THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY | DEPARTMENT OF PHYSICS

香 港 科 技 大 學
THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY

# Investigation of Many-Body Quantum Spin Properties of Organic Radicals in Metal-Organic Frameworks

Presenter: Xin LIU

Supervisor: Prof. Nian LIN

Date: 27/08/2026

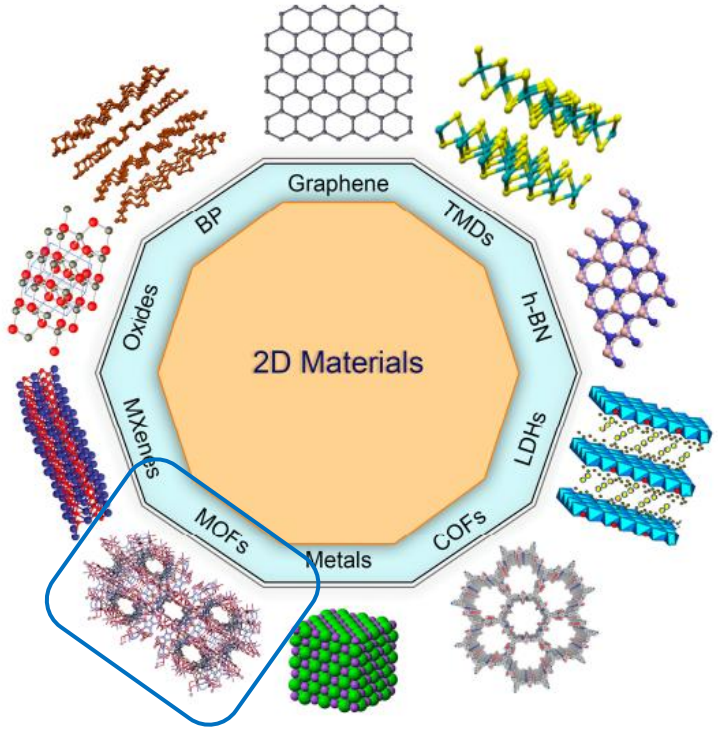


# Outline

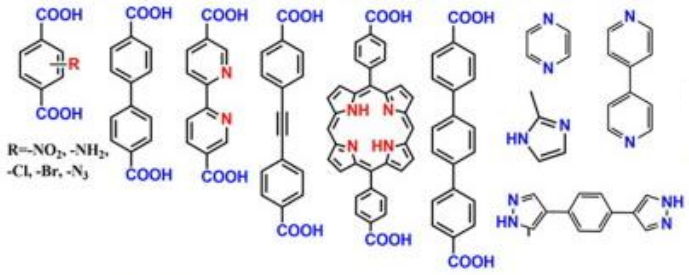
1. Introduction
2. Experimental Techniques
3. Modify Kondo Strength and Intramolecular Coupling of π-radicals
4. Enhance Intermolecular Coupling of π-Radicals using π-d-π Interaction
5. Regulate Kondo Resonance Using Metal Coordination
6. Confined Spin-Wave Excitation in Artificial π-Radical Lattice
7. Summary and Perspectives

# 1. Introduction

# From Nanomaterial to 2D-MOF

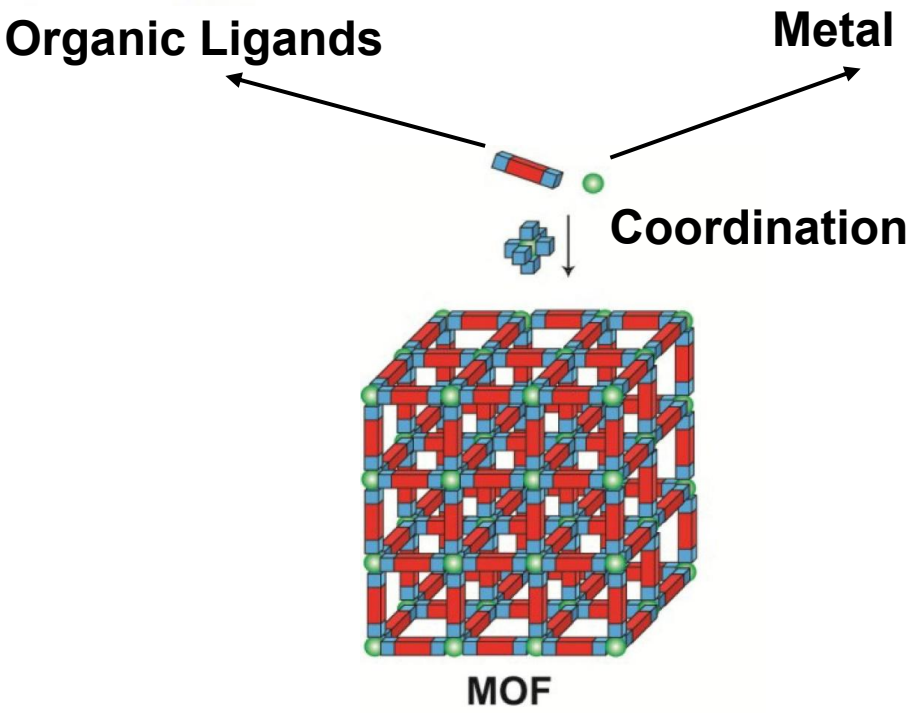



Kalantari, M.H *et al. Nanomaterials,* 2023, 13, 117.





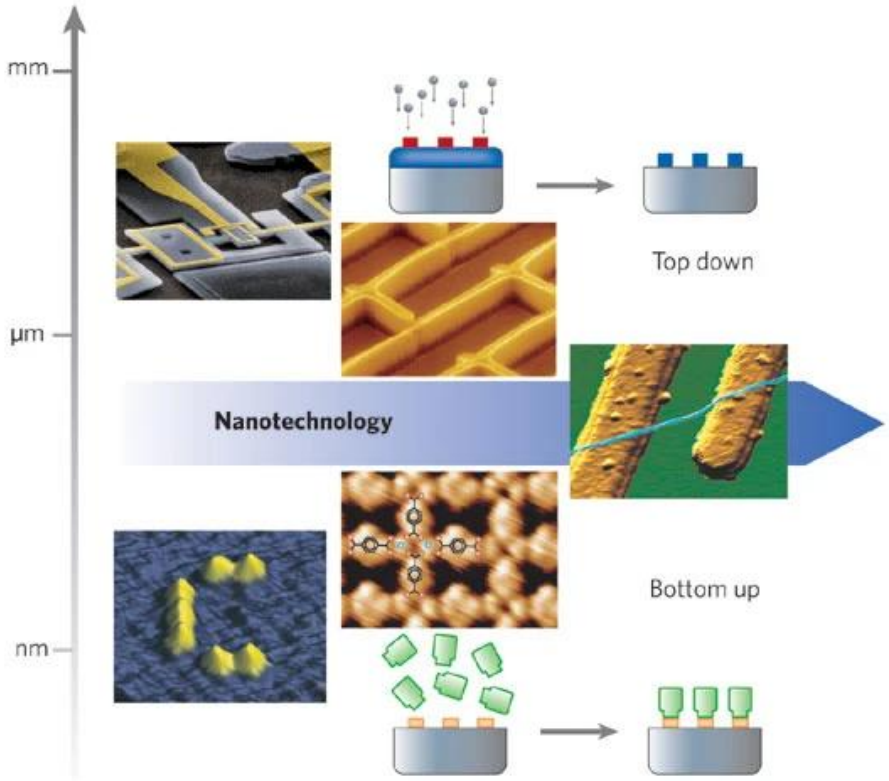




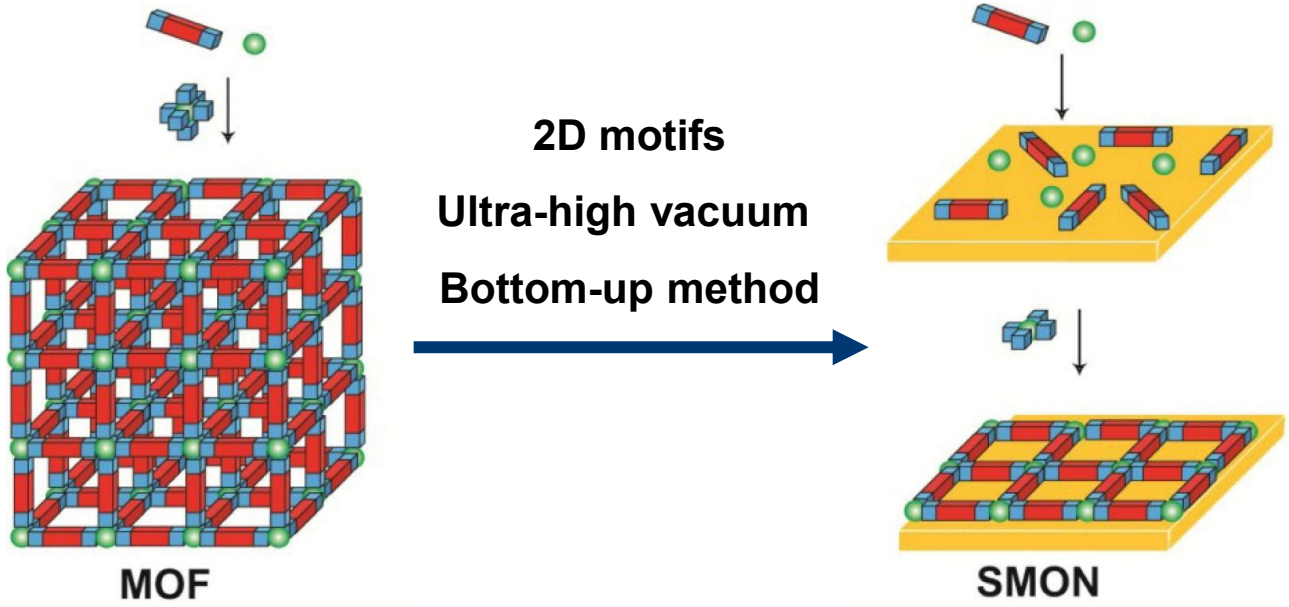

L. Dong *et al. Prog. Surf. Sci.*, 2016, 91(3), 101-135

# From Nanomaterial to 2D-MOF

## Bottom-up method: atomic precision



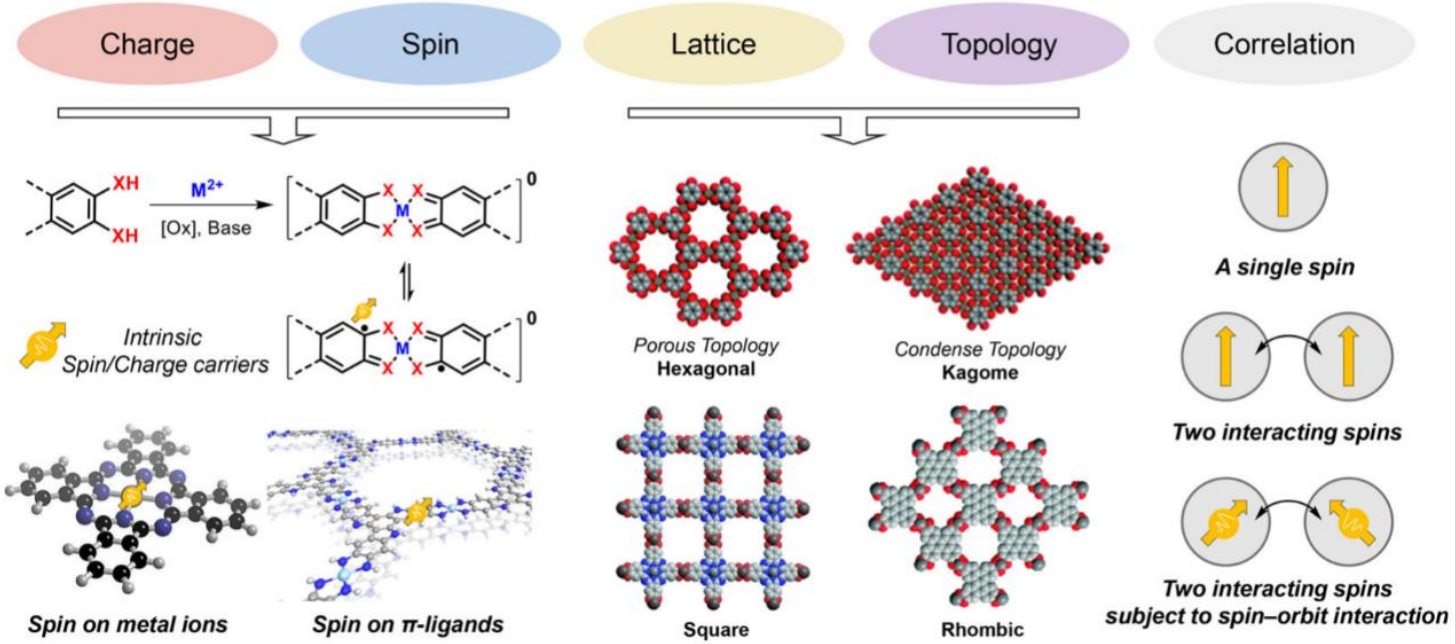

J. V. Barth *et al. Nature*, 2005, 437(7059), 671-679




L. Dong *et al. Prog. Surf. Sci.*, 2016, 91(3), 101-135

# From Nanomaterial to 2D-MOF

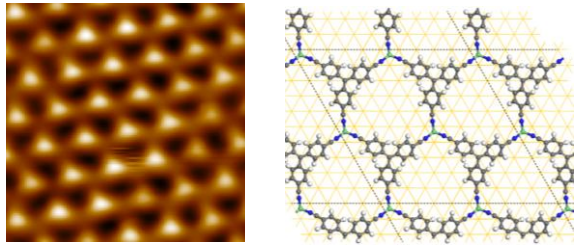
## Tunable properties of 2D-MOF




Mingchao Wang *et al. Chem. Soc. Rev.*, 2021, 50, 2764.

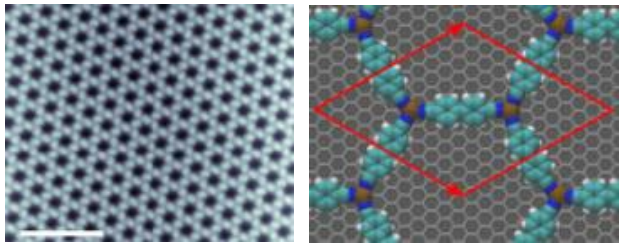
## Examples of 2D-MOF symmetry

### Triangular lattice



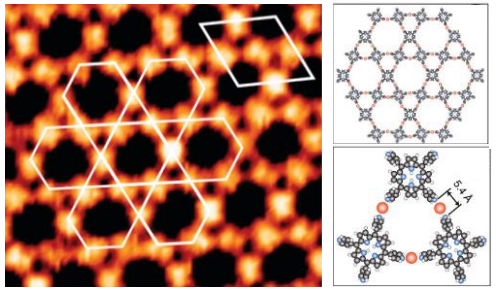
Chen C *et al. J. Am. Chem. Soc*, 2025, 147(39), 35464-35470.

### Honeycomb lattice



Kumar A *et al. Nano letters*, 2018, 18(9), 5596-5602.

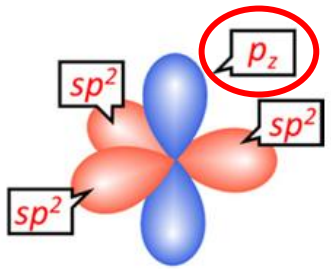
### Kagome lattice



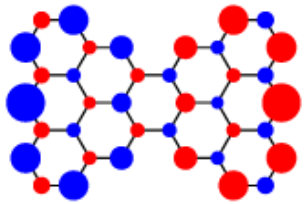

Shi Z, Lin N. *J. Am. Chem. Soc.*, 2009, 131(15), 5376-5377.

# Magnetism of π-Radical

## π-magnetism



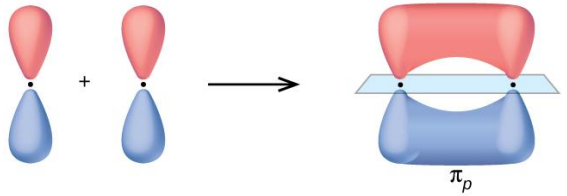

Singly occupied $p_z$ orbital



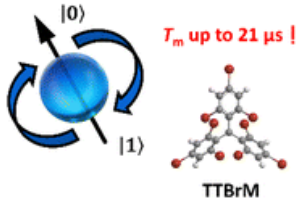
Unpaired $p_z$ electron in graphene-based materials

## Compared to other magnetisms

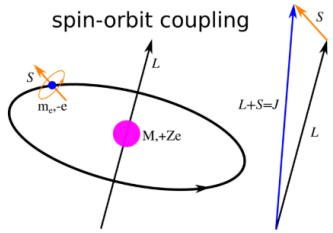
- **High delocalization**



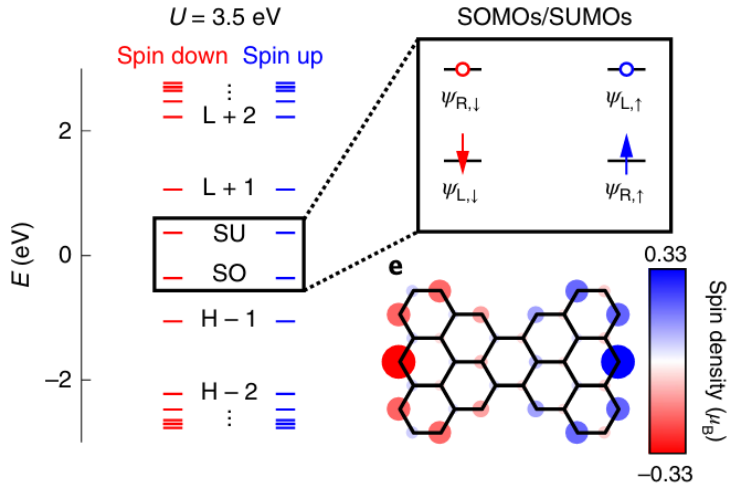

- **Long spin coherence time**



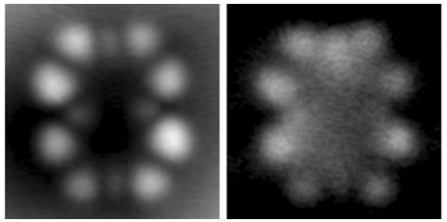

- **Weak spin-orbital coupling**




## Molecule with π-radical on surface

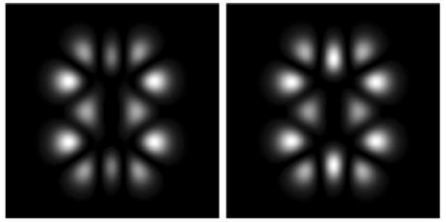



Experimental dI/dV maps



SOMO SUMO

MFH-LDOS maps

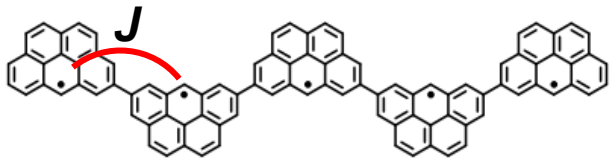


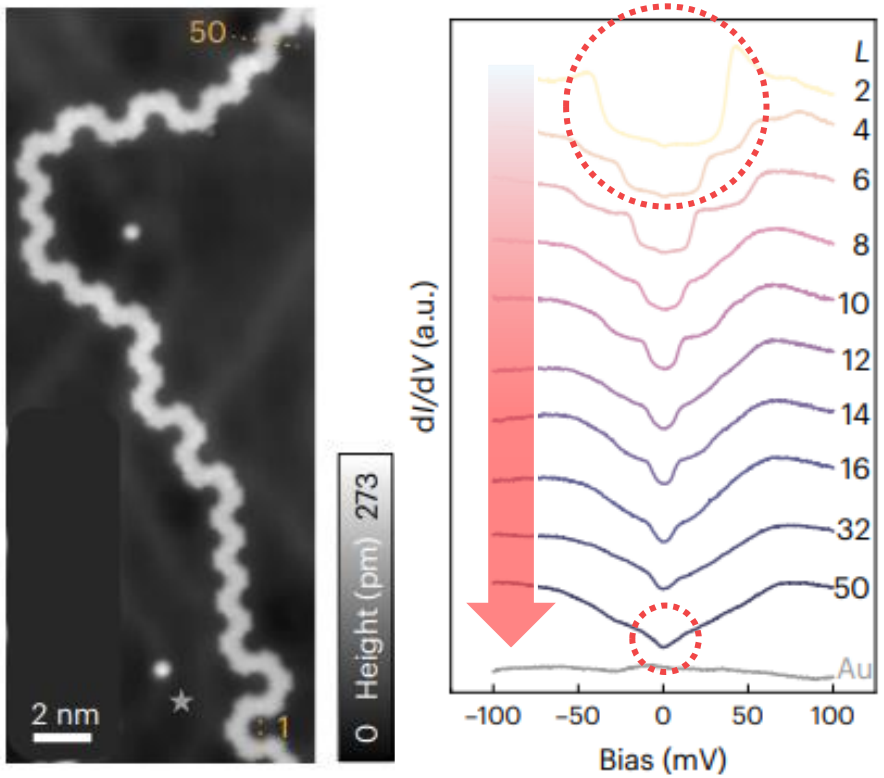
SOMO SUMO

S. Mishra *et al. Nat. Nanotechnol.*, 2020, 15, 22-28.

# Spin Correlation of π-Radicals in 2D-MOF

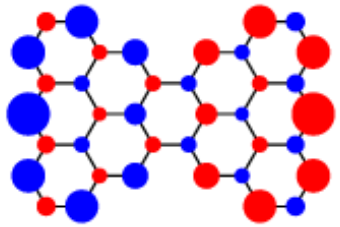
## Recent work of spin correlation of π-radicals in 1D system



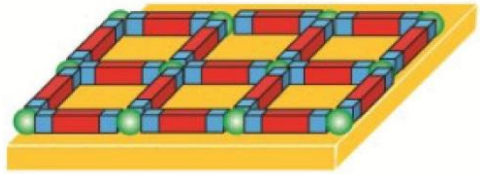




Zhao, C. *et al. Nat. Mater.* 24, 722–727 (2025).

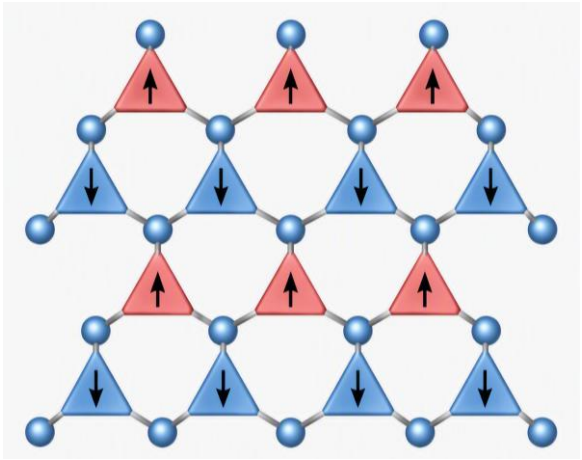
## Our goal: Many-body spin correlation of π-radicals in 2D system



Organic ligands with π-radicals



2D-MOF on surface

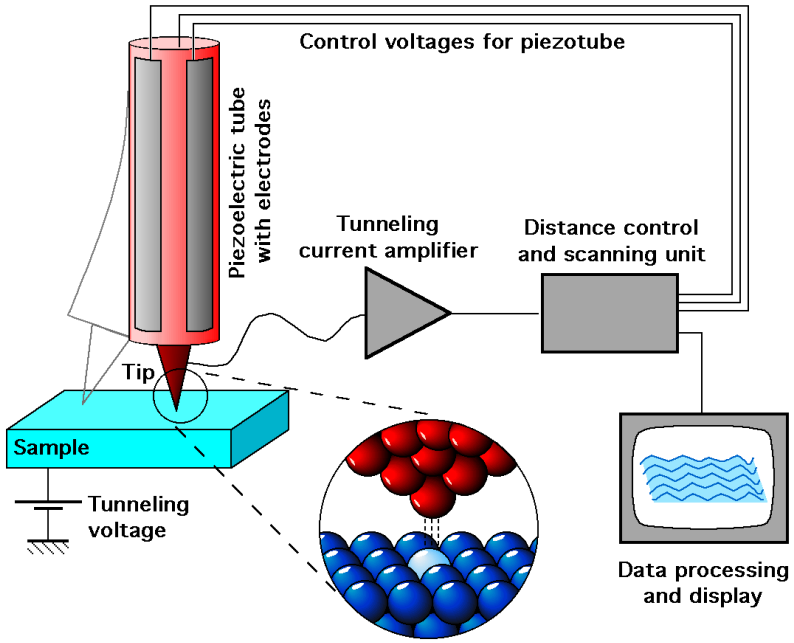


Spin correlation of π-radicals in 2D-MOF

# 2. Experimental Techniques

# Scanning Tunneling Microscopy and Spectroscopy

## Scanning Tunneling Microscopy (STM)




**Tunneling current**

**Work function**

$$I \propto V \cdot e^{-\frac{2\sqrt{2m\Phi}}{\hbar} d}$$

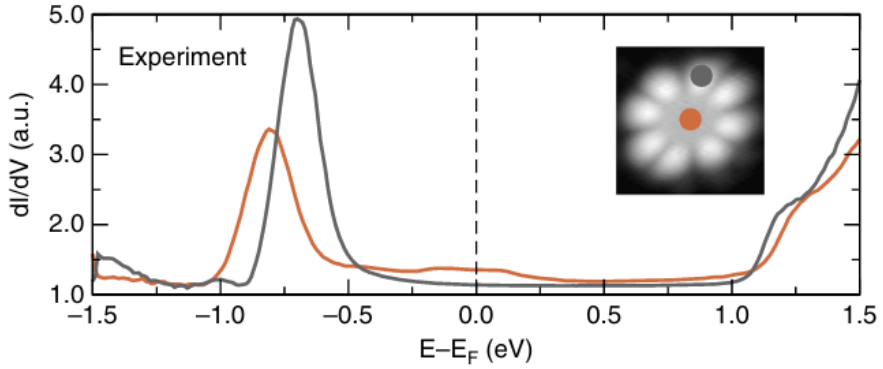
**Bias voltage**

**Distance between tip and sample**

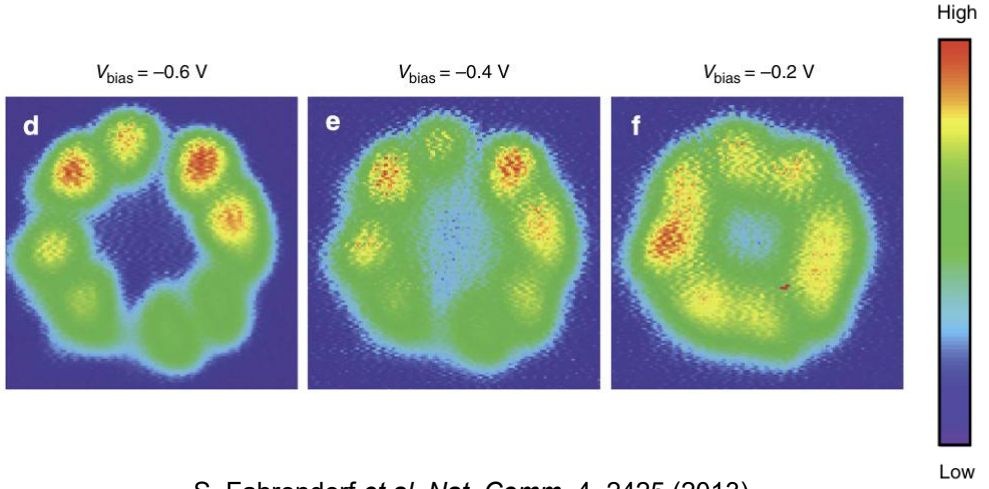
## Scanning Tunneling Spectroscopy (STS)

$$\frac{dI}{dV} \propto \rho_s(E_F + eV)$$ → **Local density of state (LDOS)**

**Site-specific dI/dV spectra**



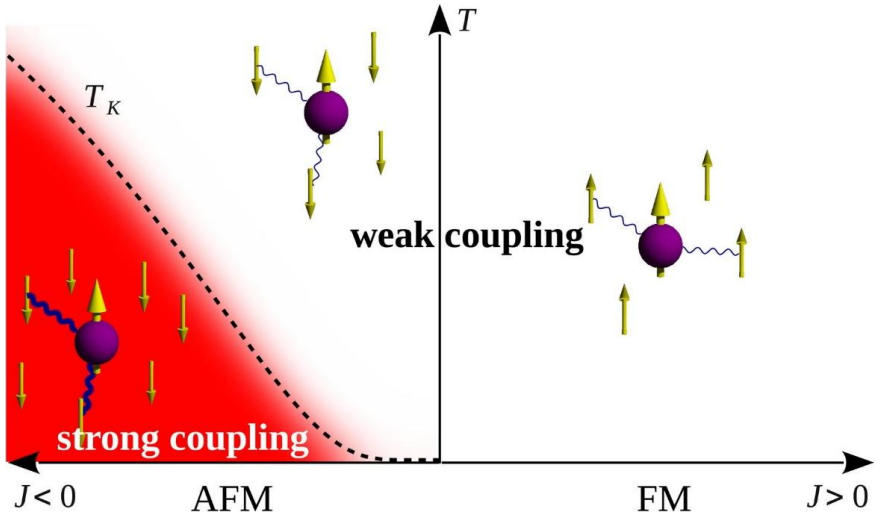

**Spatial dI/dV mapping**



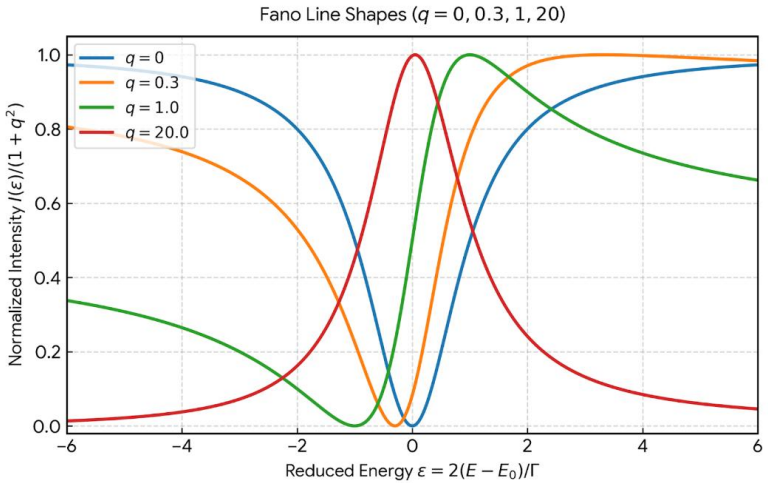

S. Fahrendorf *et al. Nat. Comm.* 4, 2425 (2013).

# Kondo Effect

## Phase diagram of Kondo effect



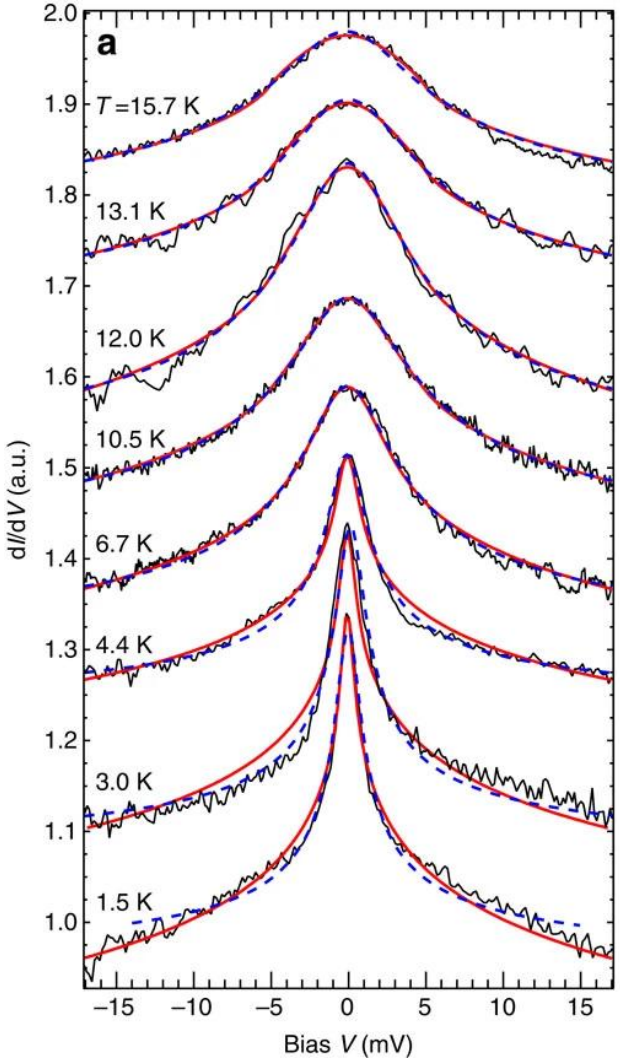

M. Ternes. *Prog. Surf. Sci.* 92(1), 83-115 (2017).




**Fano Line Formula:**

$$\frac{dI}{dV}(V) = A \cdot \frac{(q+\epsilon)^2}{1+\epsilon^2} + B(V)$$

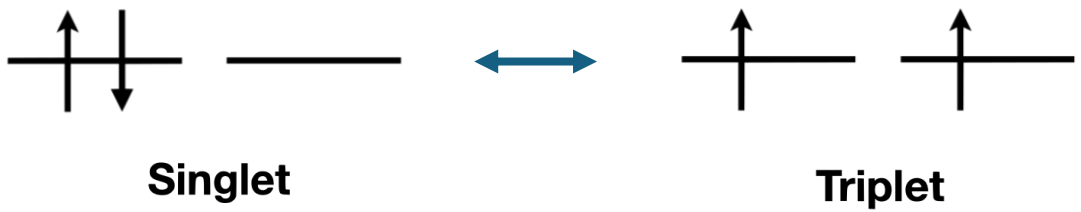
## Typical dI/dV spectra of Kondo resonance

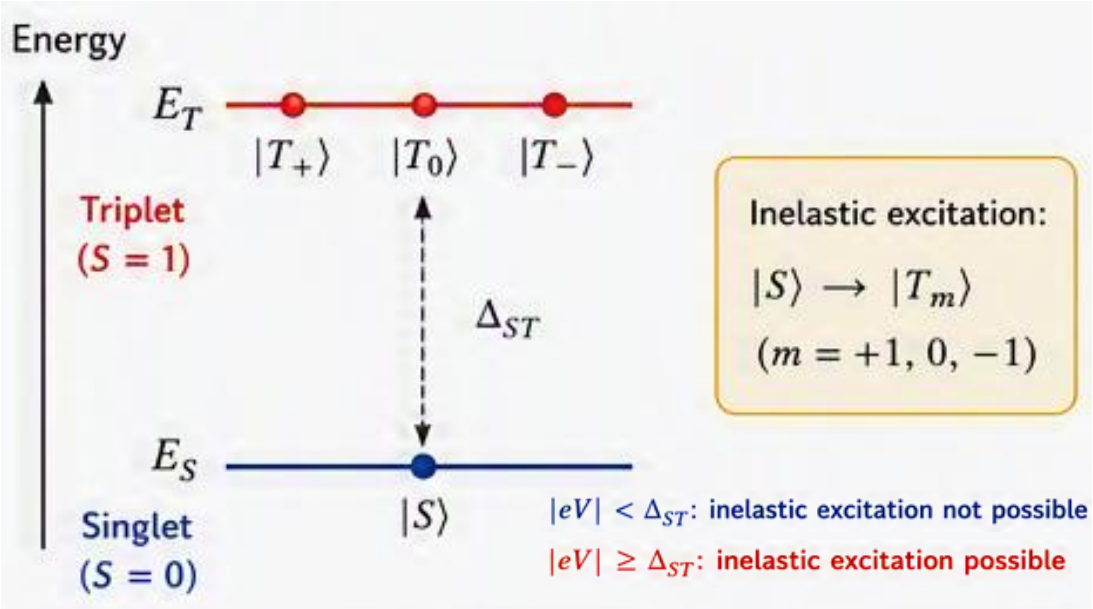



Y.-h. Zhang et al. *Nat. Comm.* 4(1), 2110 (2013).

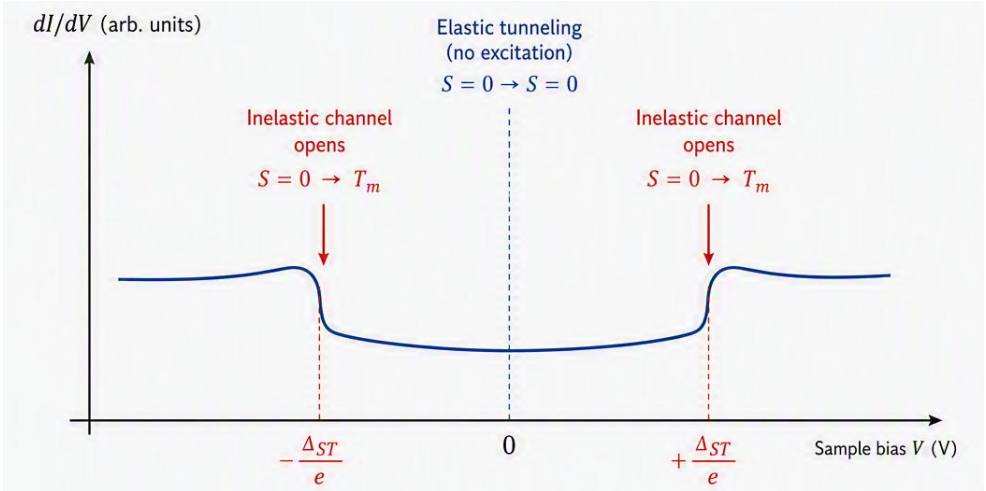
# Spin Flip Excitation

## Spin flip excitation in two-spin system

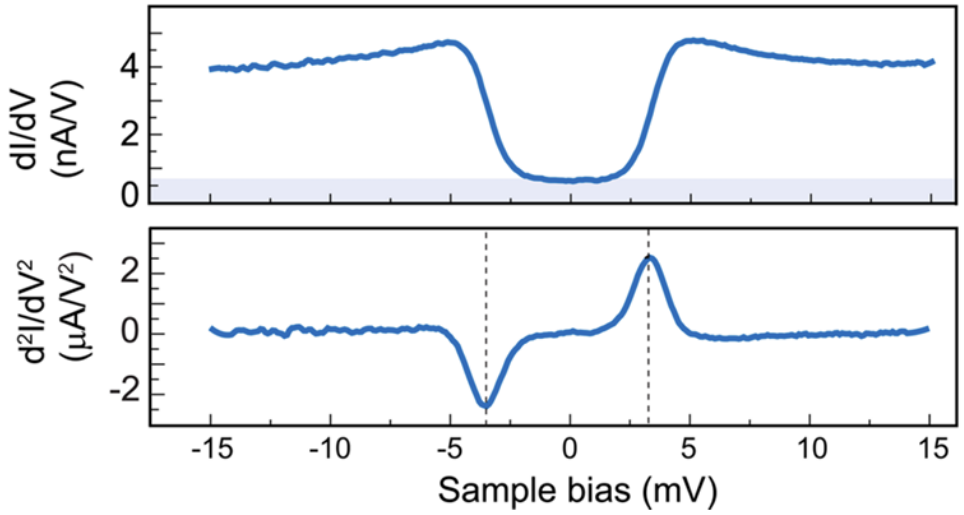



## Theoretical dI/dV spectra of spin flip excitation



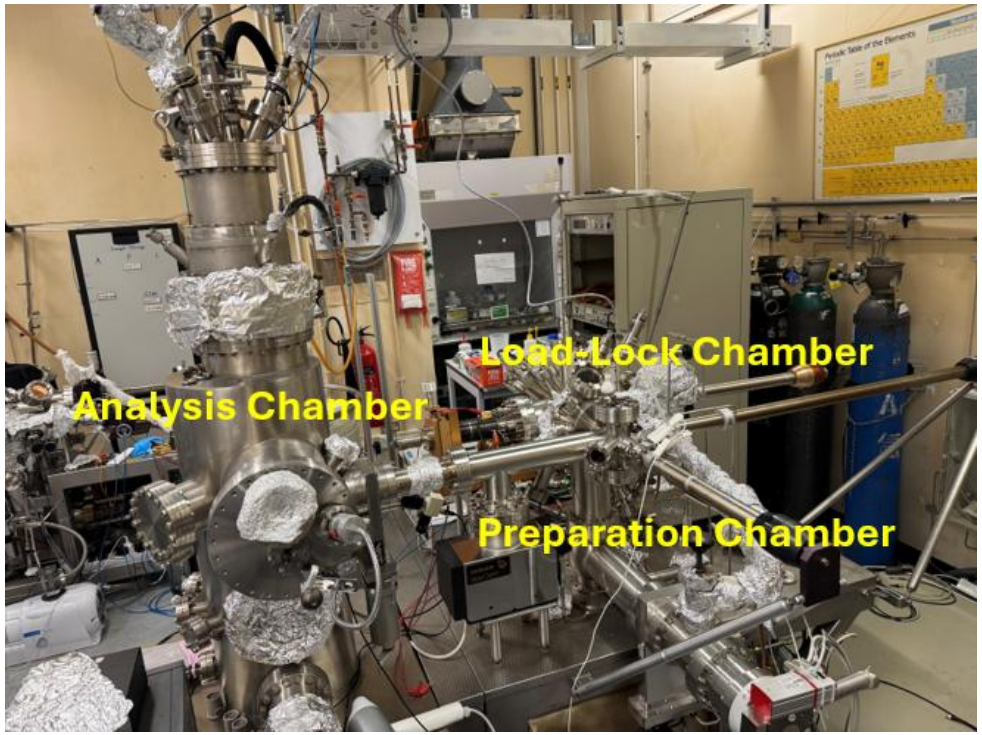

## Experimental dI/dV spectra of spin flip excitation




M. Ormaza et al. *Nano. Lett.* 17(3), 1877-1882 (2017).

# Instrument

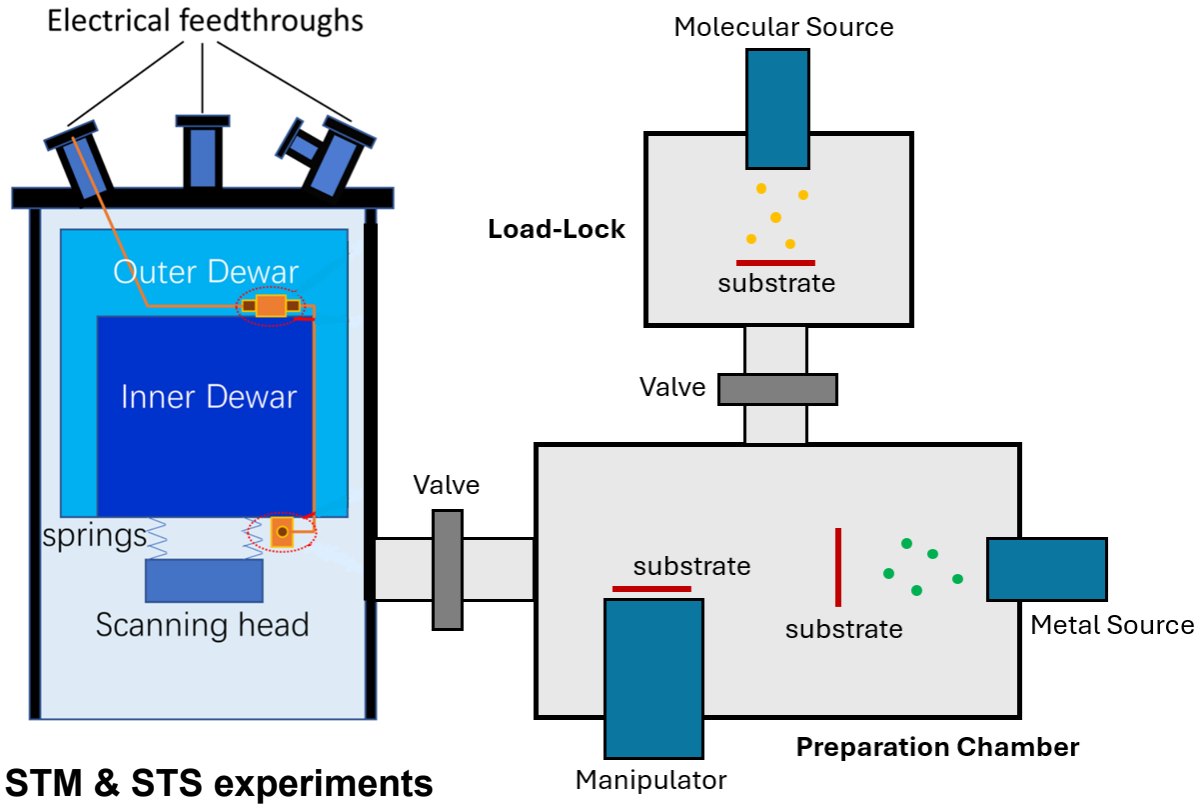
## LT-Omicron STM




**Pressure: ~3*10$^{-10}$ mbar**

**Temperature: 77K / 4.8K**

## Instrument Model



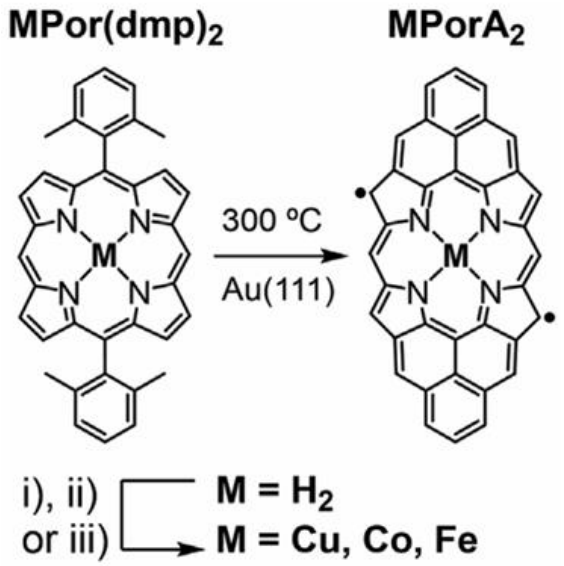

**STM & STS experiments**

**Organic Molecular Beam Epitaxy (OMBE)**
**&**
**On-surface self-assembly**

# 3. Modify Kondo Strength and Intramolecular Coupling of π-radicals

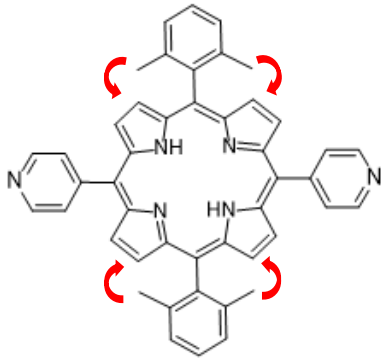
# Design of Experiment

## Former work



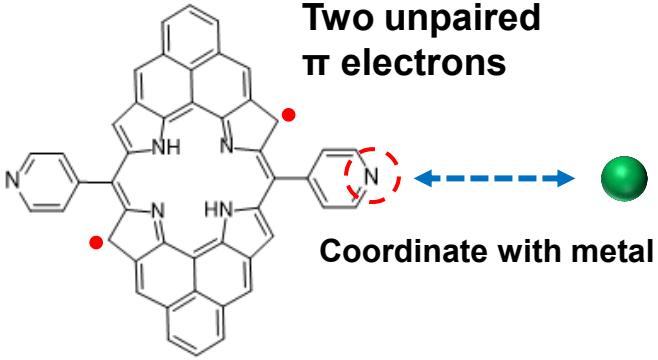

Q. Sun et al. *Adv. Sci.* 9, 105906 (2022).

## Our design



5,15-bis(2,6-dimethylphenyl)-10,20-di(pyridin-4-yl)porphyrin (Por)

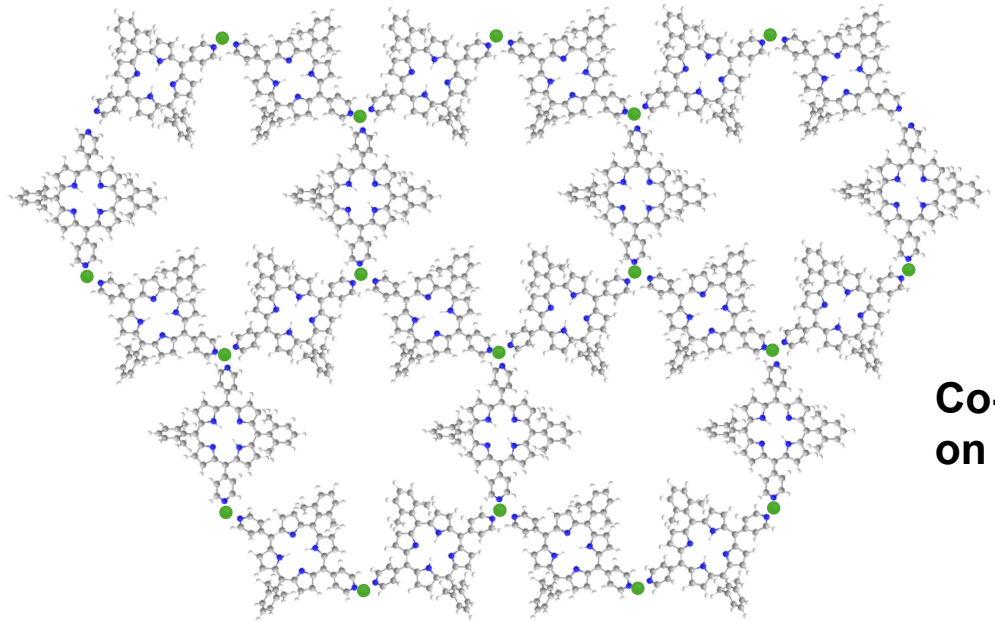
300℃
Au(111)



Two unpaired π electrons

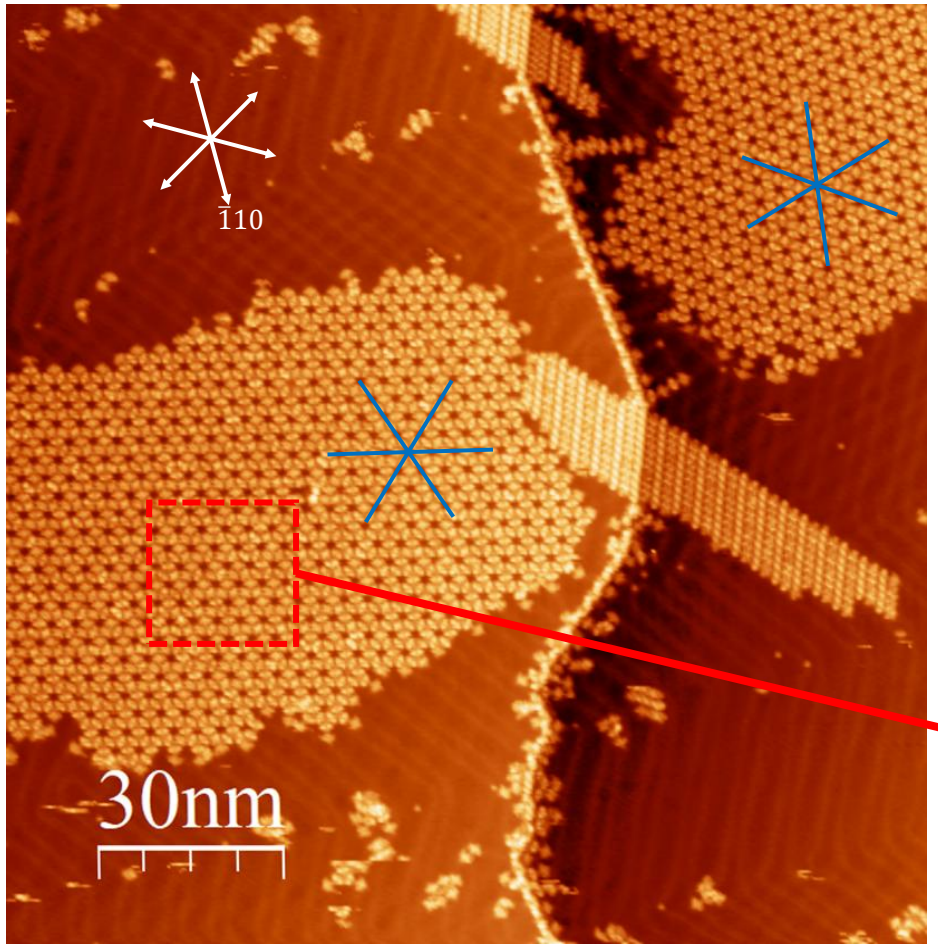
Coordinate with metal atoms (e.g., Co)

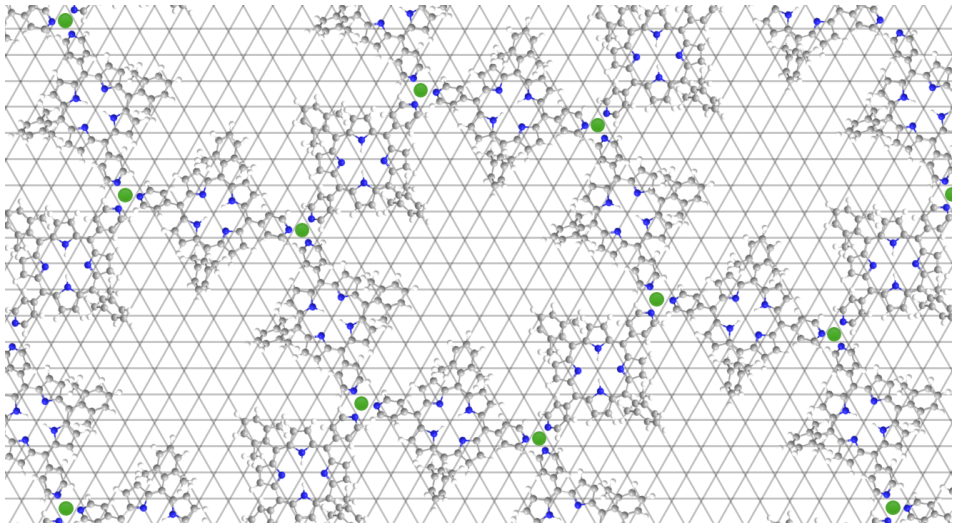
Radical Por

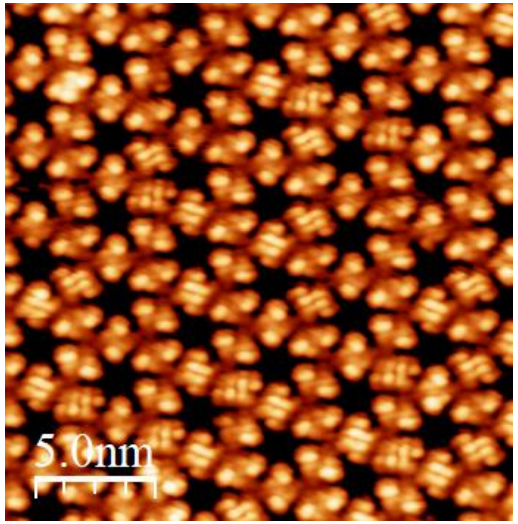


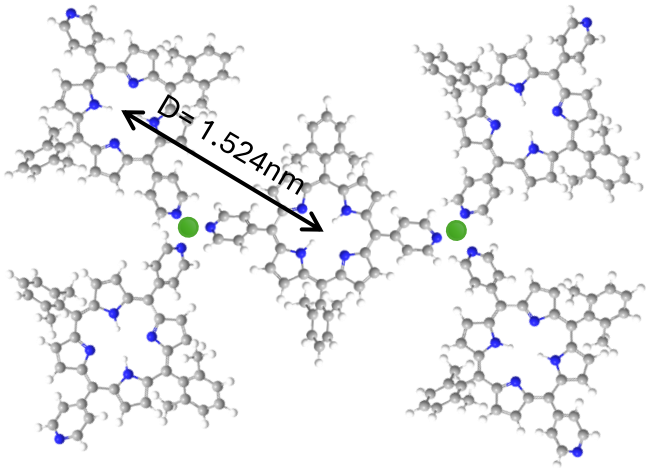
Co-Por 2D-MOF on Au(111)

# STM Topography and Model

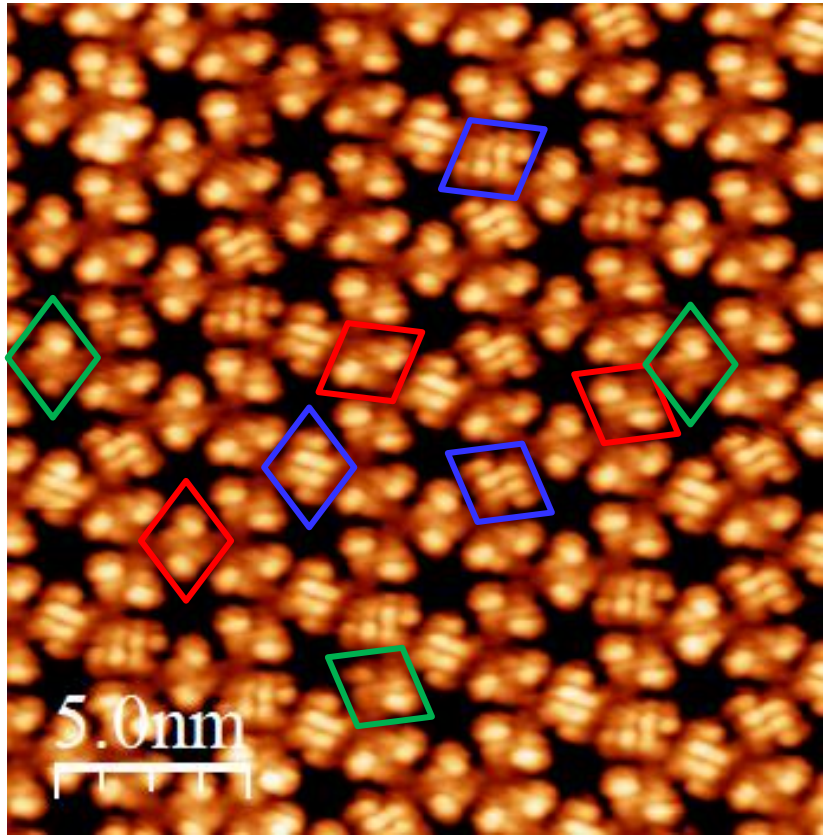


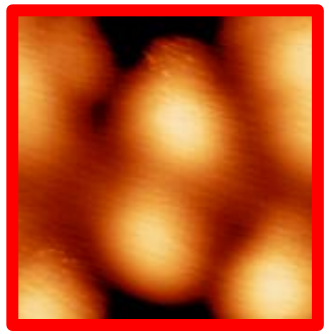


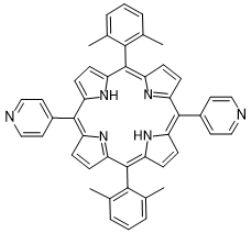



# Three Types of Por Molecules




| Annealing treatment | Type A | Type B | Type C |
|---|---|---|---|
| T=100℃, t=15min | 92% | 5% | 3% |
| T=158℃, t=2min | 70% | 15% | 15% |
| T=161℃, t=3min | 50% | 50% | 0% |

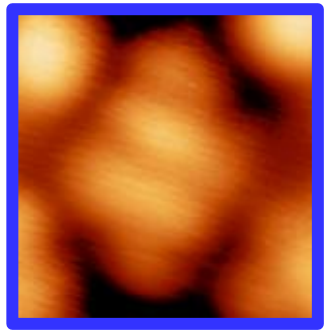


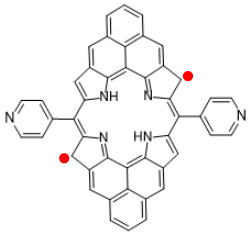


**Type A Por**

**No cyclodehydrogenation**

**No radical**



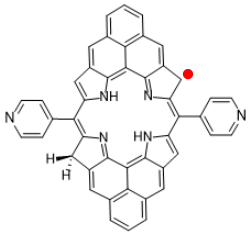


**Type B Por**

**After cyclodehydrogenation**

**Two radicals**





**Type C Por**

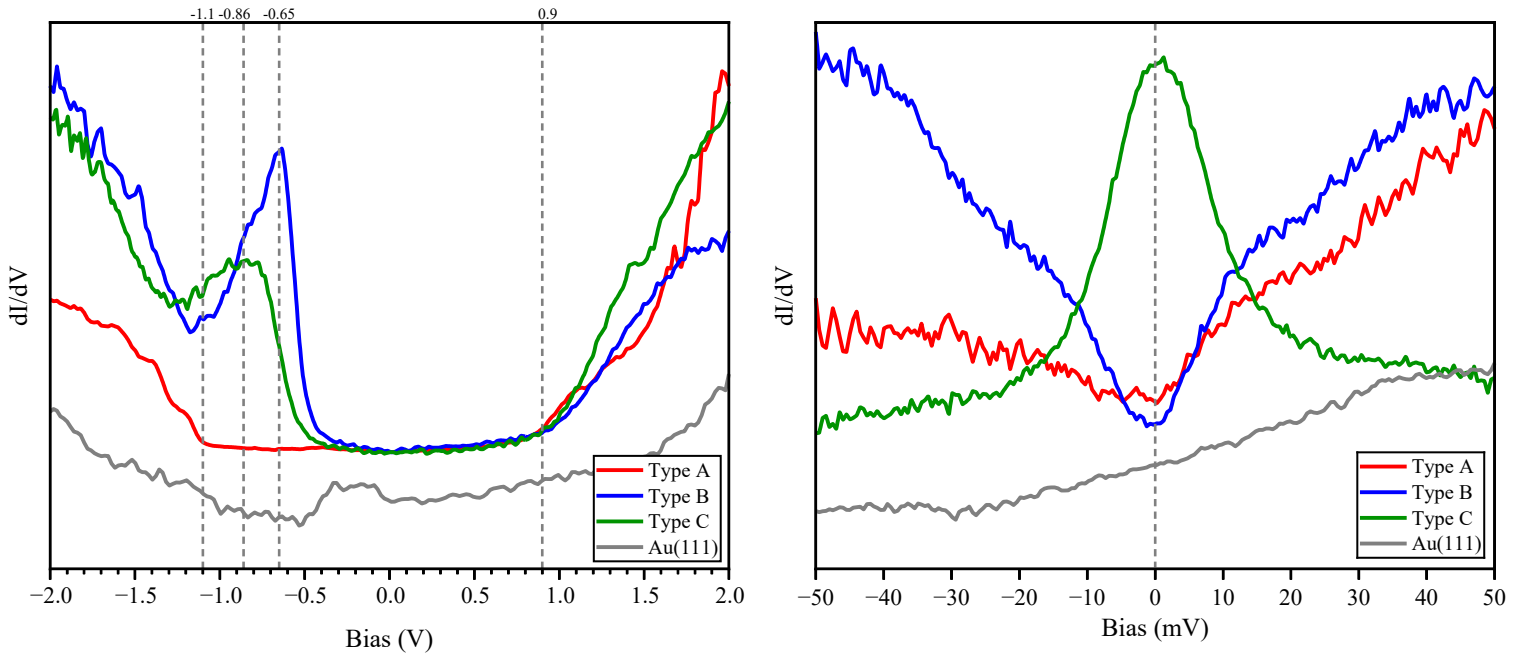
**After cyclodehydrogenation**

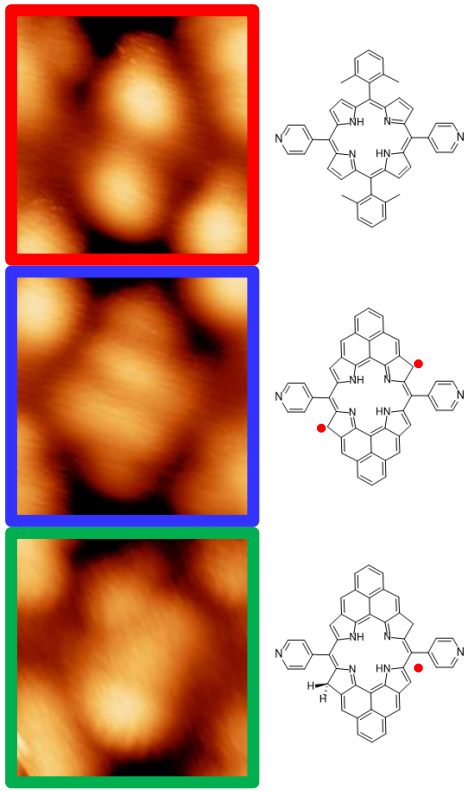
**Capture one hydrogen atom**

**One radical**

# STS Spectra and Analysis

**Experimental data of STS spectra in both large and small bias range**



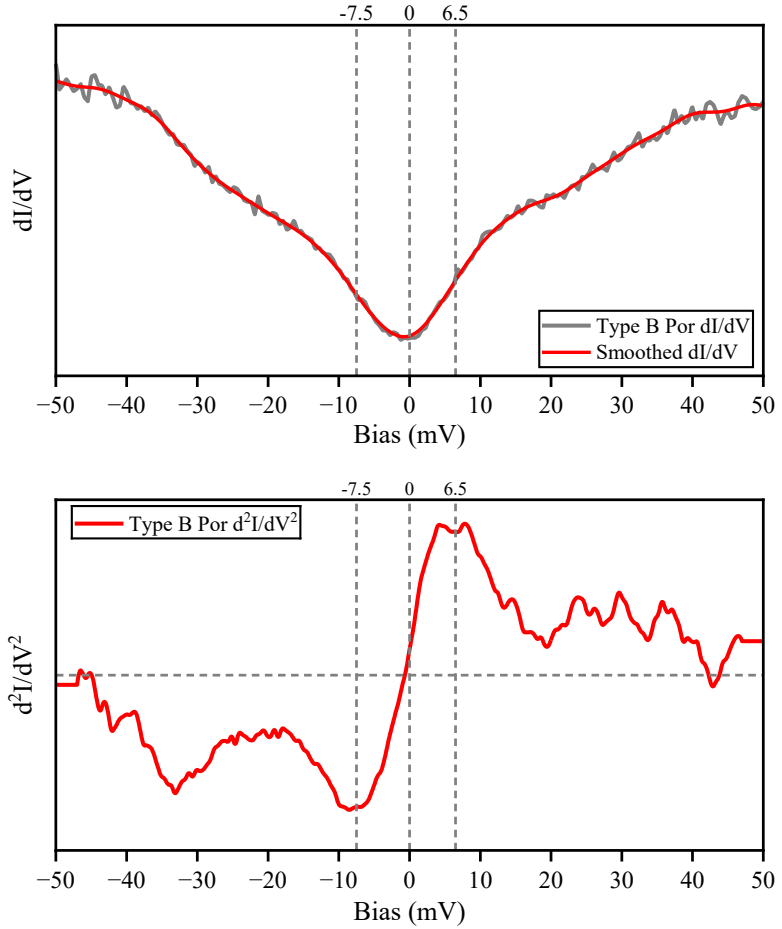
**Type A Por (0 radical)**

**Type B Por (2 radicals)**

**Type C Por (1 radical)**

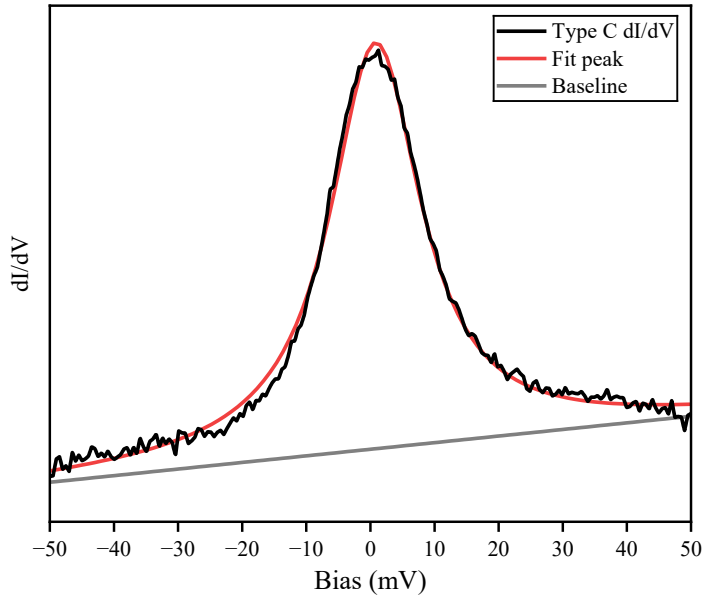
# STS Spectra and Analysis

## Spin flip excitation of Type B Por



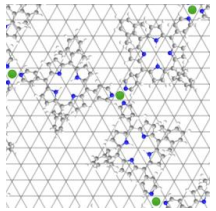
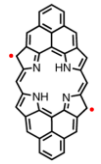
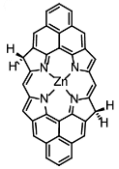
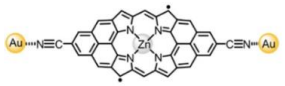

**Spin excitation energy ~7 meV**

## Kondo resonance of Type C Por




**Kondo temperature ~99.6 K**

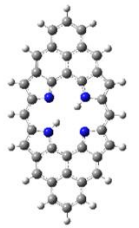
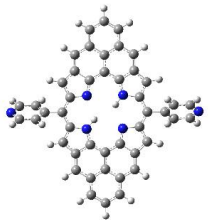
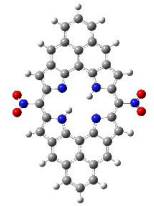
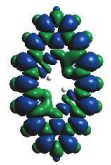
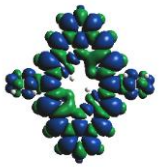
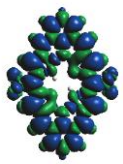
# Compare with Other Works

| Radical Por system | Model of radical Por system | Spin excitation energy (for two radicals) | Kondo temperature (for one radical) |
|---|---|---|---|
| Co-Por MOF on Au(111) (our work) |  | 7±2 meV | 99.6±11K |
| Por on Au(111) |  | 20 meV | 31K |
| ZnPor on Au(111) |  | 19.4 meV | N.A. |
| Por M on Au(111) |  | 26 meV | ~90K |

**Lower spin excitation energy** ⇨ **Weaker intramolecular coupling**

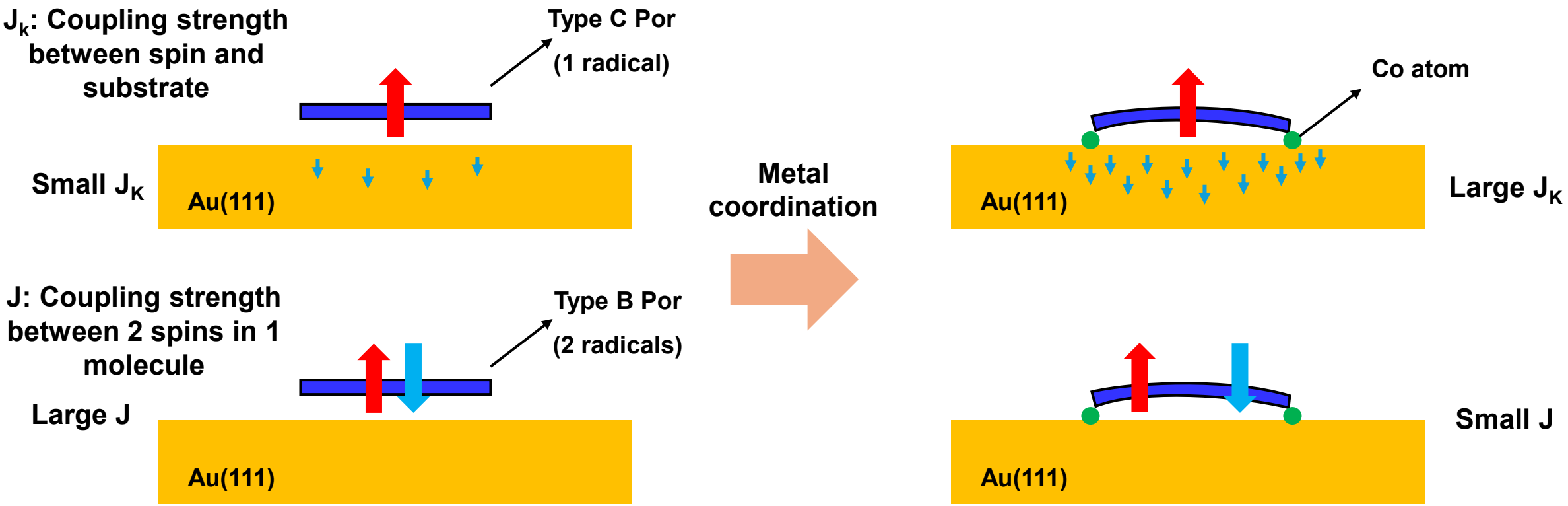
**Higher Kondo temperature** ⇨ **Stronger Kondo resonance**

## Simulation of the effect of high-electronegative connection

| Molecule |  |  |  |
|---|---|---|---|
| Excitation energy (meV) | 47.8 | 45.3 | 24.9 |
| Ground State | Triplet | Triplet | Triplet |
| Spin density map |  |  |  |

# Conclusion

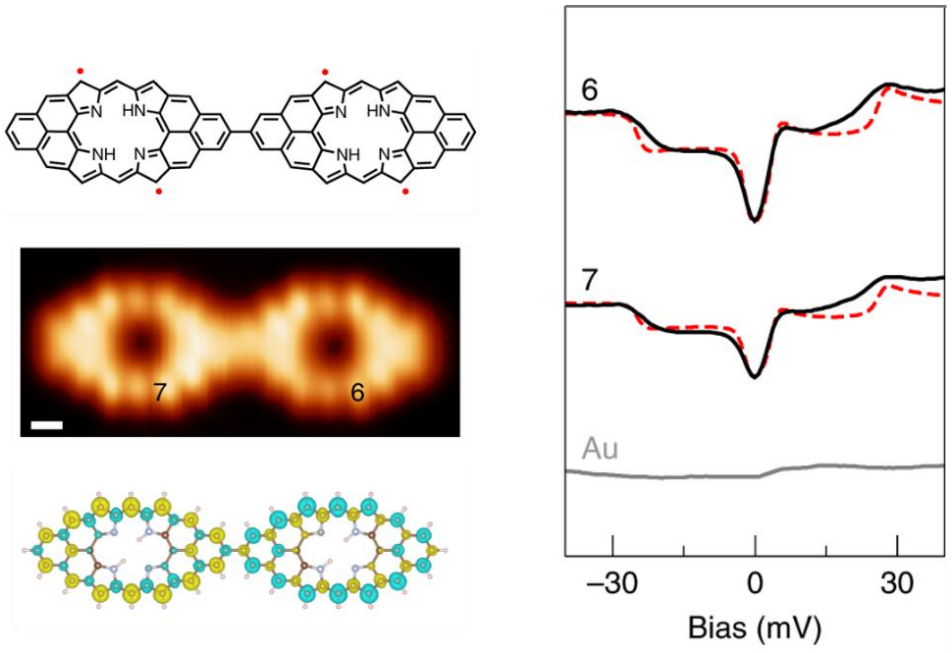
- **Metal coordination effectively enhances Kondo resonance in single-radical Por and weakens intramolecular spin coupling in double-radical Por.**



# 4. Enhance Intermolecular Coupling of π-radicals using π-d-π Interaction

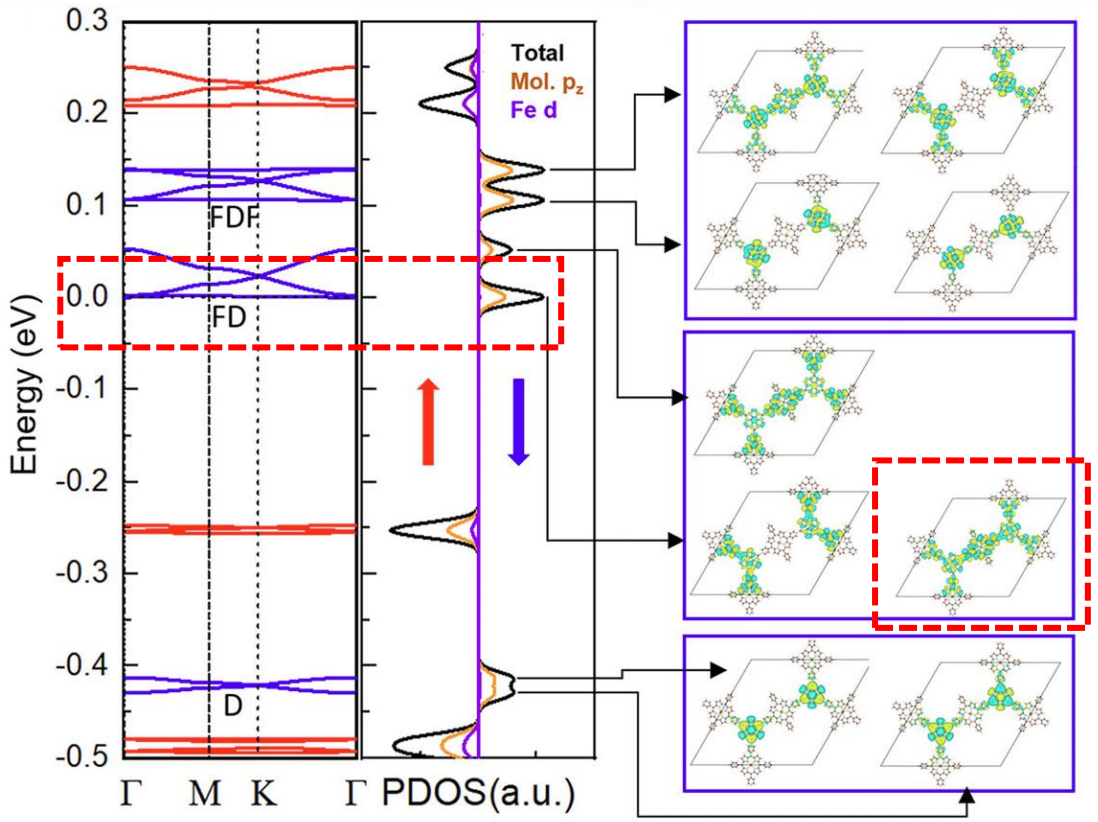
# Intermolecular coupling

## Intermolecular coupling in covalent system



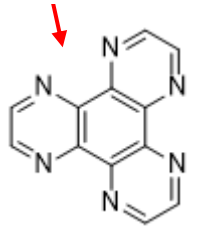

Y. Zhao et al. *Nat. Chem.* 15, 53-60 (2023).

## In 2D-MOF



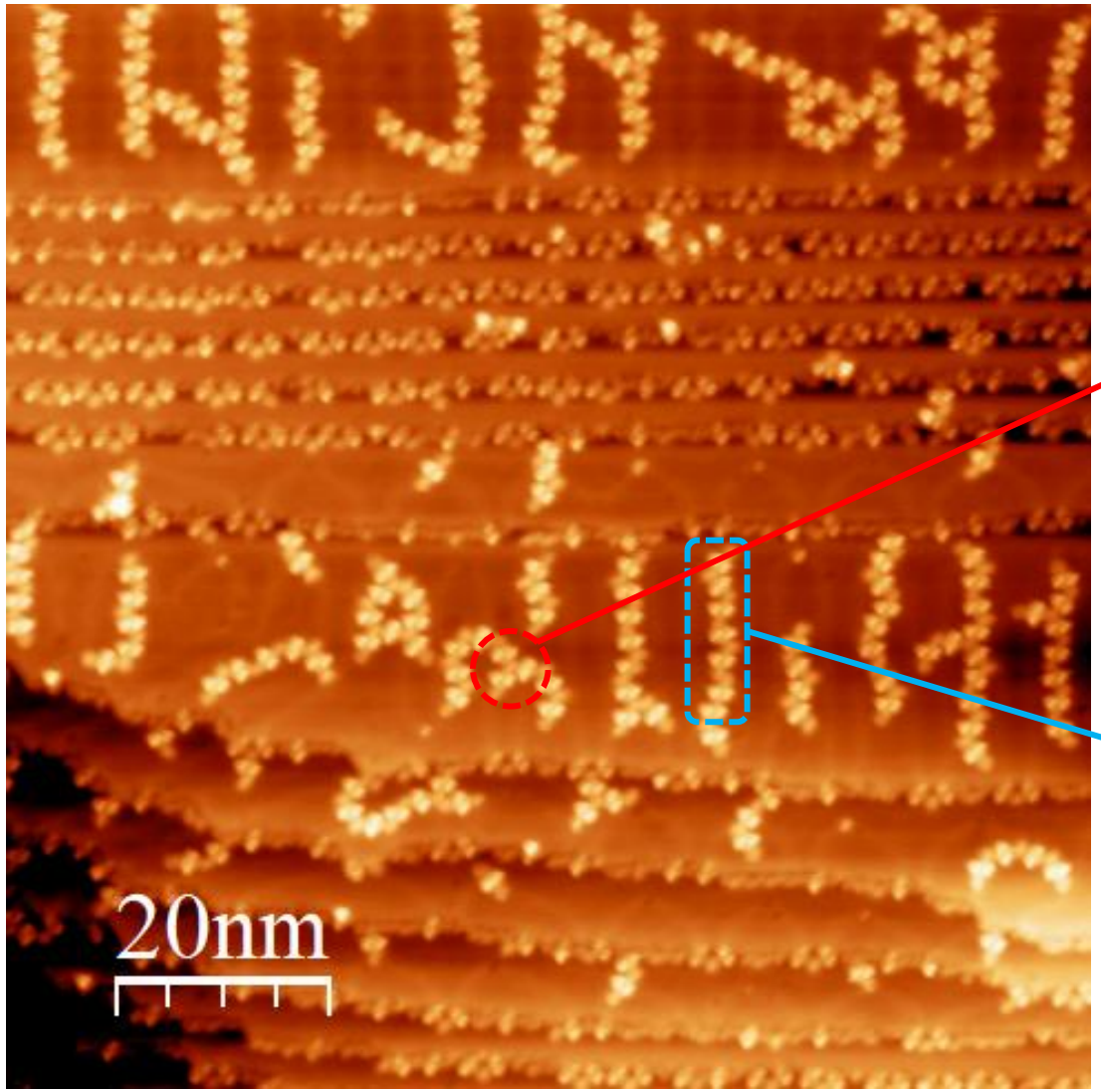

X. Wang et al. *Comm. Chem.* 6, 73 (2023).

**HAT molecule enhance π-d-π coupling in 2D-MOF**

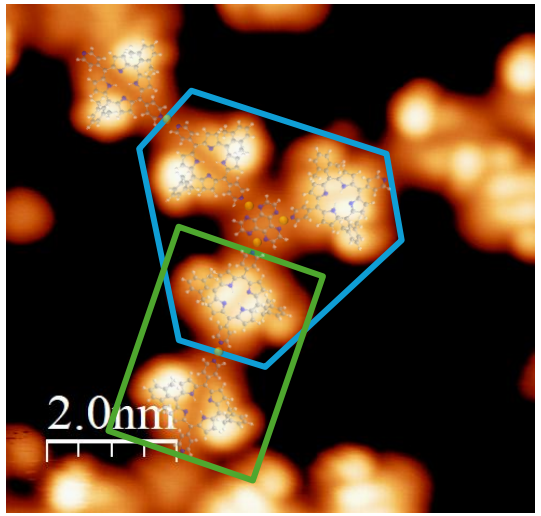


**Hexaazatriphenylene (HAT)**

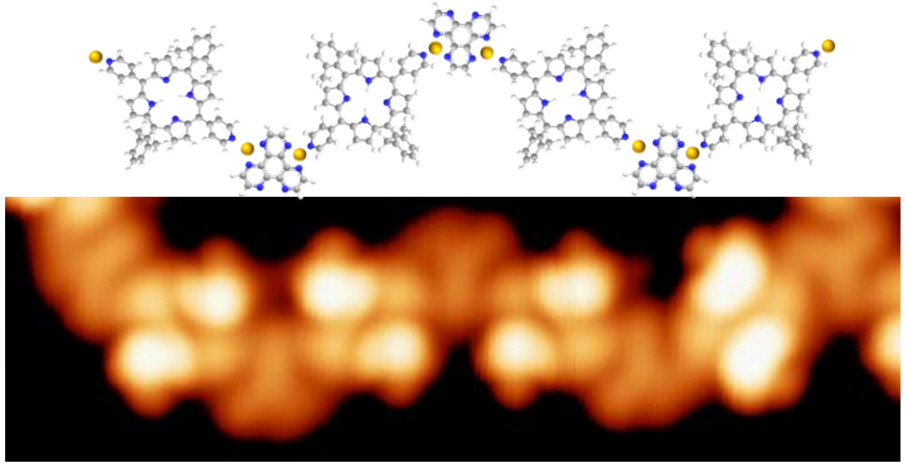
# HAT-Cu-Por Metal-Organic System




Por trimer connected to one HAT

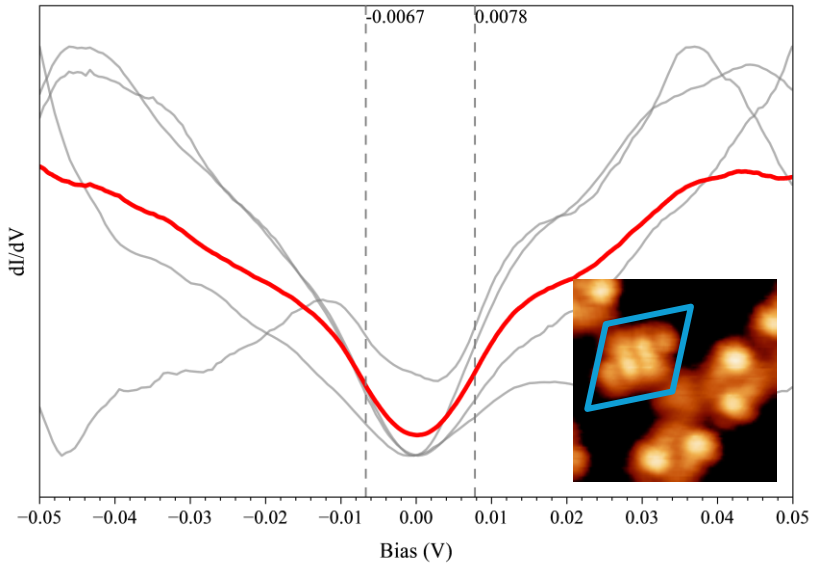


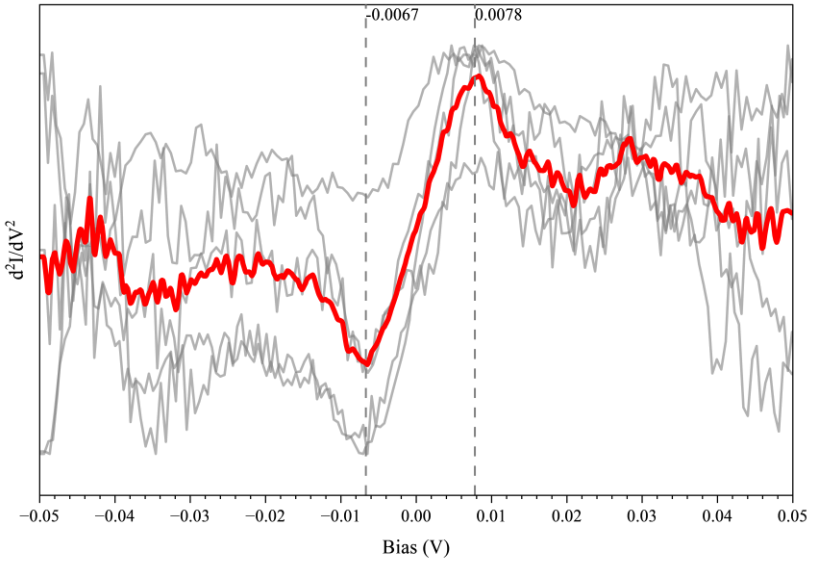

HAT-Cu-Por chain



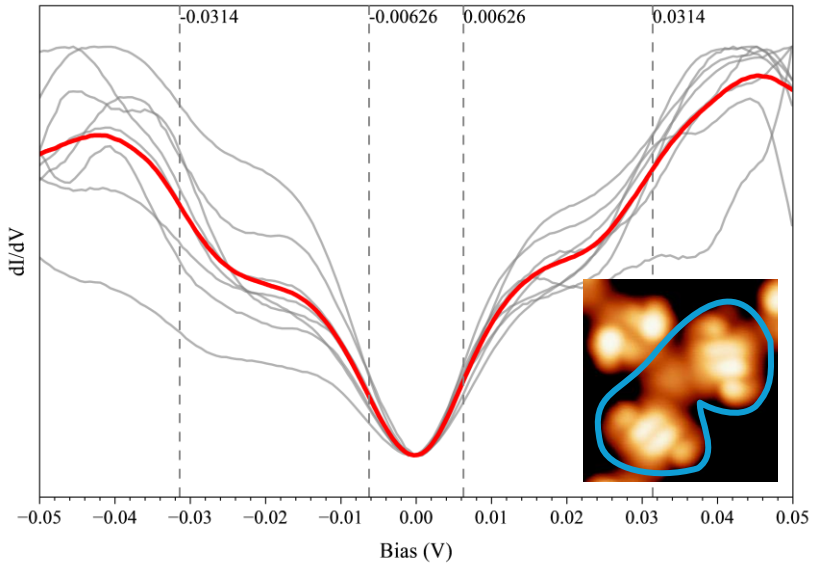
# STS Result of Type B Por Monomer and Dimer

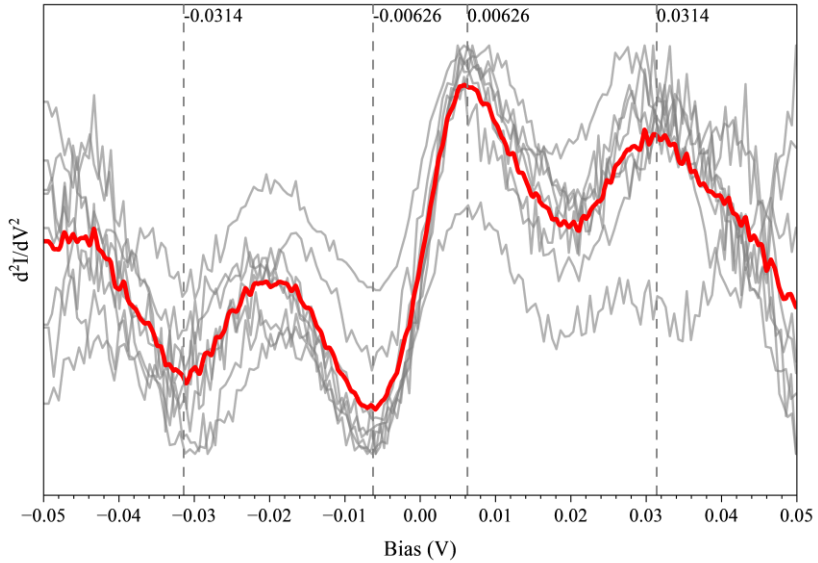
## Monomer



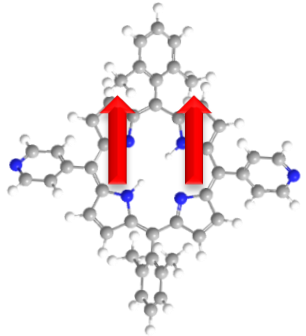




## Dimer

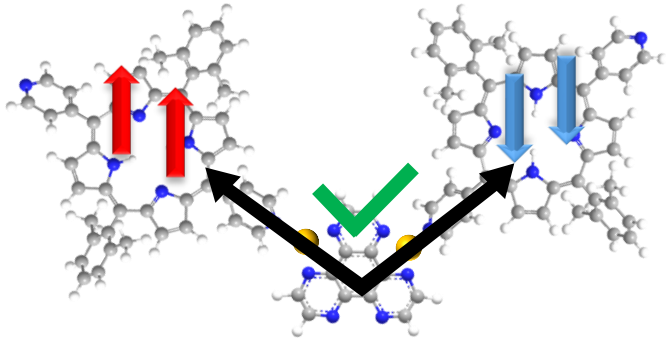



## Intramolecular coupling

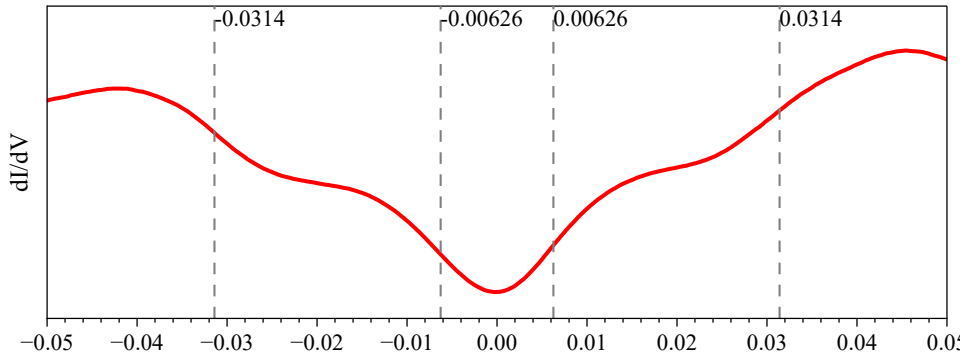


## HAT enhanced π-d-π coupling

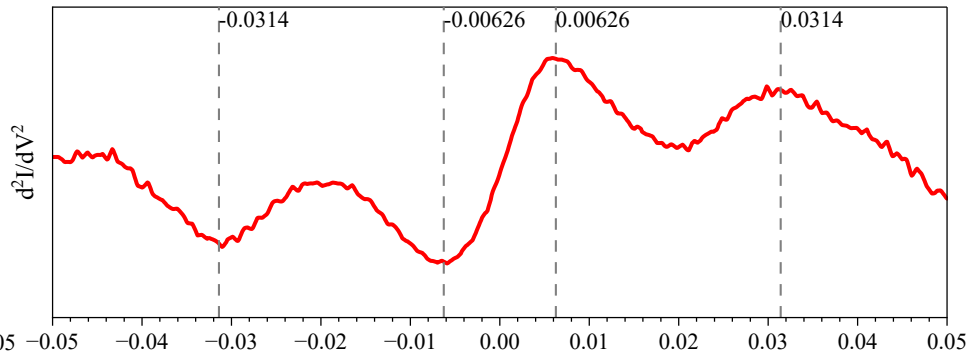


# S=1 Heisenberg Model

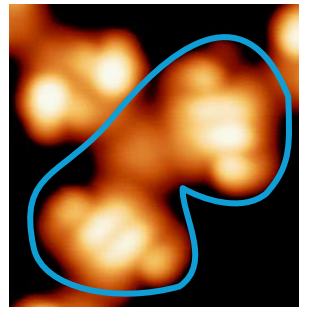
## Experimental dI/dV spectra




## Experimental $d^2I/dV^2$ spectra




## STM on dimer

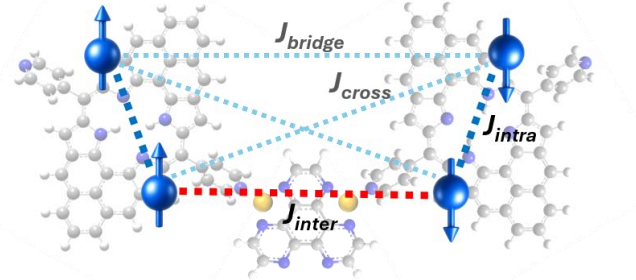


## Heisenberg model

$$\hat{\mathcal{H}} = J \sum_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1}$$

Exchange coupling

## S=1/2 Heisenberg Model




## S=1 Heisenberg model with perturbation theory

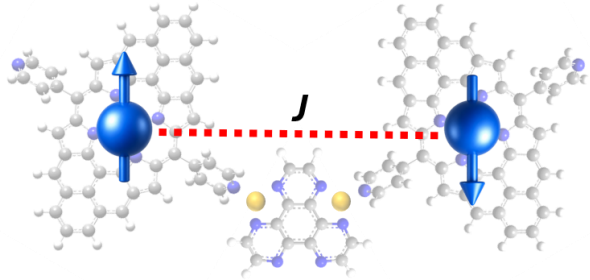
$$H = \sum_{<ij>} J_{eff} S_i S_j + \beta (S_i S_j)^2$$

Biquadratic exchange coupling

Effective exchange coupling

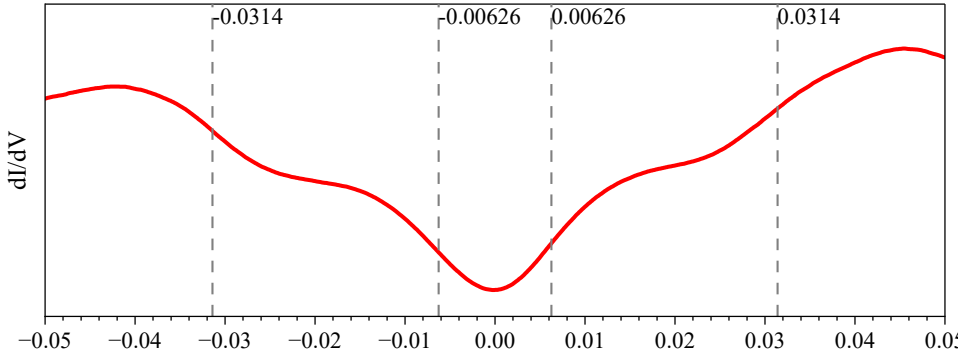
The fourth-order term

## S=1 Heisenberg Model

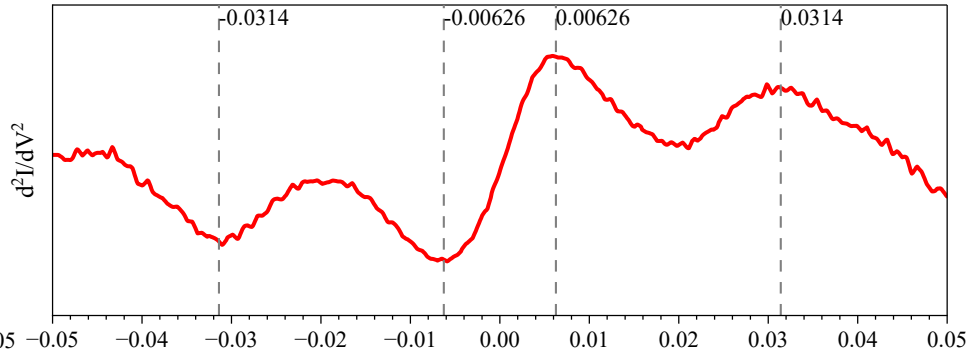


# S=1 Heisenberg Model

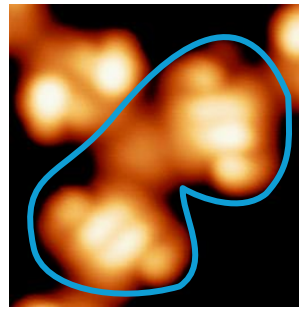
## Experimental dI/dV spectra



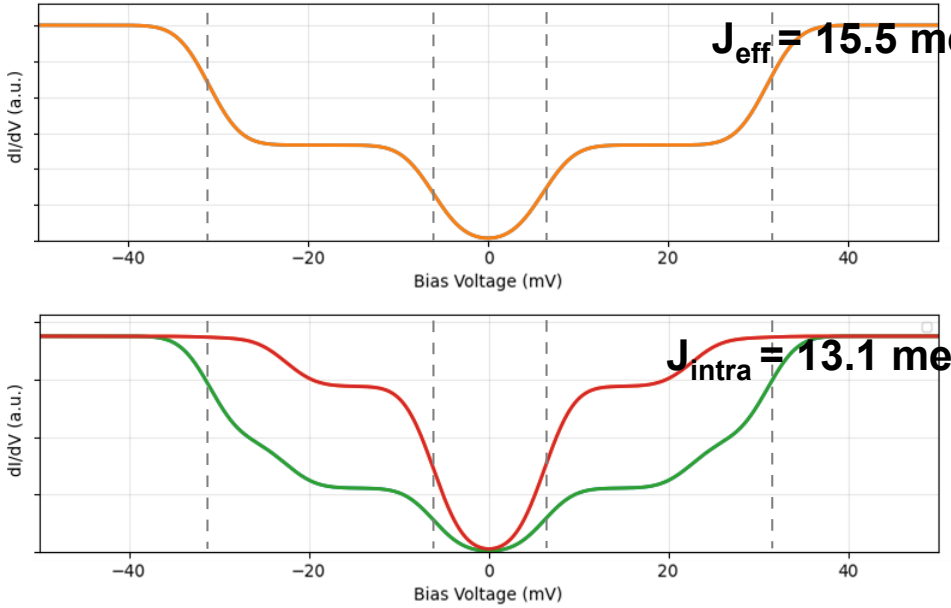

## Experimental d²I/dV² spectra



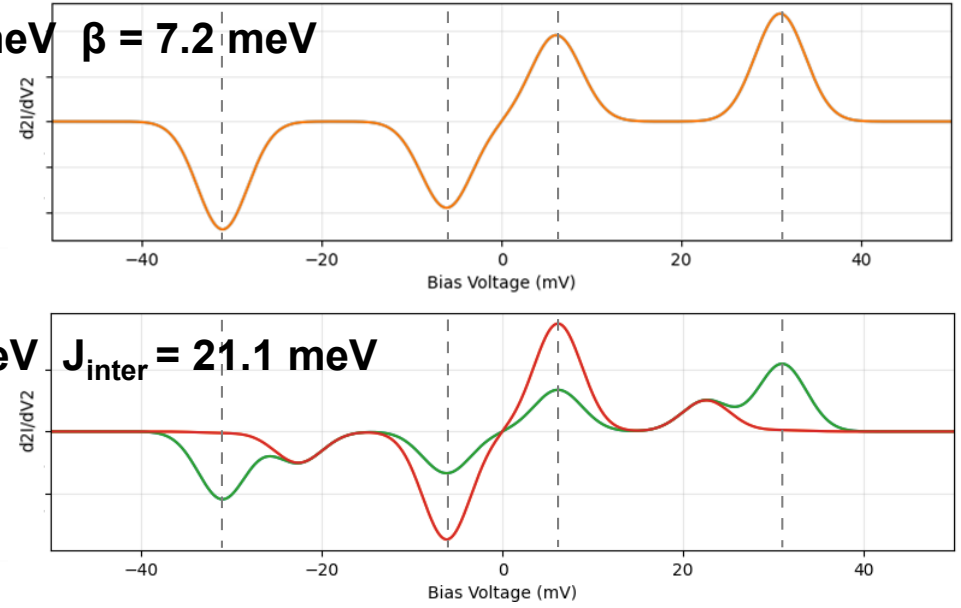

## STM on dimer



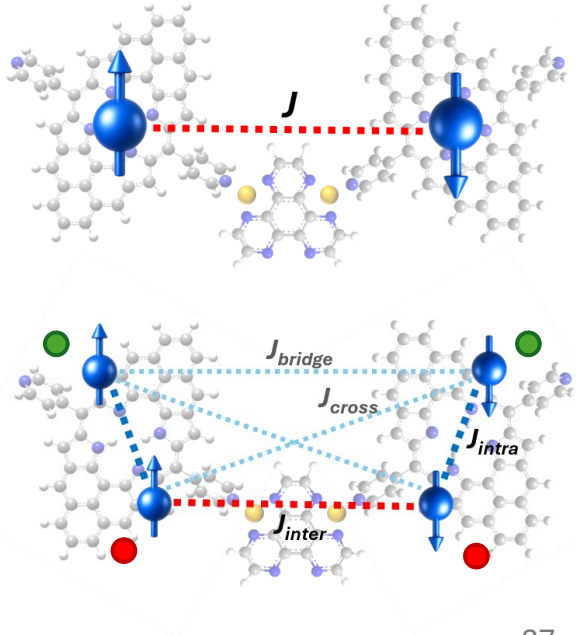
## Simulated dI/dV spectra




## Simulated d²I/dV² spectra



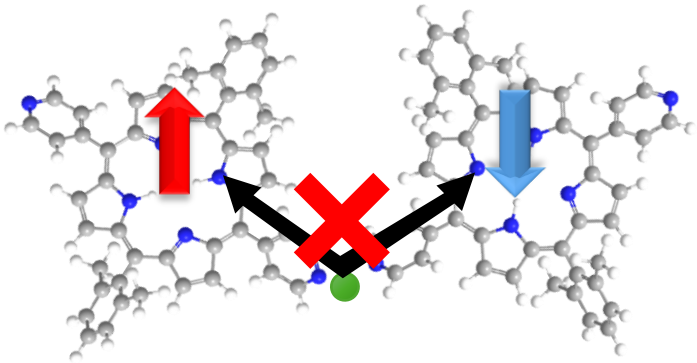

## Coupling Model



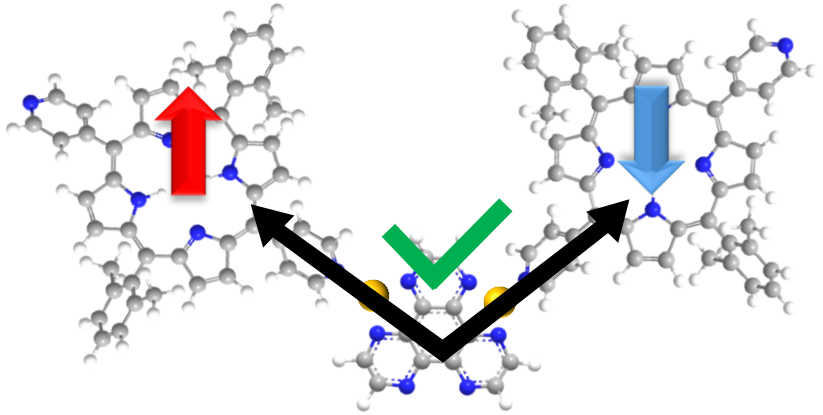
# Conclusion

- **HAT molecule opens a channel for Type B Por inter-molecular magnetic coupling and realizes π-d-π coupling in HAT-Cu-Por metal-organic system.**

**Direct π-d-π coupling**



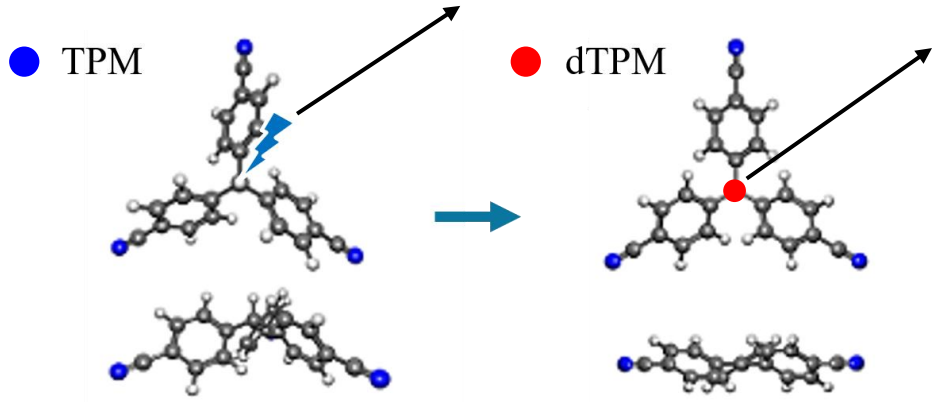
**HAT enhanced π-d-π coupling**



# 5. Regulate Kondo Resonance Using Metal Coordination

# M-TPM MOF on Au(111)

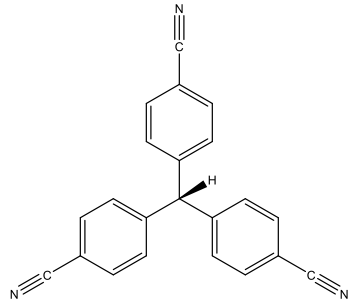
1. Pulse on the central $sp^3$ carbon




4-[bis(4-cyanophenyl)methyl]benzene-1 carbonitrile (TPM)

dTPM (with one radical)

2. Dehydrogenate and produce one radical



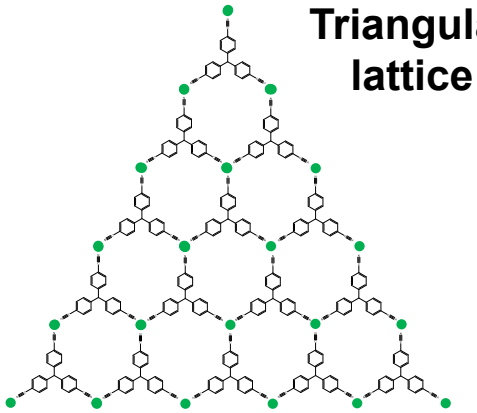
TPM

+ Metal atom M ●

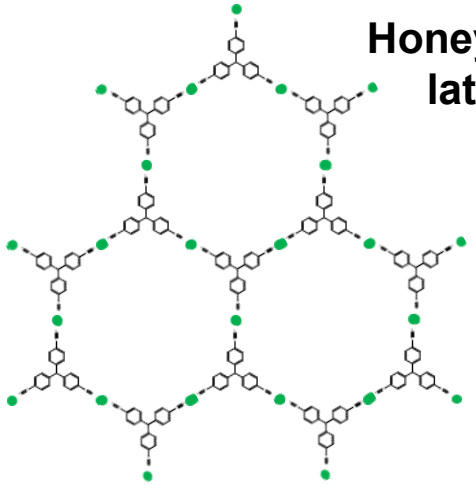
~100°C on Au(111)

M = Ni, Fe, Co

M = Cu

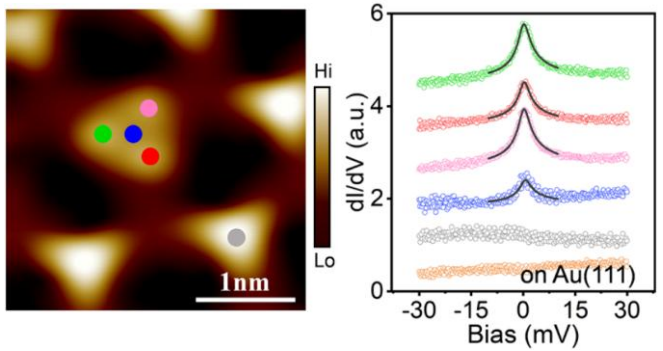


Triangular lattice



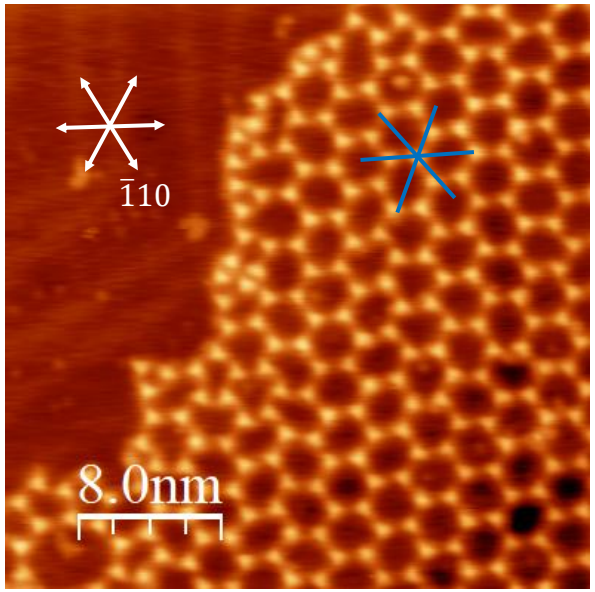
Honeycomb lattice

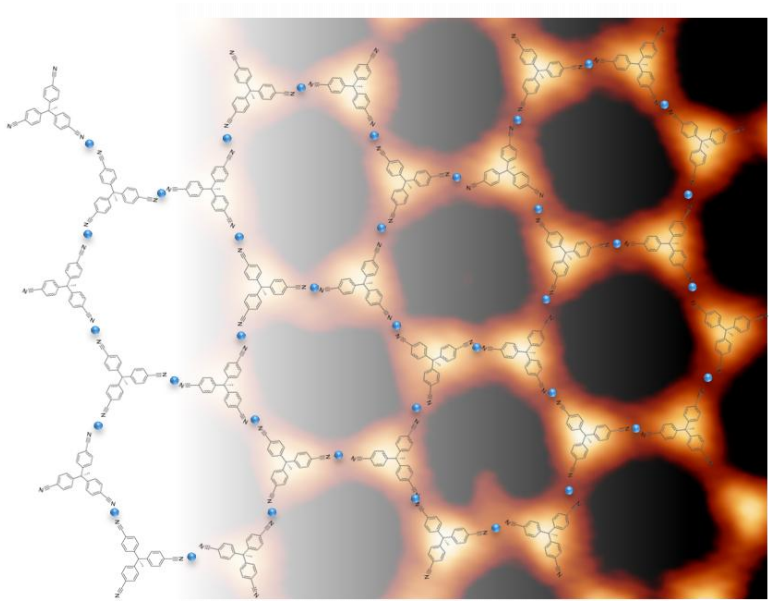
Former work of Ni-TPM MOF on Au(111)

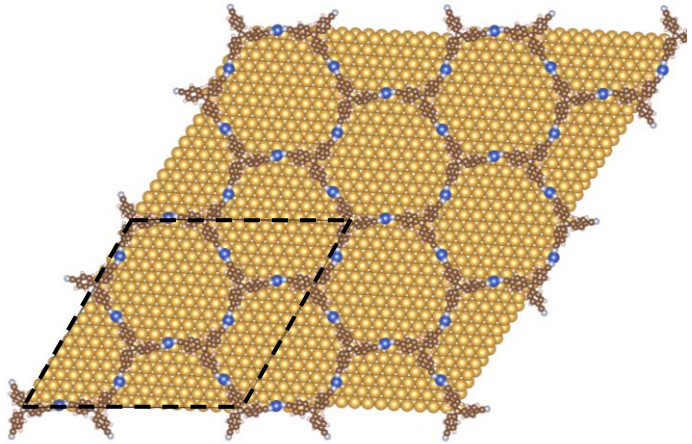


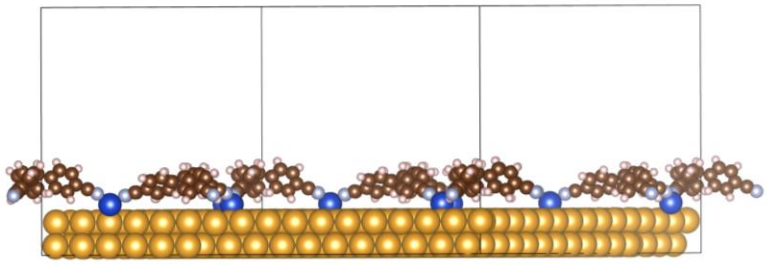

Chen C. *et al. J. Am. Chem. Soc.*, 2025, 147(39): 35464-35470.

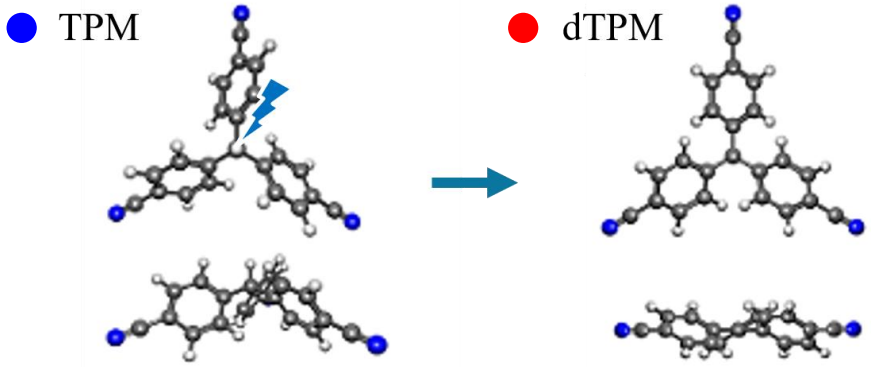
# STM and Tip Manipulation on Cu-TPM MOF

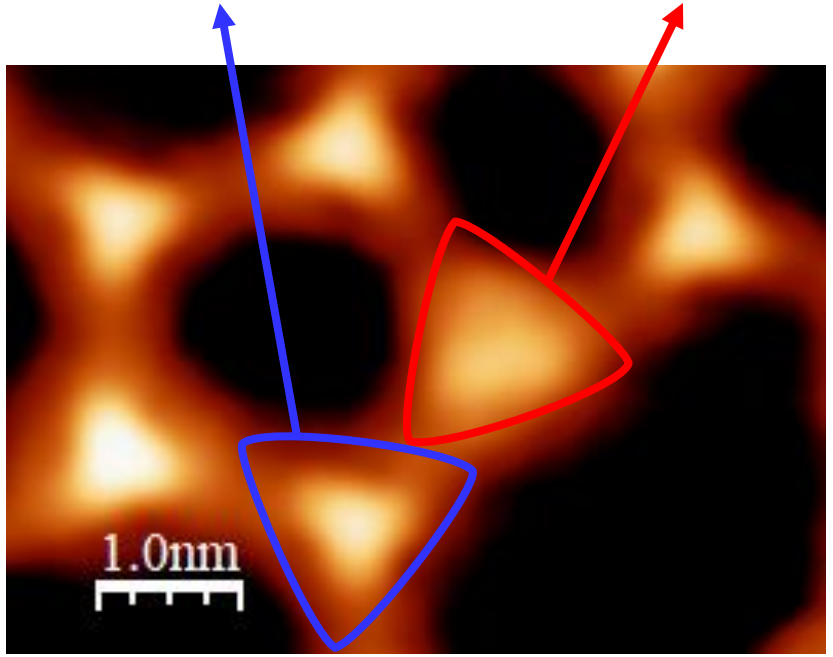




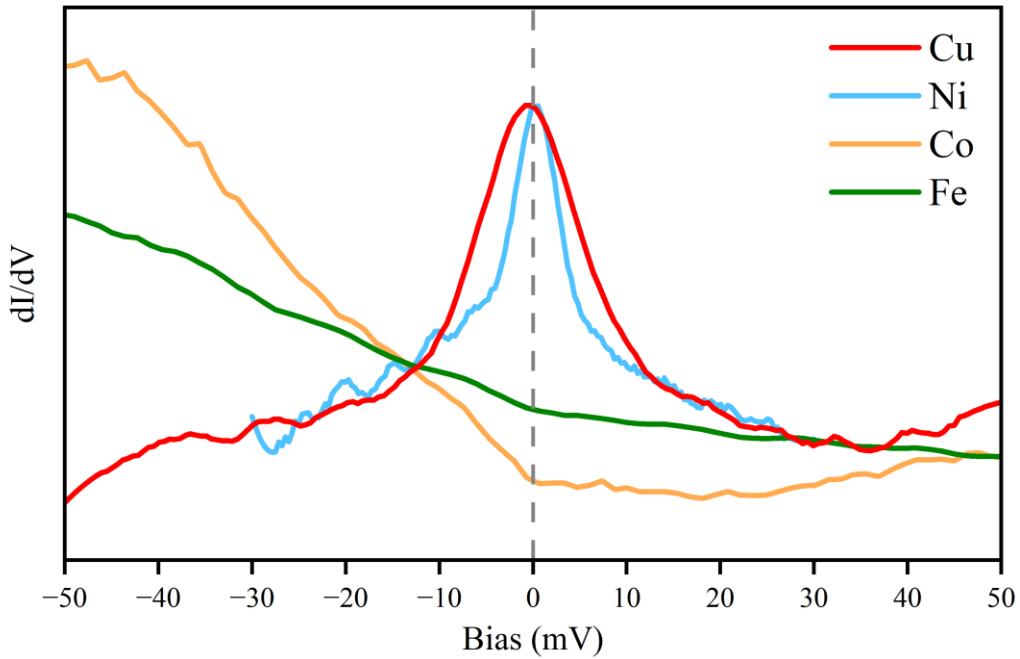




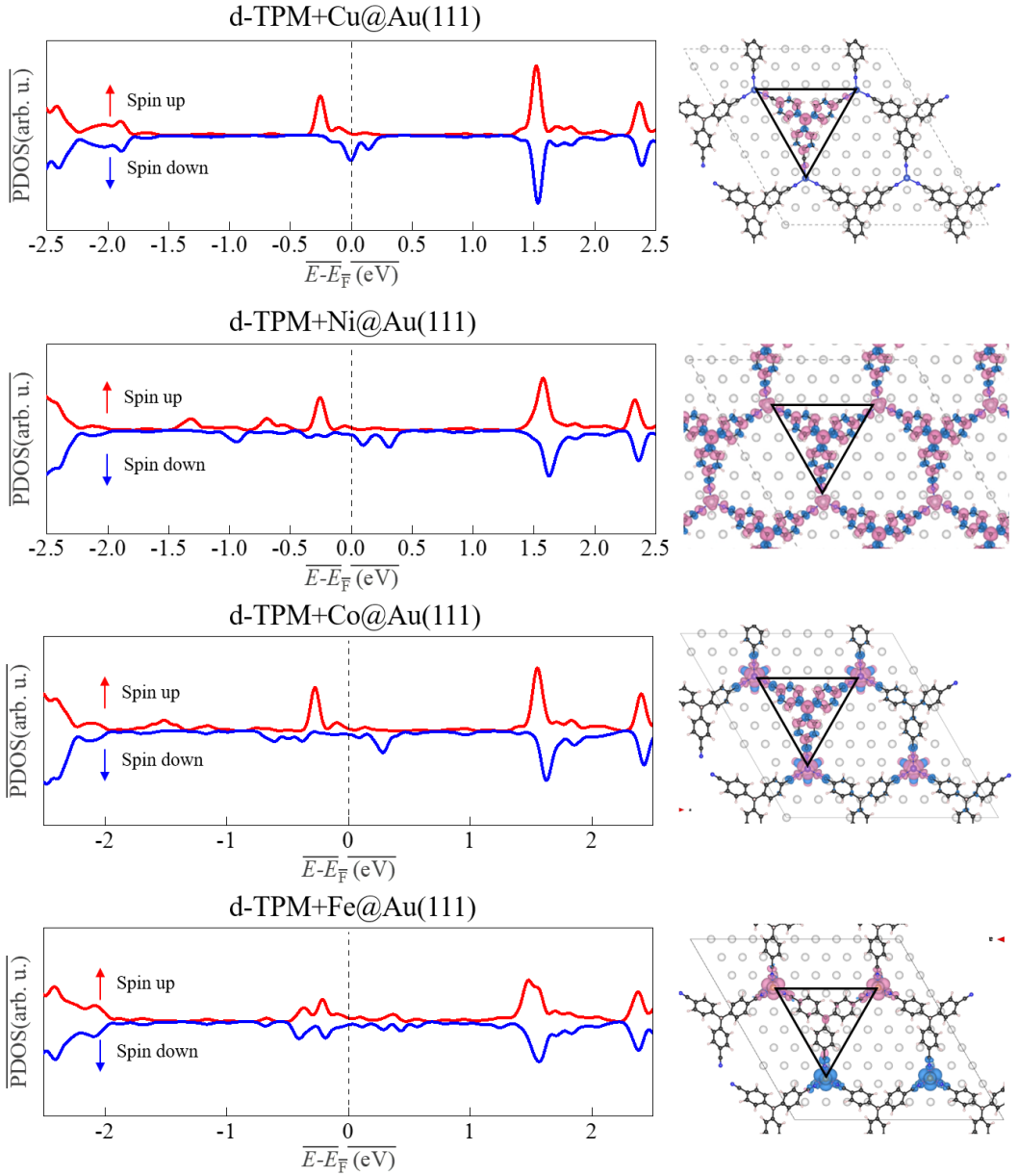
# STS and DFT simulation of dTPM in M-TPM MOF

**STS spectra of dTPM in M-TPM MOF on Au(111) near Fermi level**




**Kondo temperature**

- **Ni-TPM: 40.8K**
- **Cu-TPM: 99.4±20K**
- **Co/Fe-TPM: N.A.**



# Anderson Model

**Kondo temperature calculated using Anderson model**

$$T_K \approx \sqrt{\Gamma U}\exp\left(\frac{\pi\varepsilon_0(\varepsilon_0+U)}{\Gamma U}\right)$$

**Energy of the unpaired electron**

**Coupling strength between the magnetic impurity and the conduction electrons**

**Charging energy caused by Coulomb repulsion**

**No Kondo resonance**

**Calculated based on the SOMO & SUMO in DFT simulated LDOS**

| Type of MOF | Ni-TPM | Cu-TPM | Co-TPM | Fe-TPM |
|---|---|---|---|---|
| $\varepsilon_0$ (eV) | -0.257 | -0.207 | -0.274 | -0.187 |
| U (eV) | 0.355 | 0.252 | 0.557 | 0 |
| $T_K$ (Calculated) | 40K | 99K | 0.138K | N.A. |
| $T_K$ (Experiment) | 40.8K | 99.4K | N.A. | N.A. |

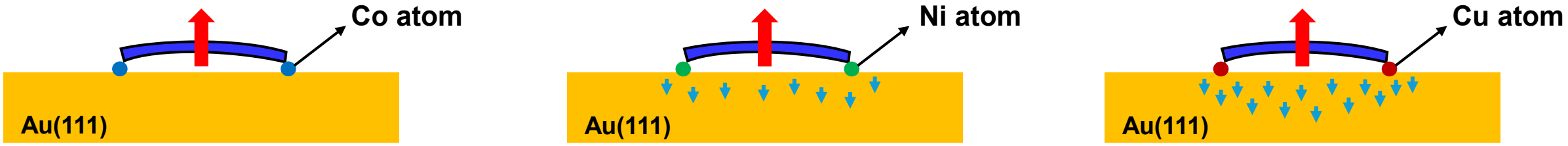
**Low $T_K$** **High $T_K$**

*set Γ as 46 meV

**move fermi level of Cu-TPM to -48meV

# Conclusion

- **Strength of Kondo resonance of dTPM molecule in M-TPM MOF on Au(111) can be regulated by substituting the coordination metal M.**




$J_K$ smaller than T
U=0.557eV

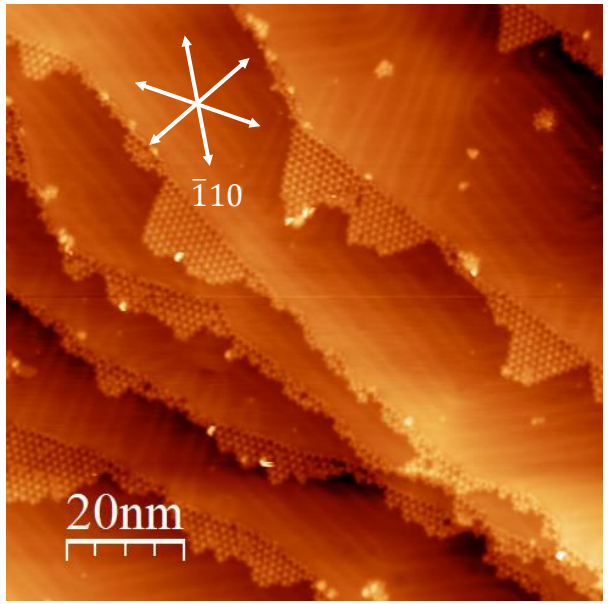
Small $J_K$
U=0.355eV

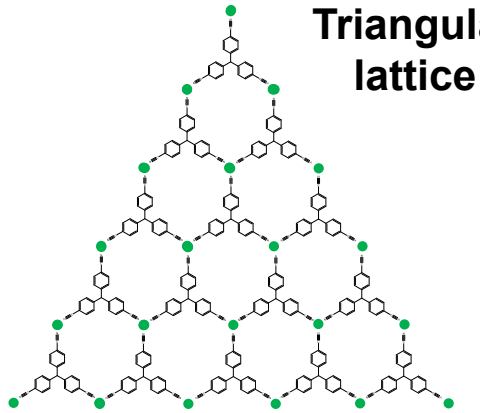
Large $J_K$
U=0.252eV

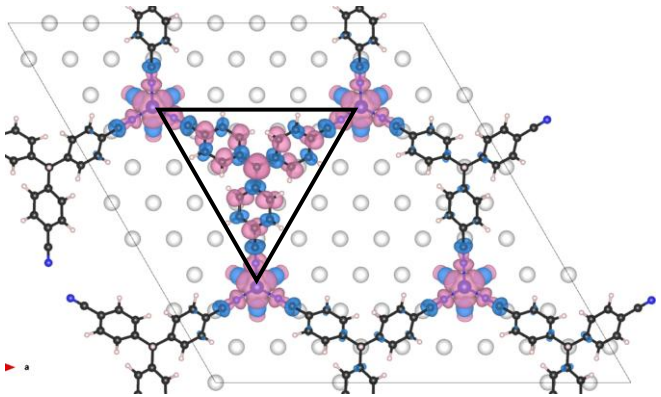
$$T_K \approx \sqrt{\Gamma U}\exp\left(\frac{\pi\varepsilon_0(\varepsilon_0+U)}{\Gamma U}\right)$$

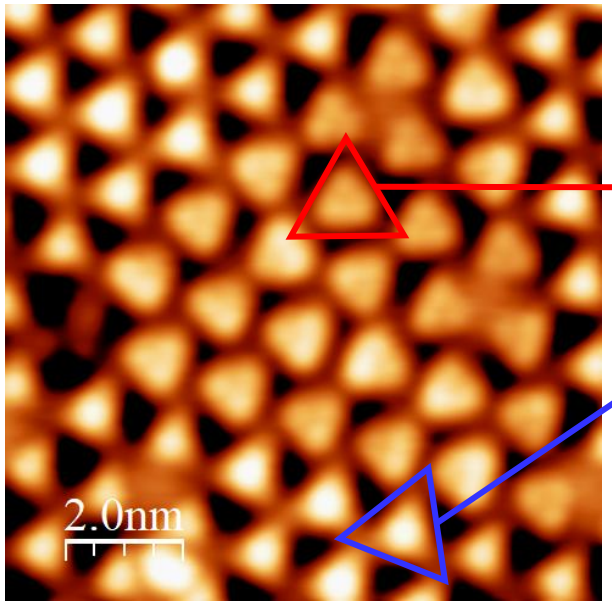
# 6. Confined Spin-Wave Excitation in Artificial π-radical Lattice

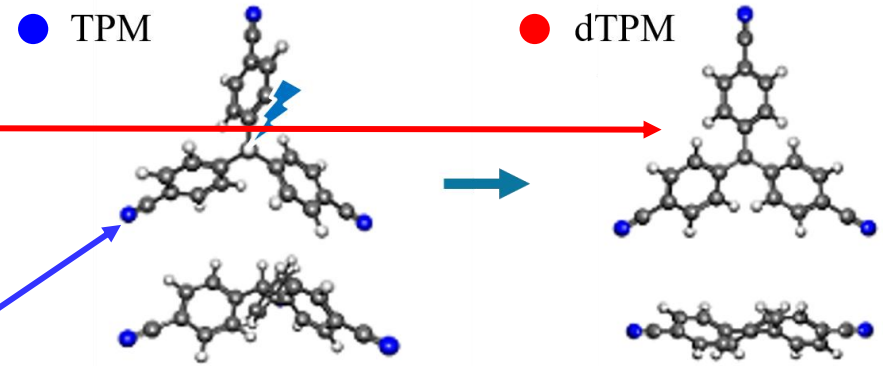
# Co-TPM MOF on Au(111)



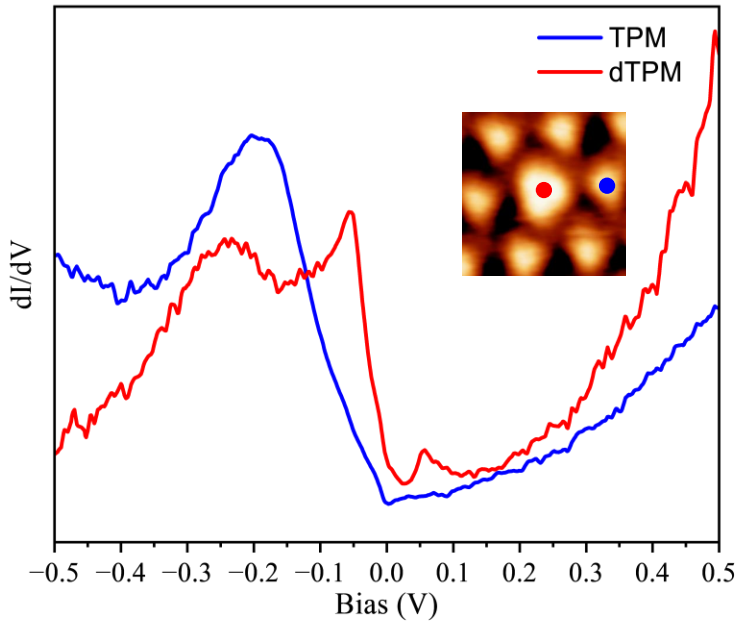



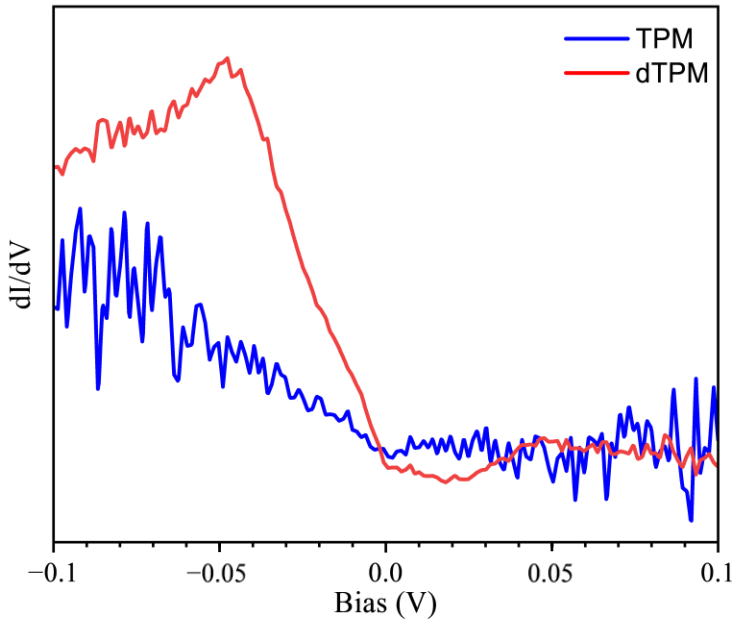



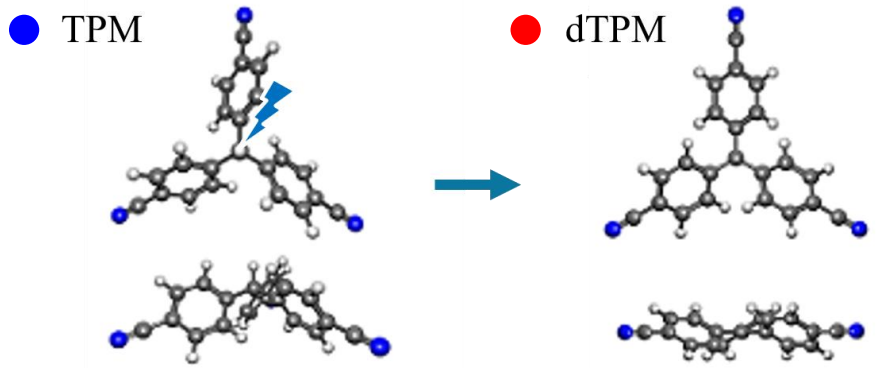


# STS of dTPM monomer in Co-TPM MOF




**DFT & Anderson Model**

**Calculated $T_k$ = 0.138 K**

**No Kondo resonance**

**Spin on dTPM unscreened**

**?**

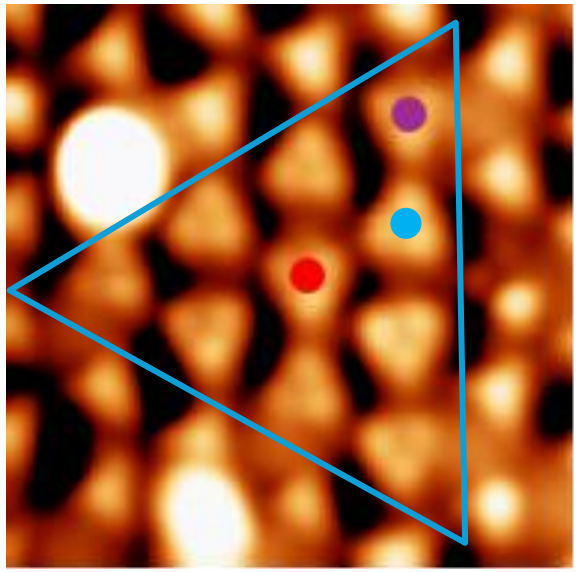
**Spin-spin coupling**

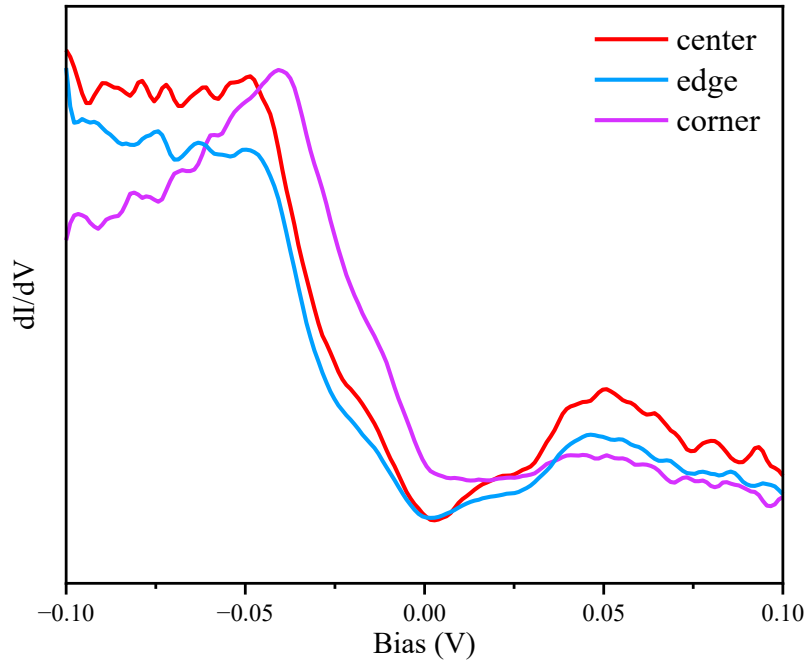
**among dTPM molecules**

# Spatial distribution of STS in triangular dTPM array

Edge number

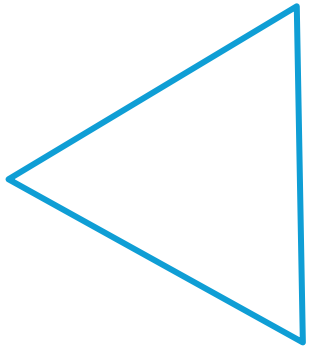
n=4

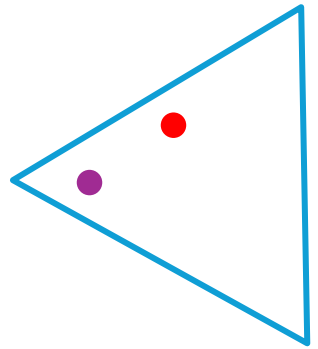


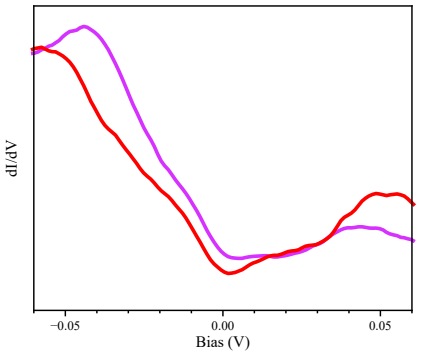



STM | dI/dV map at 40mV | STS

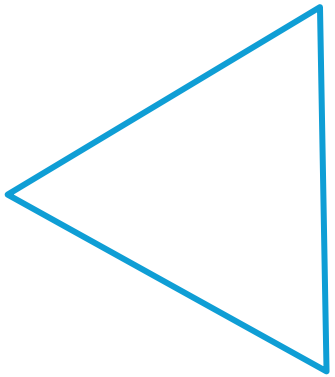
n=3

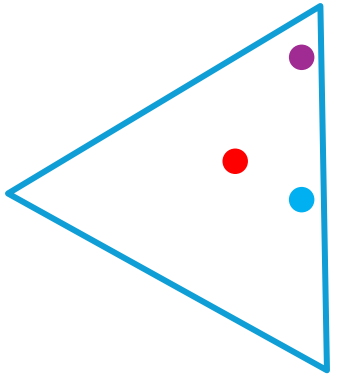


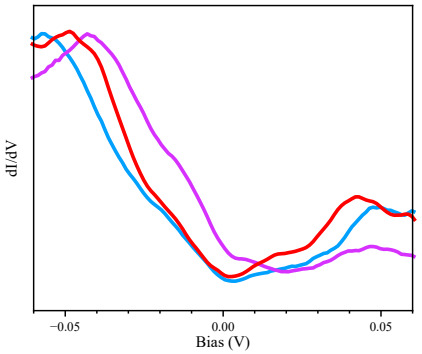




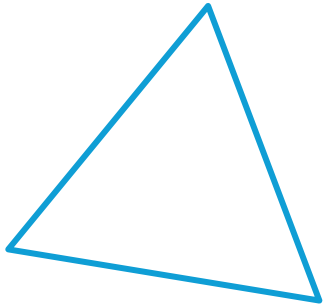

n=5

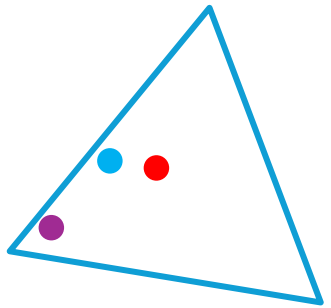


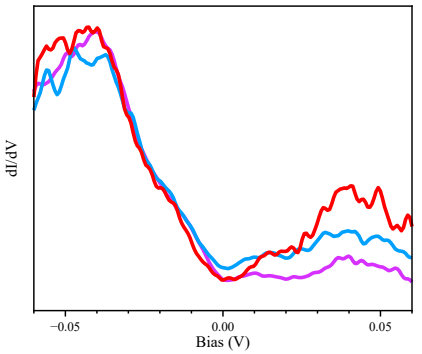





n=6







# Linear Spin Wave Theory and Spin Wave Excitation

**Ferromagnetic Heisenberg Model (J>0)**

$$H = -J \sum_{<i,j>} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

**Holstein-Primakoff transformation**

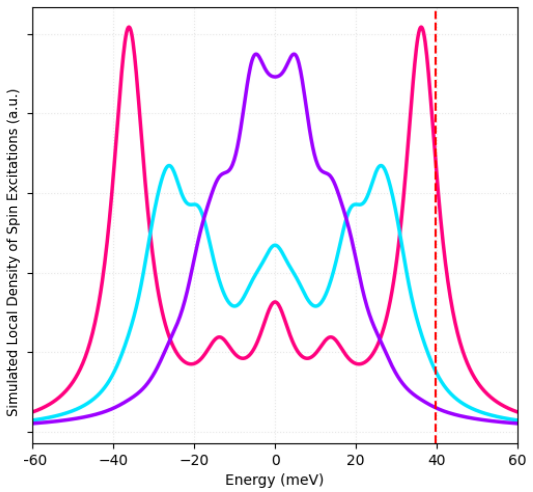
$$\begin{cases} S_i^z = S - a_i^\dagger a_i \\ S_i^+ \approx \sqrt{2S}\, a_i \\ S_i^- \approx \sqrt{2S}\, a_i^\dagger \end{cases}$$

**Hamiltonian of Magnon in Ferromagnetic Heisenberg system**

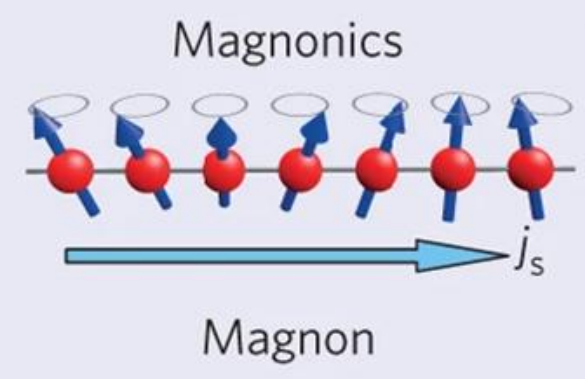
$$H_{SW} = \sum_i (JSz_i) a_i^\dagger a_i - JS \sum_{<i,j>} (a_i^\dagger a_j + a_j^\dagger a_i)$$

**In a confined spin system**

**Stand waves with different excitation energies**



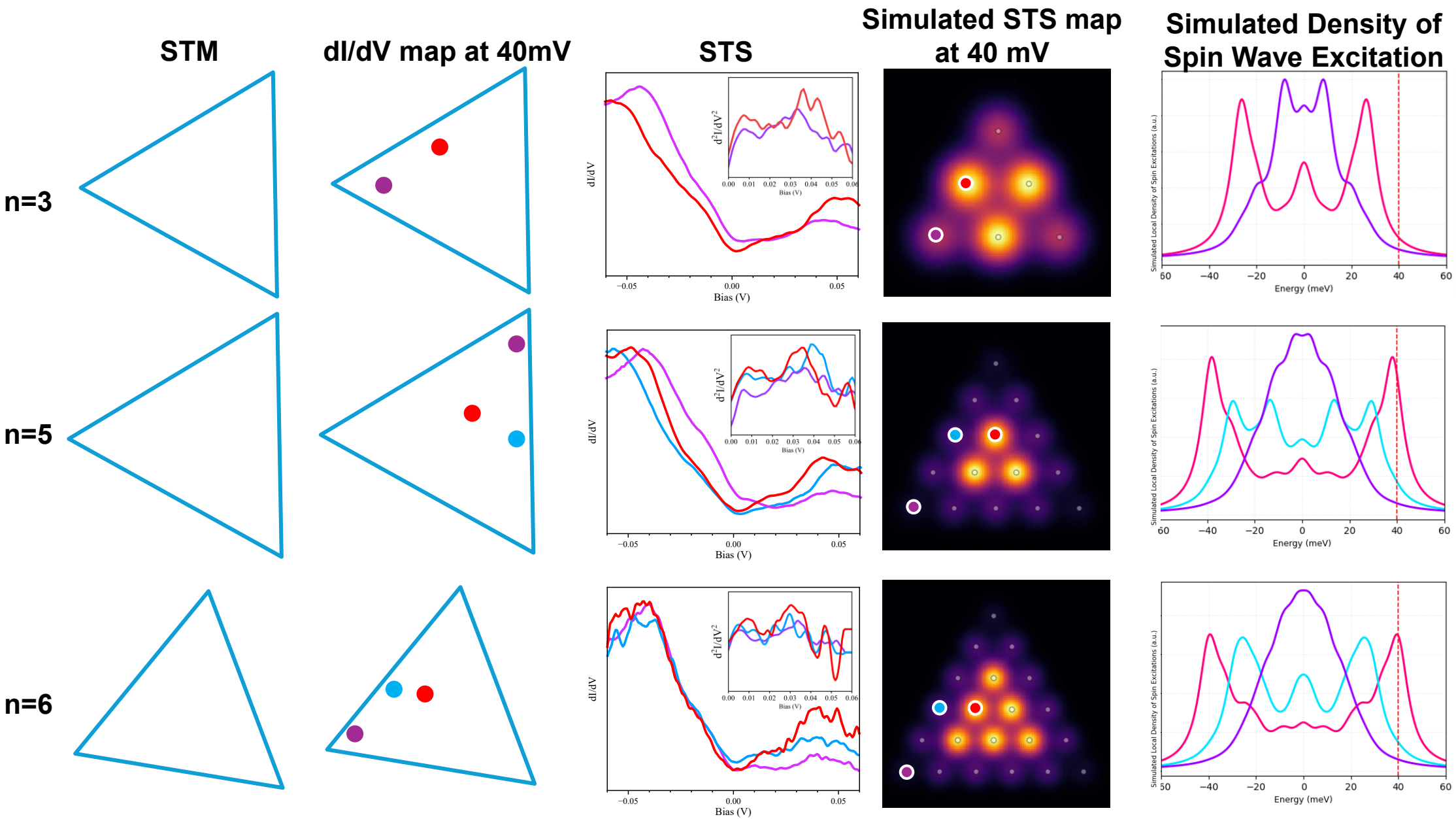

**J = 10 meV**




**Correlated spin system**

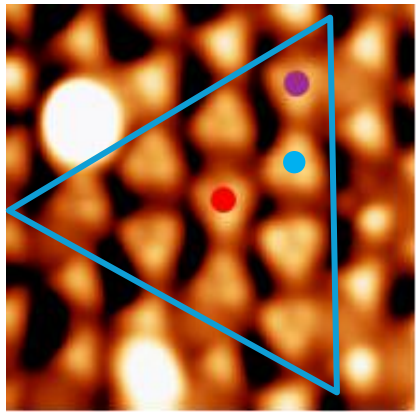
**Spin wave** ⟷ **Bosonic Quasiparticle: Magnon**

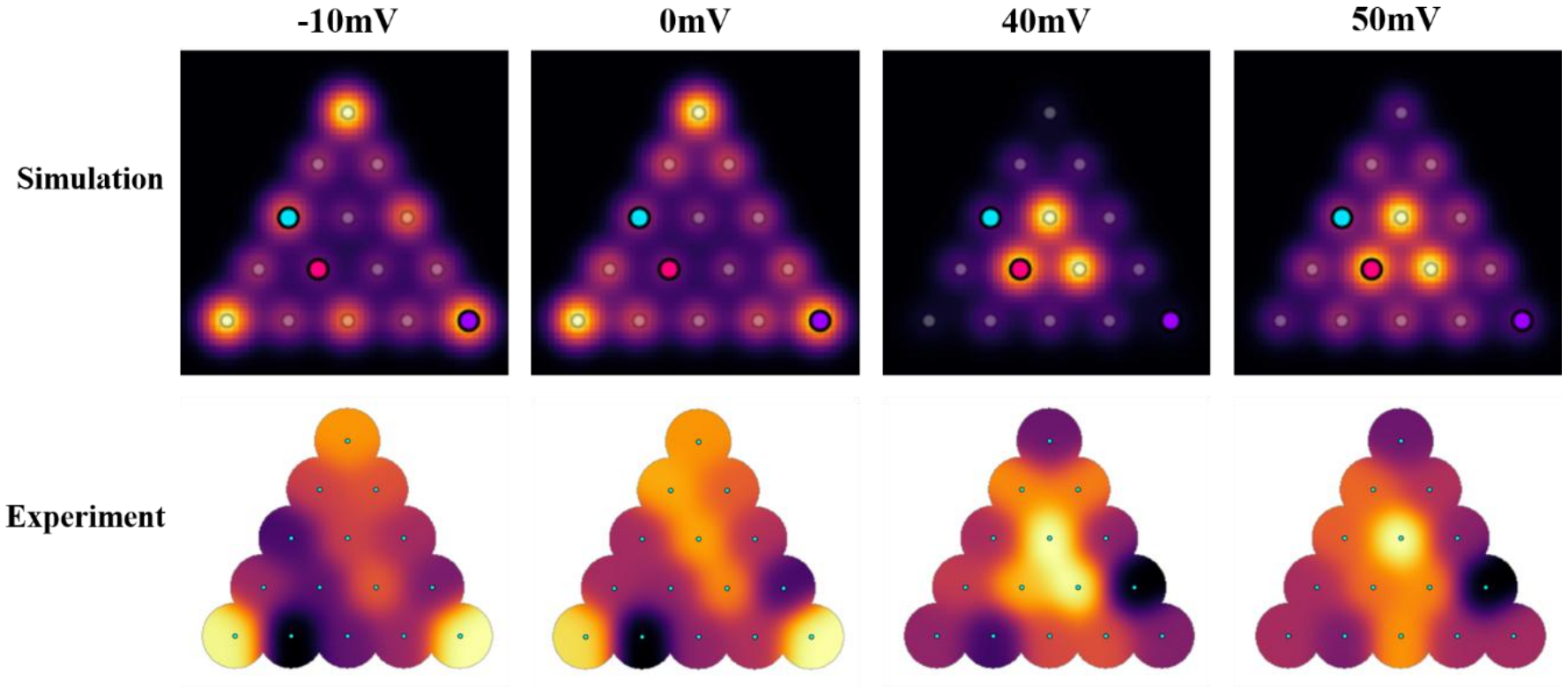
# Spin Wave Excitation in Triangular Spin Array



# Spin Wave Excitation in Triangular Spin Array

n=4

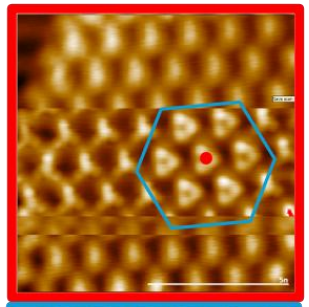




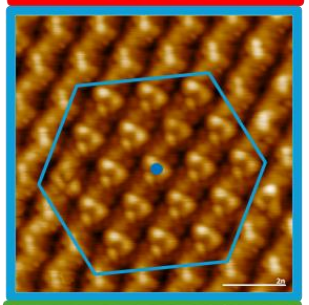

**Point-array STS map reconstructed by the point STS spectra on all sites of the triangular array**

# Spin Wave Excitation in Hexagonal Spin Array

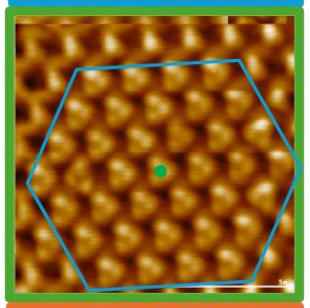
n=2



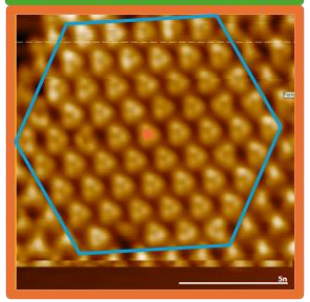
n=3



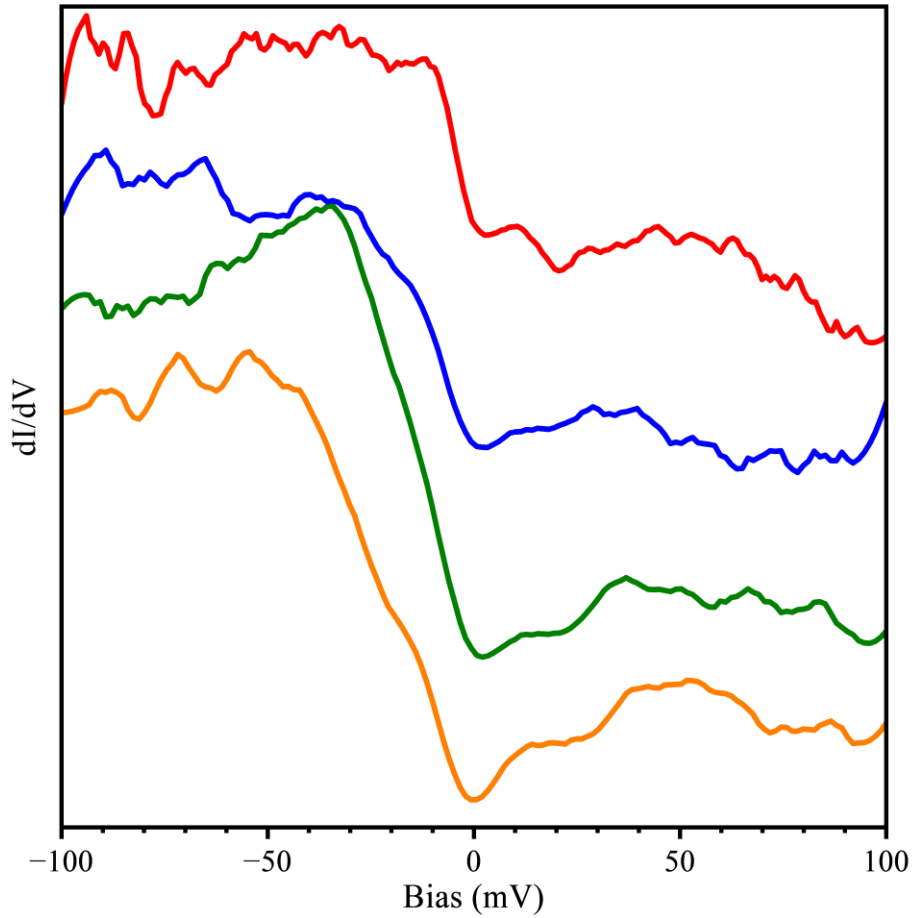
n=4



n=5

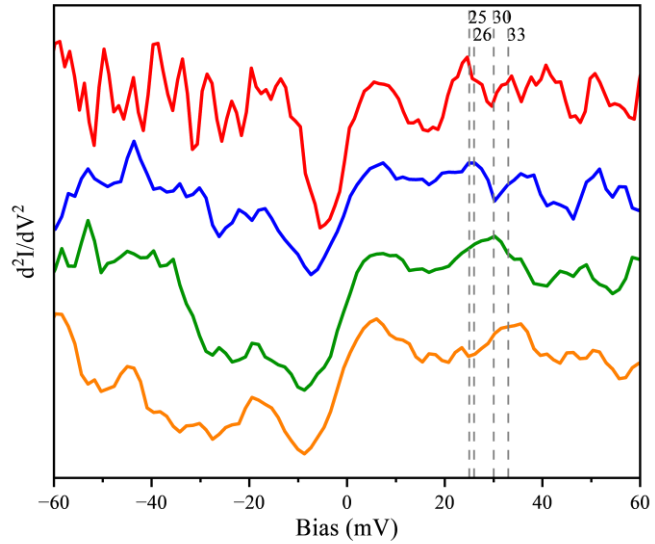


**dI/dV STS**

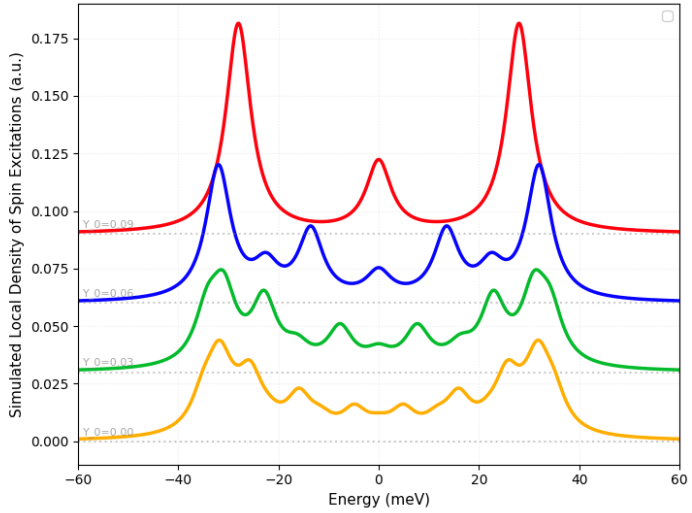



**Features more significant as *n* increases**

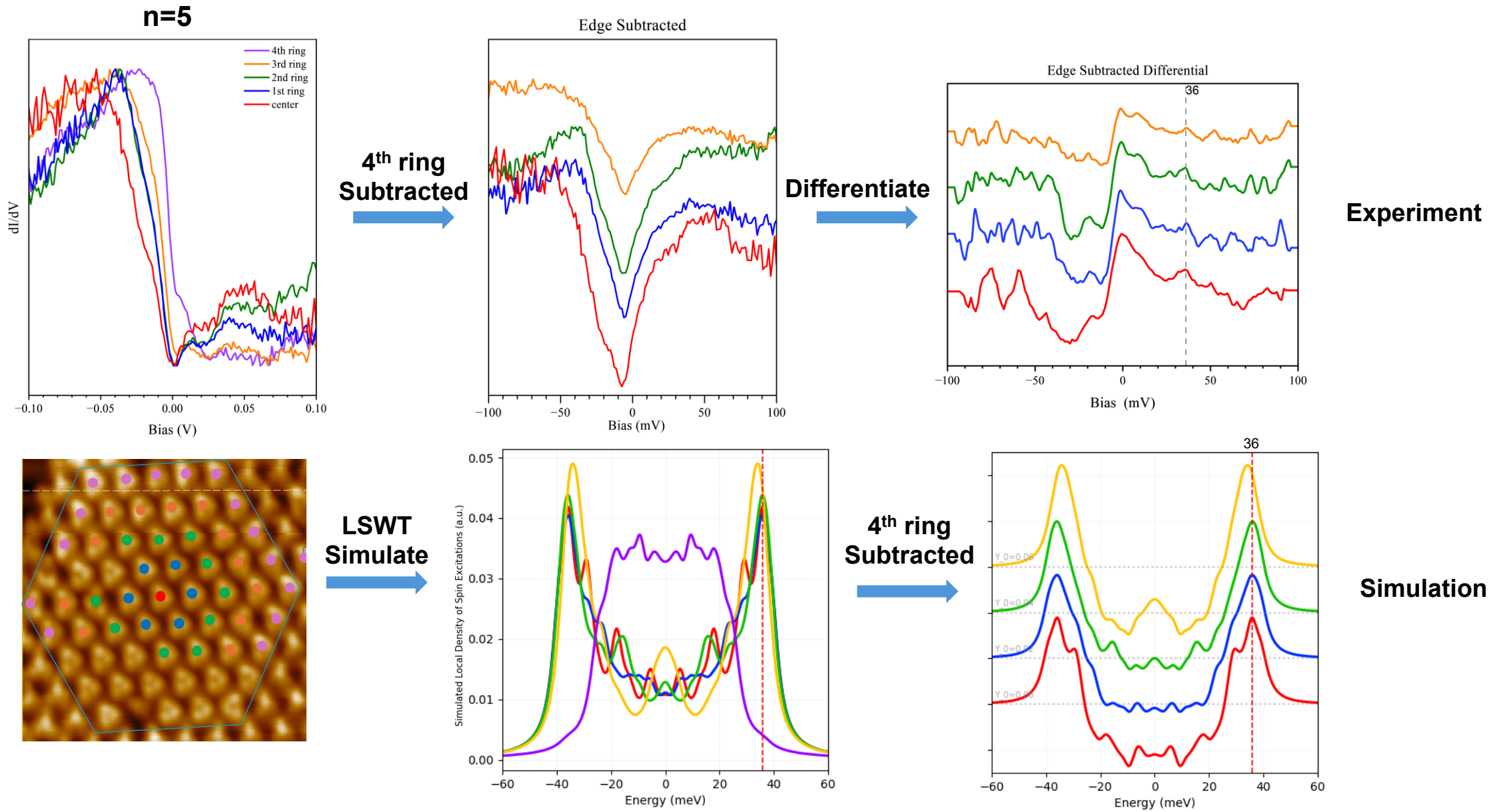
**$d^2I/dV^2$ STS**




**Simulated Density of Spin Wave Excitation**

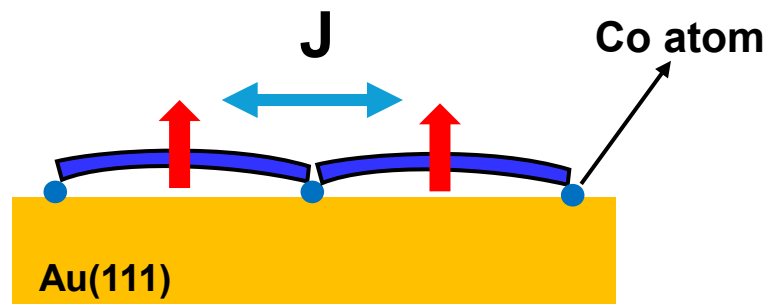


# Spin Wave Excitation in Hexagonal Spin Array



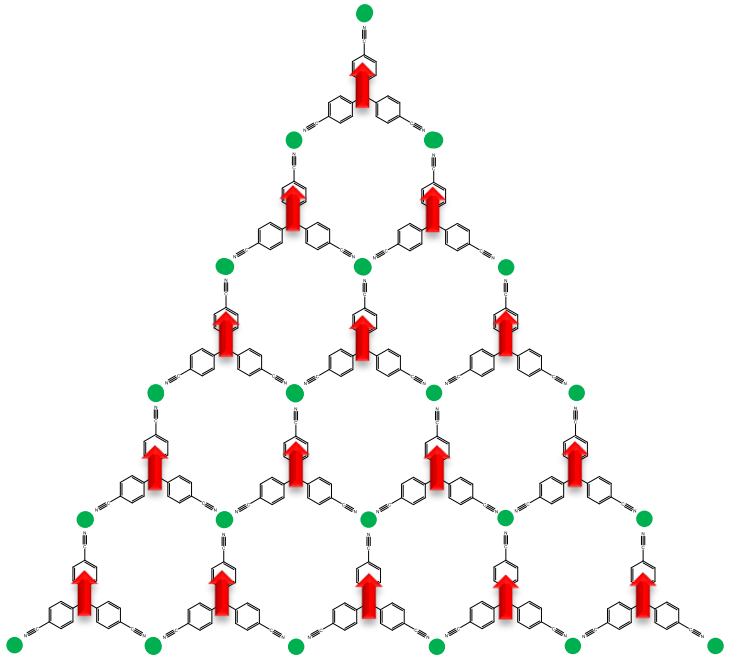
# Conclusion

- **Unscreened spins in dTPM 2D artificial lattice emerge intermolecular spin-spin coupling and exhibit confined spin wave.**




Intermolecular Spin Correlation

Construct artificial spin lattice



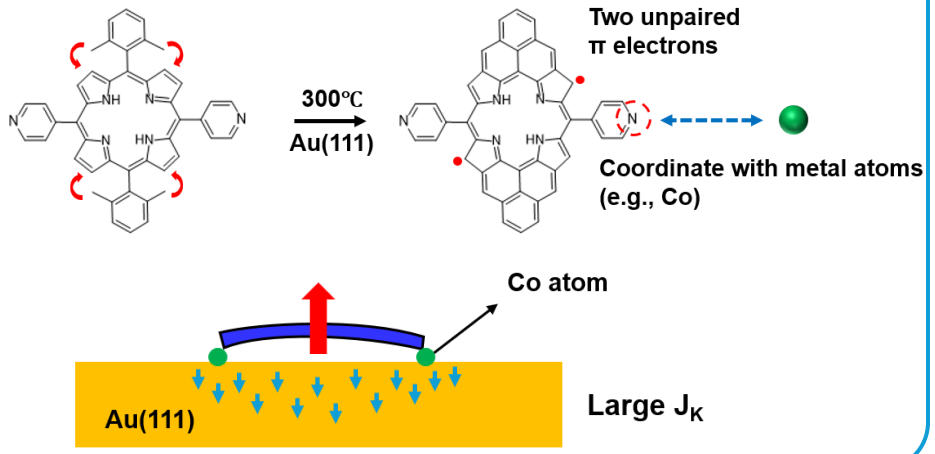
# 7. Summary and Perspectives

# Summary

## Our goal: Many-body spin correlation of π-radicals in 2D system

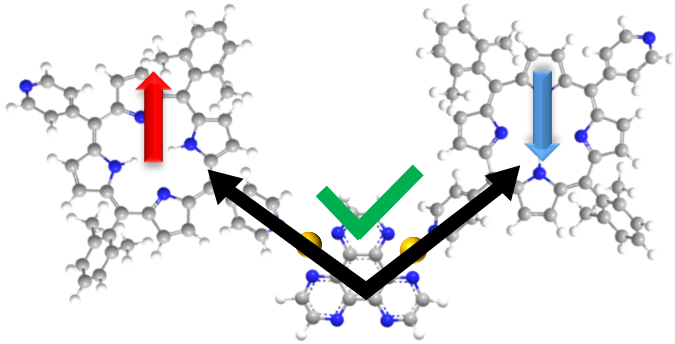
Annealing method

### Formation of π-radical in 2D MOF




HAT molecule

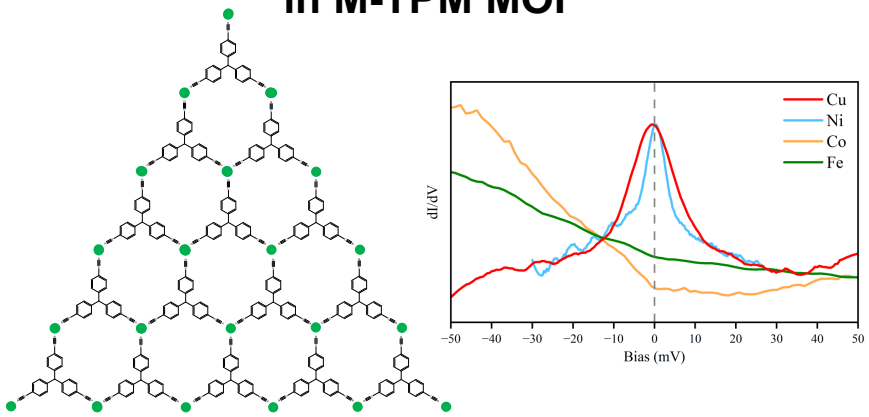
### π-d-π coupling realized



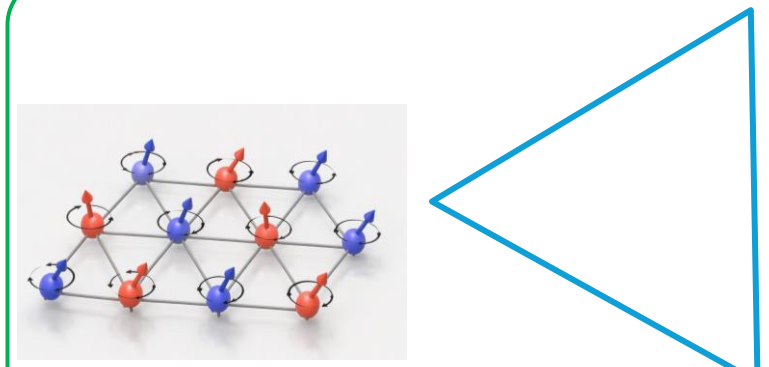
HAT-Cu-Por MOF on Au(111)

Tip manipulation

### Regulation of Kondo screening in M-TPM MOF

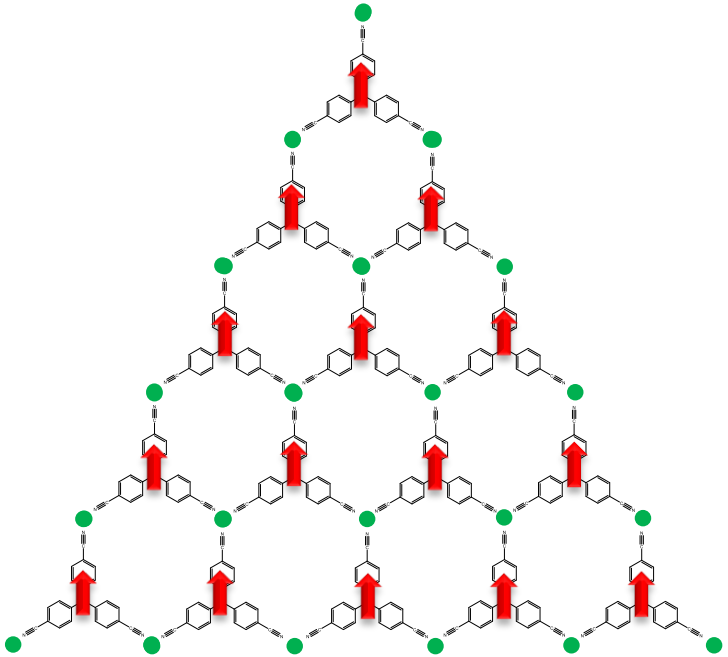



Quenched Kondo effect



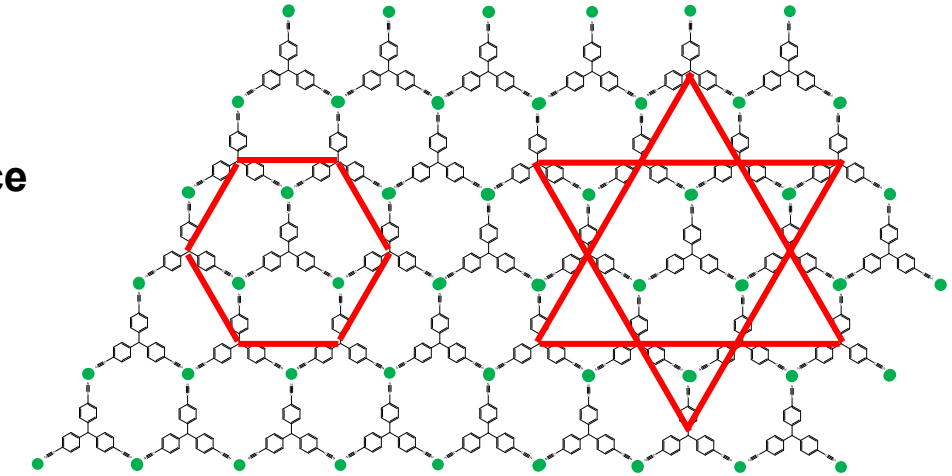
Confined spin wave in 2D artificial spin lattice

# Perspective



Confined spin wave in
2D artificial spin lattice

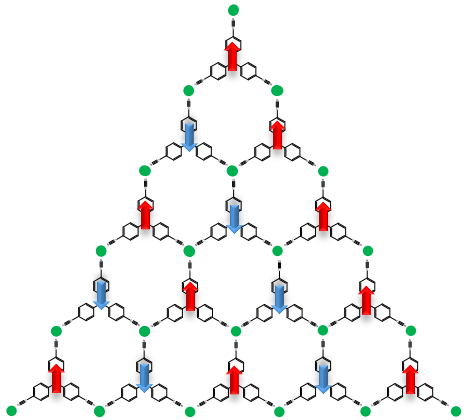
Artificially construct spin lattice
with different symmetry

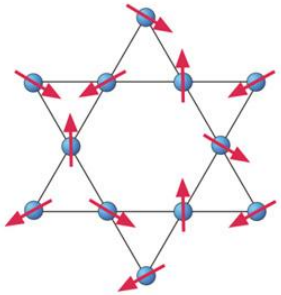


Hexagonal lattice, Kagome lattice, …

Modify metal or substrate

e.g. Mn, Zn, …
HOPG, TMDC, …





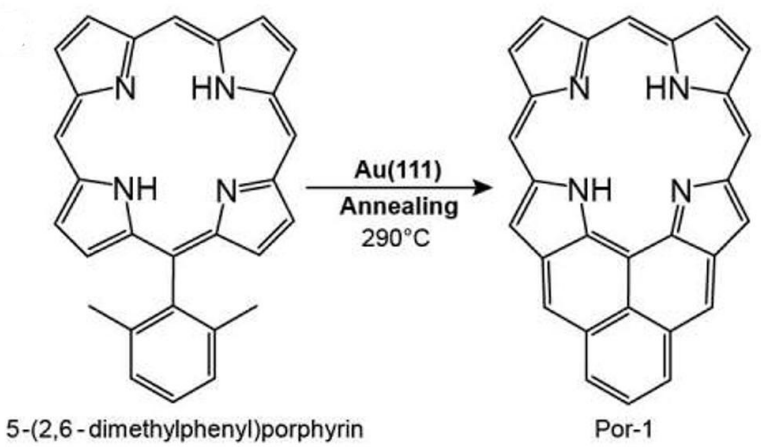
AFM coupling, Quantum spin liquid, …

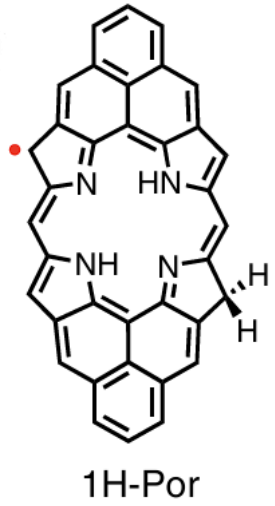
# Acknowledgements


- Thesis Supervisor:
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- Thesis Committees:
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  - Prof. Shiming Lei (HKUST)
  - Prof. Weilai Yu (HKUST)
  - Prof. Qitang Fan (USTC)
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    - Prof. Tao Lin (SZTU)
  - Organic Synthesis:
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    - Prof. Benzhong Tang (CUHK-SZ)

# Thanks for your attention!

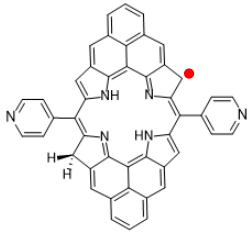
# Supporting Information




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





**Type C Por**

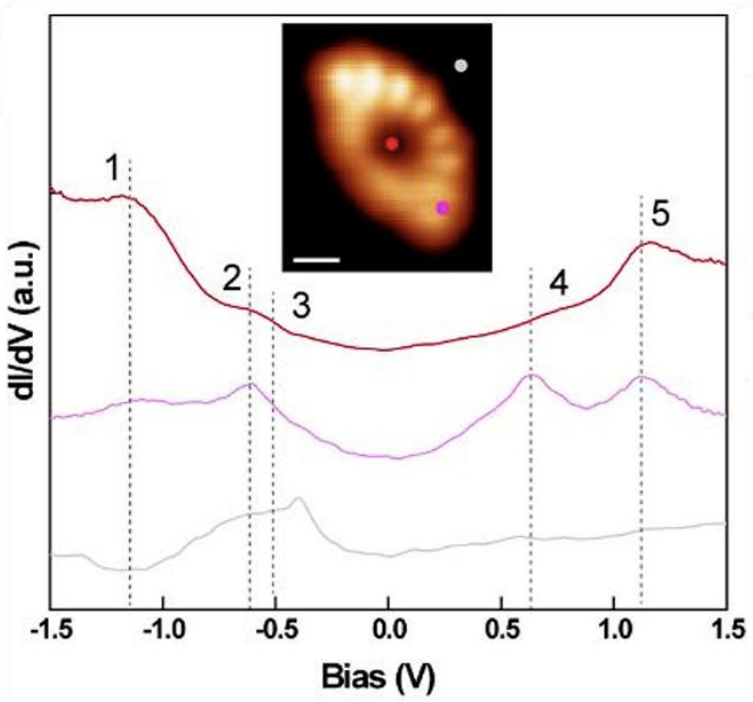
**After cyclodehydrogenation**

**Capture one hydrogen atom**

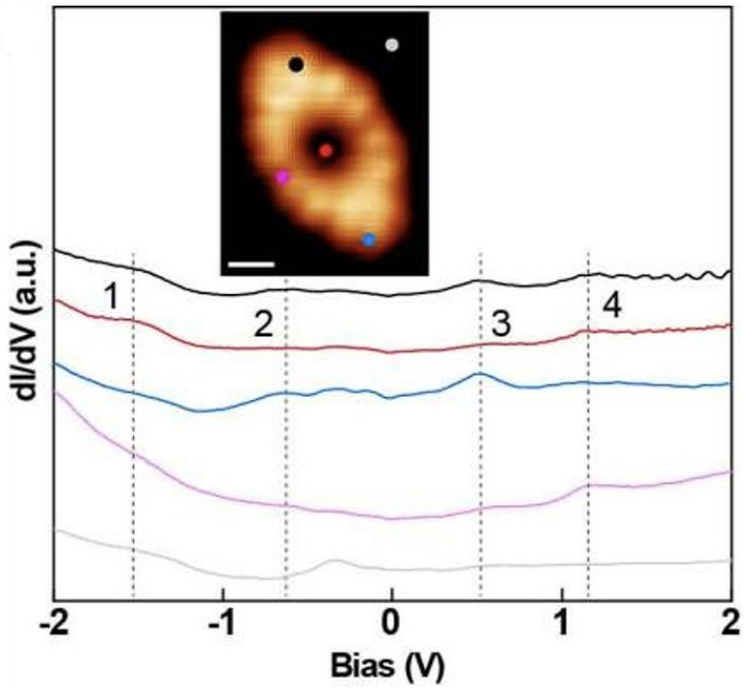
**One radical**

# Supporting Information

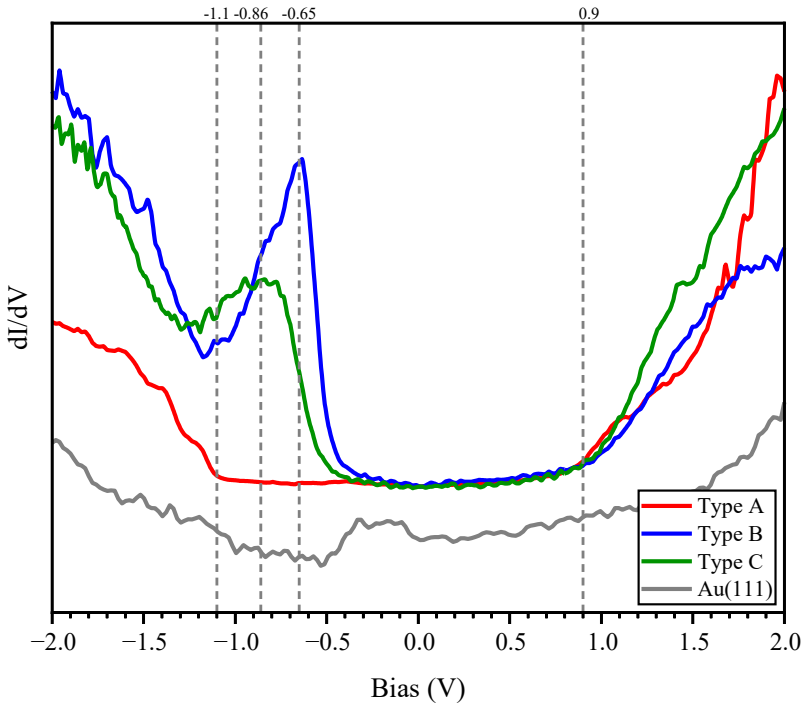
**1H-Por**
**(1 radical)**




**Por**
**(2 radicals)**




**Type A, B, C Porphyrin**
**(0, 2, 1 radicals)**




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