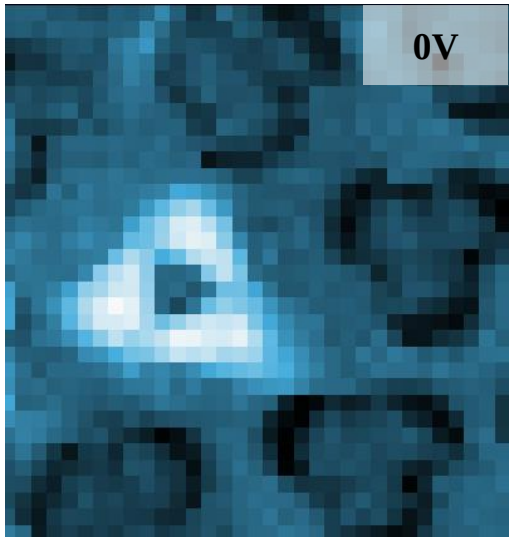


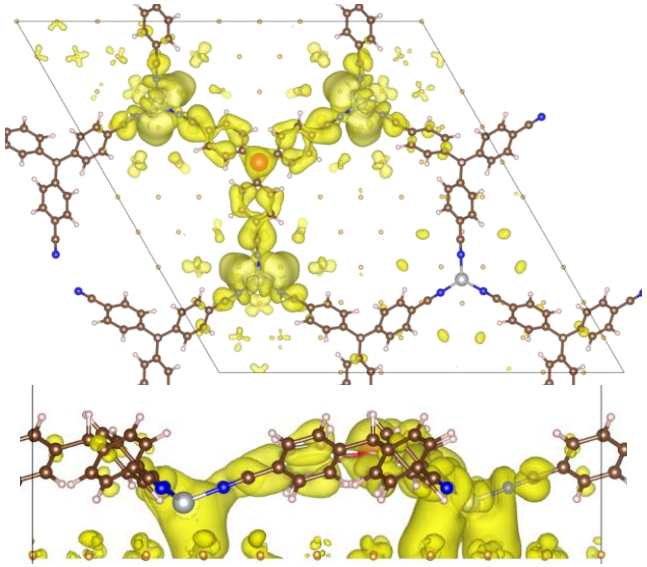


DFT calculated magnetic moment(mμB)



$$FWHM = \sqrt{(\alpha k_B T_{eff})^2 + (2k_B T_K)^2}$$





-0.38 eV

- Kondo screening through Ni

Conclusion

Experimental Achievement

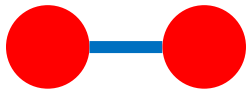
- Synthesize 2D MOF consisting of TPM molecules and Ni atoms on an Au(111) substrate
- Use tip manipulation to induce dehydrogenation reactions on single molecules to generate S= 1/2 organic radicals
- Observe the Kondo effect through the STS spectrum

DFT calculation

- Presence of the spin in d-TPM molecule
- Kondo screening mechanism through Ni channel

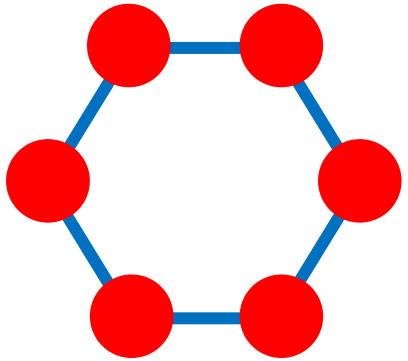
Part 4 Tip-manipulated radical linear structures

- Radical dimers



- Linear radical trimers

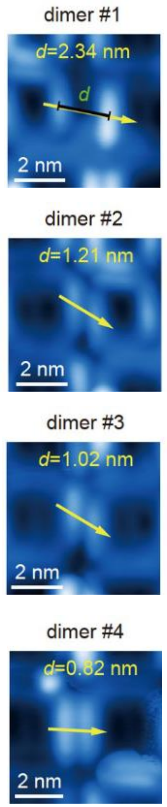
- Six-membered radical rings

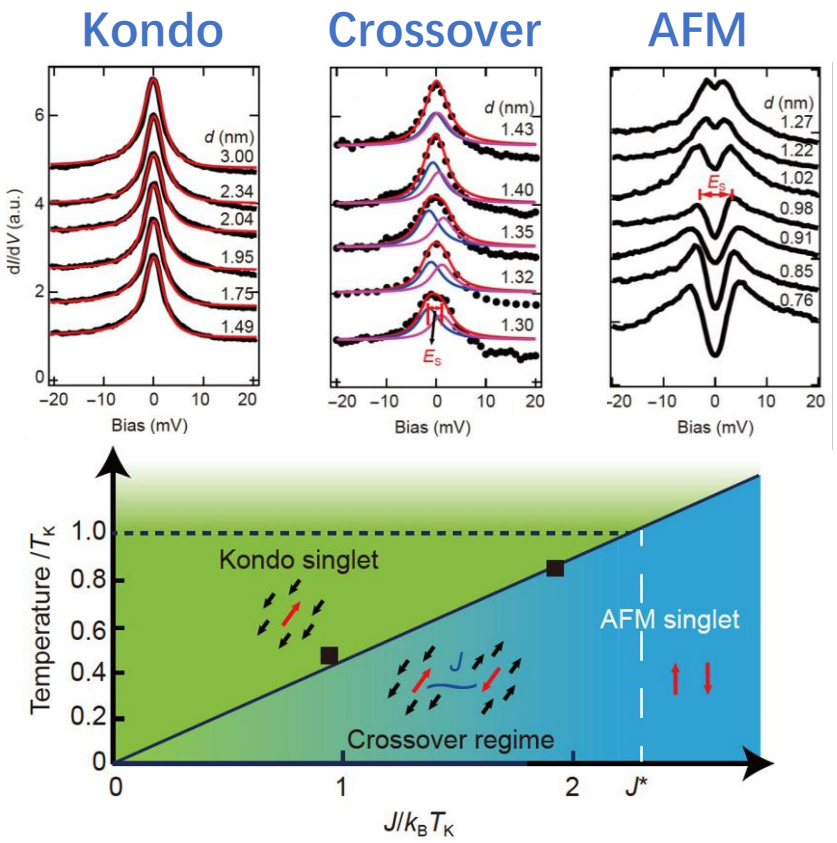


Background: Linear multi-body Kondo structure

Two-impurity Kondo problem:

- Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction
  - Kondo regime ($|J_{RKKY}| \ll k_B T_K$)
  - Crossover regime
  - AFM regime ($|J_{RKKY}| > 2.2 \sim 2.5 k_B T_K$)





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Radical dimers

Feature: Broaden zero bias peaks

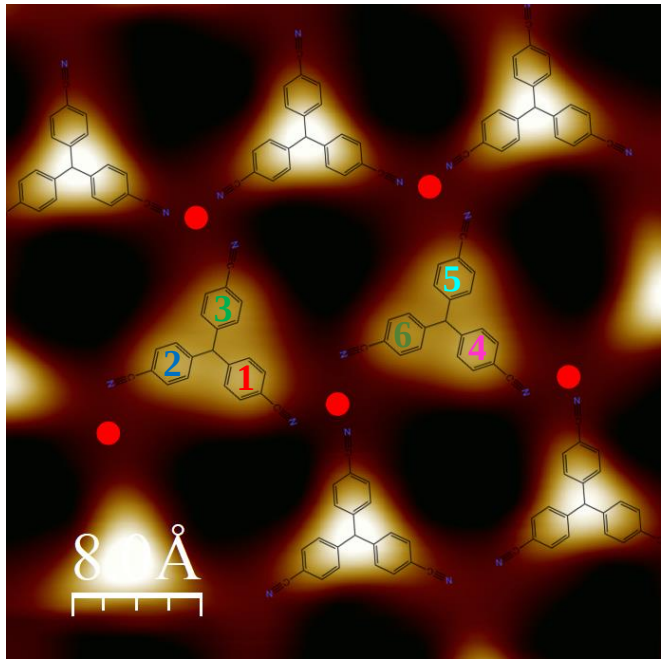
- Fitted by two split Fano lineshape with the HWHM of the monomer Fano lineshape
- Splitting energy (E_S) = 2*J_{RKKY}
- J_{RKKY} falls in a range of 0.9 ~ 1.4meV
- $k_B T_K = 3.5meV$

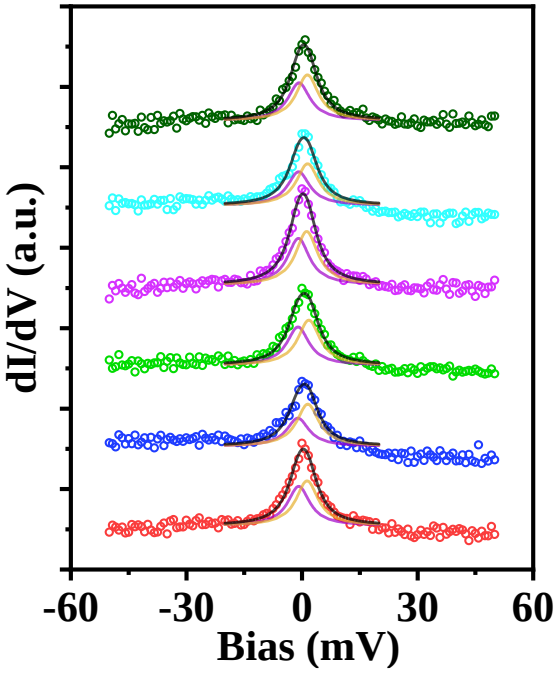
  The dimers undergo a crossover transition from a Kondo state to an AFM state.

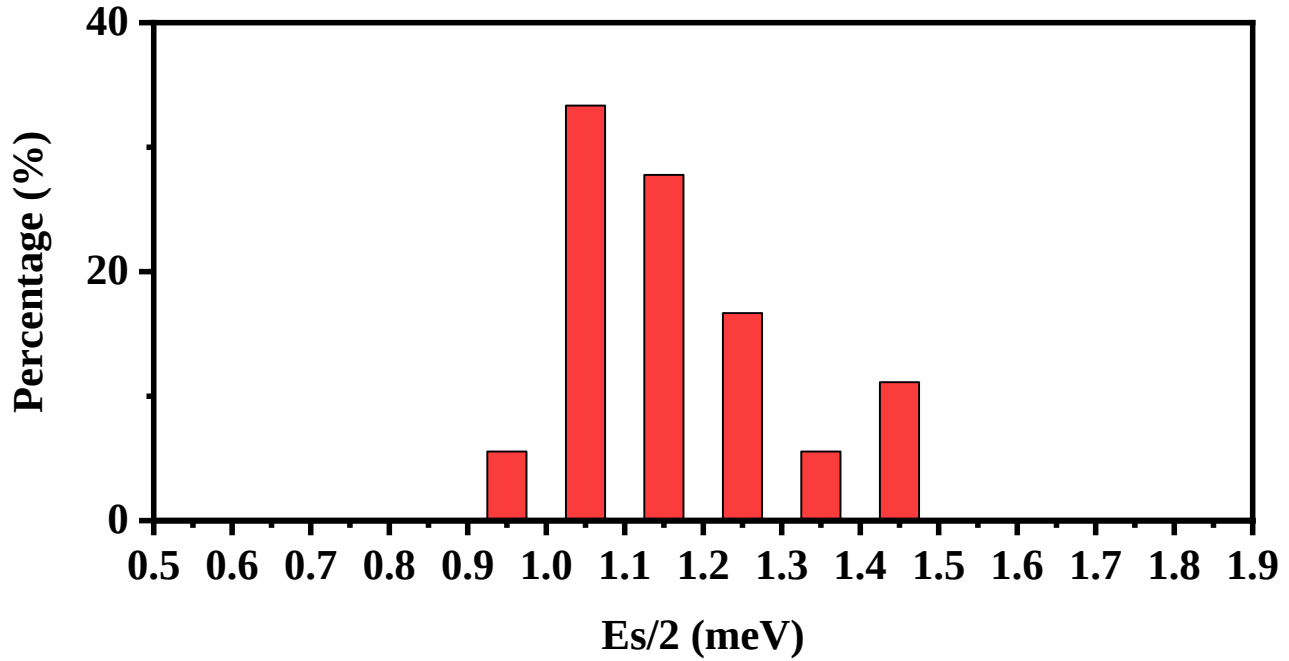
~~Kondo regime~~ ($|J_{RKKY}| \ll k_B T_K$)

Crossover regime

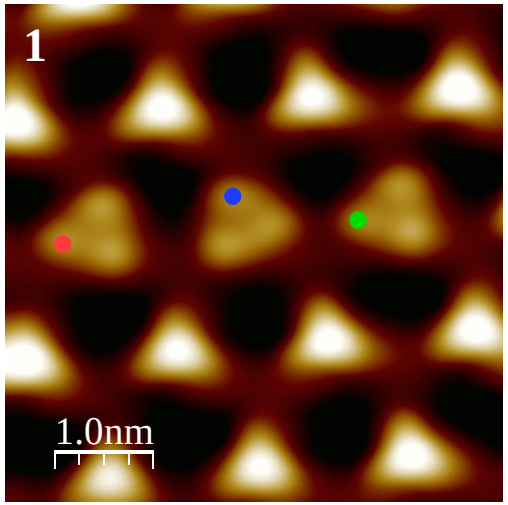
~~AFM regime~~ ($|J_{RKKY}| > 2.2 \sim 2.5 k_B T_K$)

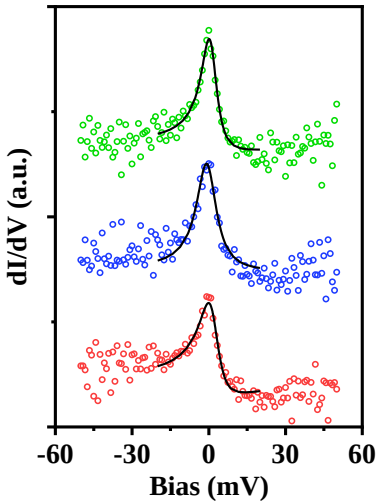


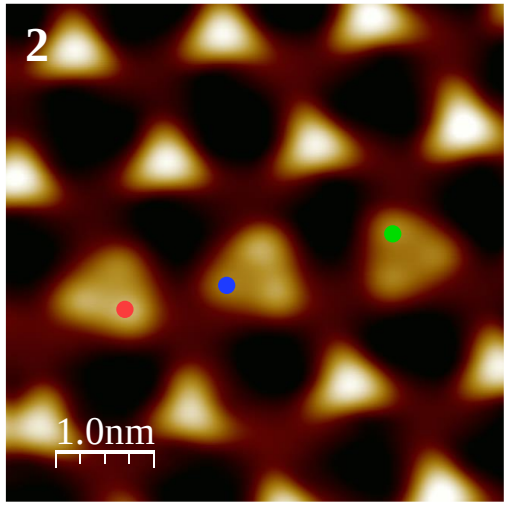


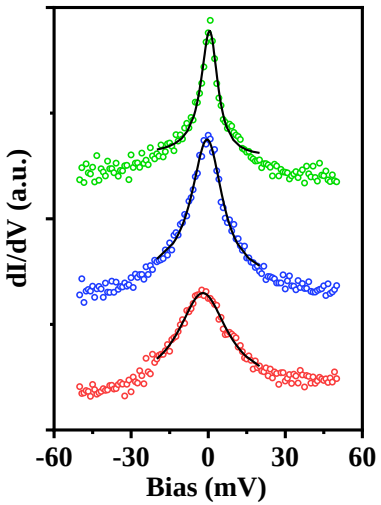


Linear radical trimers

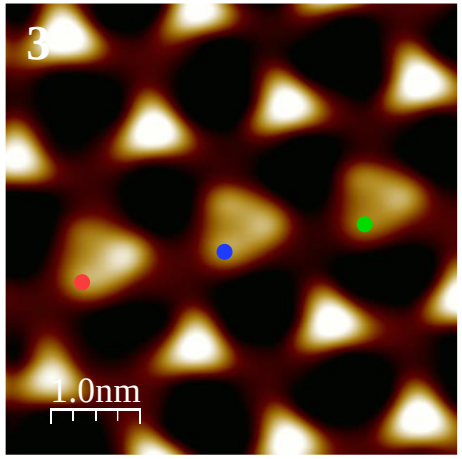


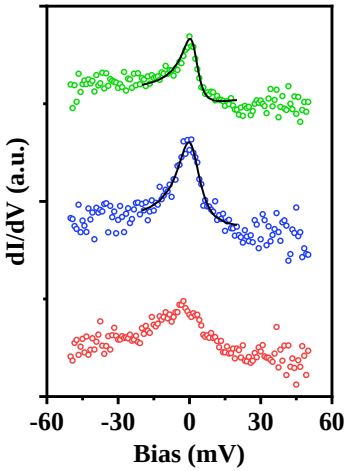


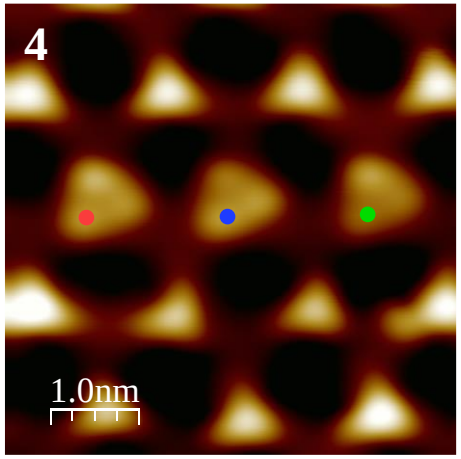


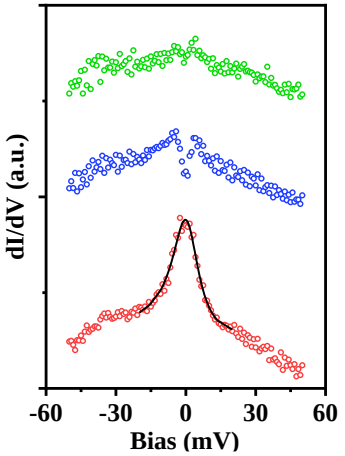


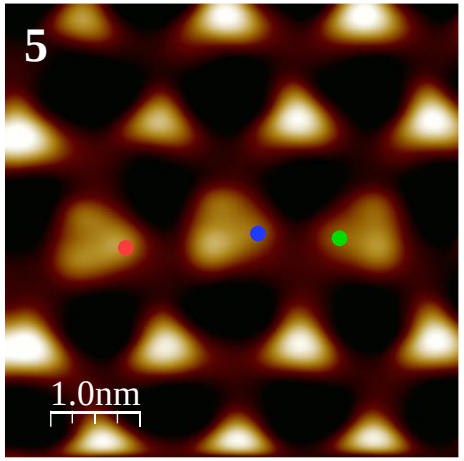
- Non-uniform spectral features

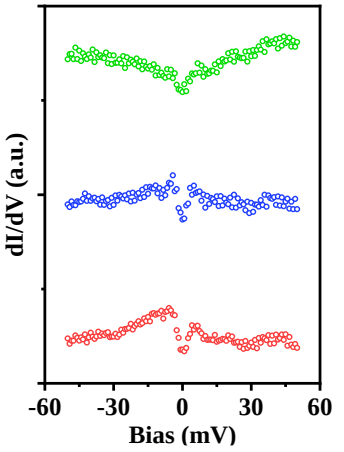






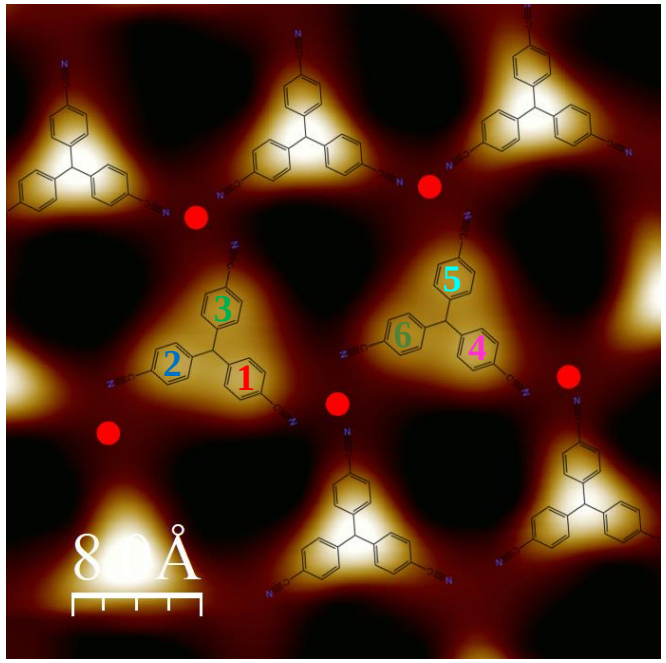


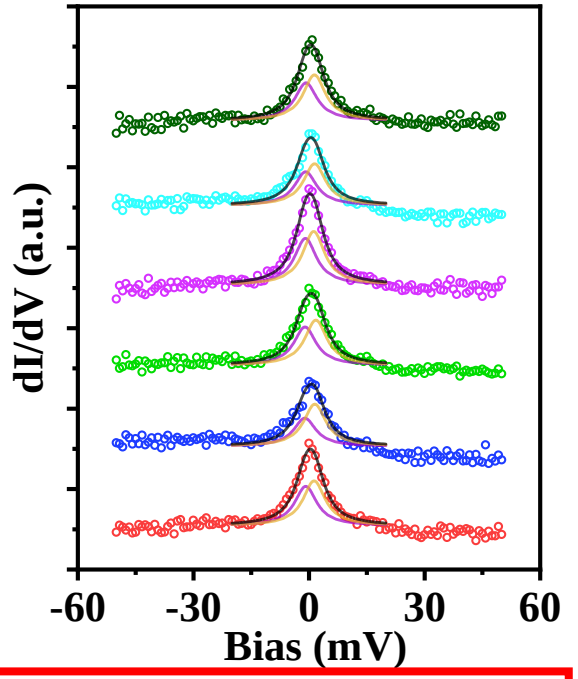


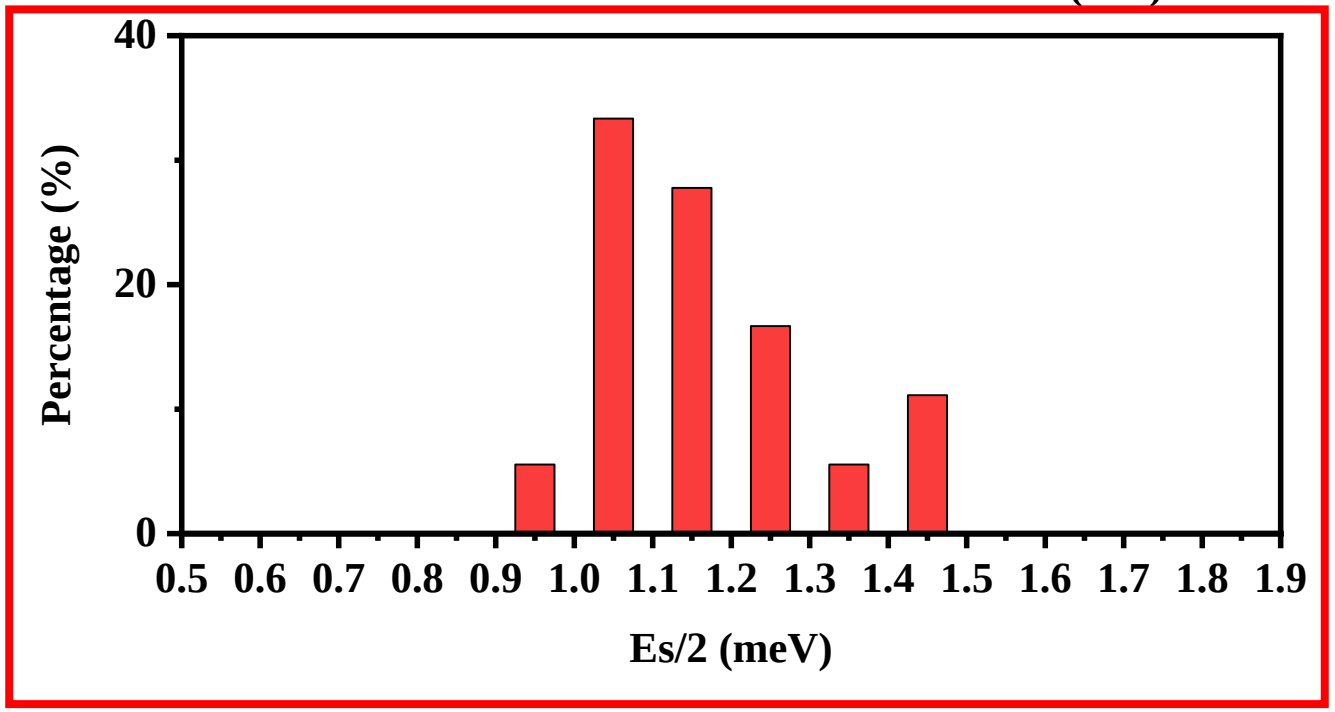


Radical dimers

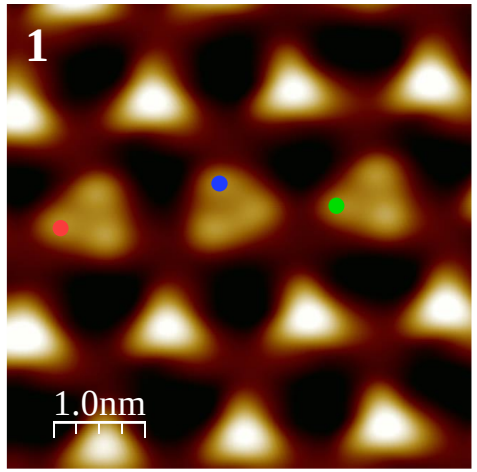
There is a fluctuation of the J_{RKKY}

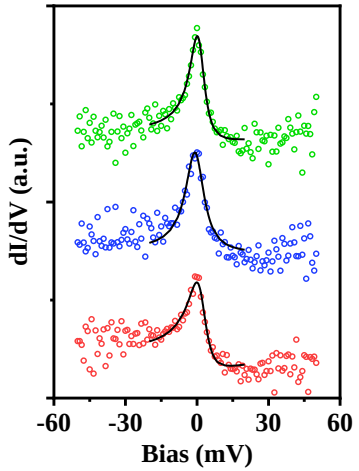


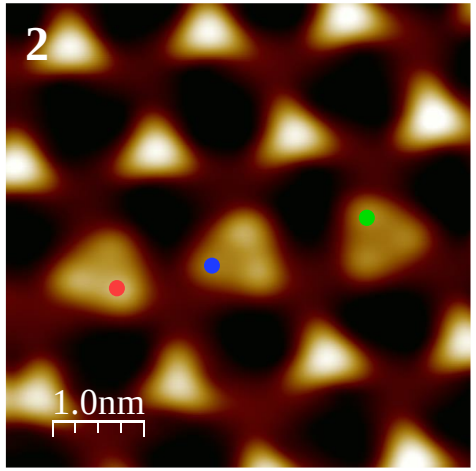


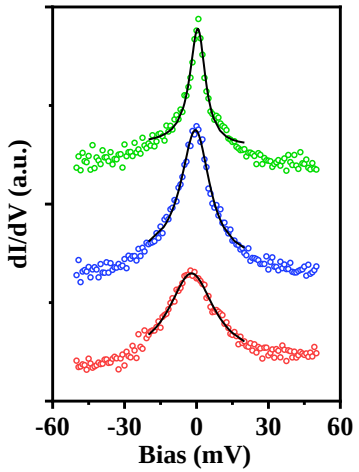


Linear radical trimers

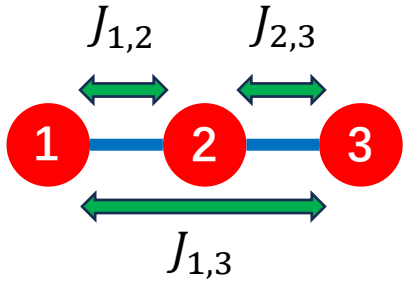


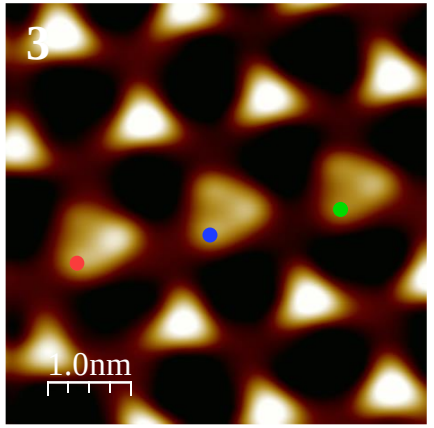


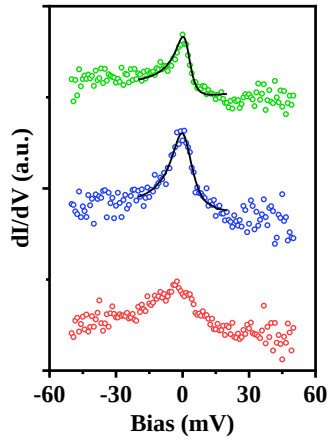


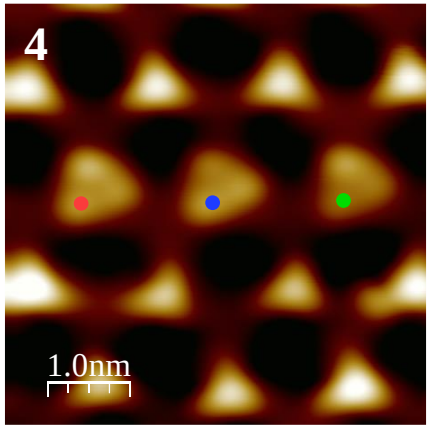


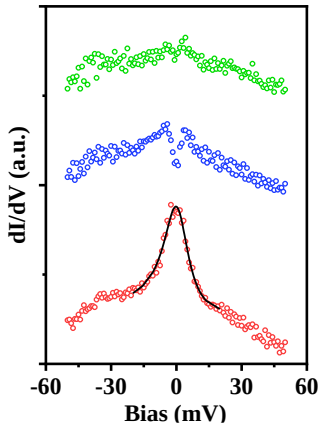
- Non-uniform spectral features due to the fluctuated J_{RKKY}

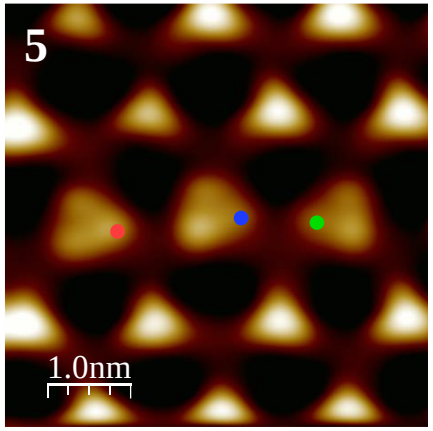


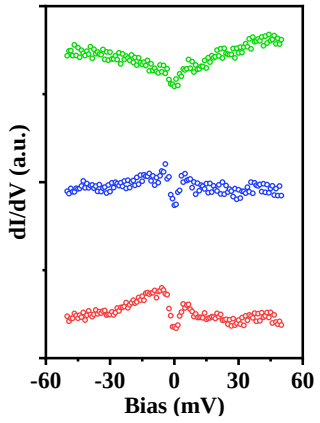




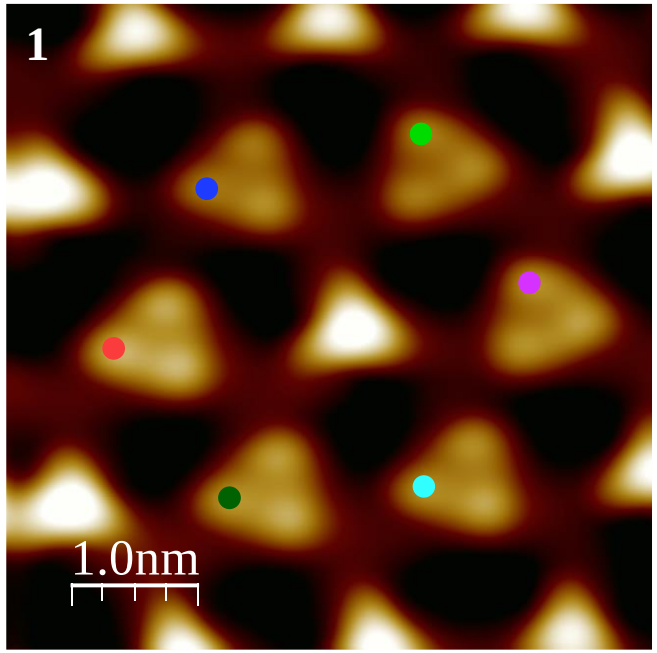


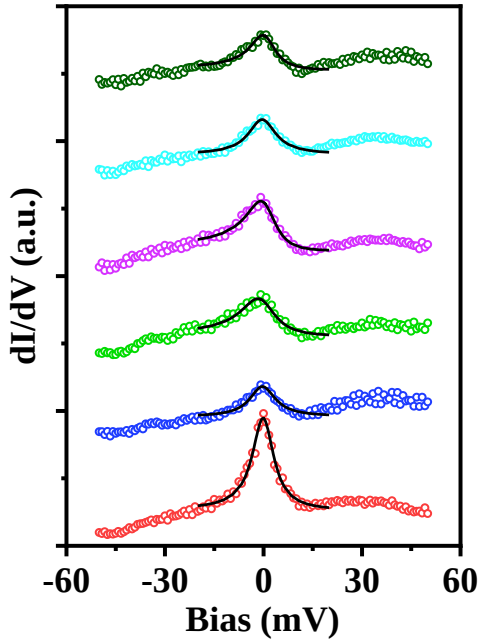


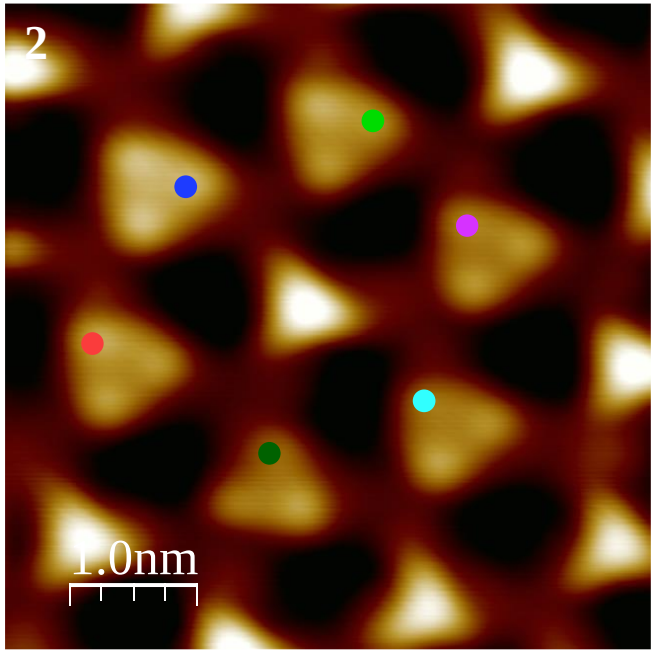


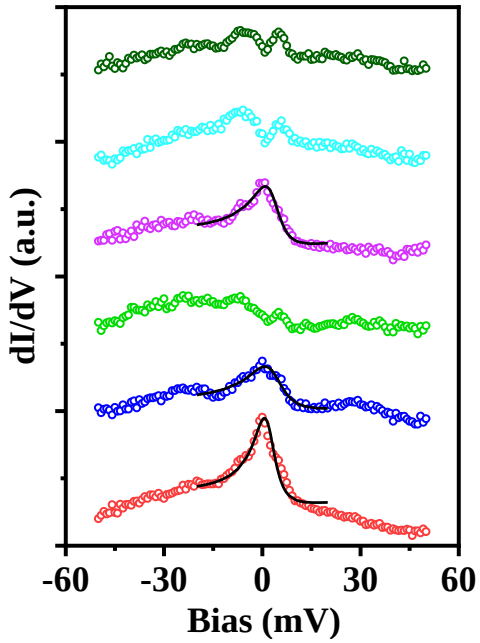


Six-membered radical rings

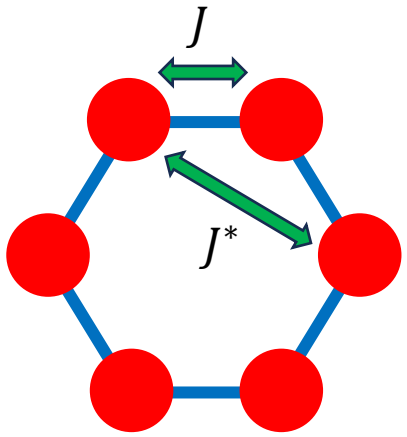








Γ/Xc(meV)						
1	4.81	5.12	5.60	6.49	4.74	3.97
2	-5.60	-6.90	5.13	-6.00	6.41	4.04
	5.30	5.60		5.20		



- **Non-uniform spectral features due to the fluctuated J_{RKKY}**
- We will try to use Quantum Monte Carlo to understand this

Conclusion

Experimental Achievement

- Generate linear radical structures including dimer, linear trimer, and six-membered ring through tip manipulation.
- RKKY interactions are at work in these structures, resulting in the observation of the broadened ZBP or dips at the Fermi level.

Problems need to be further explore

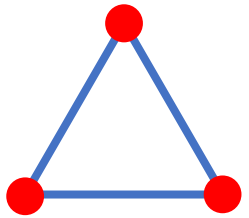
- The non-uniform features in chains and rings are beyond our understanding at the moment

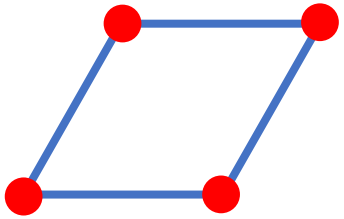
Proposal

- Non-uniform J_{RKKY} values $\rightarrow$ Non-uniform features in linear structures

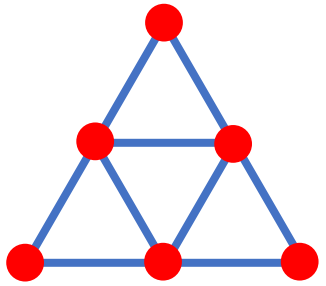
Part 5 Tip-manipulated finite 2D radical structures

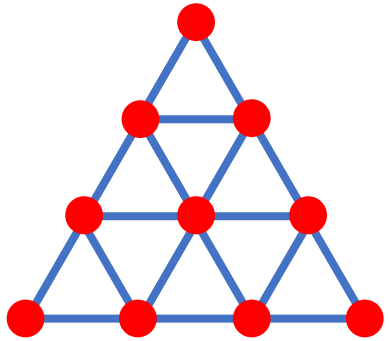
- Triangular and Rhombus Radical Arrays



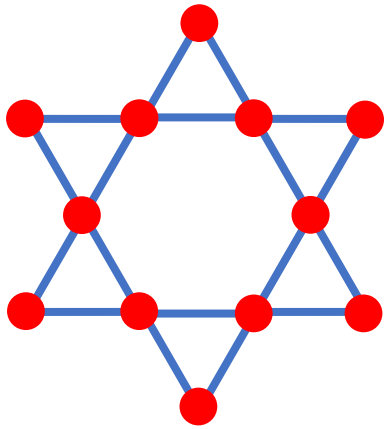


- Large triangular arrays of radicals





- David star radical structures



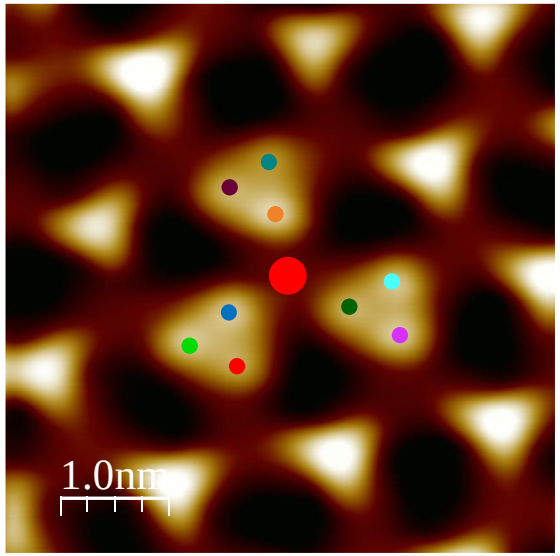
Triangular and Rhombus Radical Arrays

Observation:

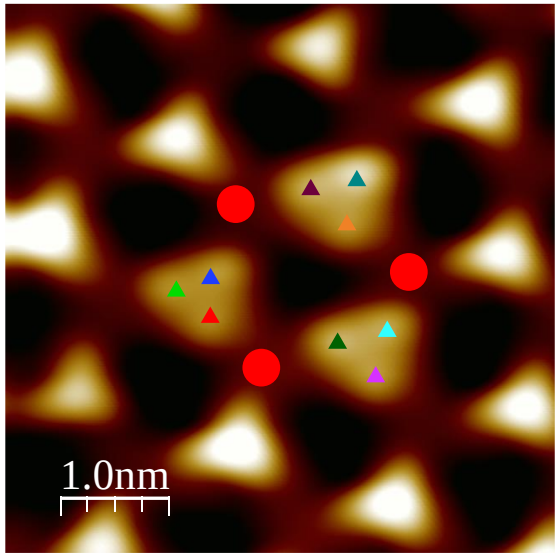
- Different configurations exhibit similar spectral features
- Zero bias dip width: 10.24 ± 1.89 meV

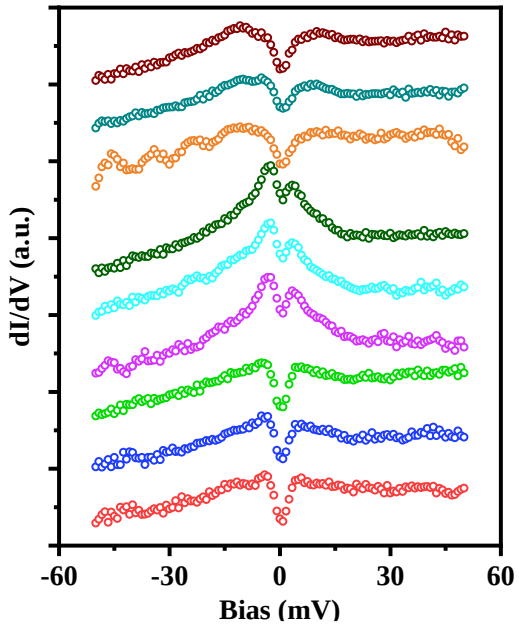
Coupling inside trimers occurs through conduction band electrons in the metal substrate, rather than through hopping via the Ni atom

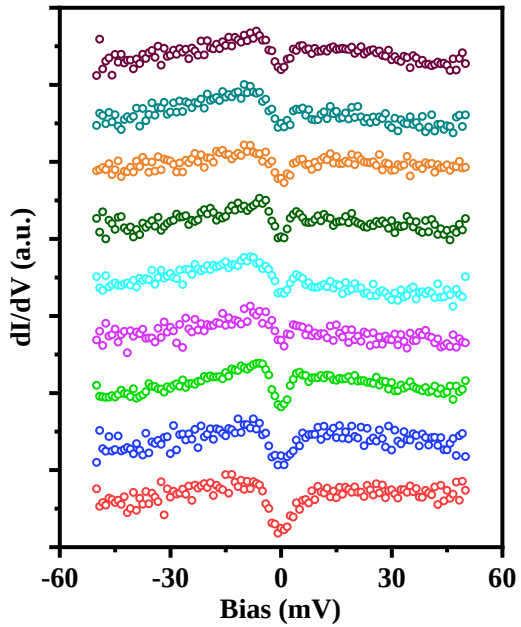
Tripod trimer



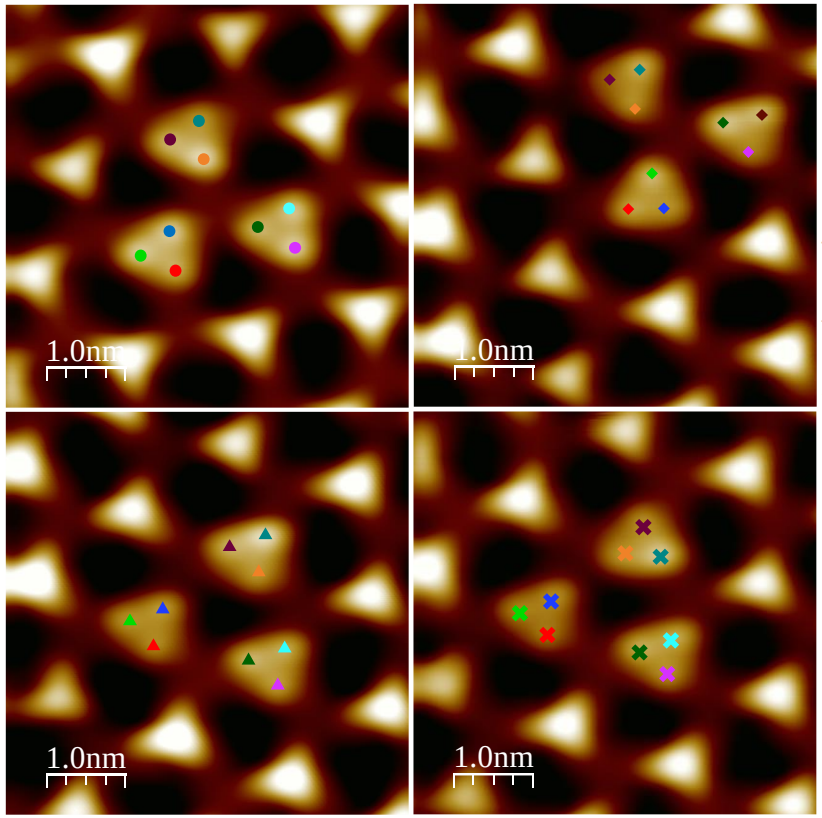
Ring trimer

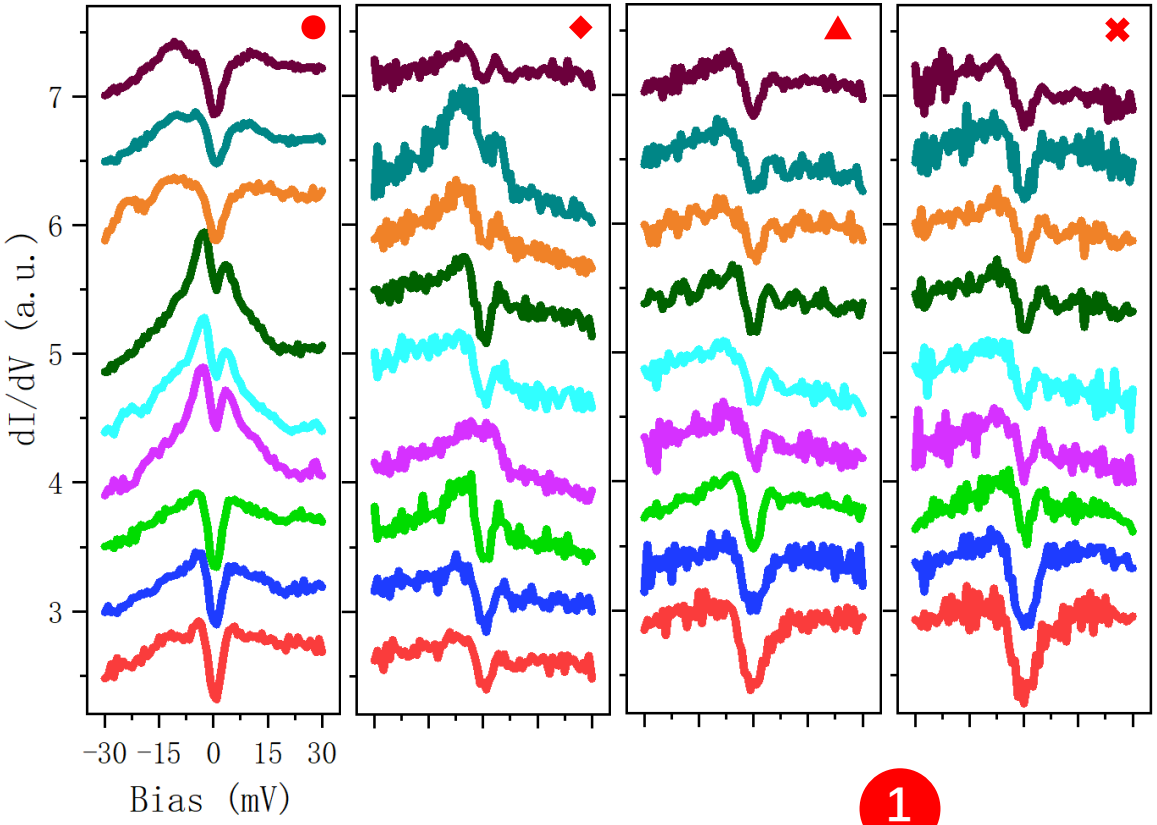


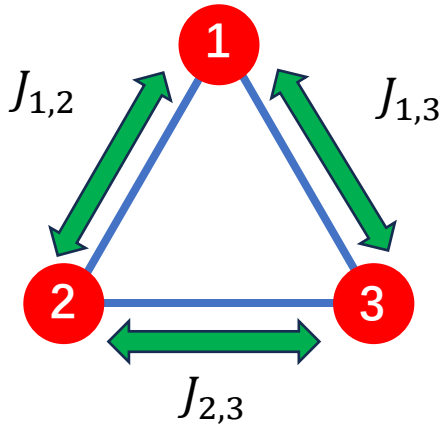




Triangular and Rhombus Radical Arrays







- **Different configurations exhibit similar spectral features**
- **Triangular trimers have robustness against the fluctuated J_{RKKY}**

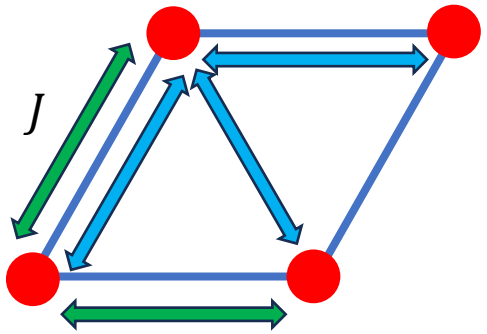
- We will try to use Quantum Monte Carlo to understand the dip feature

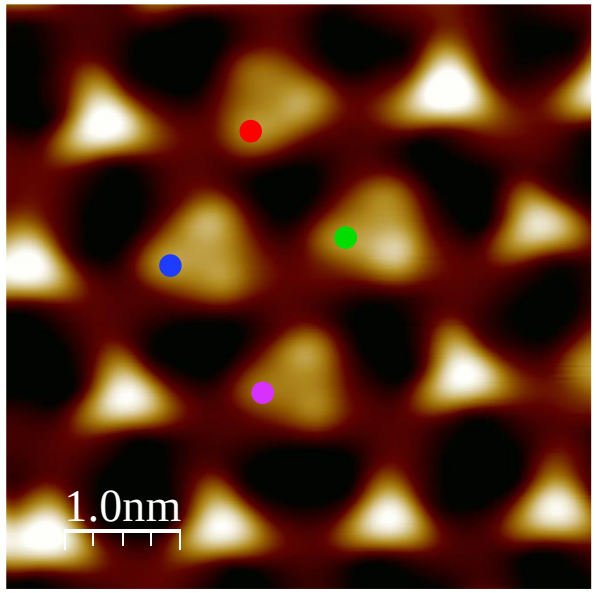
Triangular and Rhombus Radical Arrays

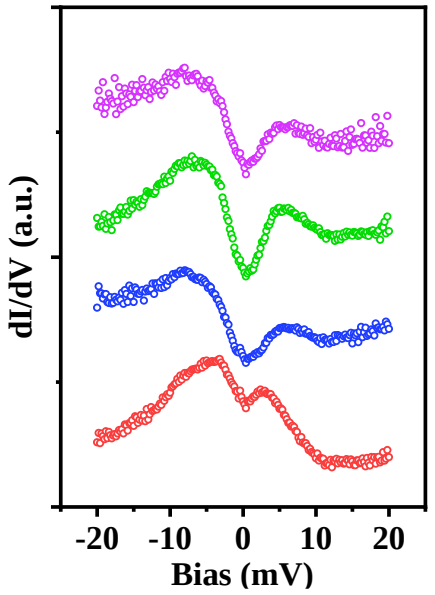
- Non-uniform spectral features

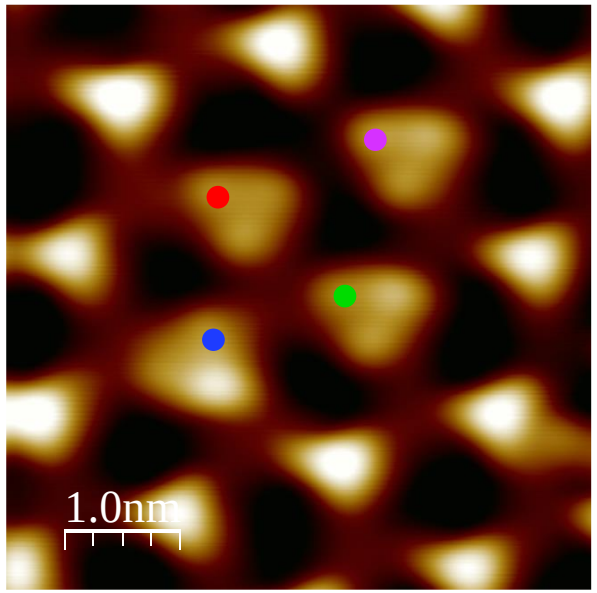
Proposal

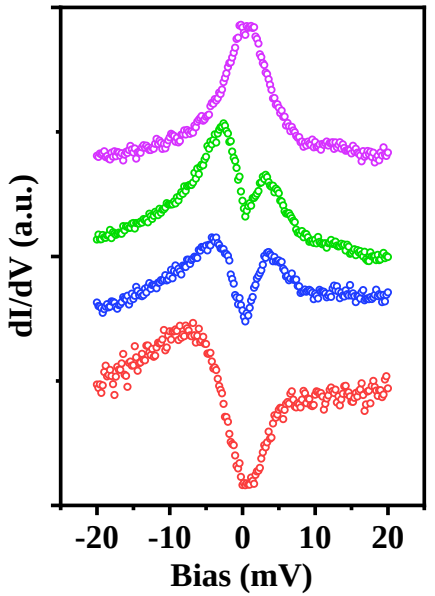
- Caused by fluctuations of the RKKY coupling strength









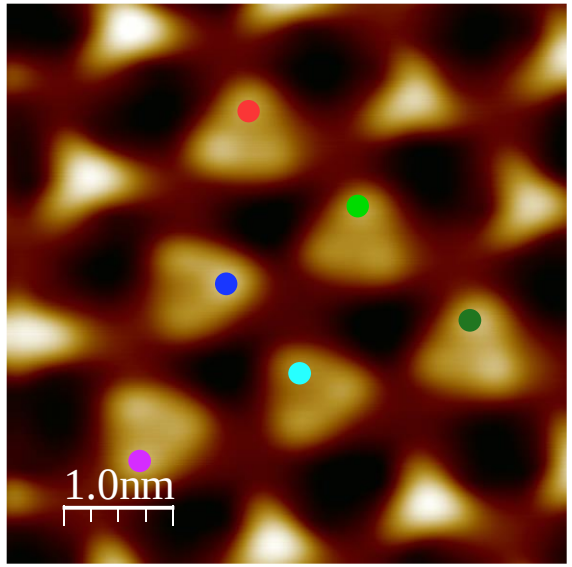


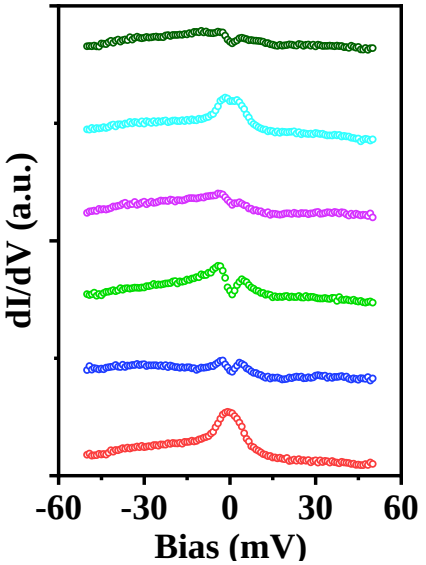
Large triangular arrays of radicals

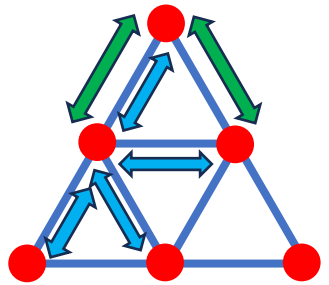
- Non-uniform and non-symmetric spectral features

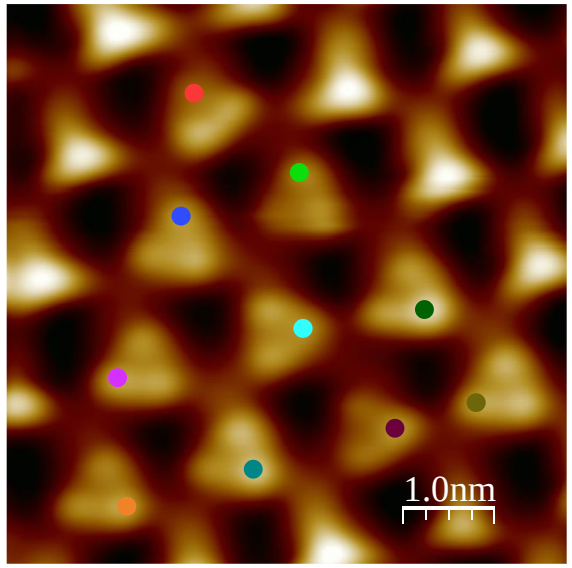
Proposal

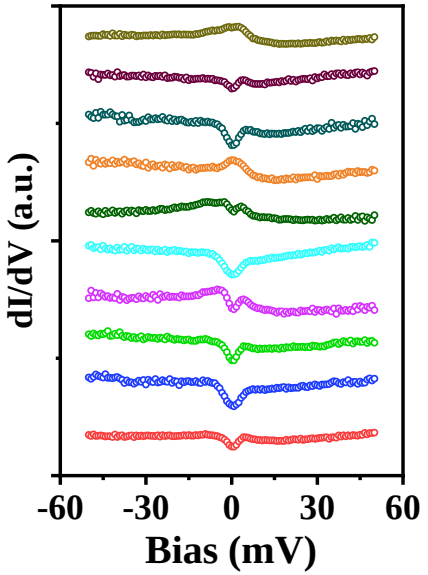
- Caused by fluctuations of the RKKY coupling strength

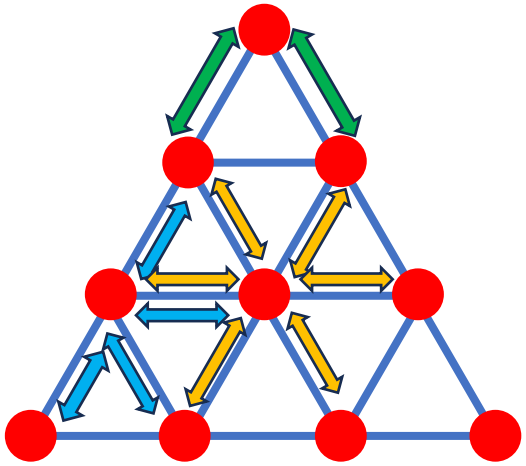










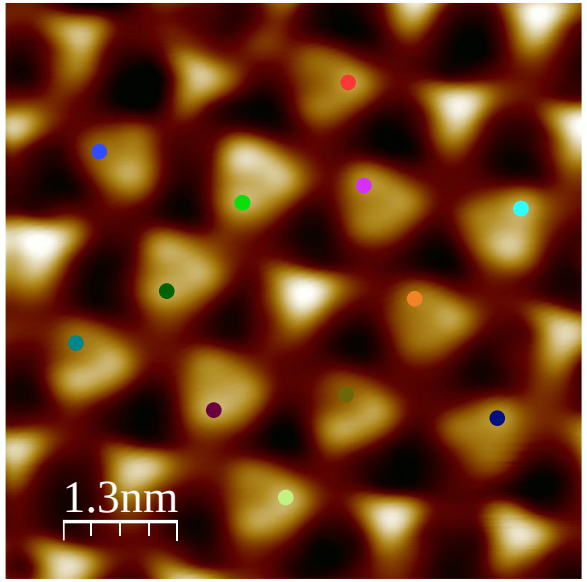


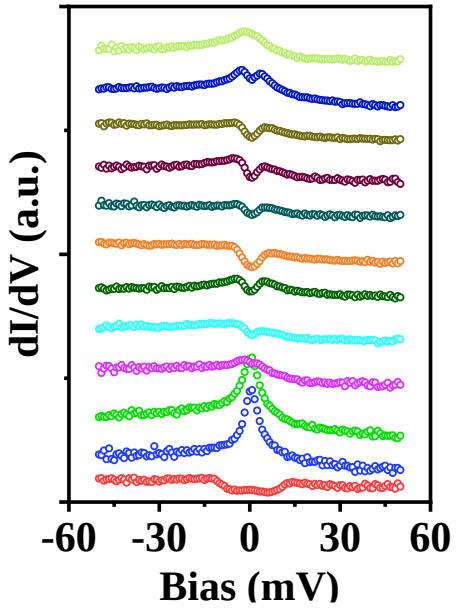
Large triangular arrays of radicals

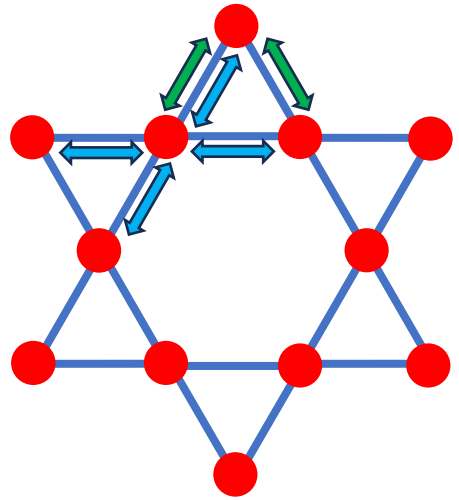
- Non-uniform and non-symmetric spectral features

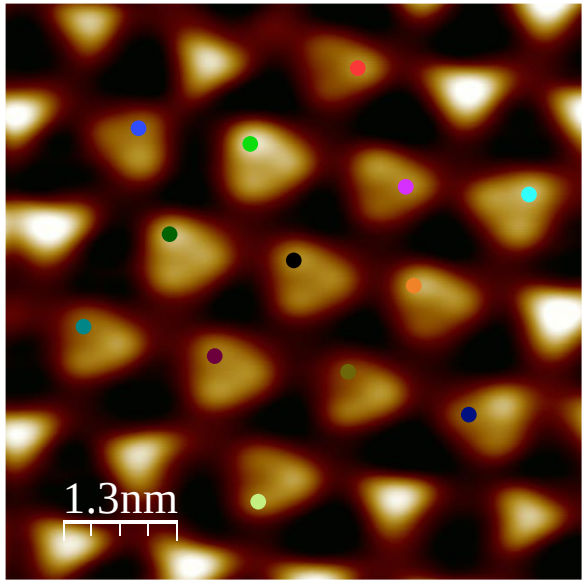
Proposal

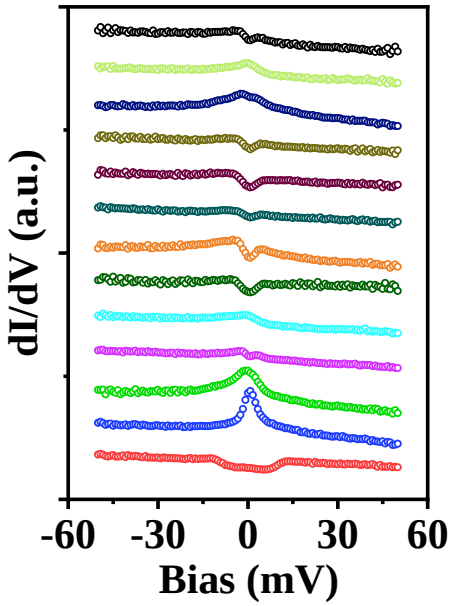
- Caused by fluctuations of the RKKY coupling strength

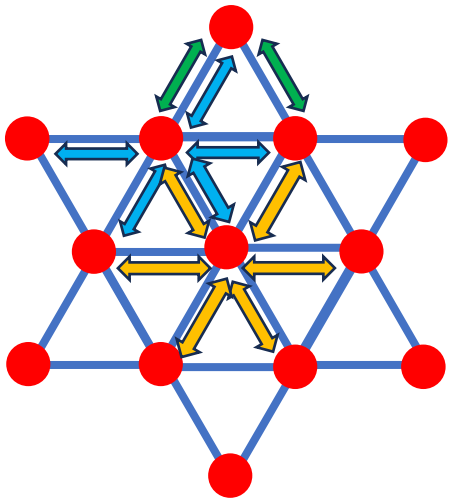












Conclusion

Experimental Achievement

- Create various multi-body radical structures, including the triangular trimer, rhombus tetramer, large triangular arrays, and David star pattern.
- Triangular trimers exhibit uniform and symmetric spectral feature
- Other larger structures exhibit non-uniform and non-symmetric spectral features

Proposal

- Non-uniform and non-symmetric spectral features in larger structures can be explained by non-uniform J_{RKKY} values.

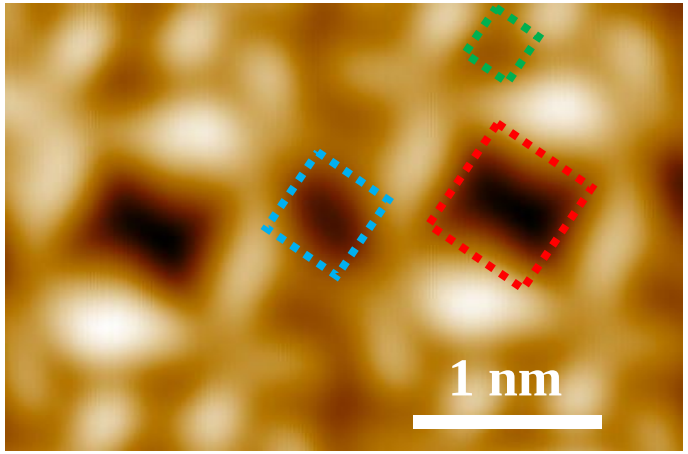
For the study

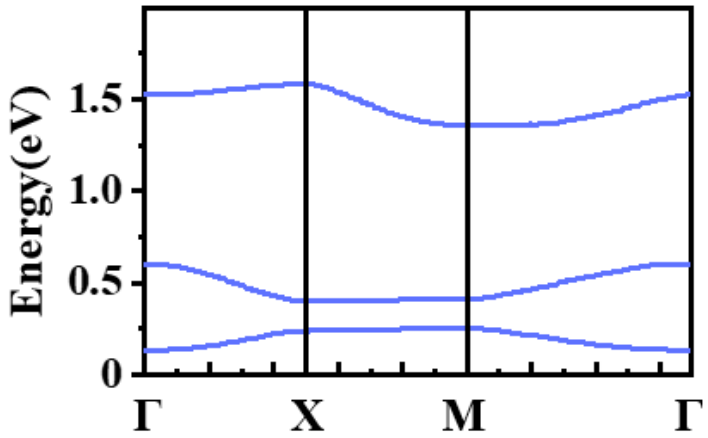
- Use Quantum Monte Carlo to understand the physic picture underlying

Part 6 Summary and Perspectives

Summary

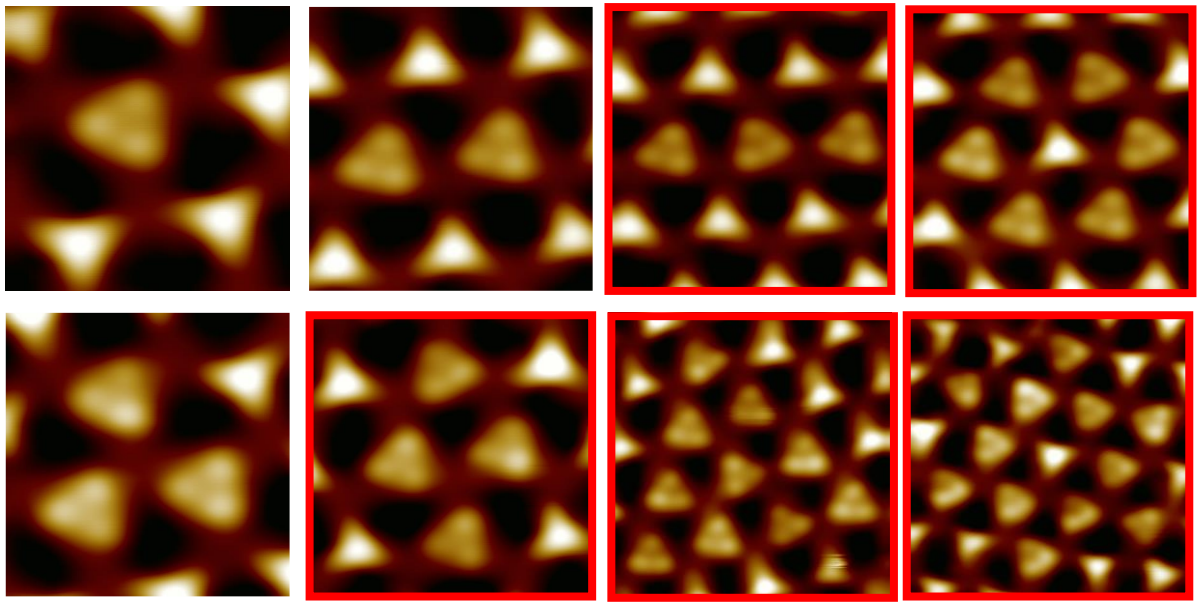
- **Isolated flat band in artificially designed Lieb lattice**



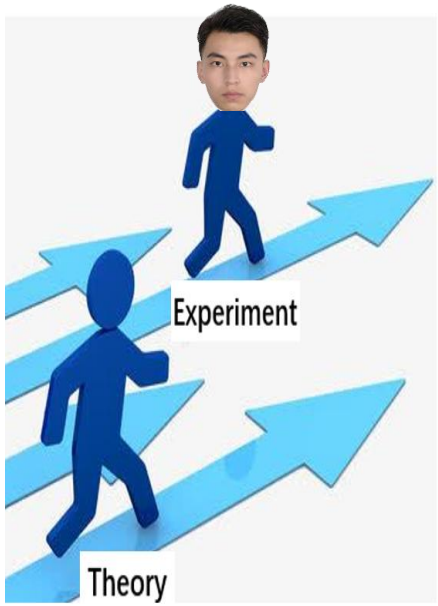


- Magnetic order
- Fractional quantum (spin) Hall effect
- Quantum anomalous Hall effect
- Raise the critical temperature of superconductors

- **Tip-manipulated Kondo structures**

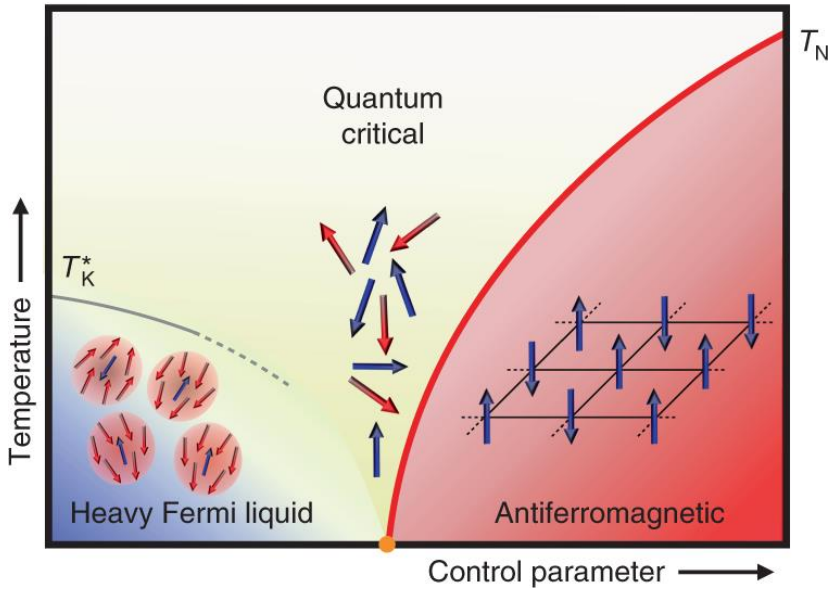


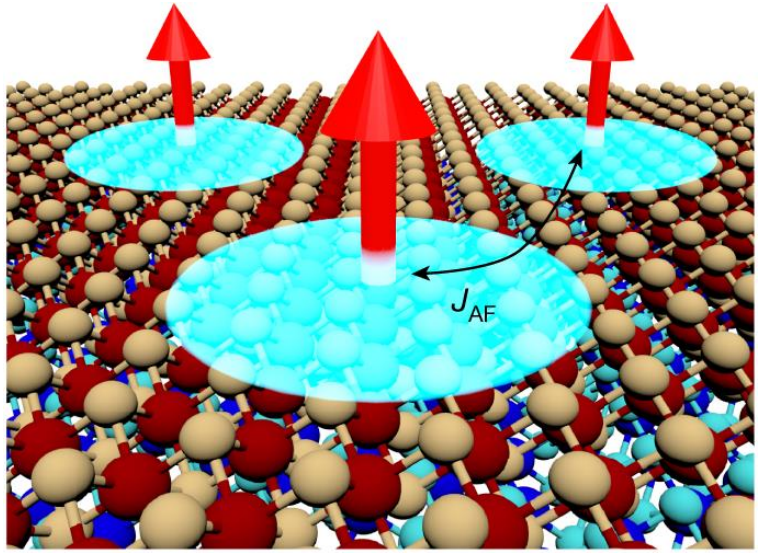
- Triangular Trimer (Robust)
- Larger structure (Non-robust)



Perspectives

Heavy-fermion system



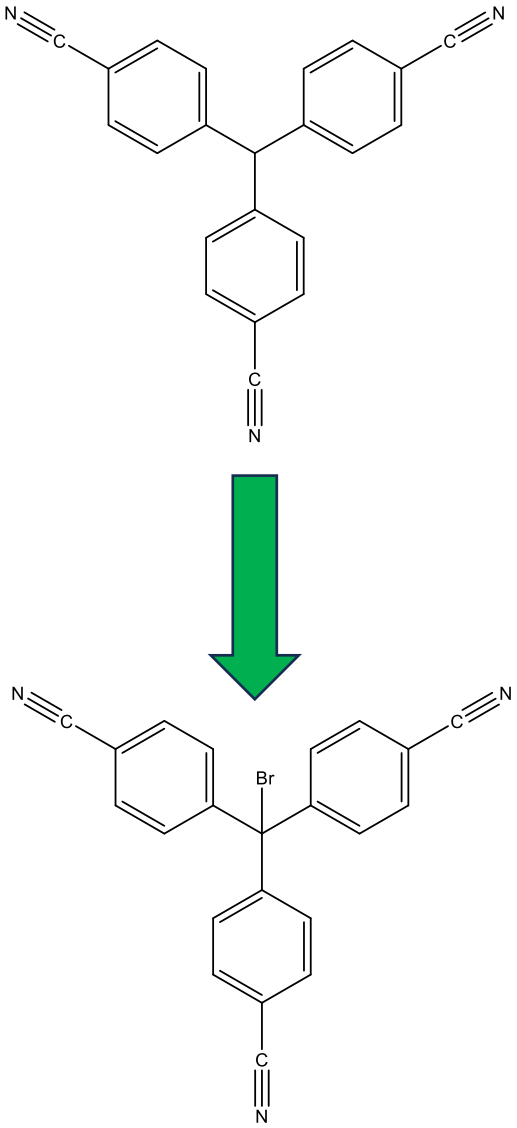


Achieved

- Kondo structures with finite size

For the study

- AI manipulation system→efficient and continuous operation→Kondo lattice
- Self-assembled Ni-TPM-Br Network→Kondo lattice



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Q&A