Synthesis and Characterization of Two-Dimensional Metal Organic Frameworks on Metal and Van der Waals Substrates

Songyu Mo

Supervisor: Prof. Nian LIN

Department of Physics
The Hong Kong University of Science and Technology

Content

1. Introduction

2. Synthesis and Characterization of 2D-cMOFs M-BHO (M=Fe, Co, Ni)

3. Characterization of spin-spin coupling induced spin excitations in 2D-cMOFs $M_3(HAT)_2$ (M=Fe, Co, Ni, Cu)

4. Narrow Bandgap 2D-cMOFs $M_3(HAT)_2$ (M= Co, Ni) Grown on a HOPG substrate

5. Summary and Perspectives

Part 1 Introduction

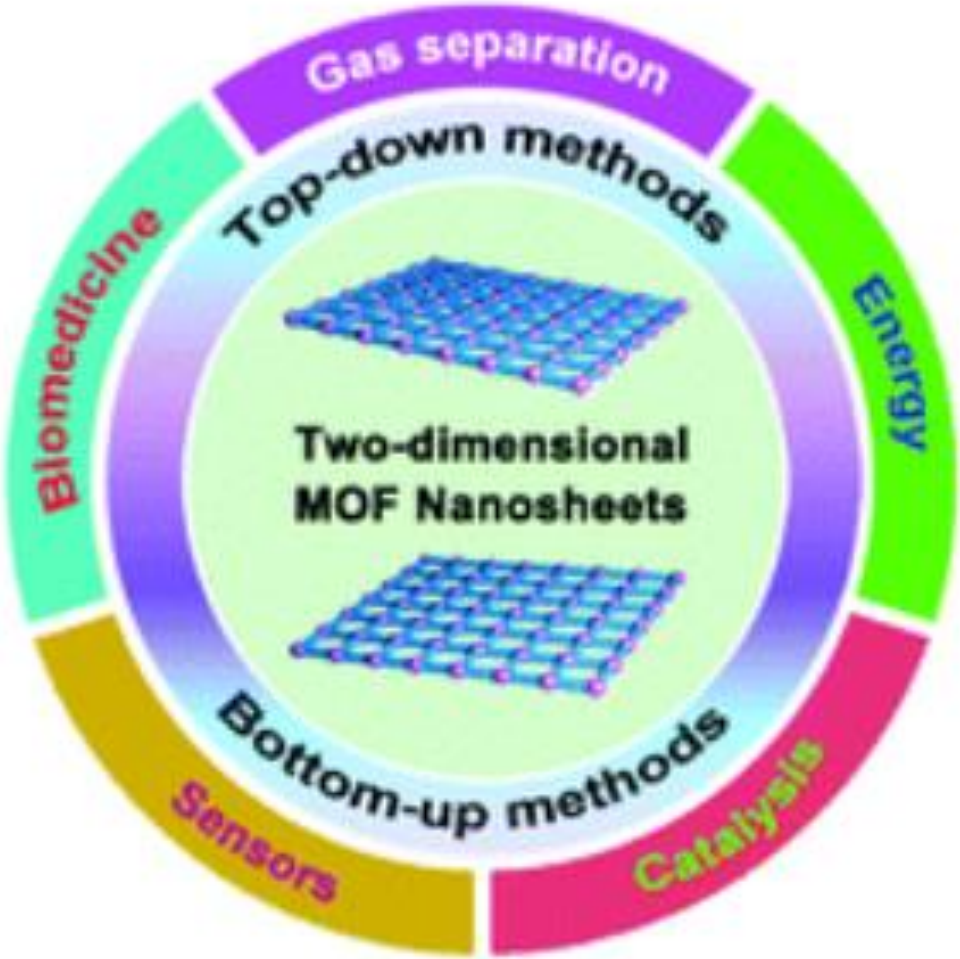
- Two-Dimensional Metal-organic frameworks (2D MOFs)
- Two-Dimensional Conjugated Metal-organic frameworks (2D-cMOFs)
- Experimental techniques: STM and STS

Synthesis and application of 2D MOFs

- Applications
  - Gas separation
  - Energy conversion and storage
  - Catalysis
  - Sensors
  - Biomedicine

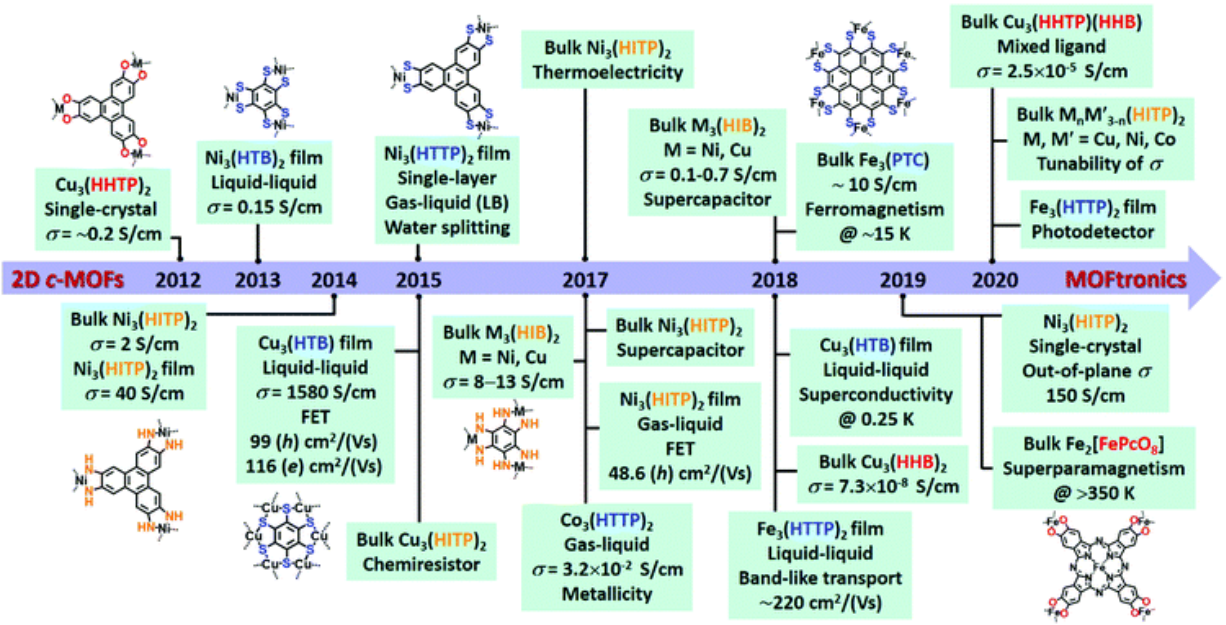
- Top-down synthesis methods
  - Sonication exfoliation
  - Mechanical exfoliation
  - Chemical exfoliation

- Bottom-up synthesis methods
  - Interfacial synthesis
  - Three-layer synthesis
  - **Self-assembly on surface** → Single-layer growth using chemical vapor deposition
    Precise characterization using surface science techniques



Chem. Soc. Rev. 47, 6267-6295 (2018)

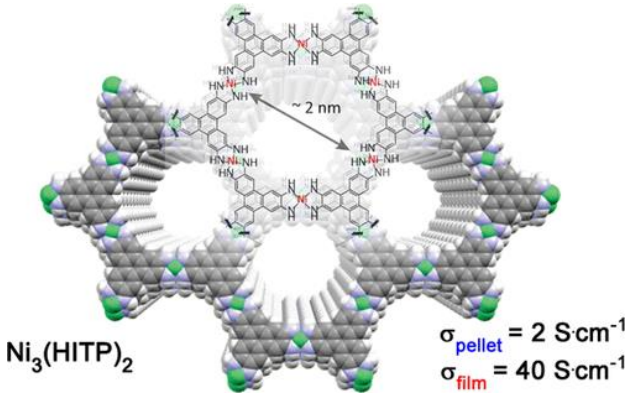
2D-cMOFs and benzene-derived organic linkers



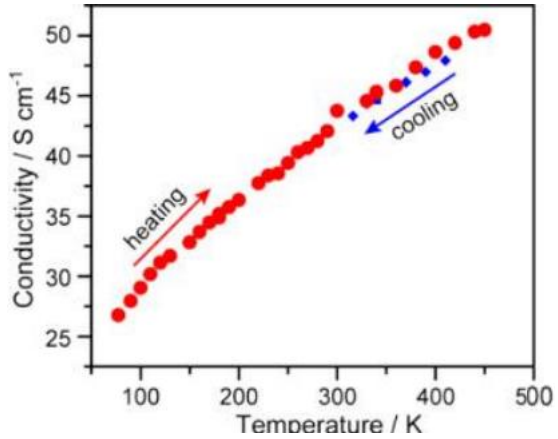
Chem. Soc. Rev. 50, 2764. (2021)

- 2D conjugated MOFs---delocalized electrons
- Properties and applications
- Not on surface
- Bulk or multilayer, not single layer

Fundamental Physical and Chemical Properties!

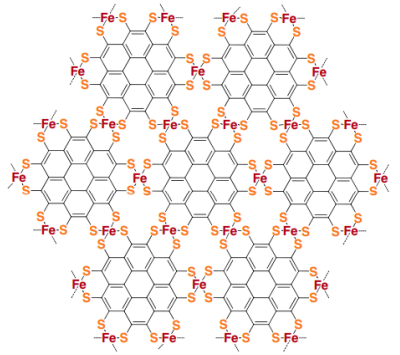


J. Am. Chem. Soc. 136, 25. (2014)

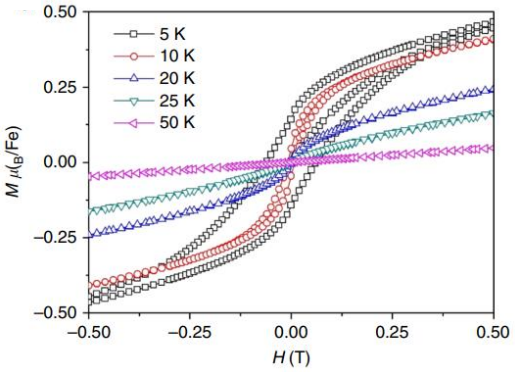


- 500nm thick film
- Conductivity 40 S/cm

Fe3PTC



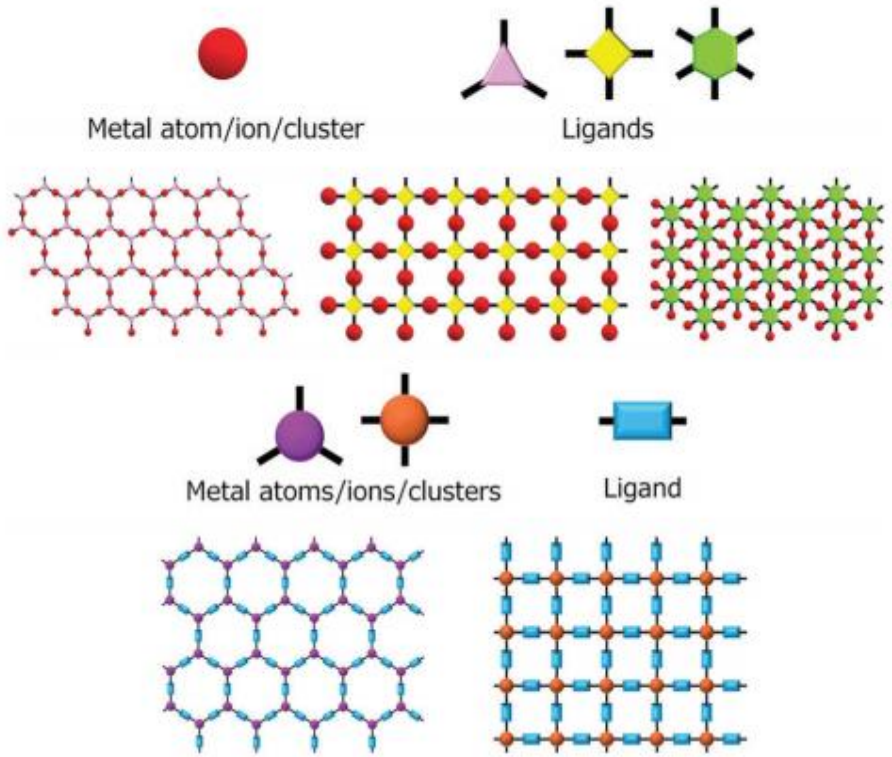
Nat. Commun., 2018, 9, 2637



- Bulk conductivity 10S/cm
- Ferromagnetism below 20K

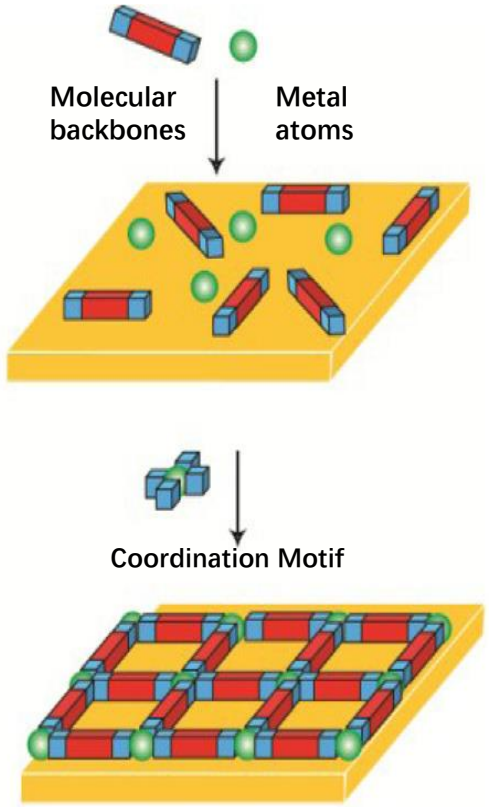
2D Metal Organic Frameworks Design

- 1 Molecular Design

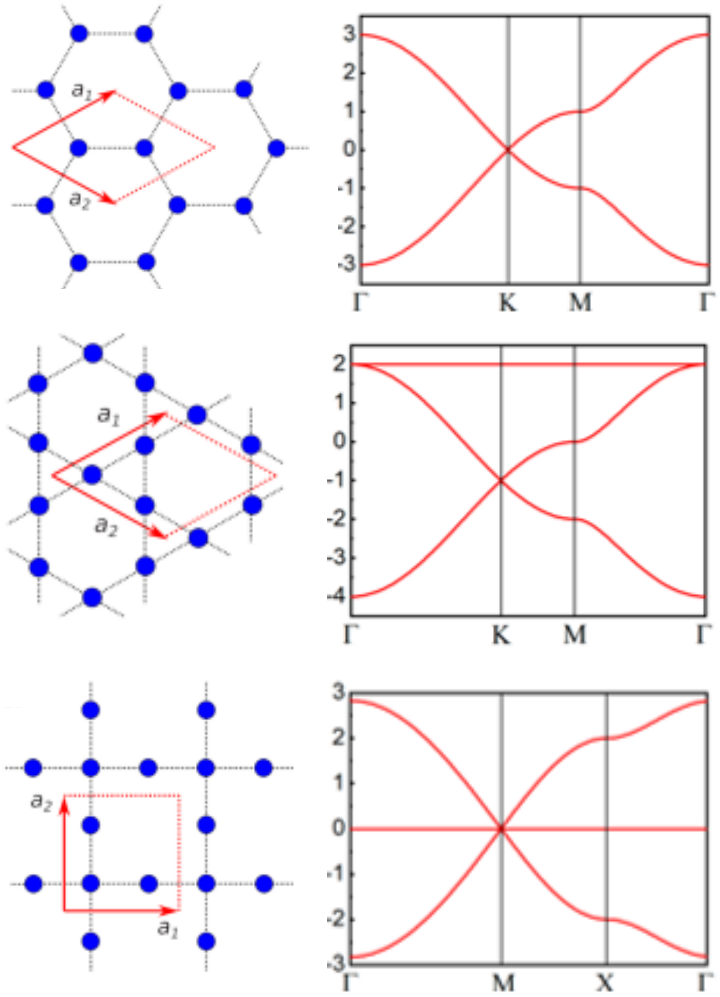


Chem. Commun. 53, 5781 (2017)

- 2 Self-Assembly

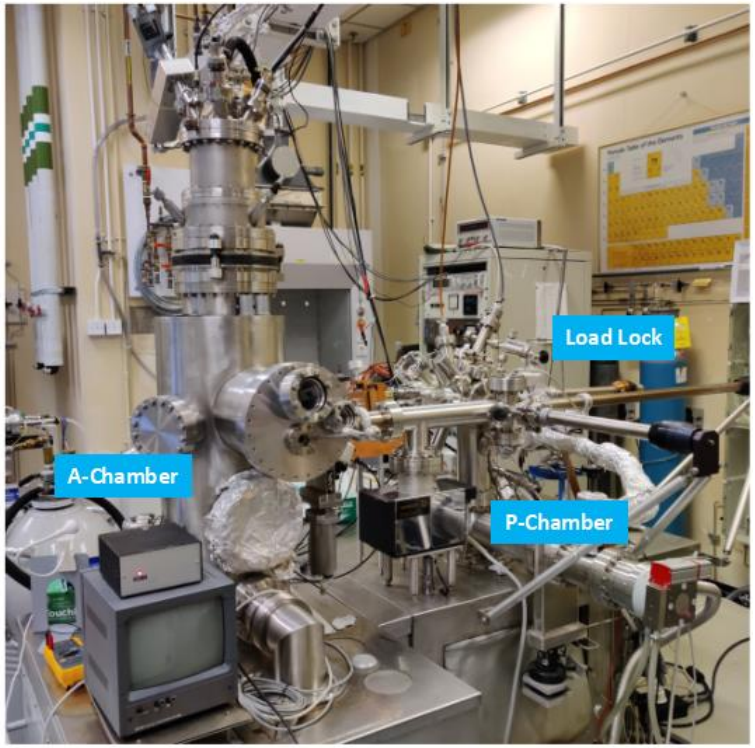


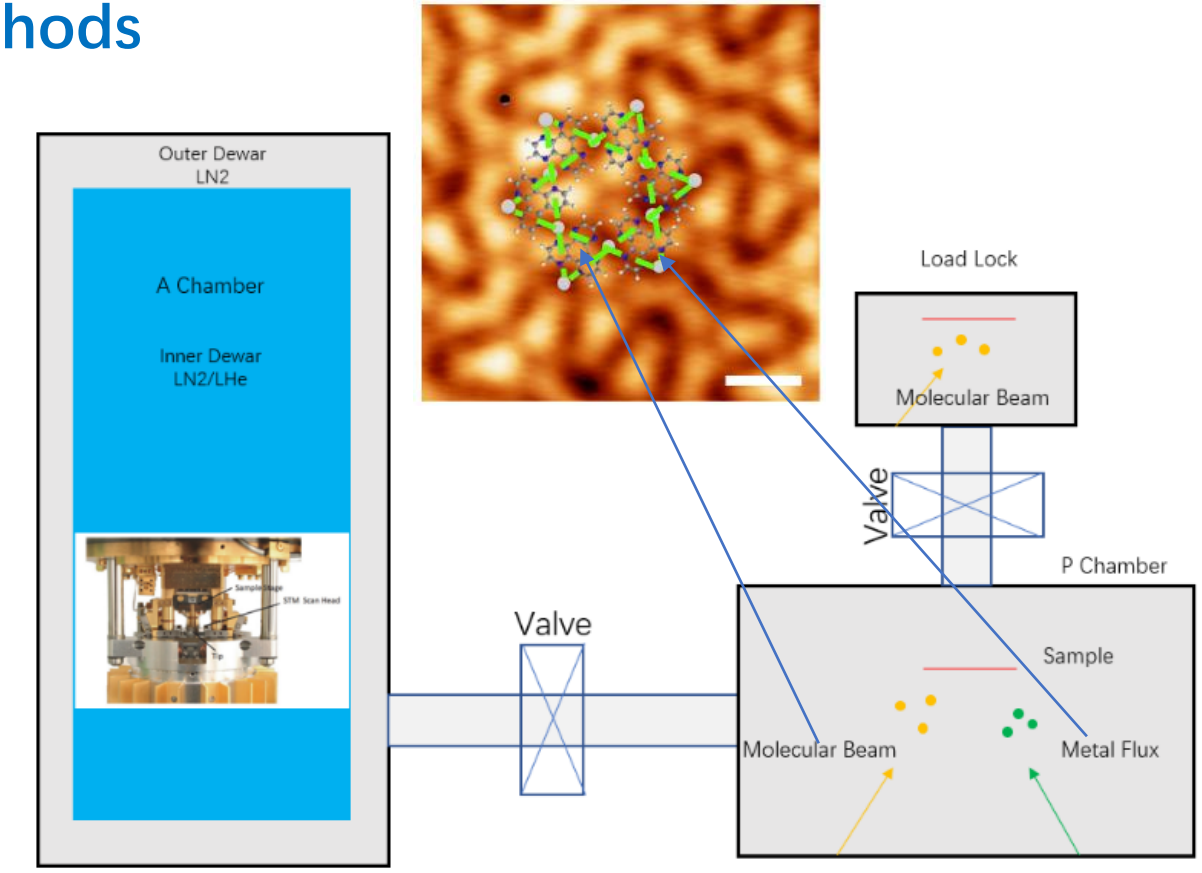
- 3 Band structure



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

Instrument and Experimental Methods





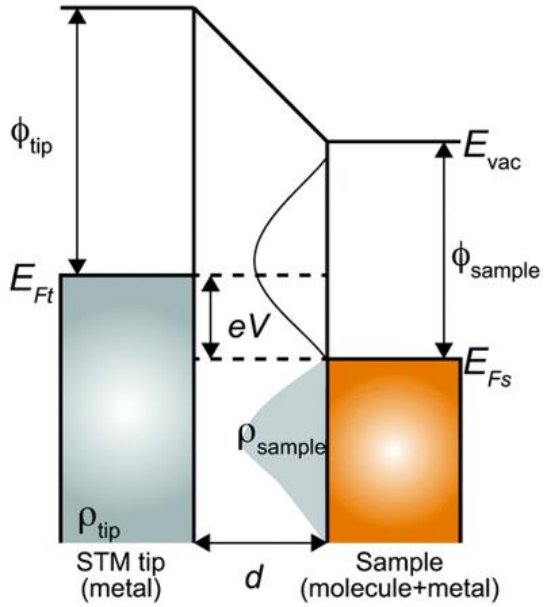
- Ultra-High Vacuum--- Free of contaminant
- Low temperature--- Stable and precise characterization
- Atomic resolution

- Substrate preparation
- Metal substrate--- Sputtering and annealing
- HOPG substrate--- Exfoliation and annealing

- Evaporation of molecules and metals
- Direct current heating
- E-beam heating

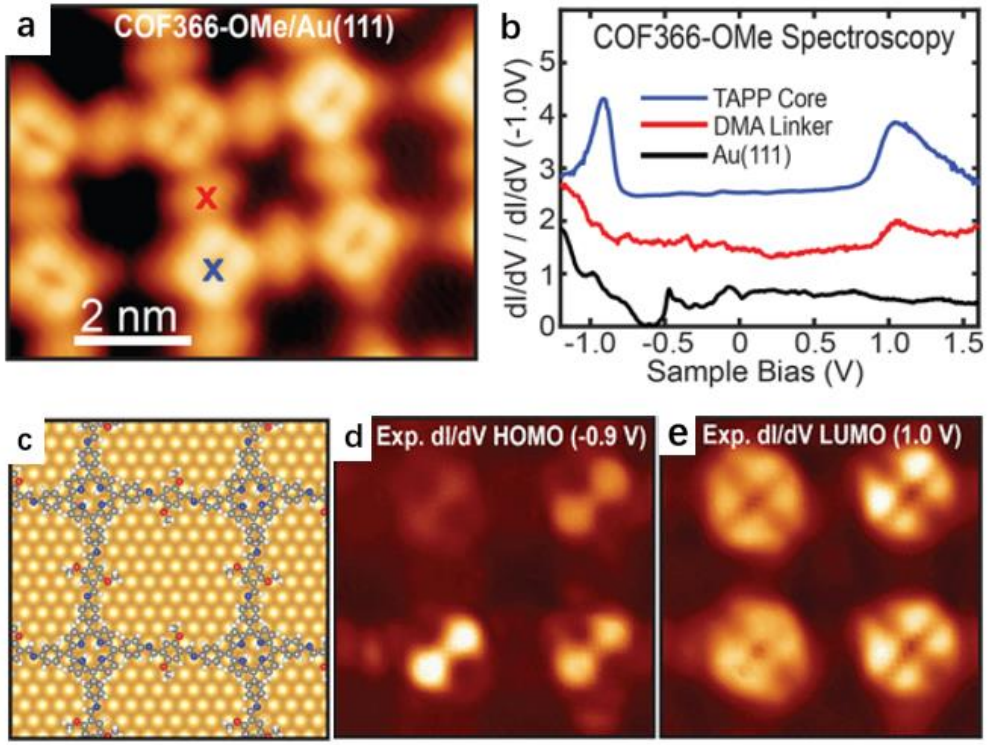
Experimental techniques -- electronic properties

Electronic properties



$$\frac{dI}{dV} \propto e\rho_{sample}(eV)\rho_{tip}(0)T'(eV,eV,d),$$

- Scanning Tunneling Spectroscopy (STS)
- Local Density of state (LDOS)
- dI/dV spectra



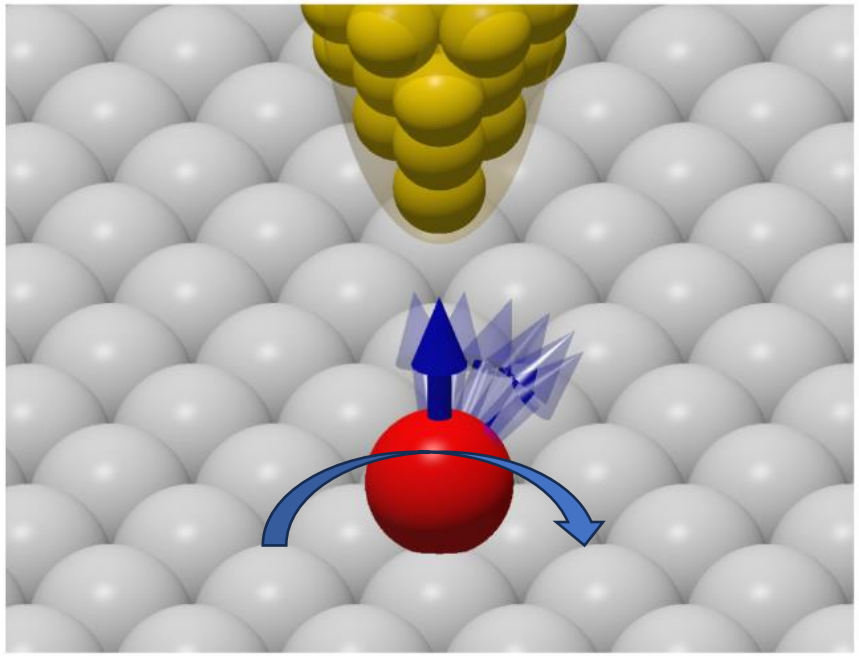
- Single point STS Peaks at -0.9V, 1.0 V
- STS Mapping HOMO, LUMO
  (spatial resolution)

Chem. Soc. Rev.44, 970 (2015)

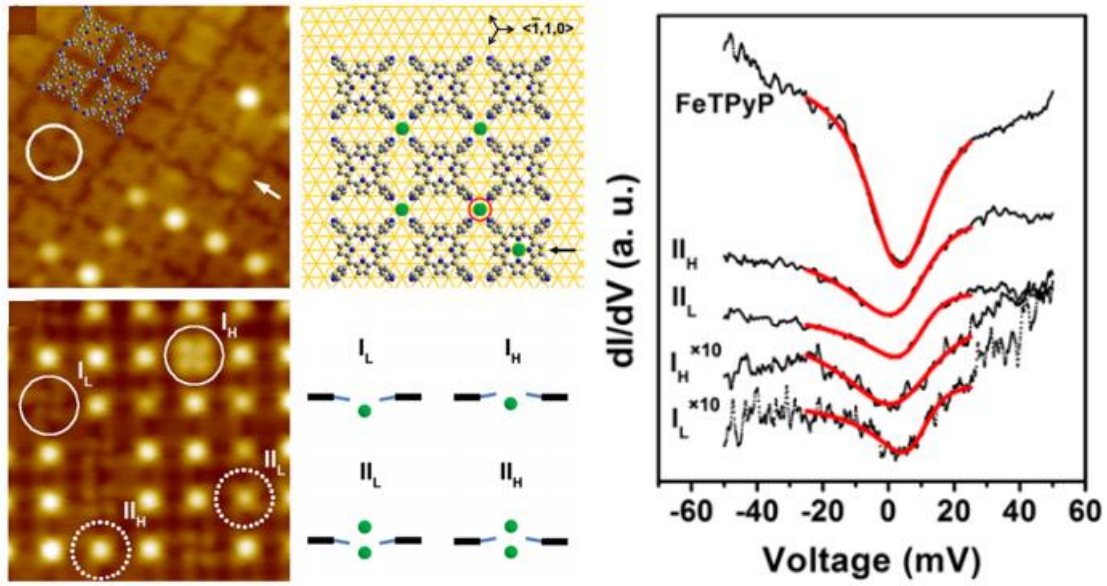
ACS Nano, 12, 385 (2017)

Experimental techniques -- magnetic properties

Kondo effect



- Scattering of localized spins with conduction electrons
- **Zero bias anomalies in asymmetric Fano line shape**

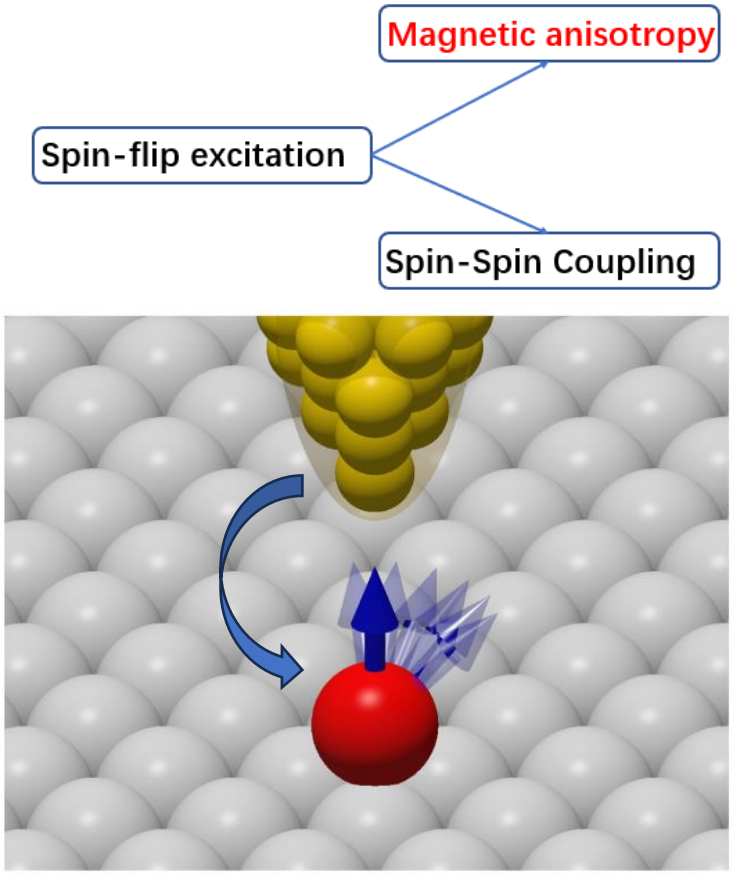


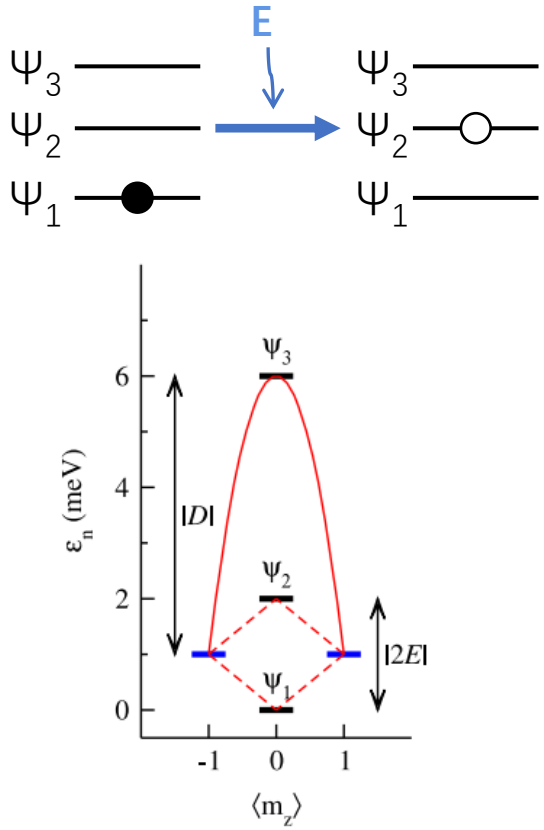
- Fe-TPyP 2D MOF
- Kondo resonance in STS spectra
- Fano function fitting---Tk~148 K

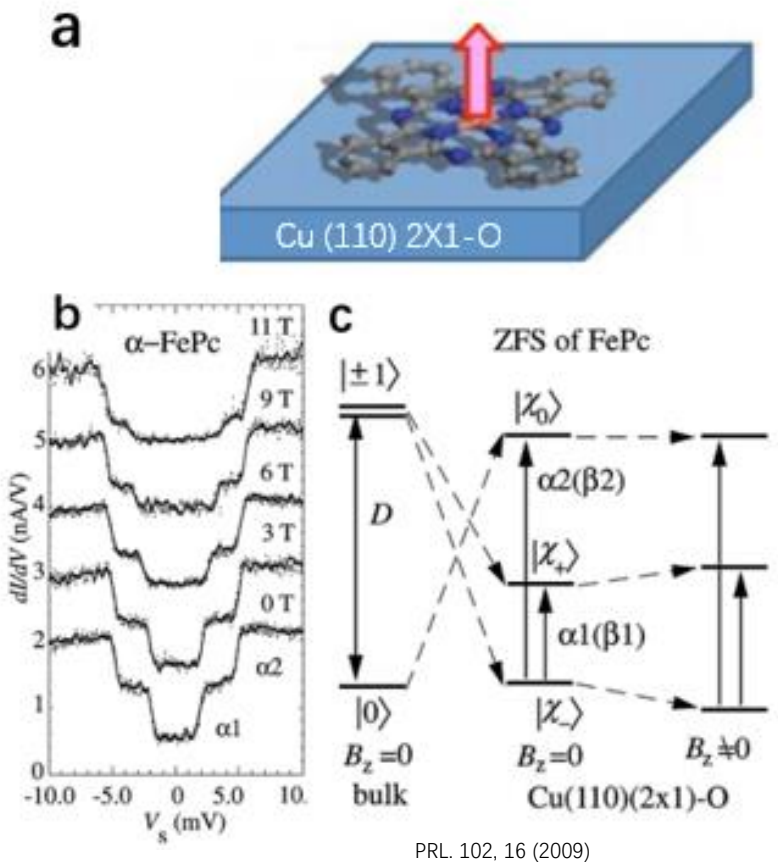
Nat Commun. 11, 6112 (2020)

ACS Nano. 8, 8310 (2014)

Experimental techniques -- magnetic properties







PRL. 102, 16 (2009)

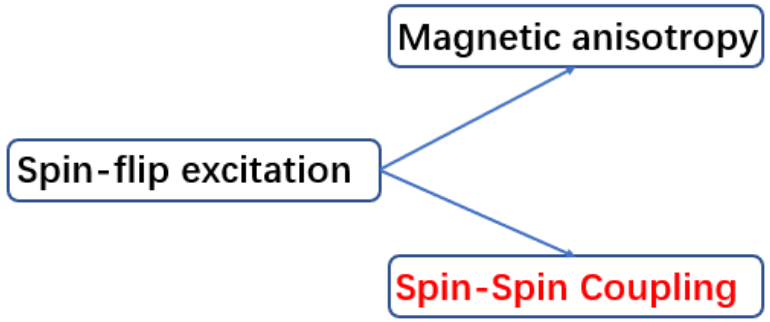
- Interaction of tunneling electrons with localized magnetic impurities
- Magnetic anisotropy lift the degeneracy, split the energy levels
- **Symmetric step like feature around Fermi level**

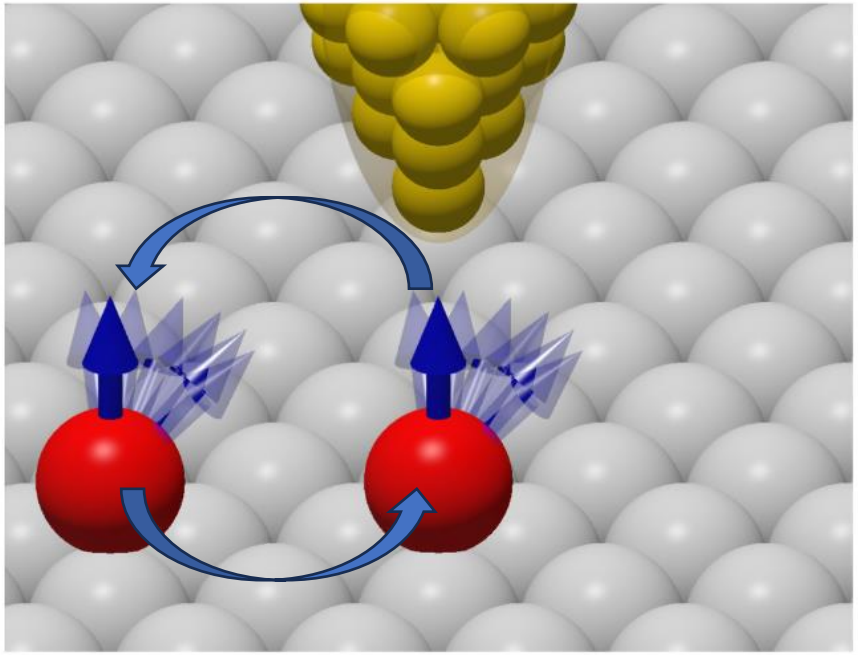
- Symmetric Step-like features
- Spin-flip excitation caused by MAE
- D=-3.8meV, E= 1.0meV

$$H_{\text{eff}} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B S_z B_z$$

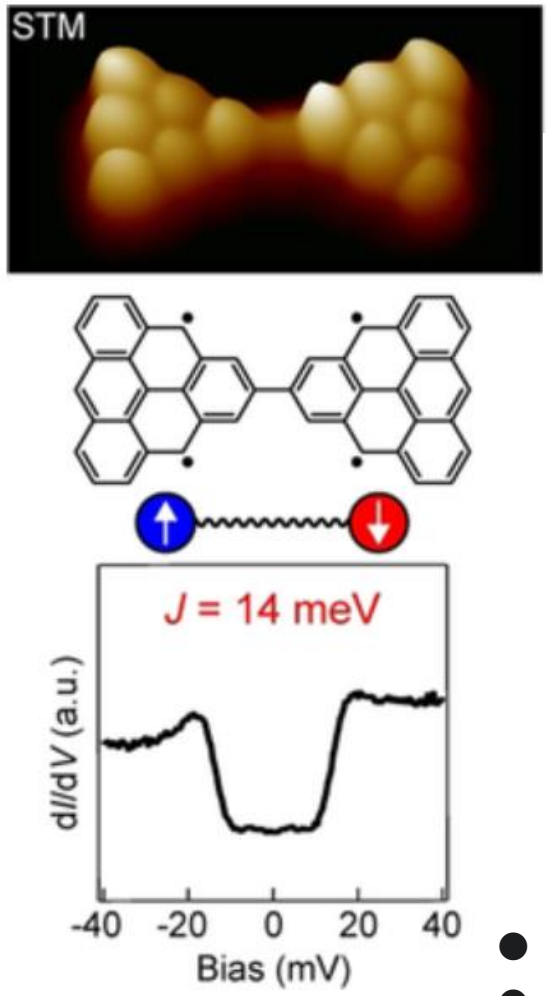
- Steps shift with increasing B

Experimental techniques -- magnetic properties

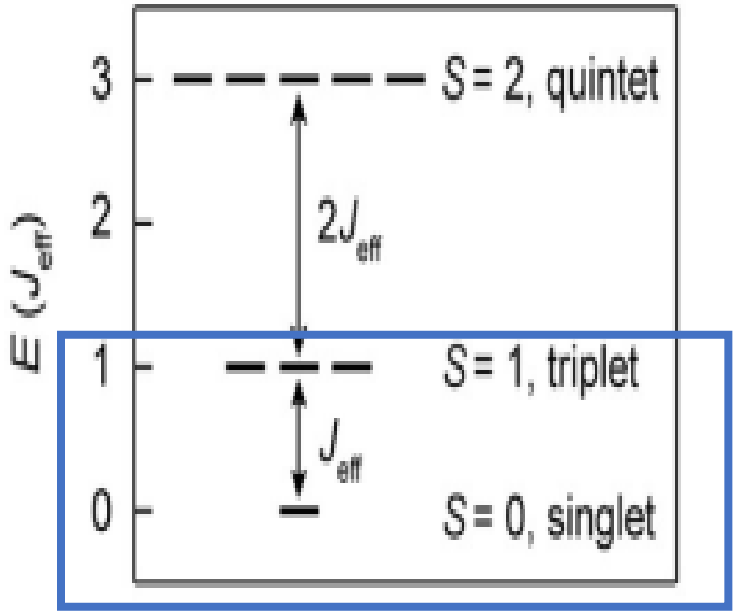




- Interaction between coupled spins
- **Symmetric step like feature around Fermi level**



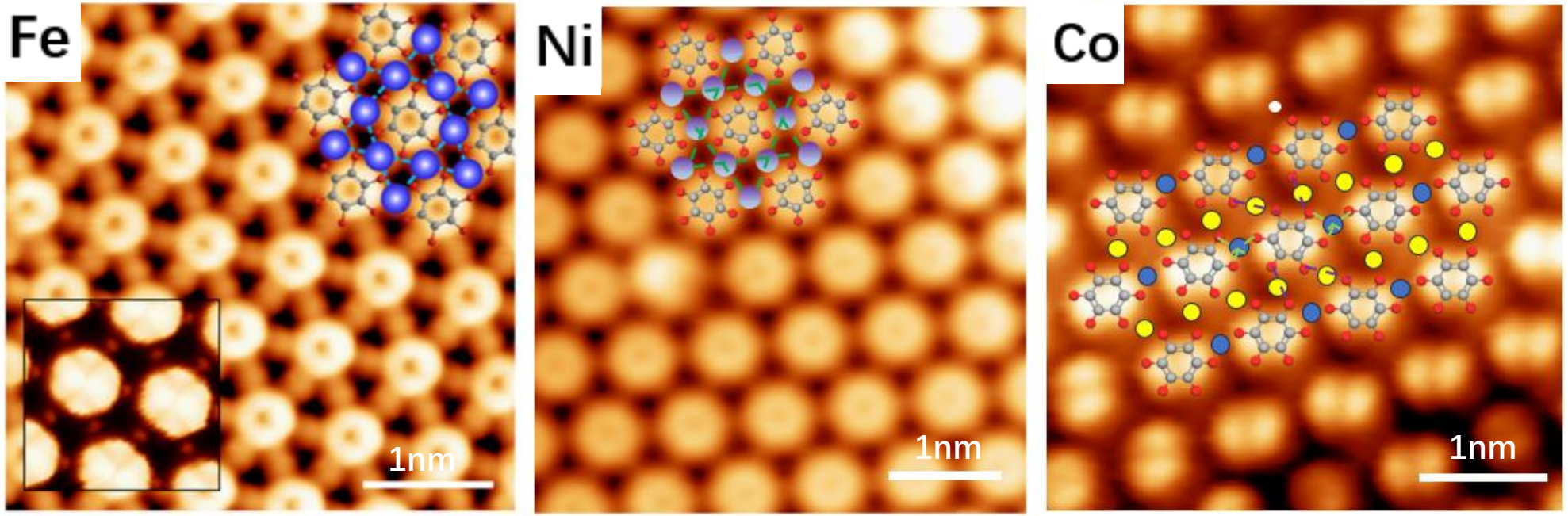
Angew. Chem. Int. Ed. 59, 12041 (2020)



- triangulene dimers
- Antiferromagnetic coupling
- Singlet to triplet transition

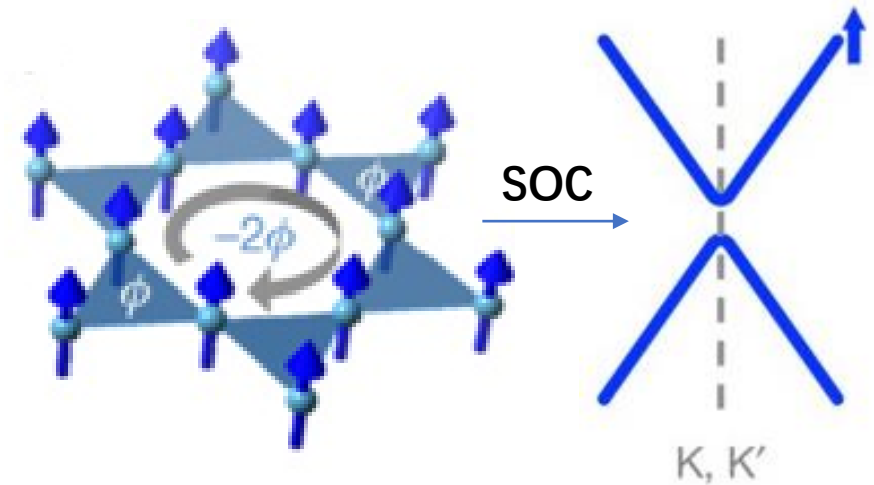
Part 2 Synthesis and Characterization of 2D-cMOFs M-BHO (M=Fe, Co, Ni)

- Sample Preparation
- $M_3(BHO_{-6H})$ (M=Fe, Ni) MOFs structures and magnetic properties
- Co-BHO structure and magnetic properties



2D Magnetic Kagome Lattice

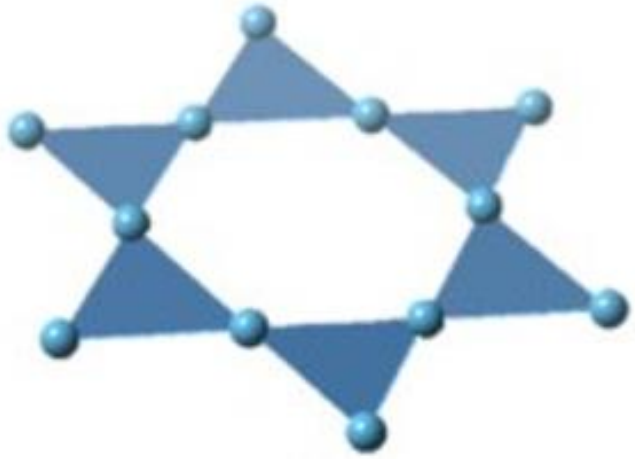
Introduction



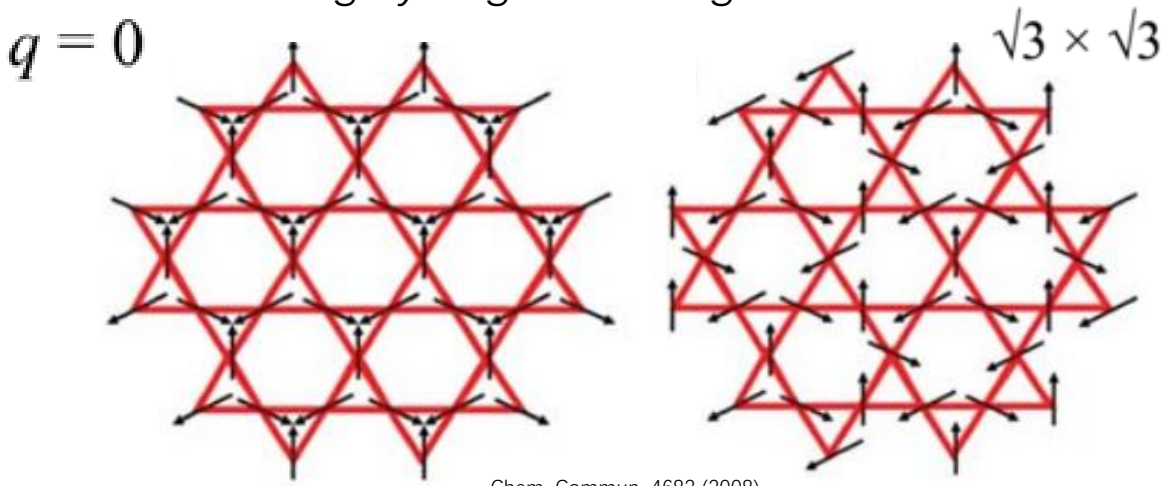
Nature. 555, 638 (2018)

- Ferromagnetism
- Split spin-degenerate Dirac bands
- QAH and FQH

- Antiferromagnetic coupling



- Geometrically frustrated
- NN interaction cannot be satisfied
- Highly degenerated ground states

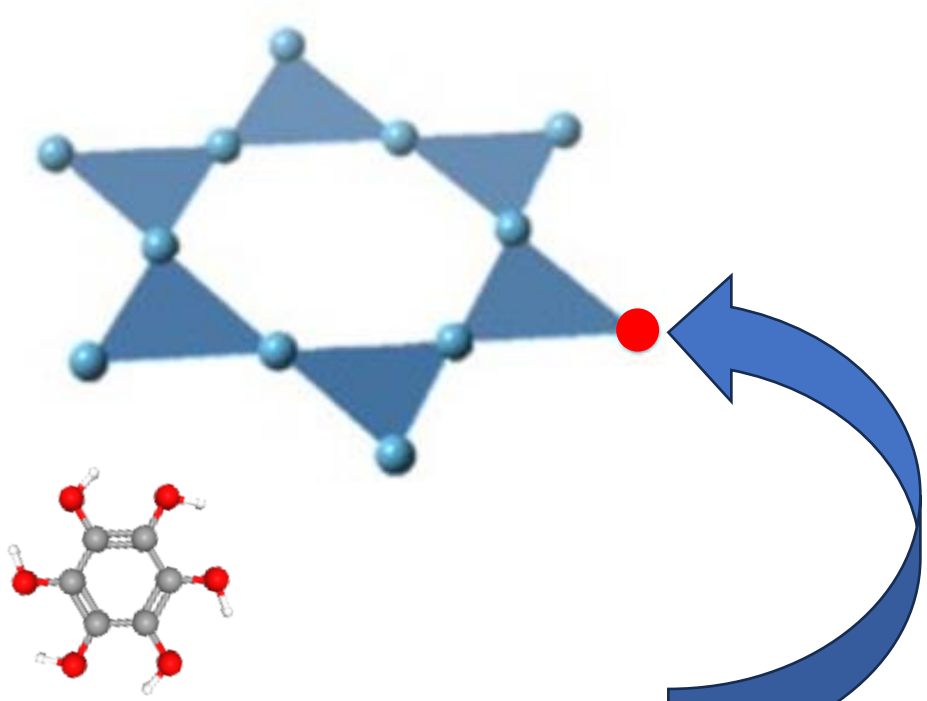


Chem. Commun. 4683 (2008)

- Two of possible highly degenerated ground states
- QSL---No long-range magnetic order

Magnetic Elements With Different d Electrons

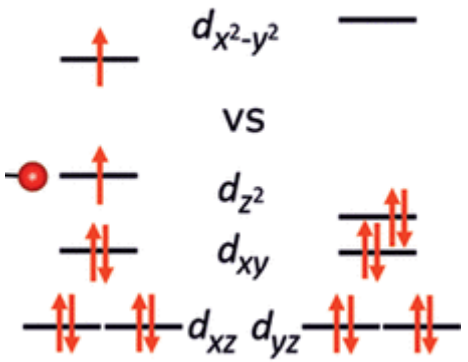
Introduction



- Metal Organic Frameworks
- Kagome lattice---BHO
- Magnetism---Fe, Co, Ni

- **Oxidation States: M(II)**

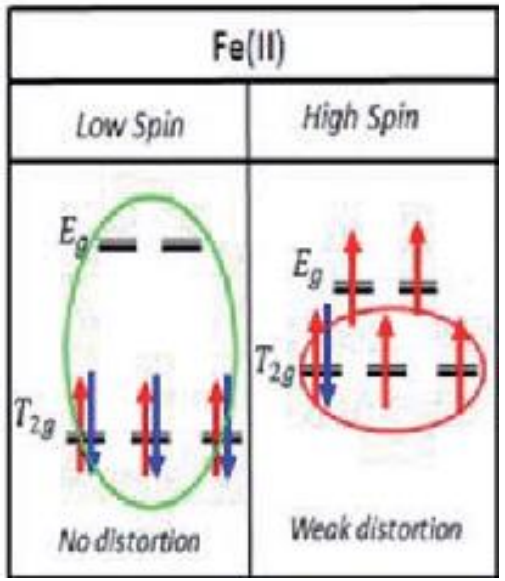
Ni High-spin vs Low-spin



- S=1 S=0

Chem. Mater. 34, 21 (2022)

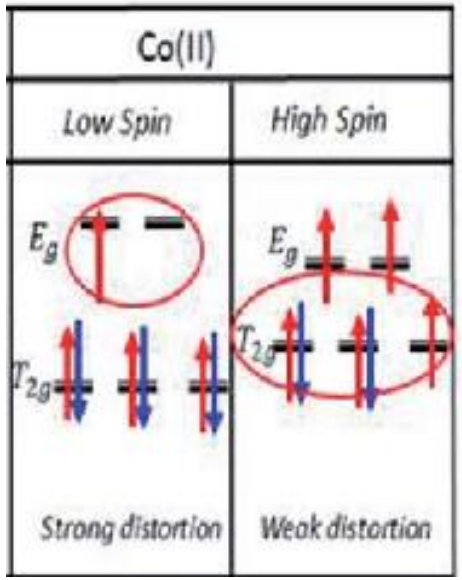
Fe



- S=0 S=2

RSC Adv.9 (2009)

Co

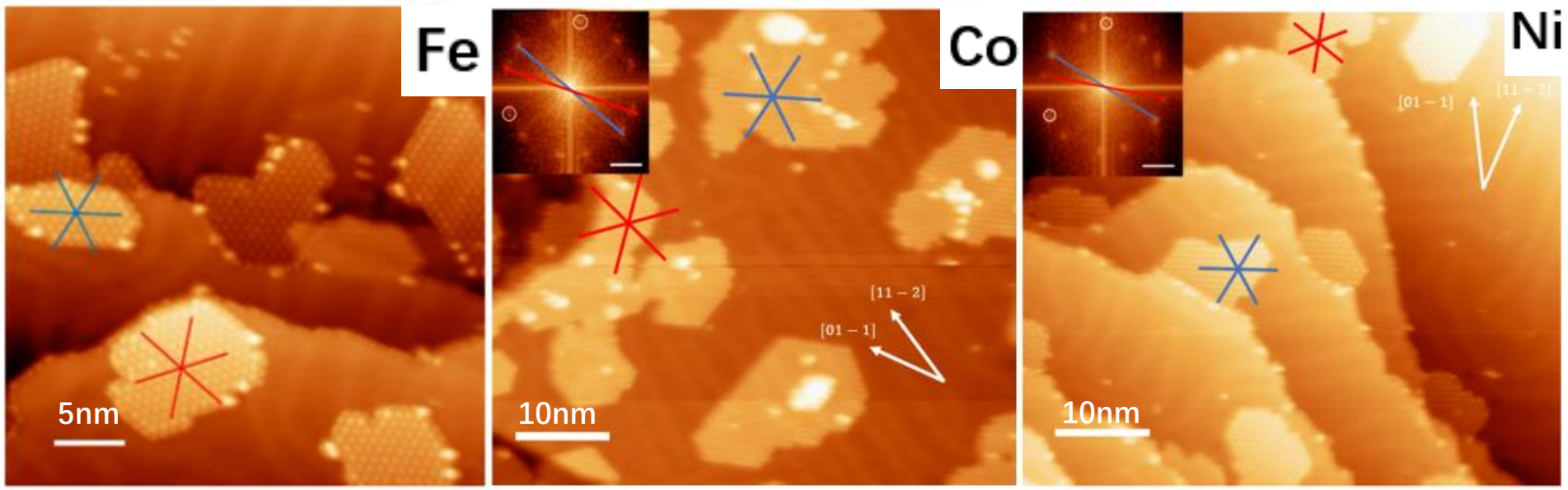


- S=1/2 S=3/2

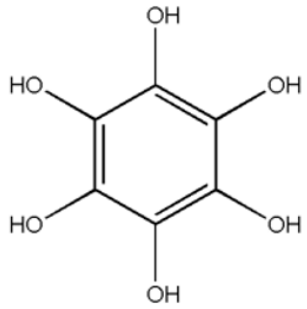
Different Spin states in different elements

M-BHO (M=Fe, Co, Ni) MOFs

Sample Preparation



- Benzene-1,2,3,4,5,6-hexaol (BHO) molecules
- Sample preparation
  - (1) Deposit BHO on Au (111) at RT
    [evaporate temperature: 410K]
  - (2) Dose metal atoms on sample
  - (3) Anneal at 430K

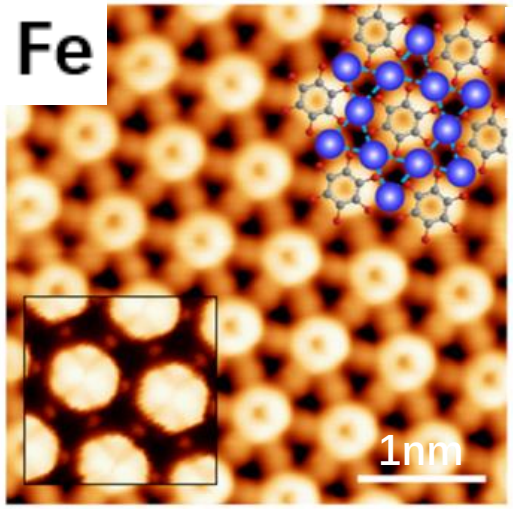


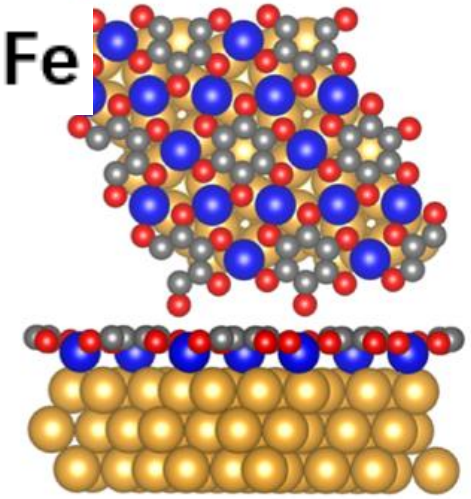
- Lattice orientations: ±10° relative to the equivalent $\langle 11\bar{2} \rangle$ directions on Au (111)

$M_3(BHO_{-6H})$ (M=Fe, Ni) MOFs

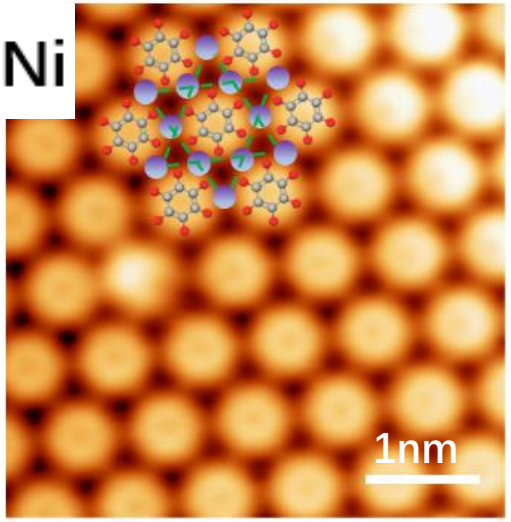
Models and DFT optimized structures

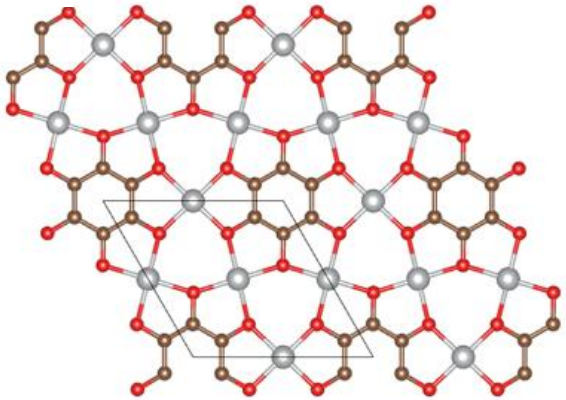
- Round shape with six-fold symmetry
- Lattice constants: 0.76nm
- Kagome lattice of Metal
- Two shorter Fe-O bond 1.98 Å and Two longer Fe-O bond 2.22 Å
- Identical Ni-O bond 2.1 Å





J. Phys. Chem. Lett. 12, 3733 (2021)





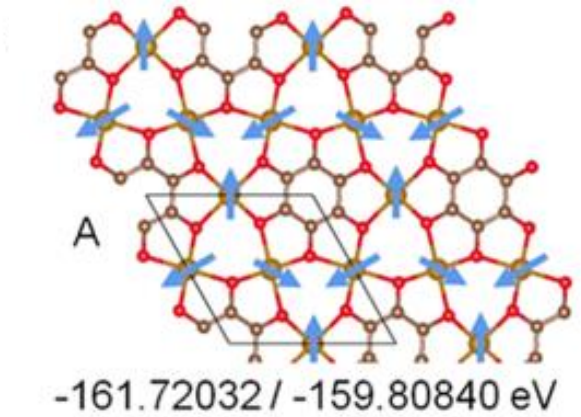
$Fe_3(BHO_{-6H})$ MOFs

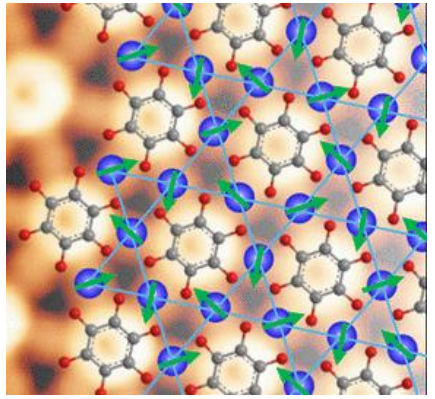
Magnetic Properties

- Lowest energy configuration---AF
- **Highly degenerated ground states**
- NN coupling J1=5.8 meV
- DFT calculated spin state S=2

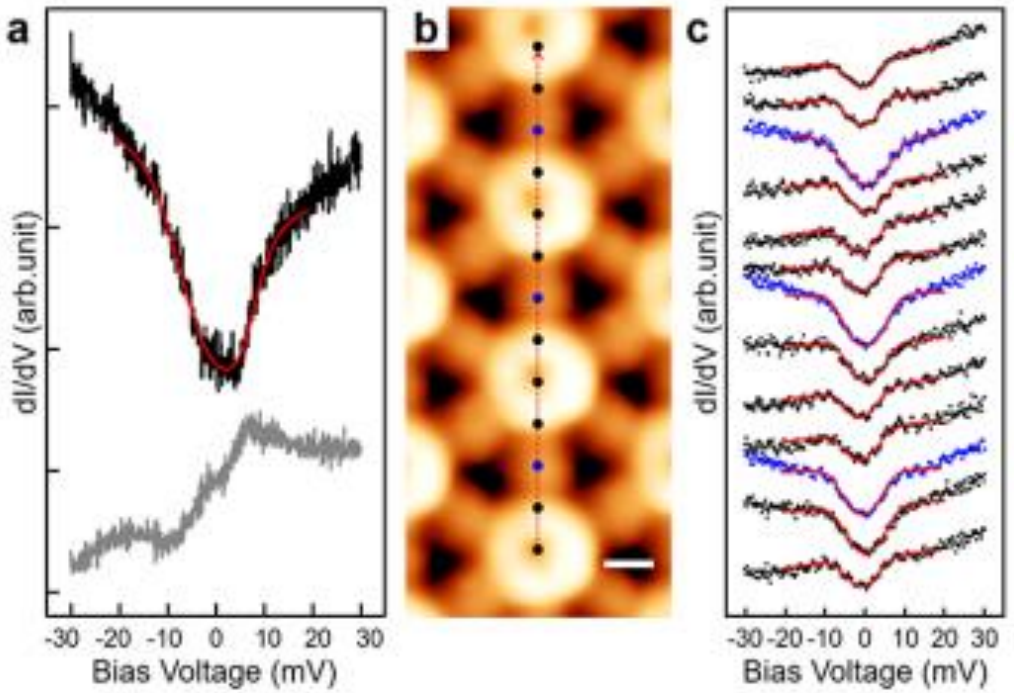
- Two steps at ±6 meV--Spin excitation features
- Fitting magnetic anisotropy easy plane D = 6meV
- Spin excitation --- global effect

Ordered spin excitation features





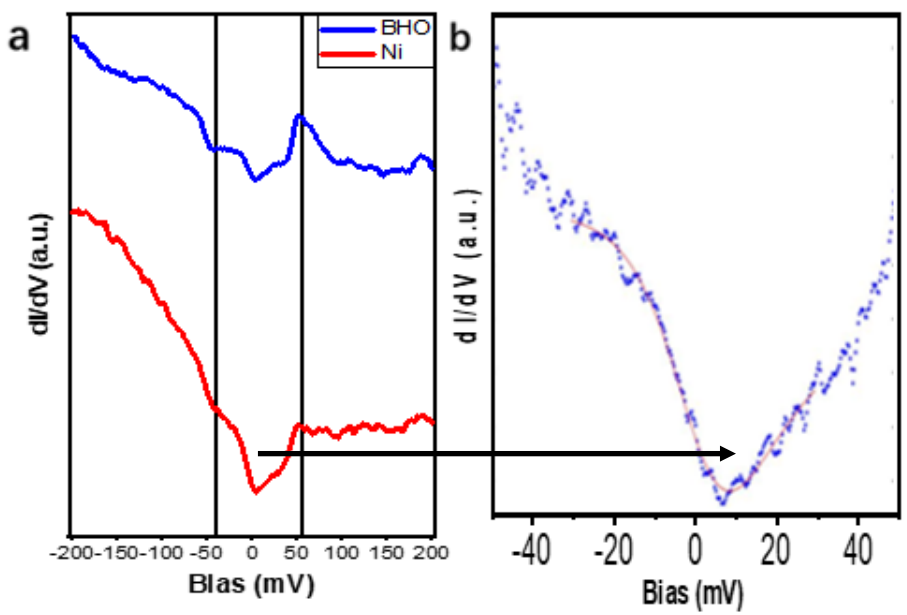
In-plane antiferromagnetic

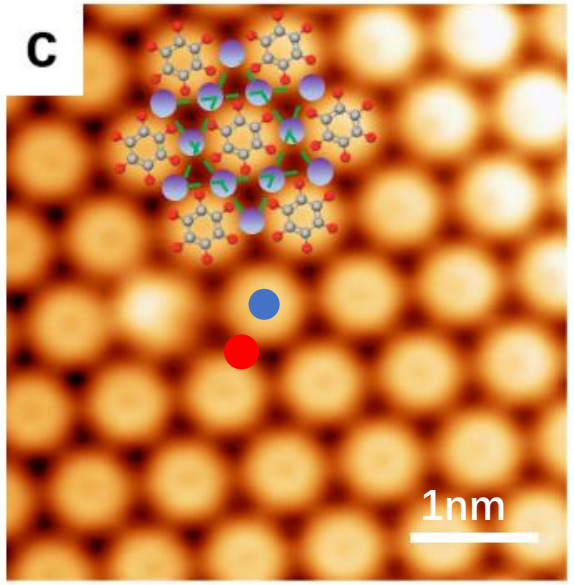


STS spectra STM image Line Mode Spectra

$Ni_3(BHO_{-6H})$ MOFs

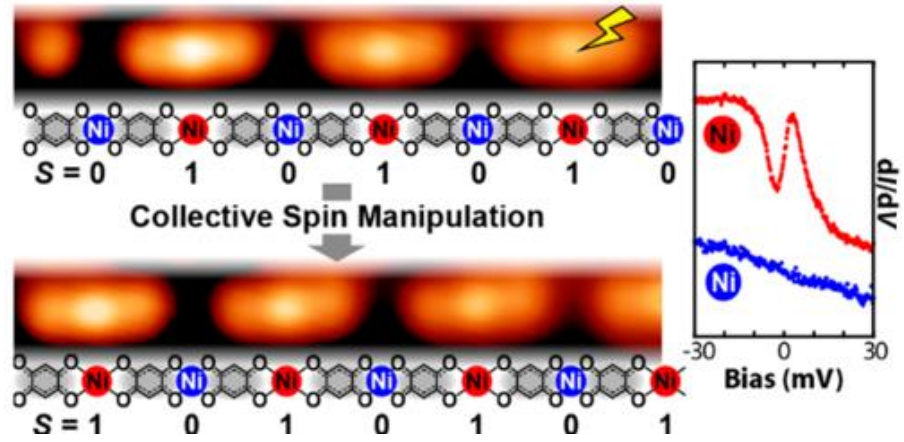
Magnetic Properties





- DFT calculated Ni spin state S=1
- No spin excitation features
- Fano function fitting: high temperature (TK~209K) screened Kondo effect?

- Ni-THB chain



ACS Nano. 14, 11283 (2020)

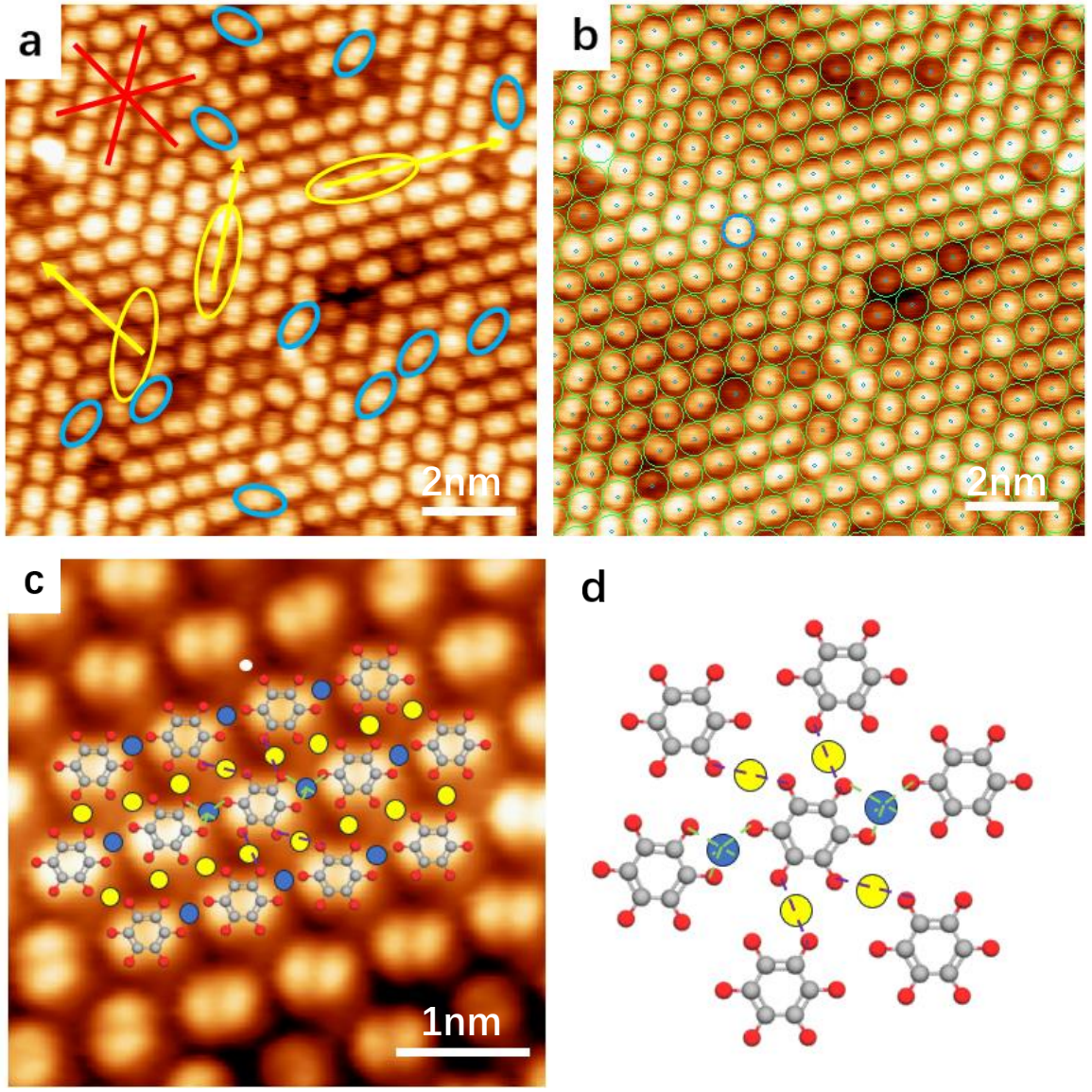
- Two types of Ni
- Two Kondo channels screening the molecular spins
- Two Fano functions
- Tk1=35K Tk2=220K

The 2D spin lattice behaves differently from the 1D spin system.
No spin excitation feature.

Co-BHO MOF

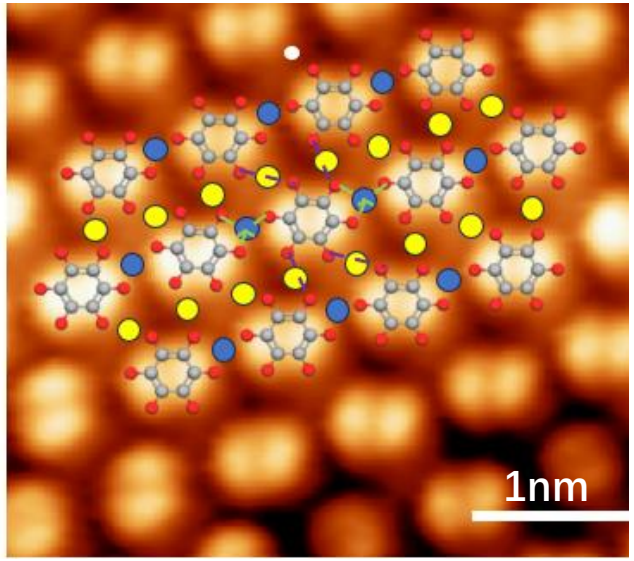
Models

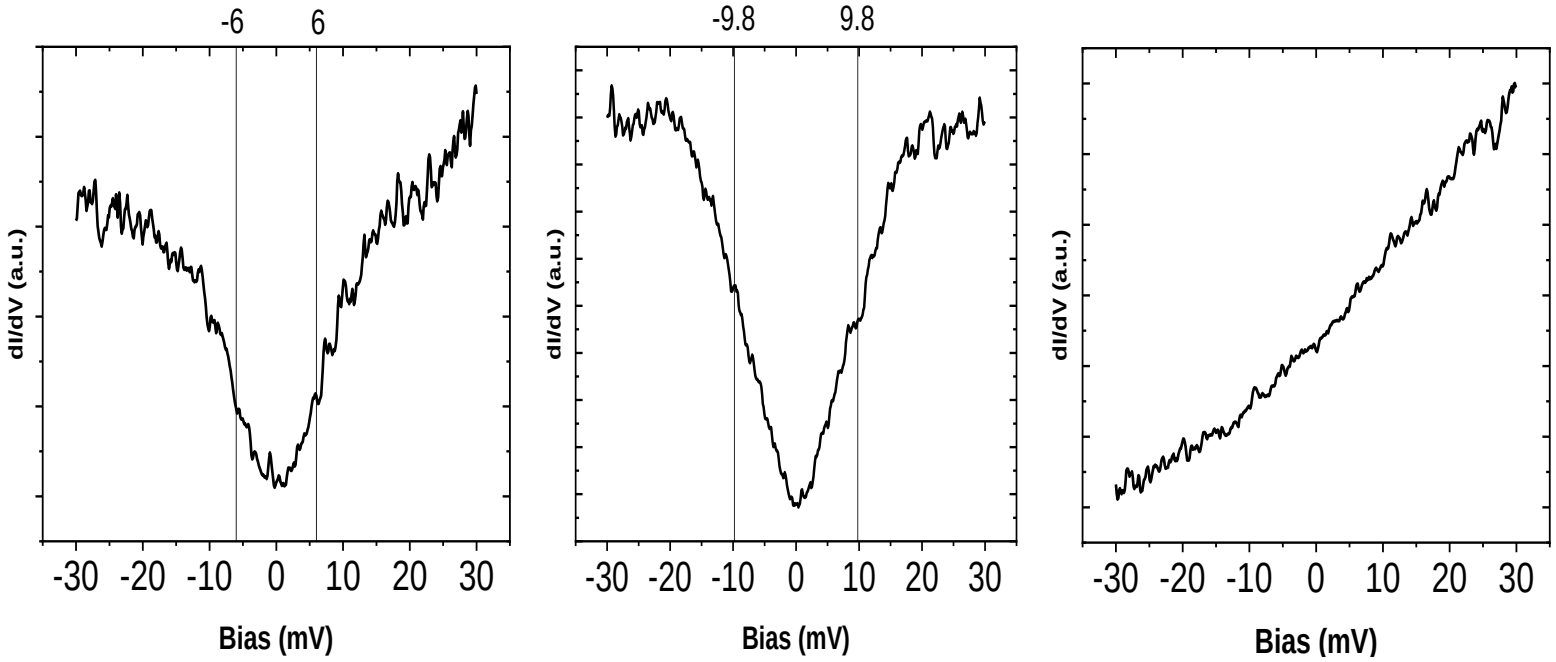
- Elliptical shaped BHO molecules---breaking of six-fold symmetry – orientated in three major directions and other minor directions.
- Same lattice as the $Fe_3(BHO_{-6H})$ and the $Ni_3(BHO_{-6H})$ MOFs with a lattice constant of 0.76nm.
- Molecules appear two half discs at negative bias.
- Non-Uniform bonding motif: Two-fold and Three-fold coordinated Co atoms.



Co-BHO MOF

Non-periodical magnetic properties





- Three types of spectral features randomly distributed.
- Excitation energy positions : 6meV, 10meV
- **Disordered spin excitation features**

M-BHO (M=Fe, Co, Ni) MOFs

Conclusion

Structure

- We synthesized a series of new 2D-cMOFs, namely $Fe_3(BHO_{-6H})$, $Ni_3(BHO_{-6H})$ and Co-BHO
- In $Fe_3(BHO_{-6H})$ and $Ni_3(BHO_{-6H})$, the metal atoms comprise a Kagome Lattice
- The Co-BHO system contains different bonding motifs

Magnetic properties

- $Fe_3(BHO_{-6H})$ shows ordered spin excitation features

DFT shows that the ground state of this system is highly degenerated containing antiferromagnetic coupled in-plane S = 2 spins;

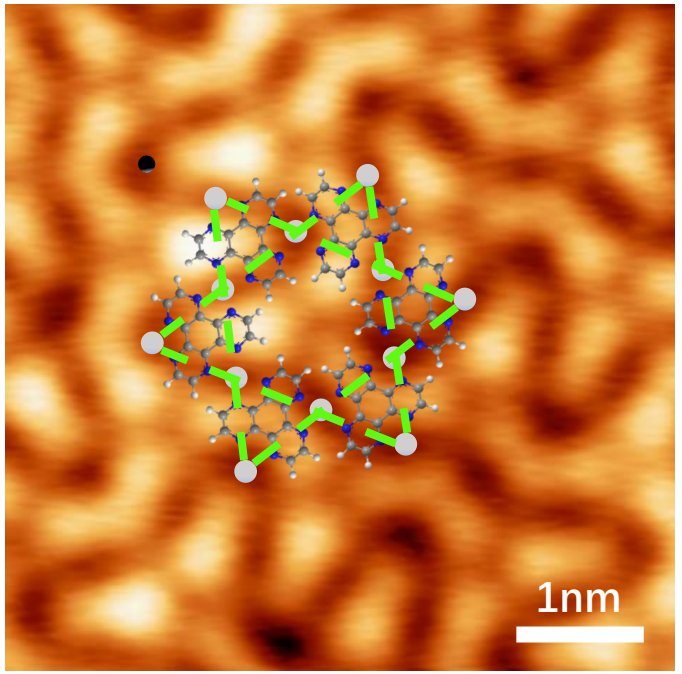
STS shows global spin excitation, which likely indicates a spin gap

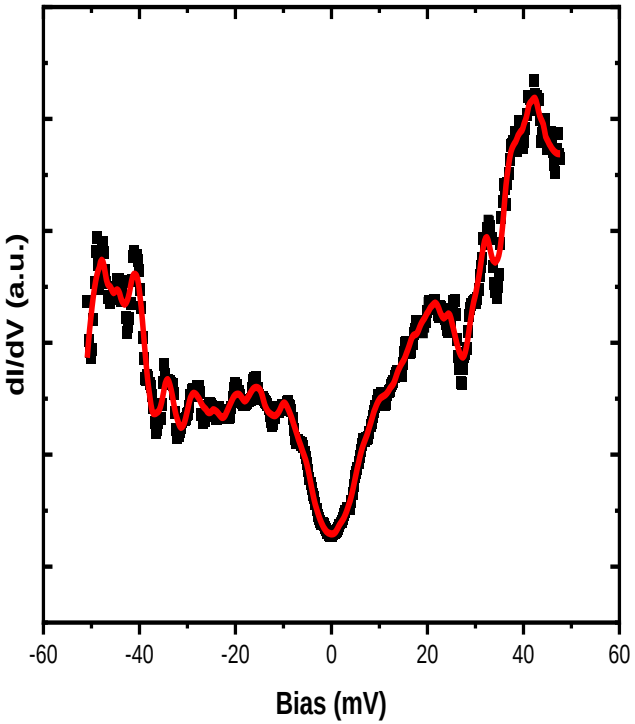
- $Ni_3(BHO_{-6H})$ shows no spin excitation feature
- Co-BHO shows disordered spin excitation features

Need theoretical study to explain

Part 3 Characterization of spin-spin coupling induced spin excitations in $M_3(HAT)_2$ (M=Fe, Co, Ni) MOFs

- Sample Preparation
- Models and DFT Calculation
- Magnetic Properties of $Cu_3(HAT)_2$ and $Ni_3(HAT)_2$
- Magnetic Properties of $Ni(HAT)_2$ and $Ni_4(HAT)_3$
- Magnetic Properties of $Ni(HAT)_2$ and $Ni_4(HAT)_3$

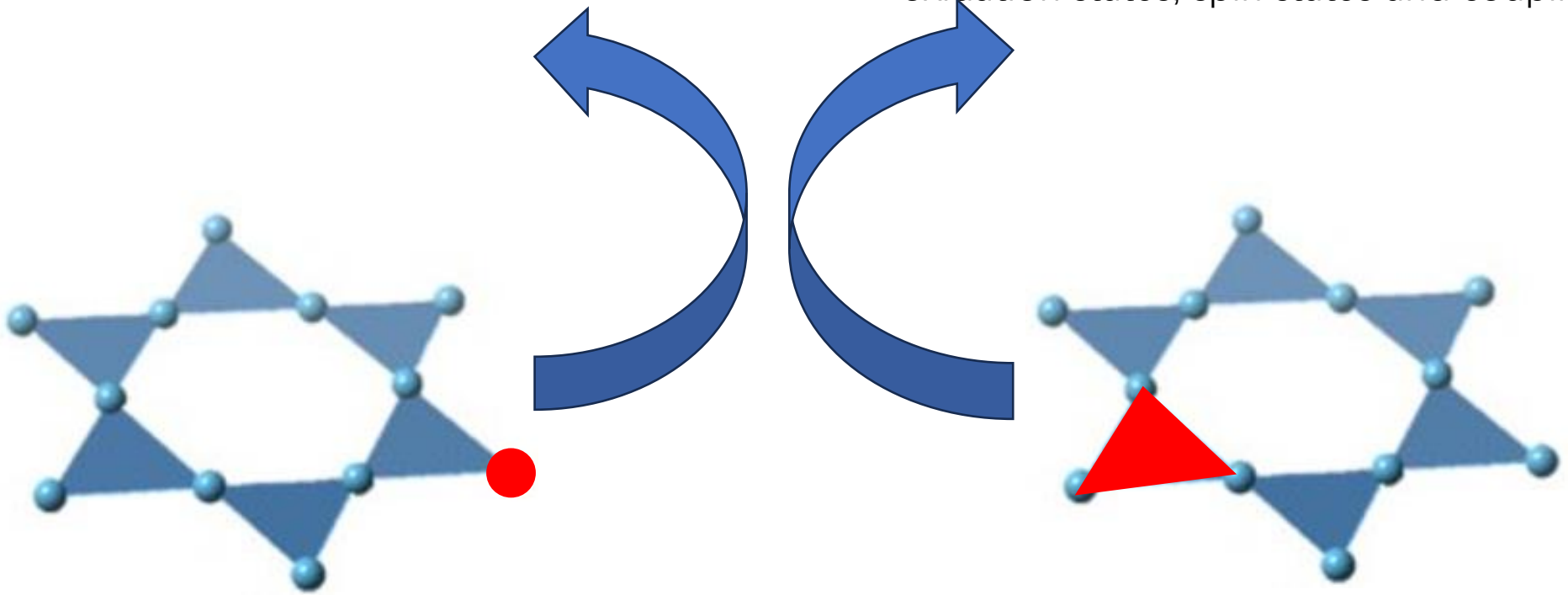


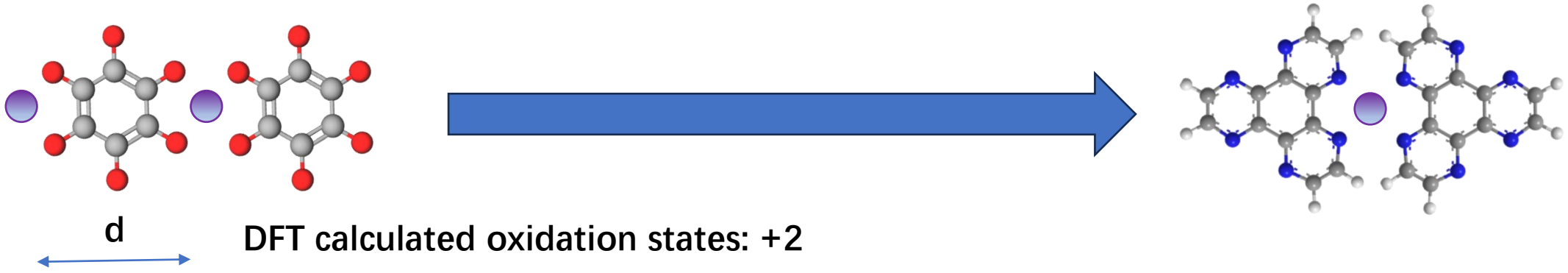


$M_3(HAT)_2$ (M=Fe, Co, Ni) MOFs

Introduction

- Change elements--- change spin states
- Change ligand---
  oxidation states, spin states and coupling pathways



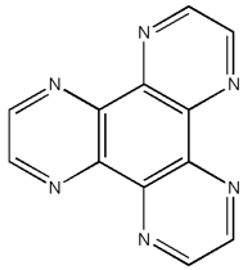


DFT calculated oxidation states: +2

$M_3(HAT)_2$ (M=Fe, Co, Ni, Cu) MOFs

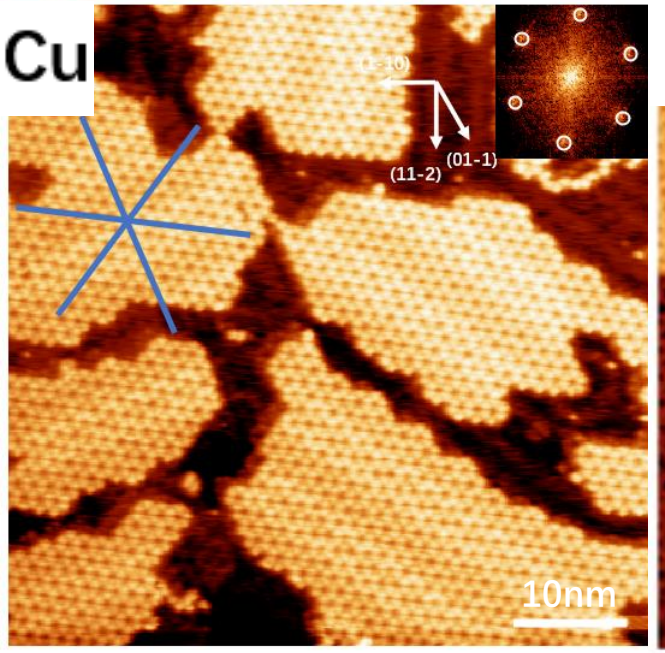
Sample Preparation

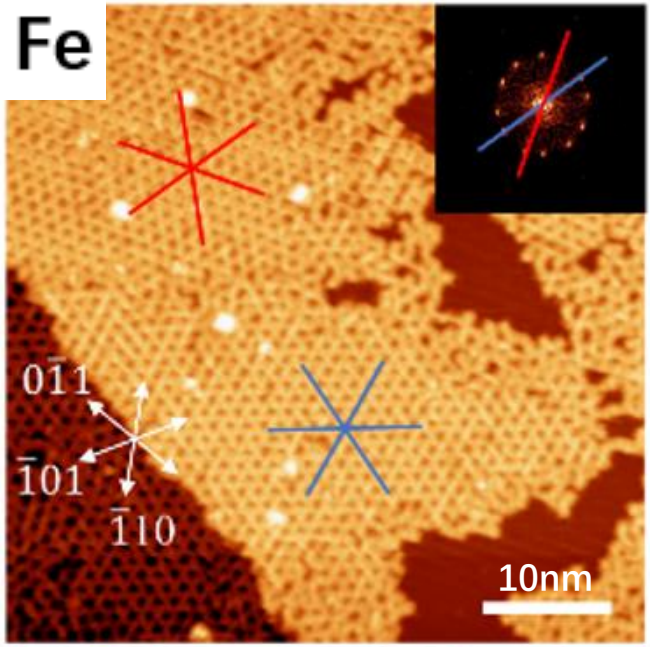
- 1,4,5,8,9,12-Hexaazatriphenylene (HAT)
- Ag(111) and Au (111) substrate

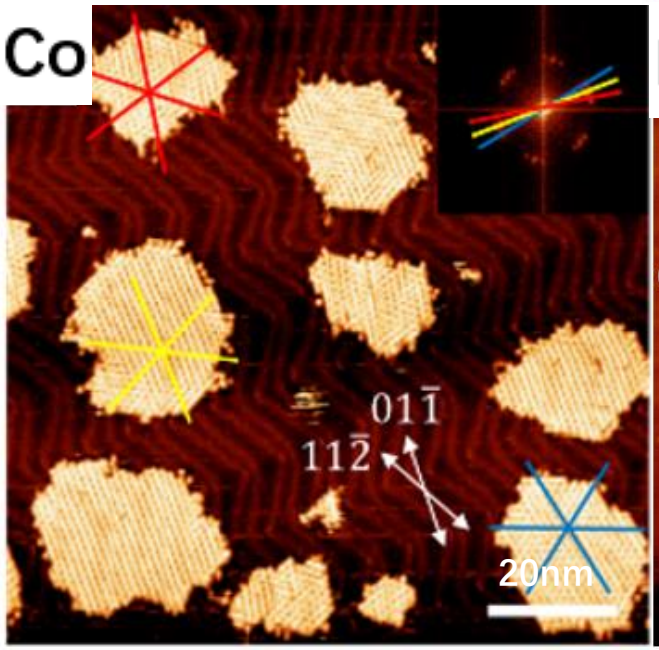


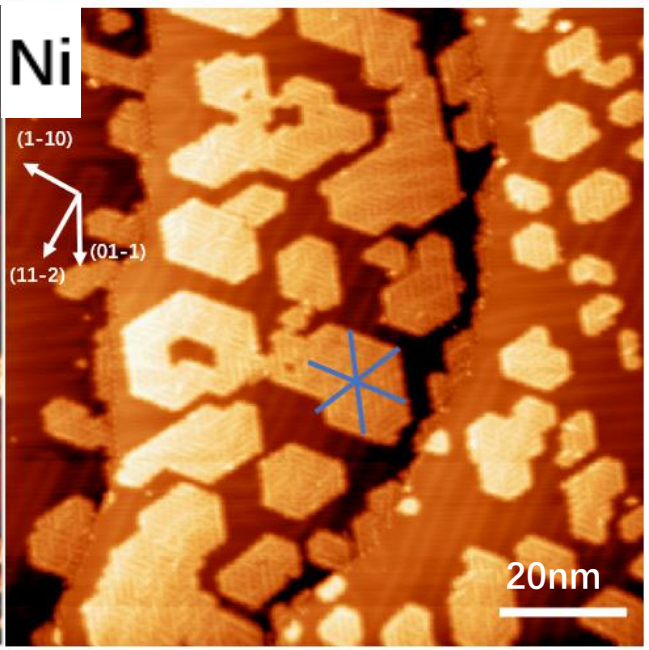
- Sample preparation
  - (1) Deposit HAT on Ag(111)/Au (111) at RT
    [evaporate temperature: 460K]
  - (2) Dose metal atoms on sample
  - (3) Anneal at 430K

- Lattice orientations:
  - (1) $Cu_3(HAT)_2$ along $\langle 01\bar{1} \rangle$
  - (2) $Fe_3(HAT)_2$ ±14° with respect to $\langle 0\bar{1}1 \rangle$
  - (3) $Co_3(HAT)_2$ yellow one is along the $\langle 01\bar{1} \rangle$
    other two ±10° with respect to $\langle 0\bar{1}1 \rangle$
  - (4) $Ni_3(HAT)_2$ along $\langle 01\bar{1} \rangle$



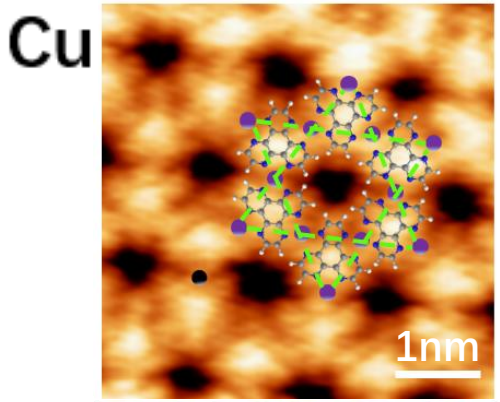


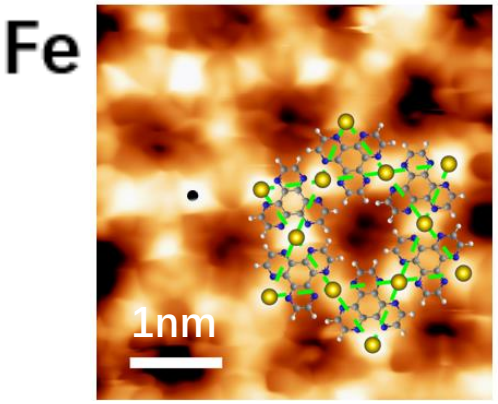


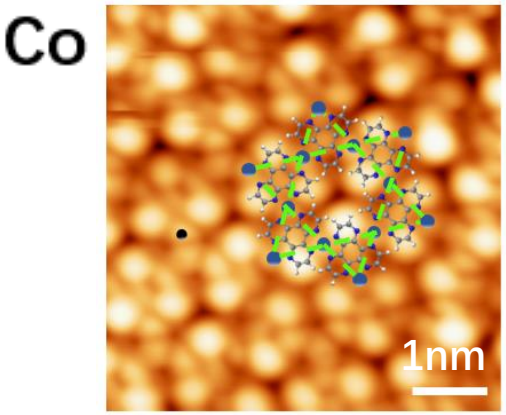


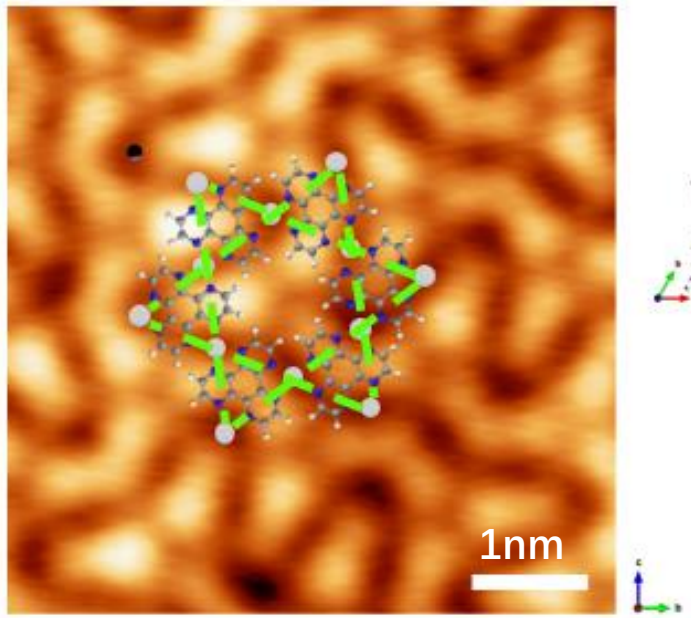
$M_3(HAT)_2$ (M=Fe, Co, Ni, Cu) MOFs

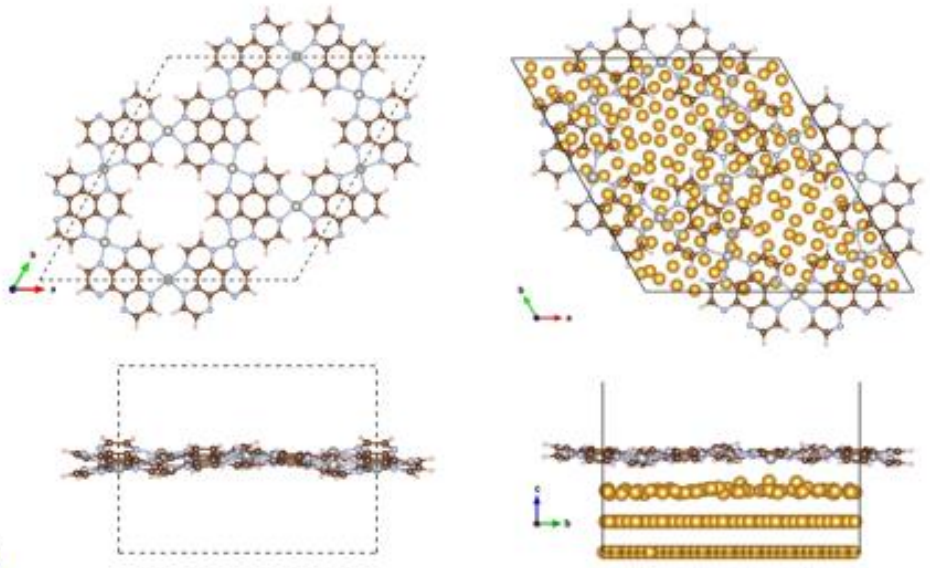
Models and DFT Optimized Structures











- Lattice constants:
  - (1) $Cu_3(HAT)_2$ 1.42nm (2) $Fe_3(HAT)_2$ 1.38nm
  - (3) $Co_3(HAT)_2$ 1.38nm (4) $Ni_3(HAT)_2$ 1.37nm
- Structures:
  - (1) Honeycomb lattice of HAT molecules, Kagome lattice of metal atoms
  - (2) bulked: HAT molecular backbones tilt up to 23°
  - (3) less bulked on substrate, HAT molecular backbones tilt up to 15°

$M_3(HAT)_2$ (M=Fe, Co, Ni) MOFs

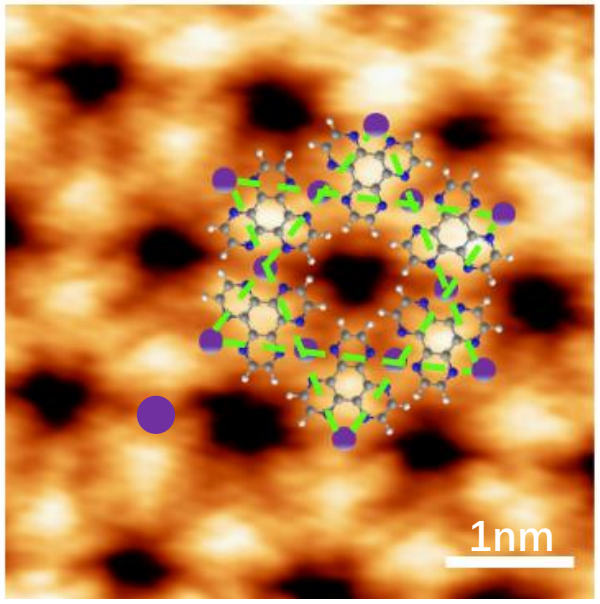
DFT Calculations

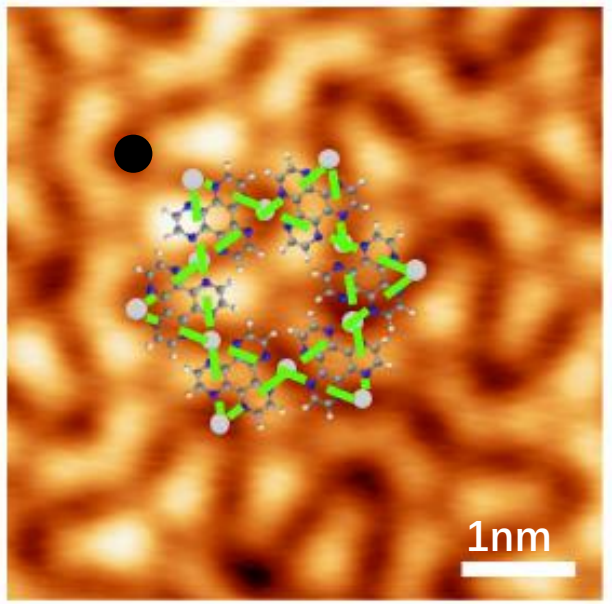
	Averaged Local Magnetic Moment (μB per atom)	Spin State	MAE (meV per atom)	Coupling
$Fe_3(HAT)_2$	3.667	S=2	0.06 out of plane	FM
$Co_3(HAT)_2$	2.555	S=1 or S=3/2	0.04 Out of plane	FM
$Ni_3(HAT)_2$ Freestanding	1.073	S=1/2	0.087 Out of plane	AFM
$Ni_3(HAT)_2$ on Au (111)	1.116	S=1/2	/	AFM

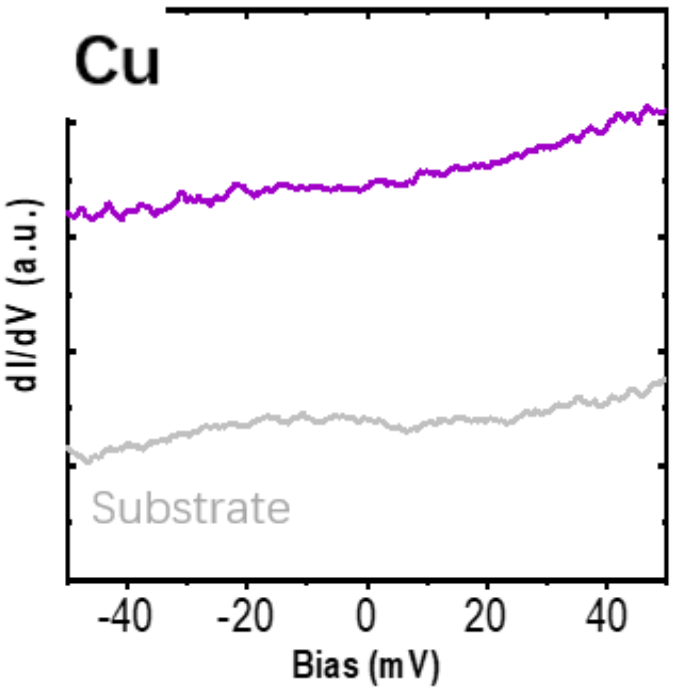
$Cu_3(HAT)_2$ and $Ni_3(HAT)_2$

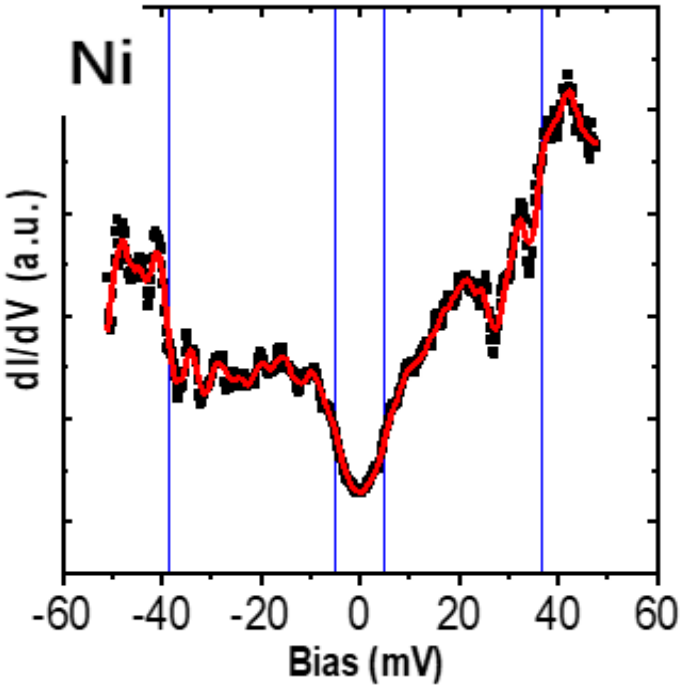
Magnetic Properties

- No excitation feature at Cu (S=0)
- Double-Step like feature at Ni sites
  Step edges: ±5 mV and ±37.8 mV
- The Double-Step like feature is a spin excitation.
- Without magnetic field, MAE is impossible to induce spin-flip excitation for S=1/2 (Ni)
- **We propose the double-step excitation of Ni is associated with Spin-Spin Coupling in the Kagome lattice.**





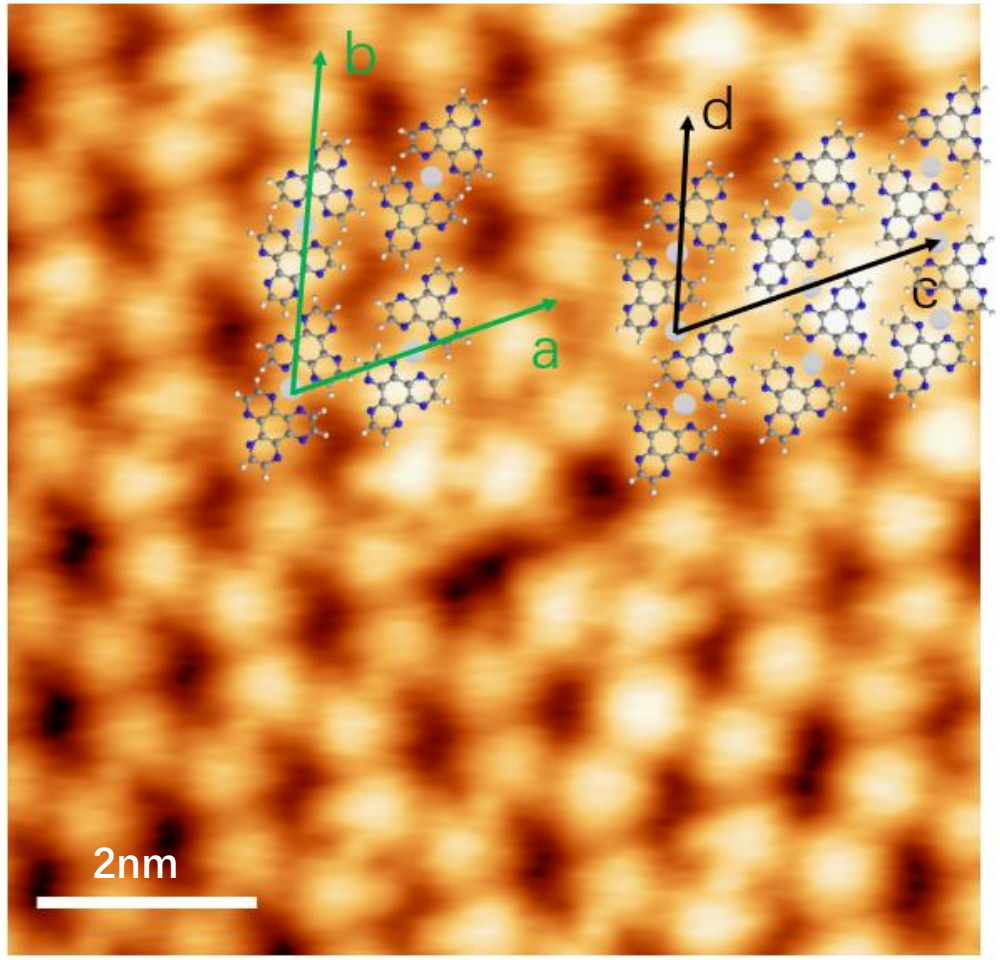


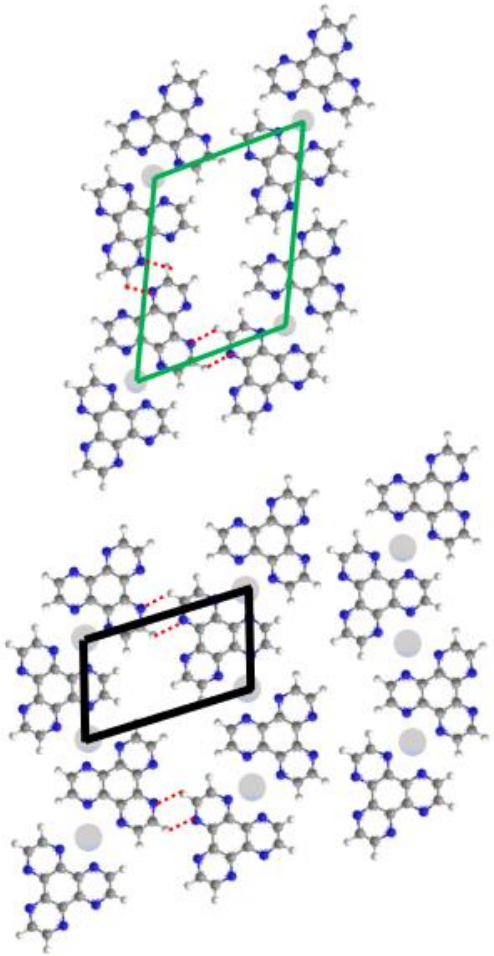


$Ni(HAT)_2$ and $Ni_3(HAT)_4$

Ni-HAT Metal organic Composite Structures

- $Ni(HAT)_2$ dimer: one Ni atom is coordinated with two HAT molecules forming a mono-Ni complex.
- $Ni_4(HAT)_3$ tetramer: three Ni atoms are coordinated with four HAT molecules forming a tri-Ni chain.





$Ni(HAT)_2$ and $Ni_4(HAT)_3$

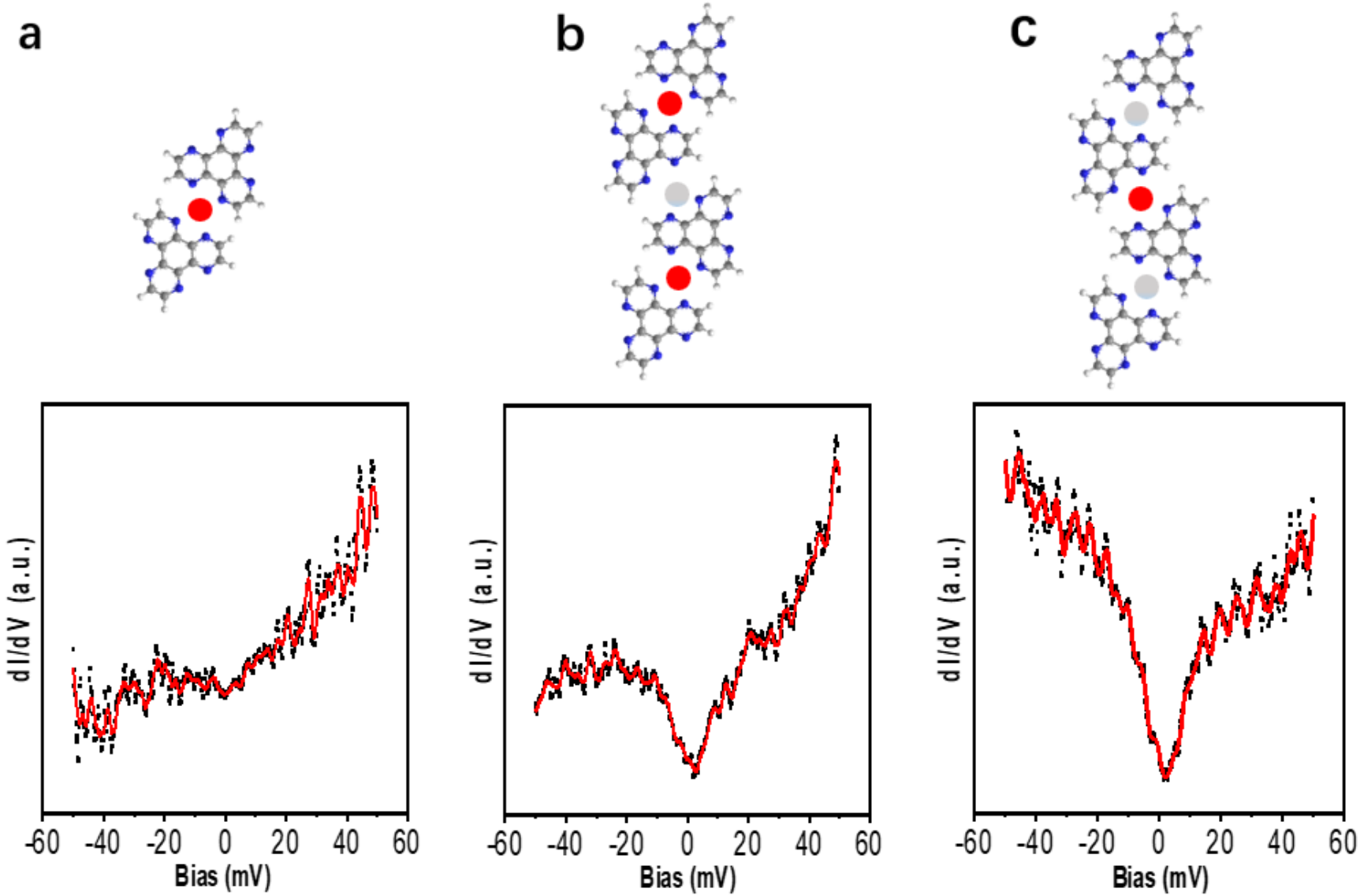
Magnetic Properties

a. Mono-Ni: No excitation feature

b. Side Ni in a tri-Ni chain: excitation at ±6.2 mV

c. Middle Ni in a tri-Ni chain: excitation at ±5.9 mV

The excitation is caused by Spin-Spin Coupling



0-neighbor Ni

1-neighbor Ni

2-neighbor Ni

$Fe_3(HAT)_2$ and $Co_3(HAT)_2$

Magnetic Properties

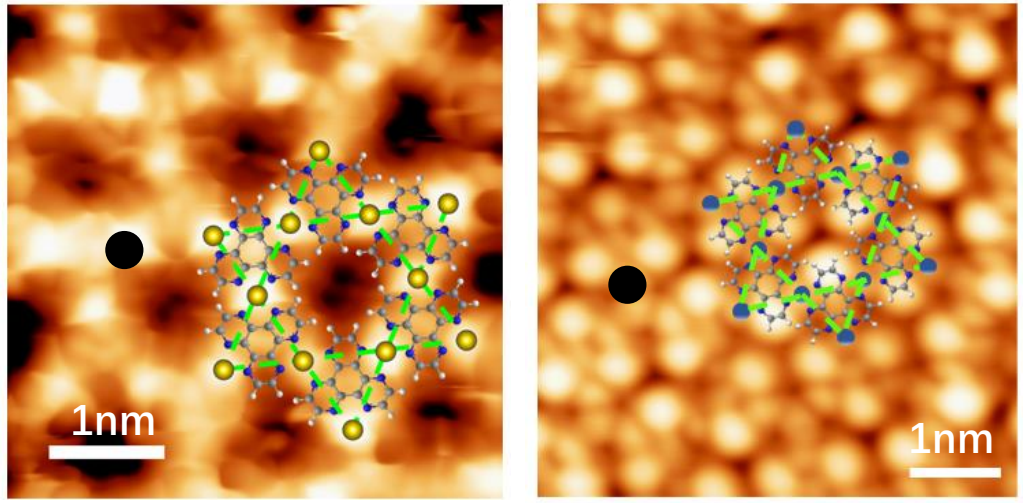
- Double-step structure symmetric about V=0
  - (1) $Fe_3(HAT)_2$
  - Step edges: ±3.6 mV & ±16 mV
  - (2) $Co_3(HAT)_2$
  - Step edges: ±3.2 mV & ±26.3 mV
- Spin Hamiltonian

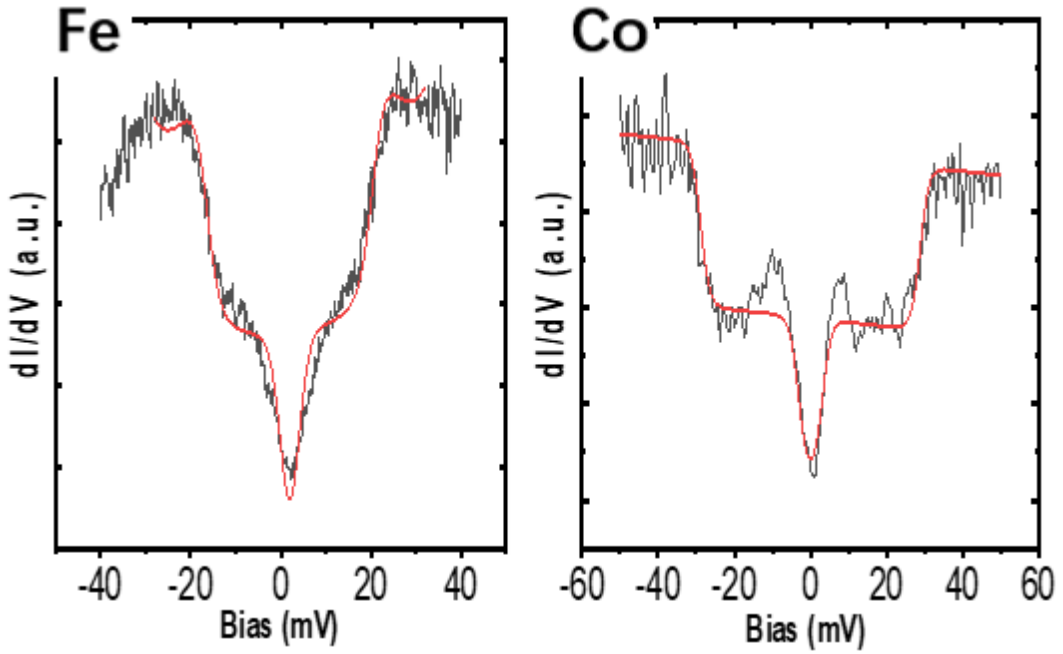
$$H_S = \sum_i H_S(i) + \sum_{i,j} J_{ij} \vec{S}(i) \cdot \vec{S}(j)$$

$$H_S = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g\mu\vec{B} \cdot \vec{S}$$

- Assume no spin-spin coupling (J=0)

  Fitting of the experimental data shows a large magnetic anisotropy:
  - (1) $Fe_3(HAT)_2$ D=-7.09meV
  - (2) $Co_3(HAT)_2$ D=-27.3 meV
- DFT calculated MAE:
  - (1) $Fe_3(HAT)_2$ D=0.06 meV out of plane
  - (2) $Co_3(HAT)_2$ D=0.04 meV out of plane





The spin excitation is originated from spin-spin coupling instead of MAE

$M_3(HAT)_2$ (M=Fe, Co, Ni, Cu) MOFs

Conclusion

- We synthesized 2D-cMOFs $M_3(HAT)_2$ (M= Fe, Co, Ni, Cu) on the Au (111) and Ag (111) surface. These MOFs are all constructed by a honeycomb lattice of HAT molecules and a Kagome lattice of M atoms.

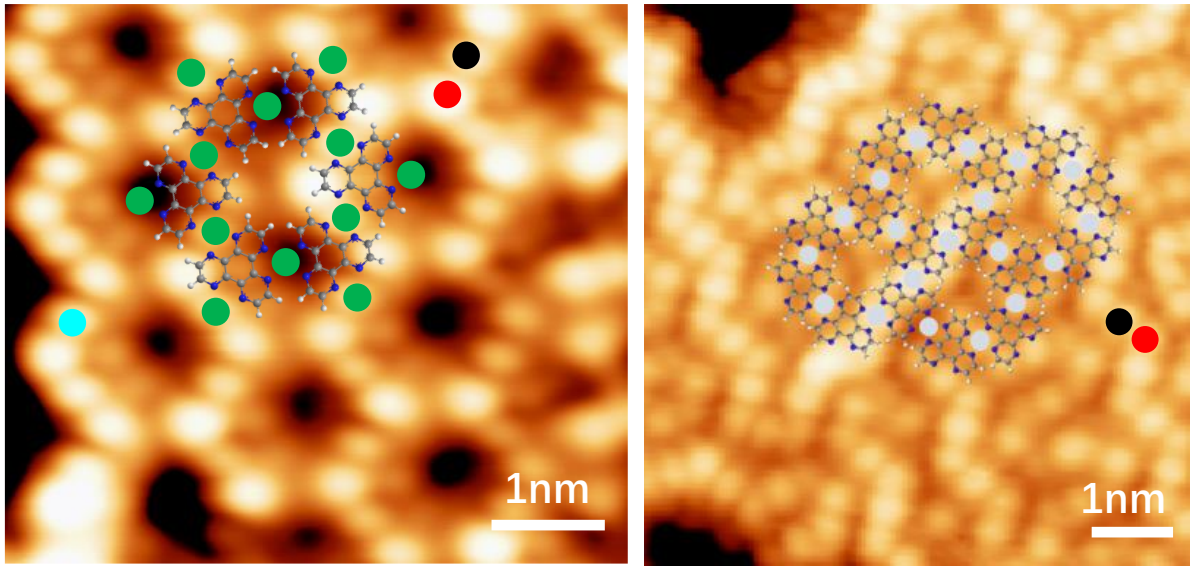
- Spin excitation is observed in all three (Fe, Co, Ni) MOFs.

- $Ni_3(HAT)_2$ is an antiferromagnetic coupled S=1/2 system, and the double-step spin excitation originates from **spin-spin coupling**. It is a candidate for realizing **QSL states.**

- $Fe_3(HAT)_2$ (S=2) and $Co_3(HAT)_2$ (S=1 or S=3/2) are ferromagnetic coupled system. The mismatch between fitted MAE and DFT calculated MAE suggest that the spin excitations originate from **spin-spin coupling** instead of MAE.

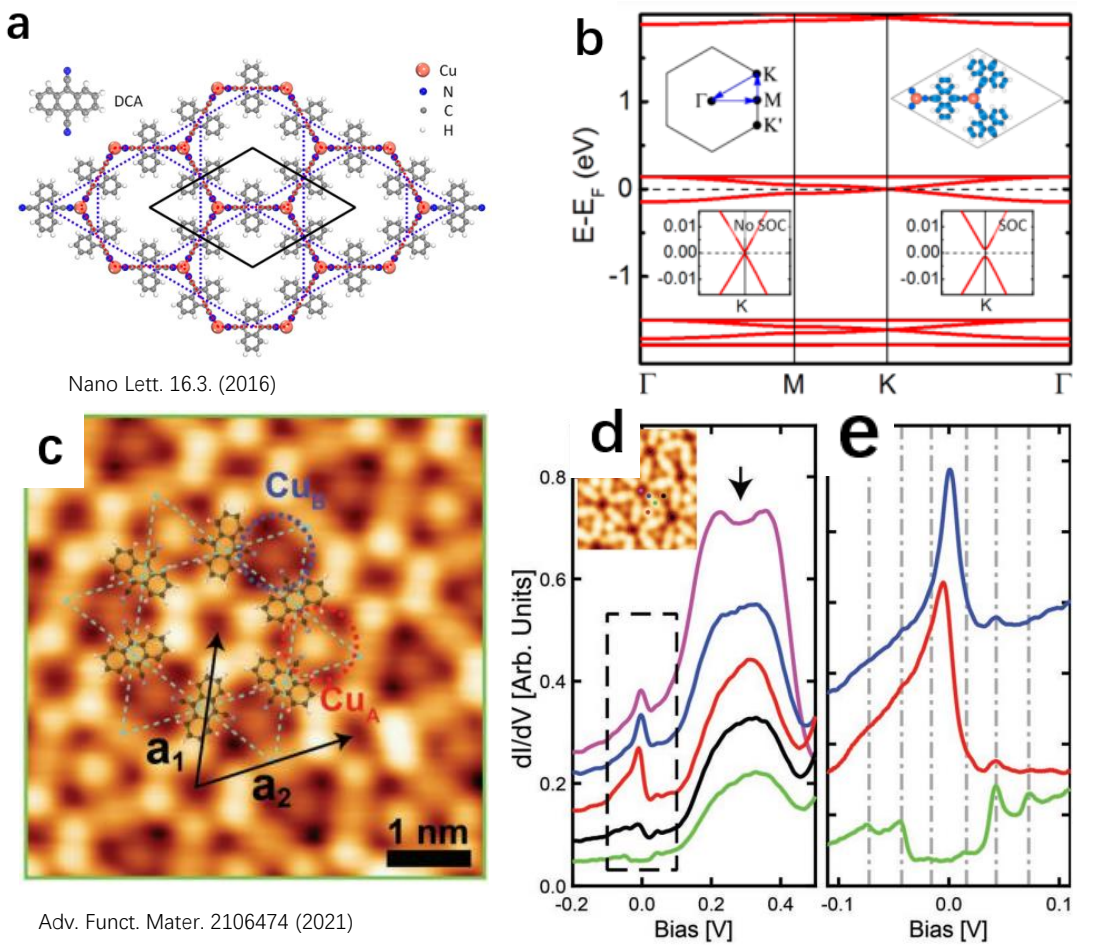
Part 4 Narrow Bandgap 2D-cMOFs $M_3(HAT)_2$ (M= Ni, Co) Grown on HOPG substrate

- HAT molecular phase
- Sample Preparation
- $\mathbf{Ni_3(HAT)_2}$ models, DFT optimized structures, electronic properties on Au (111) and HOPG
- $\mathbf{Co_3(HAT)_2}$ models, DFT optimized structures, electronic properties on Au (111) and HOPG



Metal Substrate Versus Inert Substrate

Introduction

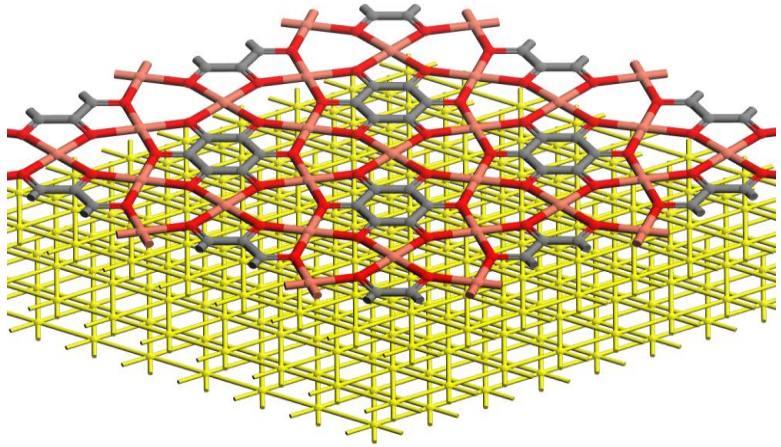


Nano Lett. 16.3. (2016)

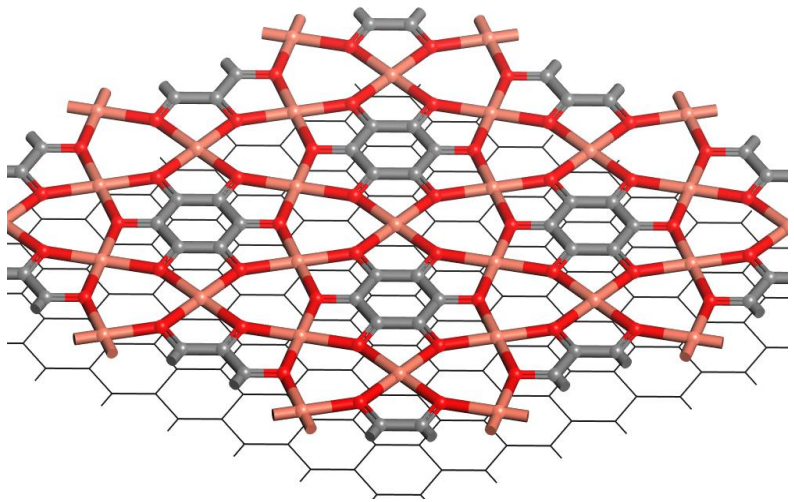
Adv. Funct. Mater. 2106474 (2021)

- Theoretical prediction of many quantum phases
- Intrinsic organic topological insulators
- Screened by Ag (111)

- Metal substrate (most) Intrinsic properties are screened



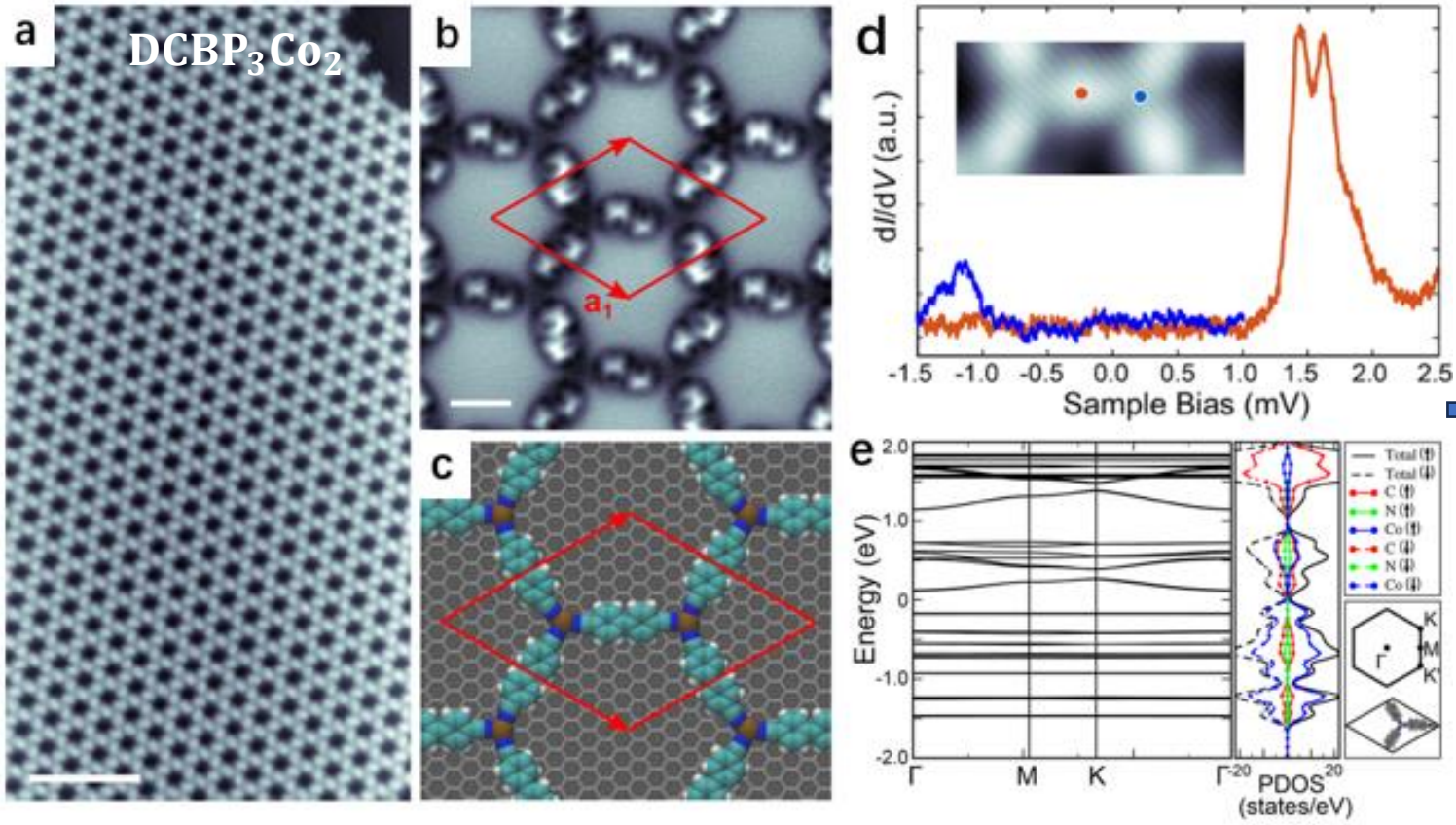
- Inert (VdW) substrate



Intrinsic properties are preserved

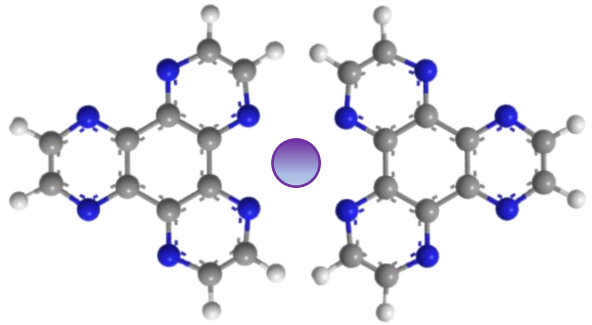
MOFs on Van der Waals Substrate

Introduction



Nano Lett. 18, 5596 (2018)

- DFT well described occupied states
- Underestimated gap
- Other DOS are missing



- Ligand

Unidentate ligand---bidentate ligand
M(CN)3---MN4
Conjugated ligand

- Substrate

G/Ir (111)---bulk HOPG

- STS and DFT

HAT/HOPG Molecular Phase

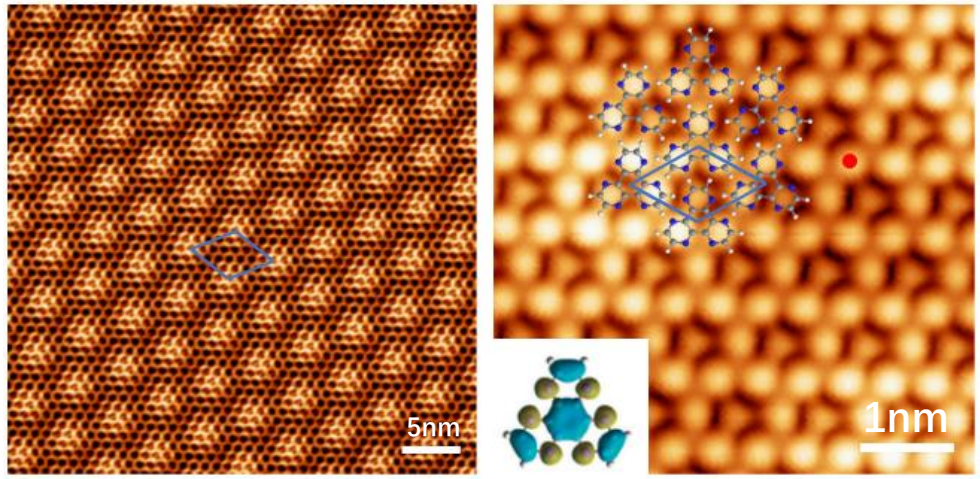
Structure and Electronic Properties

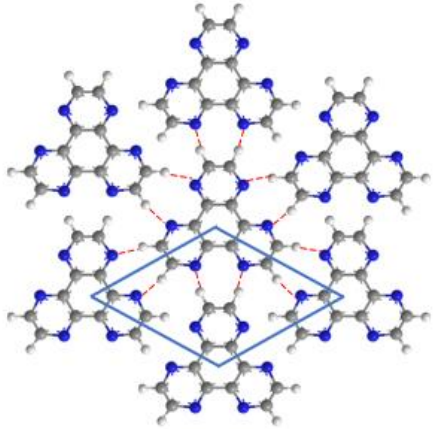
- 1,4,5,8,9,12-Hexaazatriphenylene (HAT)
  Evaporation Temperature: 460K
- HOPG substrate at RT

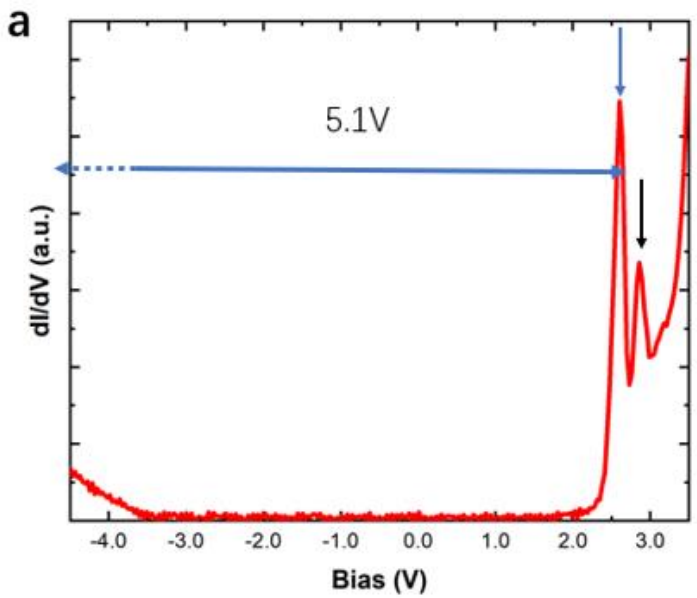
- Moire period: 4.4nm
- Lattice constant: 0.8nm
- Two peaks: 2.62V, 2.82V
- Gap larger than 5.1V experimentally

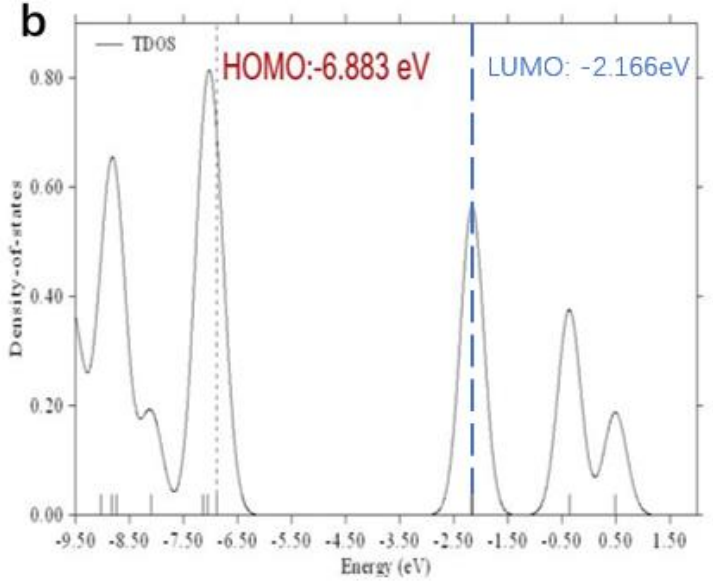
- 2.62V LUMO-LUMO+2
- 2.82V Vibronic peak
- HOMO not detected
- Theoretical Gap: 4.72eV

- Weak interaction between HAT and HOPG





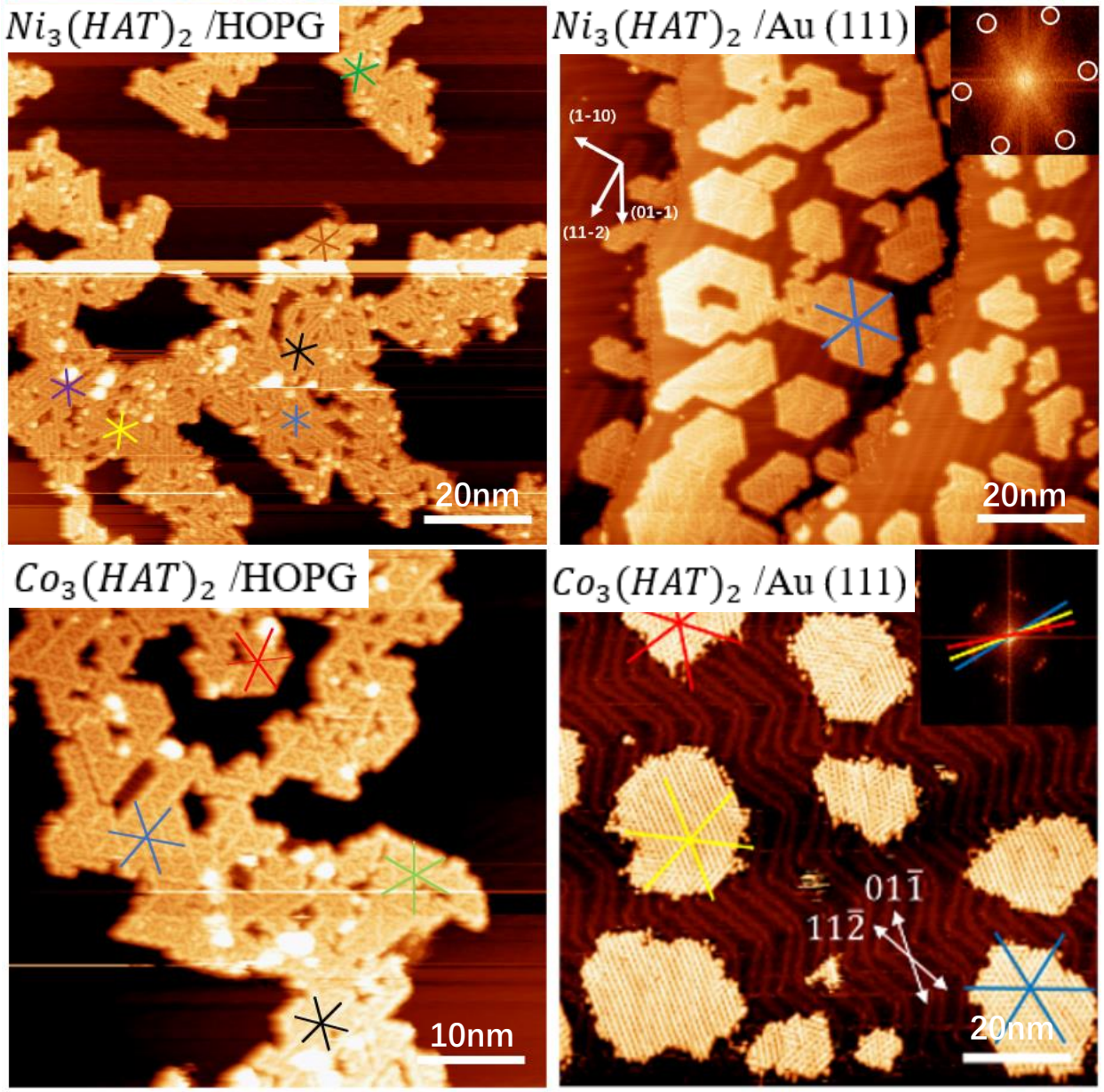




$M_3(HAT)_2$ (M= Ni, Co) MOFs/HOPG and Au (111)

Sample Preparation

- Dose Co, Ni on HAT islands
- Annealing at 430K
- Lattice Orientations
  - (1) $Ni_3(HAT)_2$
    - Six on HOPG
    - One on Au (111)
  - (2) $Co_3(HAT)_2$
    - Four on HOPG
    - Three on Au (111)
- Weak interaction
- Single Domain Size
  - (1) $Ni_3(HAT)_2$
    - 10nm*10nm on HOPG
    - 30nm*30nm on Au (111)
  - (2) $Co_3(HAT)_2$
    - 8nm*8nm on HOPG
    - 18nm*18nm on Au(111)

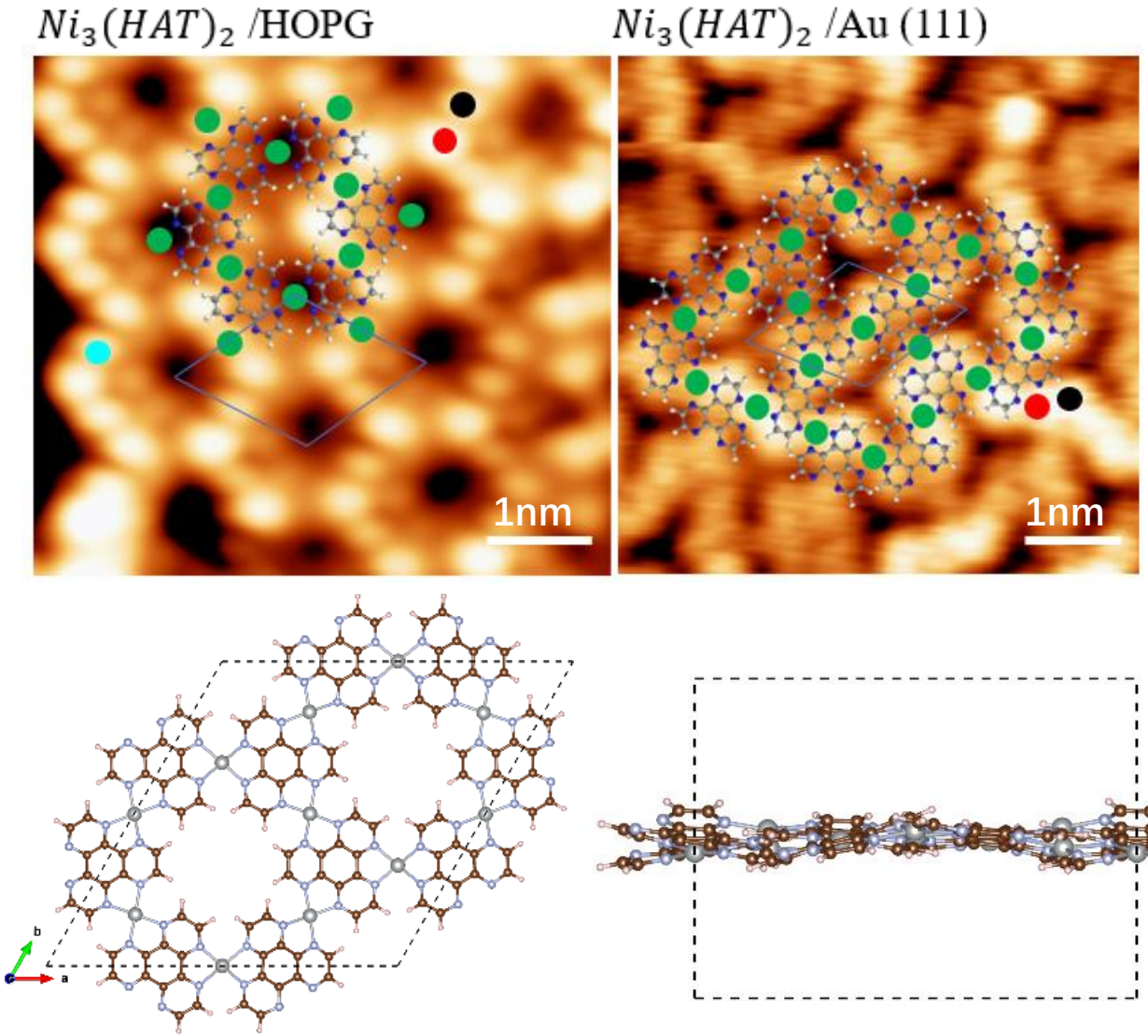


$Ni_3(HAT)_2$ /HOPG and Au (111)

Models and DFT Optimized Structures

- Lattice constant:
  (1) $Ni_3(HAT)_2$ /HOPG 1.36nm
  (2) $Ni_3(HAT)_2$ /Au (111) 1.37nm
- Models: Kagome lattice of Ni
  Honeycomb lattice of HAT
- Bulked: HAT molecular backbones tilt up to 23°
- Non-periodic feature on Au (111):
  Tilting directions and angles of HAT molecules are more random and influenced by underlying Au (111)

- More periodic feature on HOPG:
  Decouple---All the molecules are less influenced by the substrate and tend to tilt in an ordered way



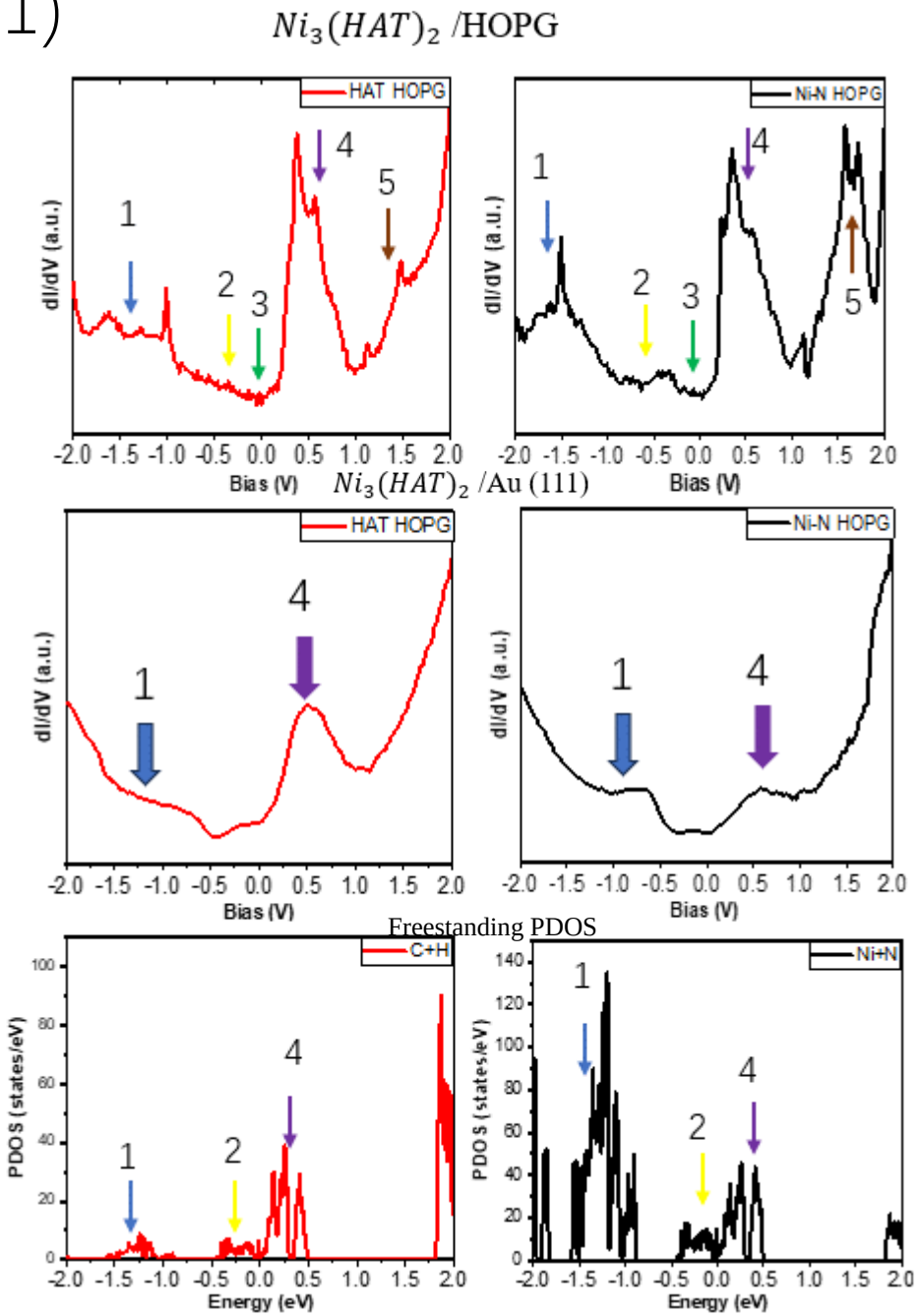
$Ni_3(HAT)_2$ /HOPG and Au (111)

Electronic Properties

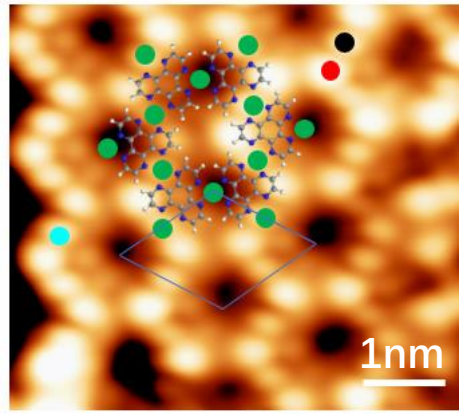
- $Ni_3(HAT)_2$ /HOPG Spectra
- $Ni_3(HAT)_2$ /Au (111) Spectra
- DFT calculated Freestanding PDOS
- Gap like feature, sharp peaks/dips

- Peak 4 vs Broad peak 4: same states
  Narrower, Stronger, Component Peak

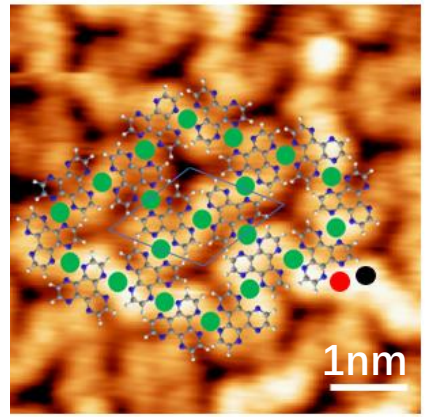
Effectively Decoupled, the intrinsic properties are largely preserved on HOPG, strongly screened on Au (111)



$Ni_3(HAT)_2$ /HOPG



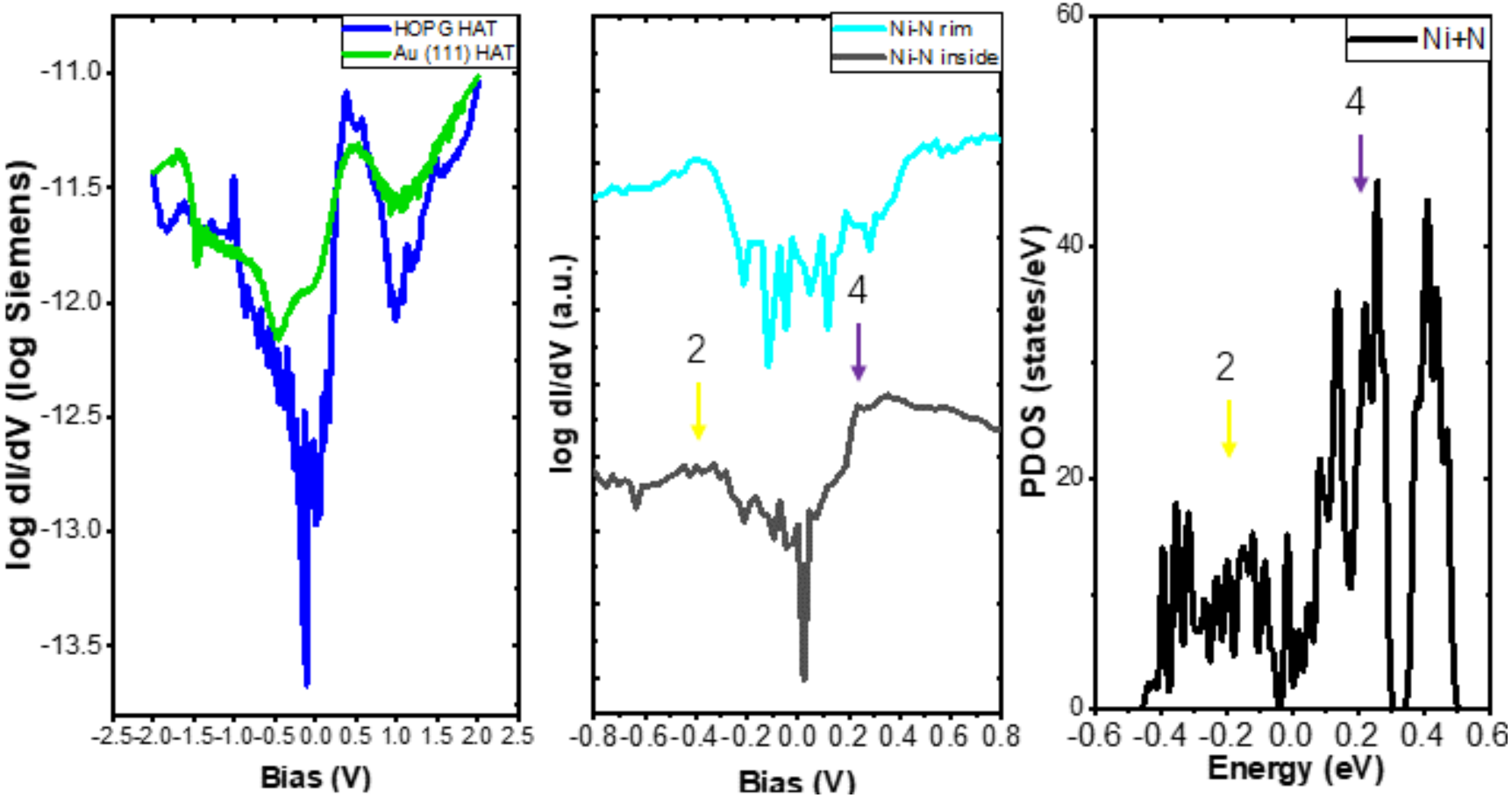
$Ni_3(HAT)_2$ /Au (111)

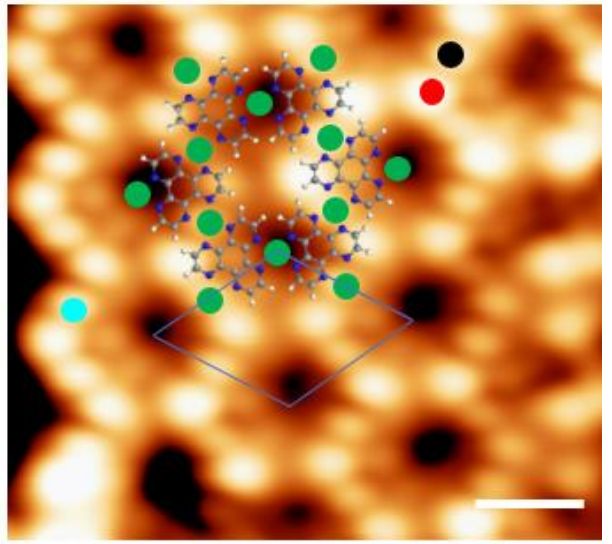


- Red: HAT corners
- Black: Ni-N

$Ni_3(HAT)_2$ /HOPG and Au (111)

Electronic Properties---Bandgap



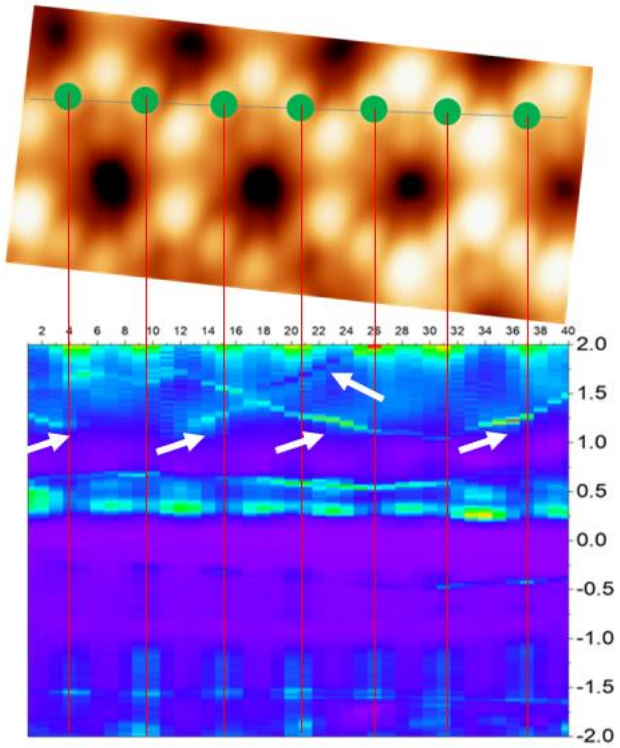


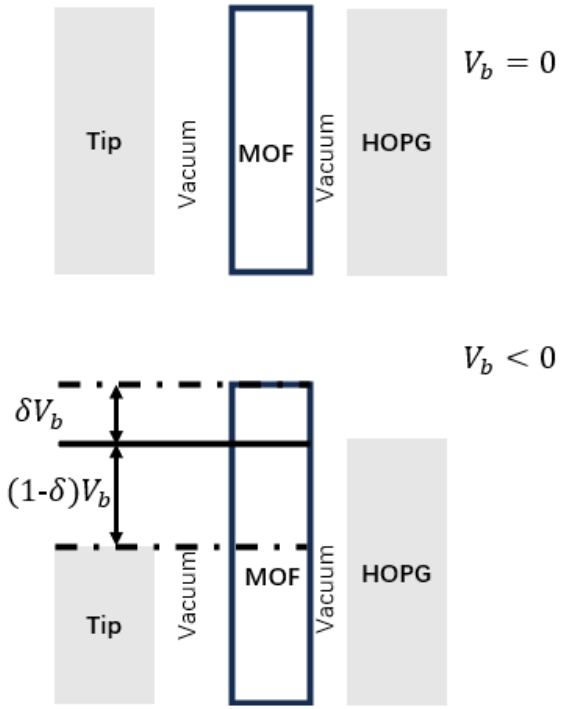
- Edge Ni: Cyan
- Interior Ni: Black

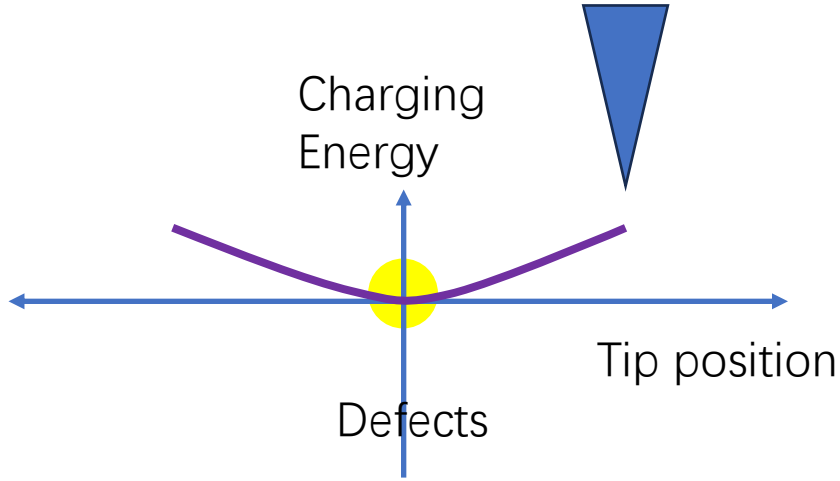
- logarithmic-scale dI/dV spectra: nearly zero density of states on HOPG
- Interior Ni-N site: 0.16V gap
- Edge Ni-N site: 0.4V gap
- DFT calculations show no gap---size of domain is too small
- Narrow bandgap 2D MOF

$Ni_3(HAT)_2$ /HOPG and Au (111)

Charging States







- White arrows in -1.1V to -1.9V: Charging effects
- Double barrier junction: Tip-MOF and MOF-HOPG junctions
- Energy shifting defects act like charge traps

Weak interaction

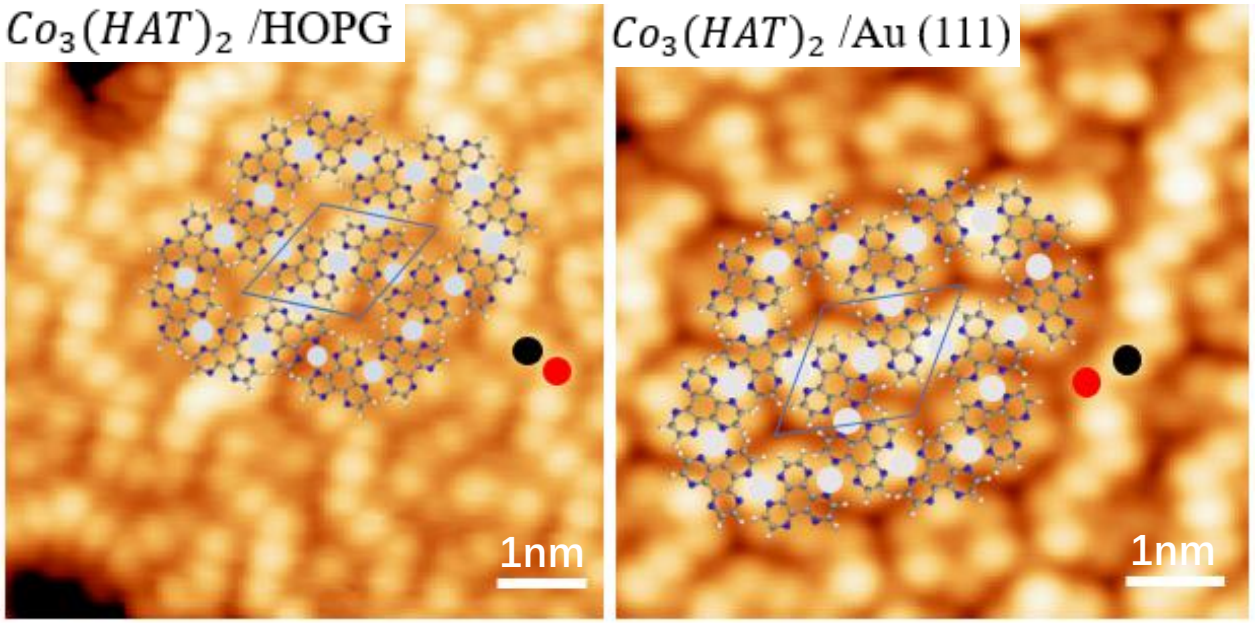
$Co_3(HAT)_2$ /HOPG and Au (111)

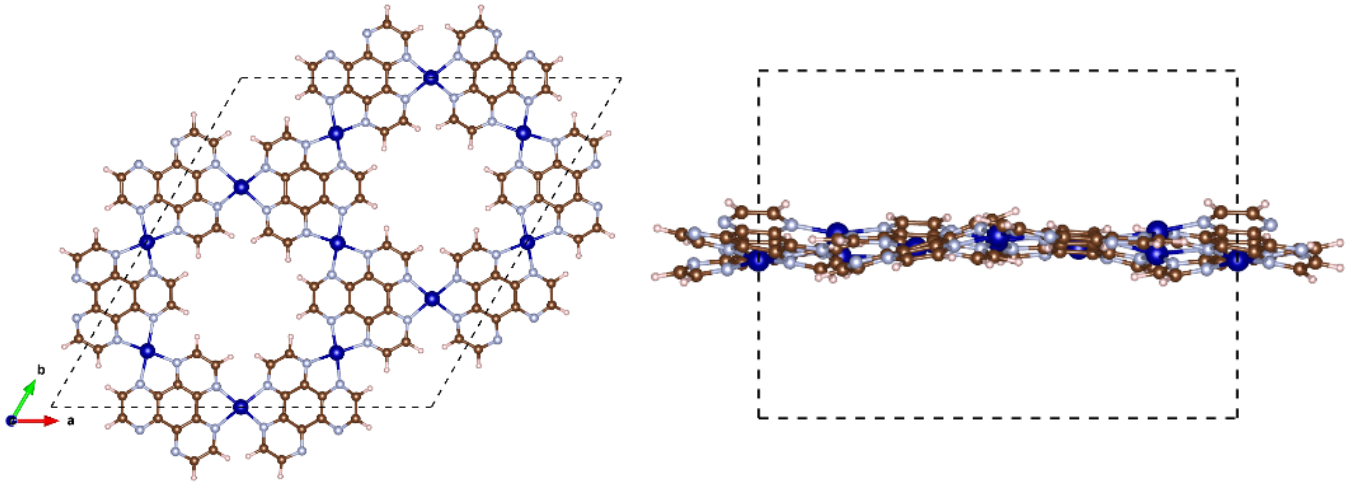
Models and DFT Optimized Structures

- Lattice constant:
  (1) $Co_3(HAT)_2$ /HOPG 1.35nm
  (2) $Co_3(HAT)_2$ /Au (111) 1.38nm

- Models: Kagome lattice of Co
  Honeycomb lattice of HAT

- Bulked: HAT molecular backbones tilt up to 23°





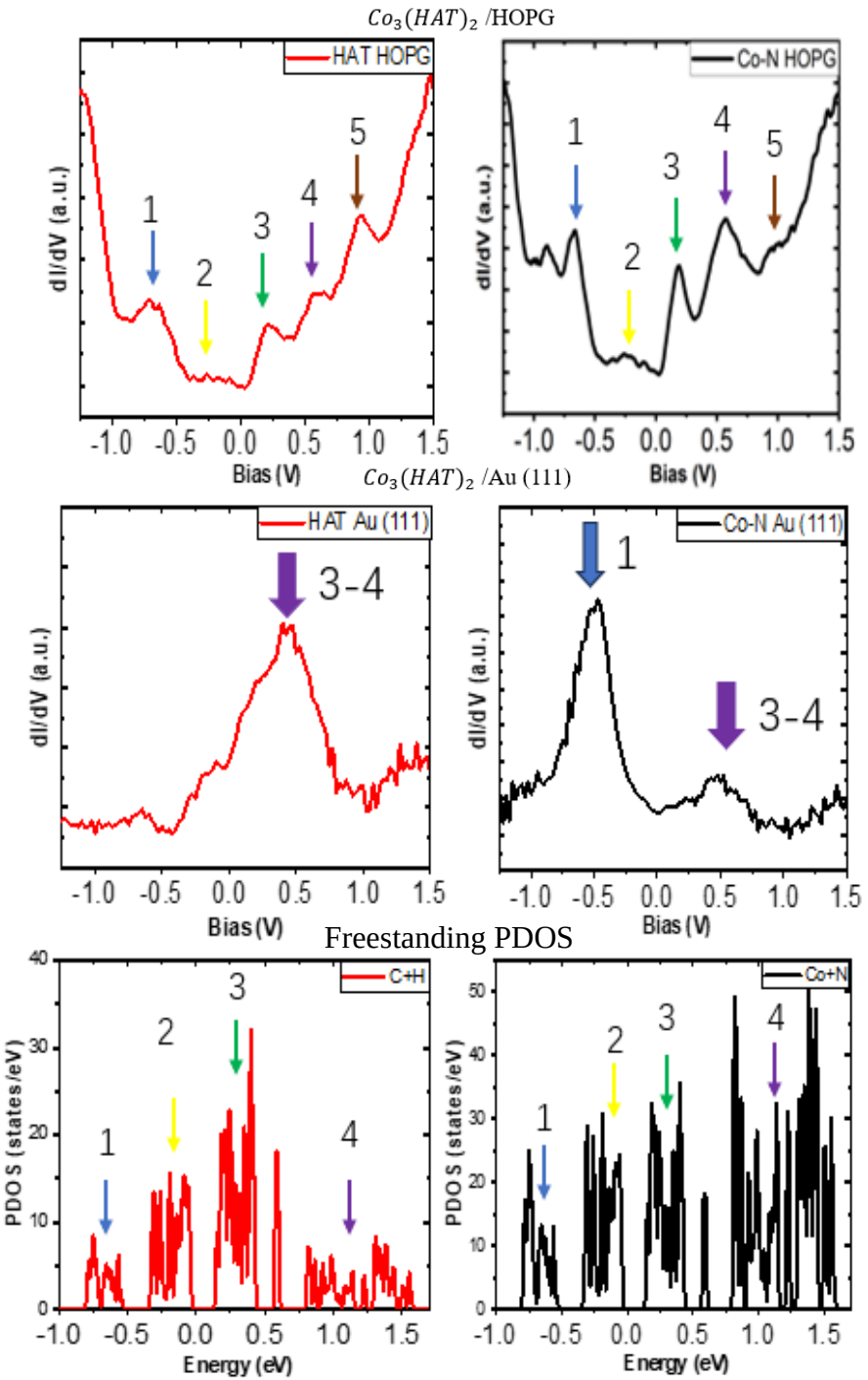
$Co_3(HAT)_2$ /HOPG and Au (111)

Electronic properties

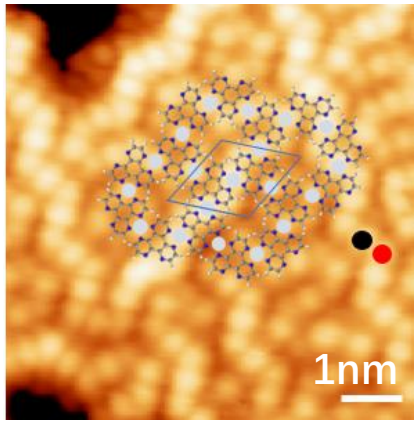
- $Co_3(HAT)_2$ /HOPG Spectra
- $Co_3(HAT)_2$ /Au (111) Spectra
- DFT calculated Freestanding PDOS

- Peak 3 and peak 4 well resolved on HOPG
  Peak 3-4 on Au (111)
- Peak 1 at HAT sites is missing on Au (111)

Effectively Decoupled, the intrinsic properties are largely preserved on HOPG, strongly screened on Au (111)

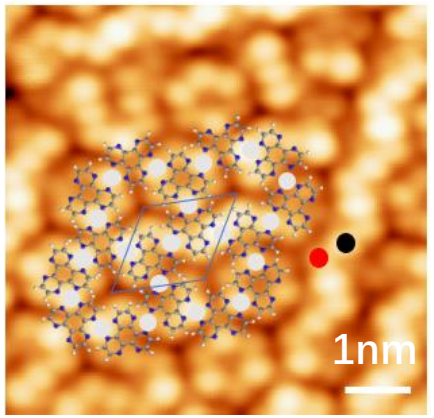


$Co_3(HAT)_2$ /HOPG



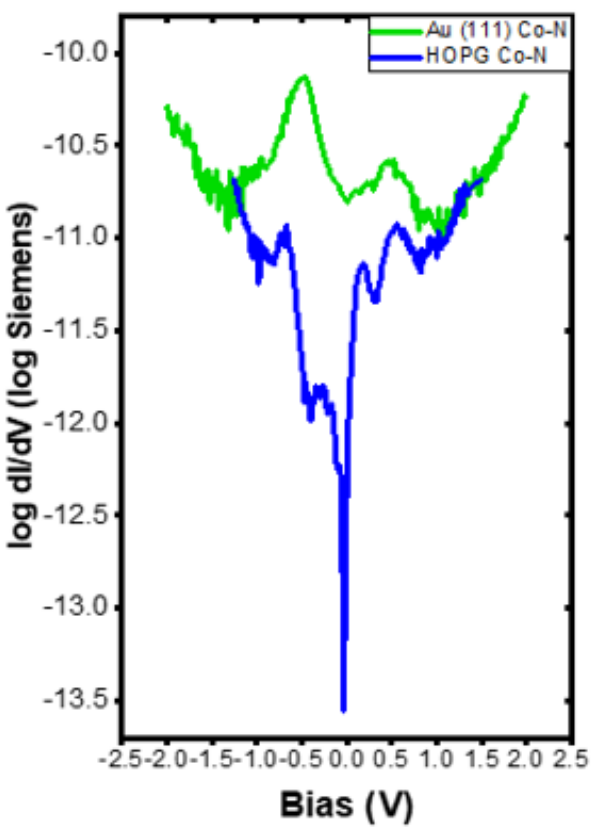
- Red: HAT corner
- Black: Ni-N

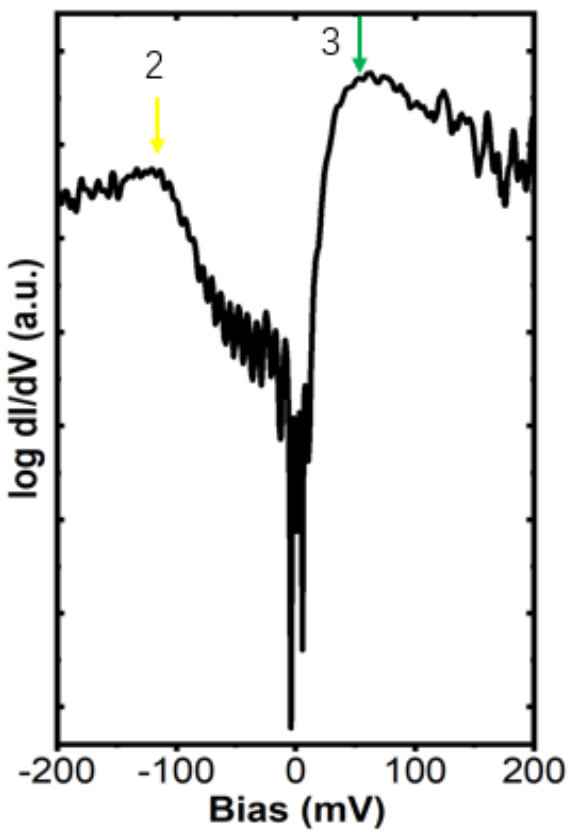
$Co_3(HAT)_2$ /Au (111)

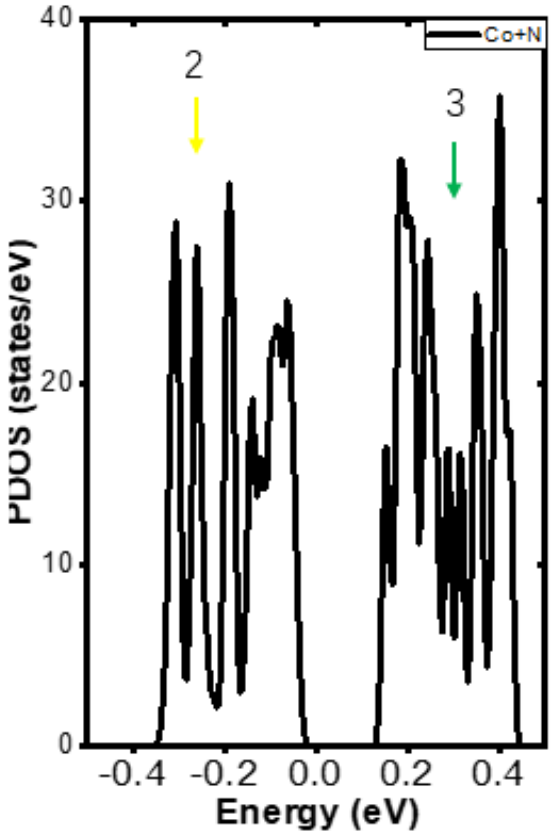


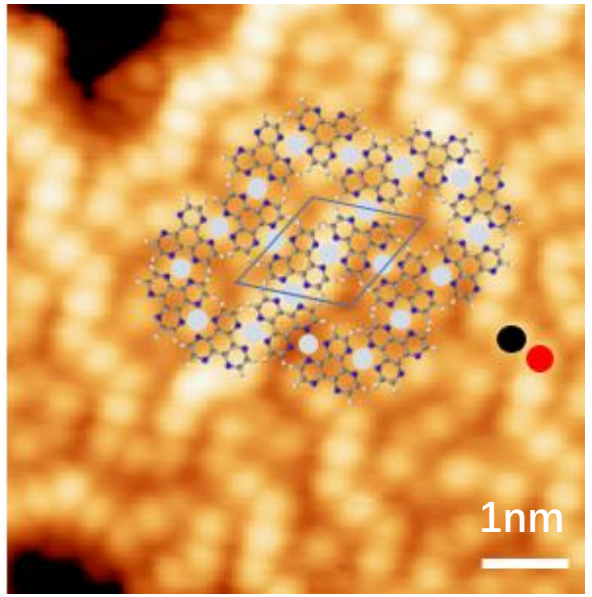
$Co_3(HAT)_2$ /HOPG and Au (111)

Electronic Properties---Bandgap









- Black: Co-N

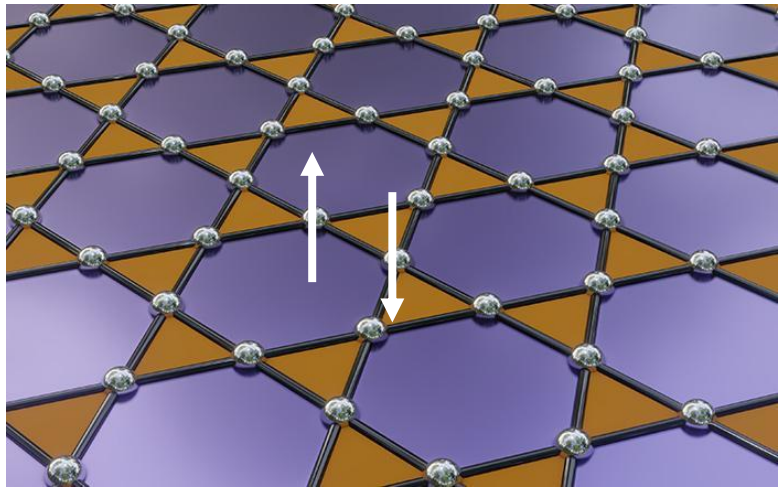
- logarithmic-scale dI/dV spectra: nearly zero density of states on HOPG
- Bandgap: 14mV
- DFT calculations show a 0.14V bandgap---the adsorption on HOPG enhances the delocalization of electrons in the MOF, leading to a narrower bandgap
- Narrow bandgap 2D MOF

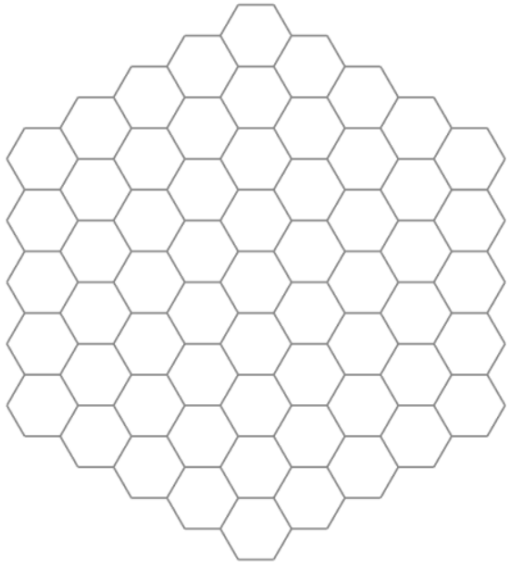
$M_3(HAT)_2$ (M=Ni, Co) MOFs/HOPG and Au (111)

Conclusion

- successfully synthesized $Ni_3(HAT)_2$ and $Co_3(HAT)_2$ MOFs on both Au (111) and HOPG substrates
- Their structures are nearly identical, indicating the synthesis of $M_3(HAT)_2$ does not rely on substrate
- The interaction between the MOFs with HOPG is much weaker than with Au (111), resulting in effective electronic decoupling of the MOFs from HOPG
- STS data confirm that $Ni_3(HAT)_2$ is a narrow bandgap MOF with bandgap below 0.2V, and $Co_3(HAT)_2$ inherently possess an extremely narrow bandgap below 15meV

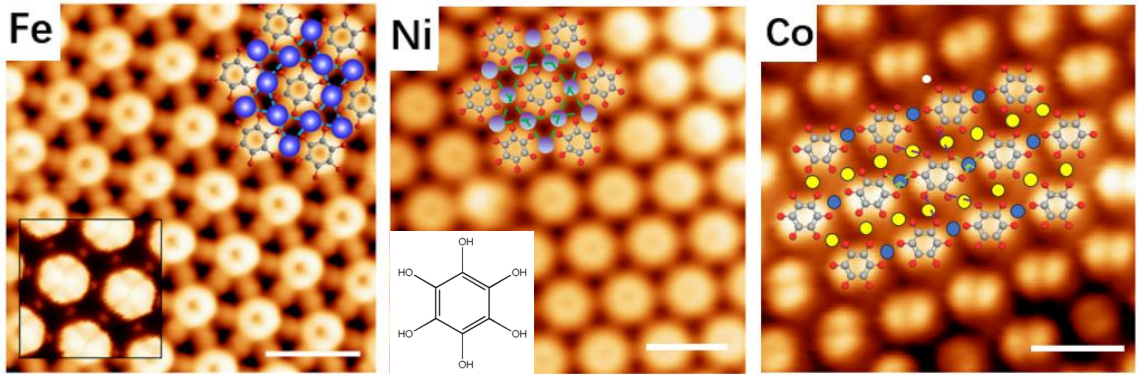
Part 5 Summary and perspectives

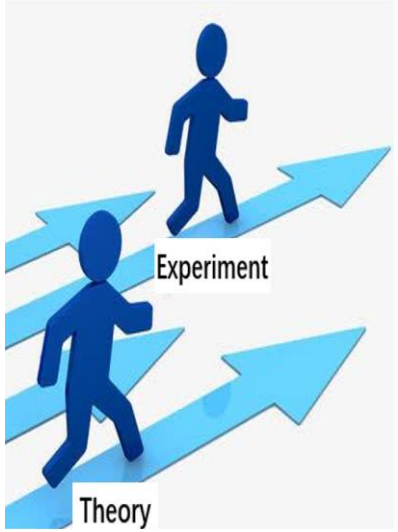


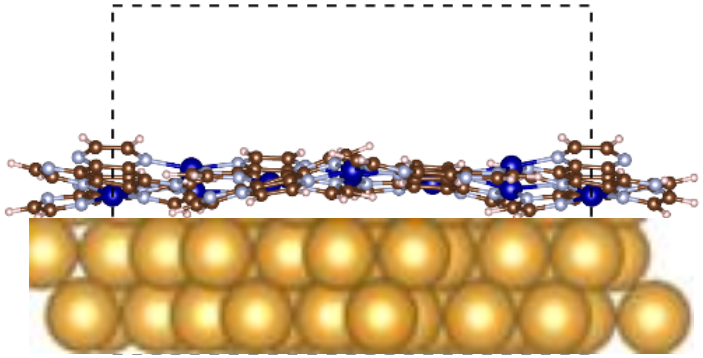


Summary

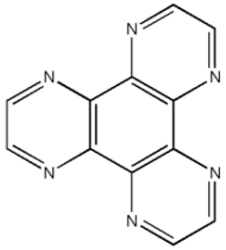
Three Projects

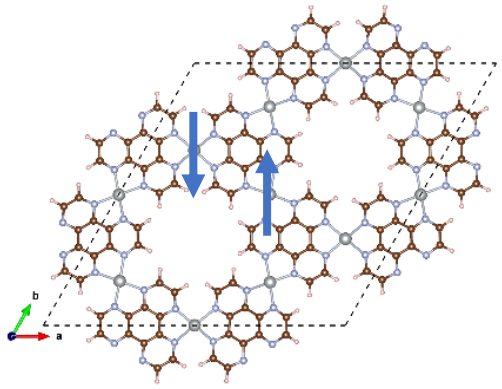


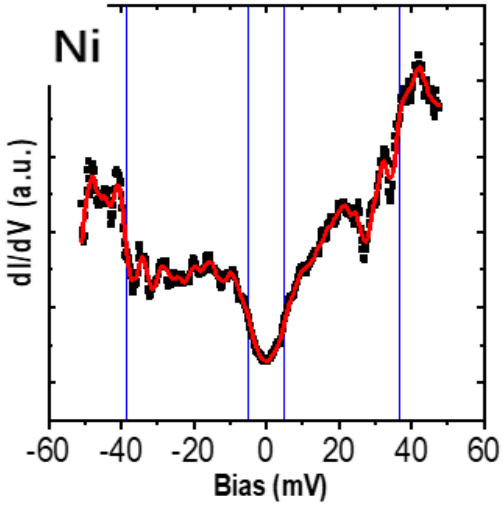




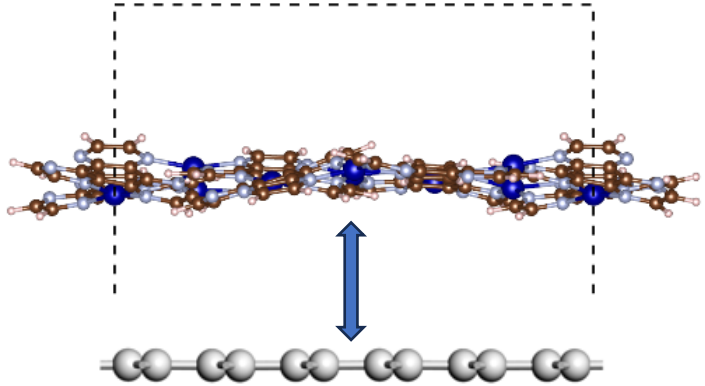
- BHO + Ni, Co/ Au(111) MOFs







- HAT + Fe ,Co, Ni, Cu/ metal MOFs



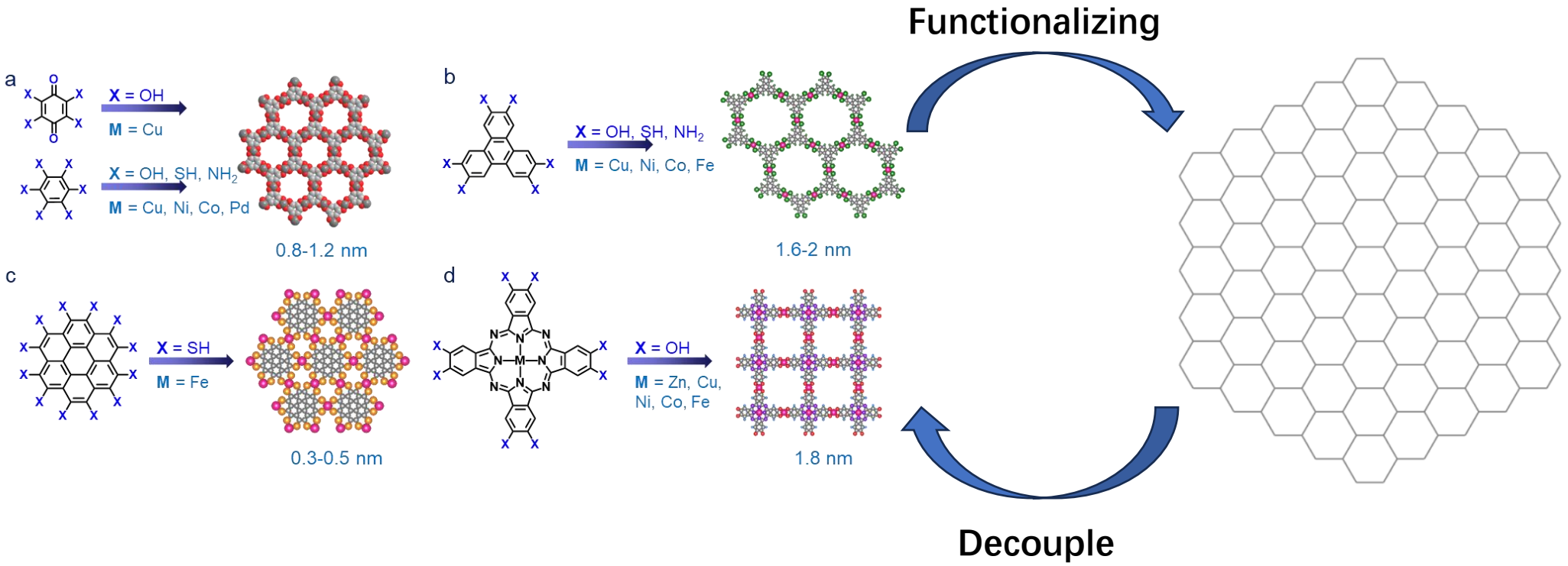
- HAT + Ni, Co / HOPG MOFs

Perspectives

2D-cMOFs On metal Substrate

- **STS with external magnetic field---**magnetic ground states and spin-changing transitions of the collective spins
- **XAS and XMCD-**--spin and orbital moment, spin state, magnetic ordering, magnetic anisotropy
- **ESR STM**---collective magnetic states and their energy levels

2D-cMOFs On Graphene Substrate



Acknowledgements

Supervisor：

- Prof. Nian Lin

Thesis Examination Committee:

- Prof. Beifang Chen (*Chairman*)
- Prof. Wei Ji
- Prof. Jianwei Sun
- Prof. Iam Keong Sou
- Prof. Qin Xu
- Prof. Nian Lin (*Supervisor*)

Collaborators:

- Prof. Li Huang (DFT)
- Prof. Peinian Liu (Molecule synthesis)

Colleagues:

- Dr. Bowen Xia
- Dr. En Li
- Dr. Muqing Hua
- Dr. Xiaobo Wang
- Dr. Yifan Gao
- Dr. Ziang Gao
- Mr. Chengkun Lyu
- Mr. Chengyi Chen
- Mr. Henan Chen
- Mr. Xin Liu