Investigating Electronic and Magnetic Properties of Metal Atoms Coordinated in Metal-Organic Structures

Muqing HUA

Supervisor: Prof. Nian LIN

Department of Physics
The Hong Kong University of Science and Technology

Content

1. Introduction
2. Characterization of the electrostatic potential of Cu atoms embeded in metal-organic nanoporous networks
3. Collective Spin Manipulation in Antiferroelastic Spin-Crossover Metallo-Supramolecular Chains
4. Design and Characterization of an Antiferromagnetic Kagome Lattice in a Two-Dimensional Metal-Organic Framework
5. Characterization of spin excitation in a Two-Dimensional Metal-Organic Network
6. Summary and perspectives

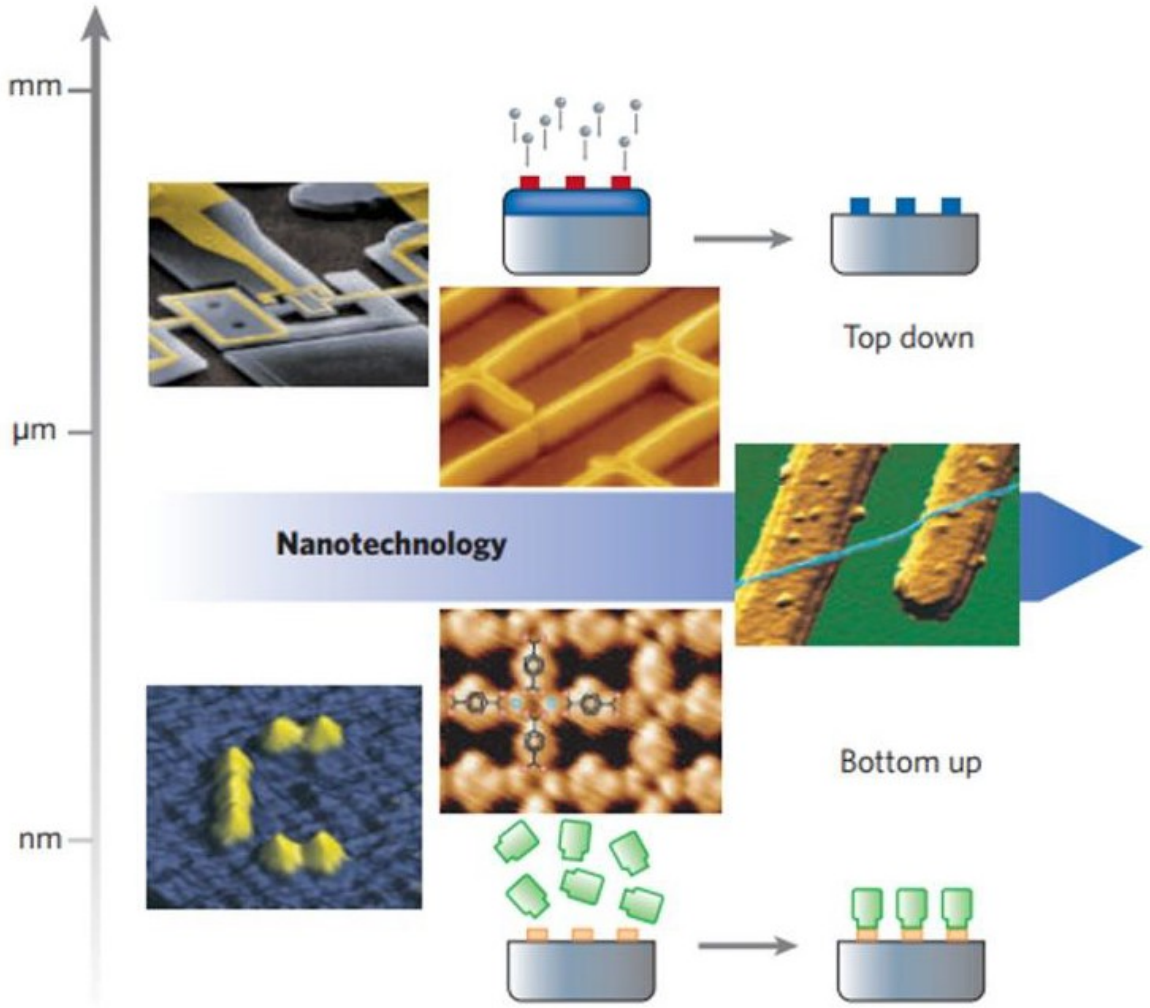
Part 1 Introduction

- Metal-organic frameworks (MOFs)
- General set-up of STM

1. Introduction

Top-down & botton-up strategies

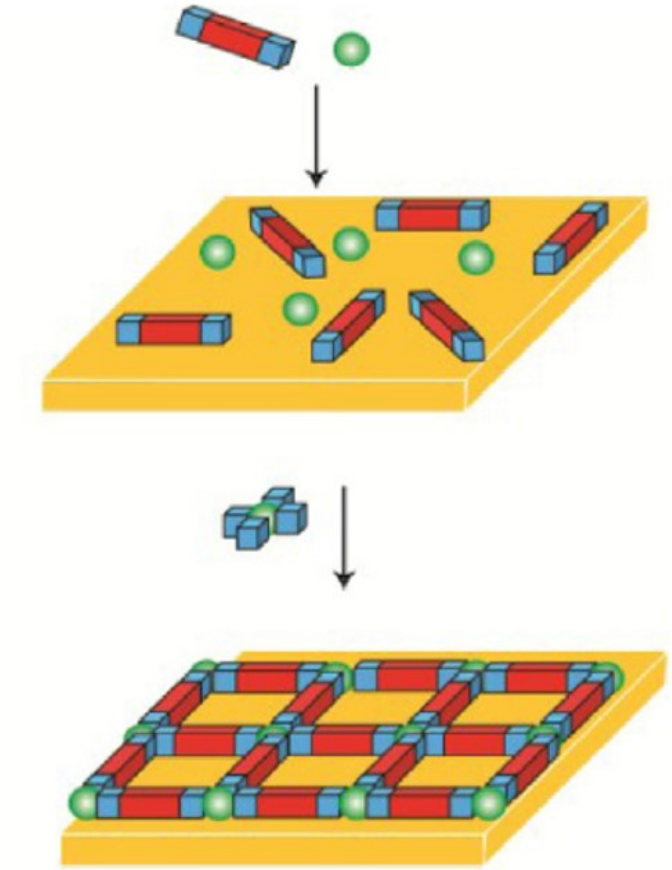
- Top-down and botton-up strategies in nanoscience and nanotechnology
- Top-down techniques have approached ~ 10 nm scales
- Self-assembly is one of the typical bottom-up techniques



J. V. Barth, G. Costantini, K. J. N. Kern, and t. a. c. o. r. f. N. journals, 67 (2010).

1. Introduction

Building On-surface Metal-organic frameworks (MOFs)



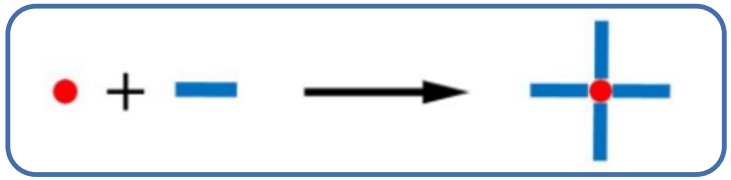
- Molecular building blocks + Metal centers
- Metal substrate
- Coordination motif
- Metal-organic frameworks

L. Dong, Z. A. Gao, and N. J. P. i. S. S. Lin, 91, 101 (2016).

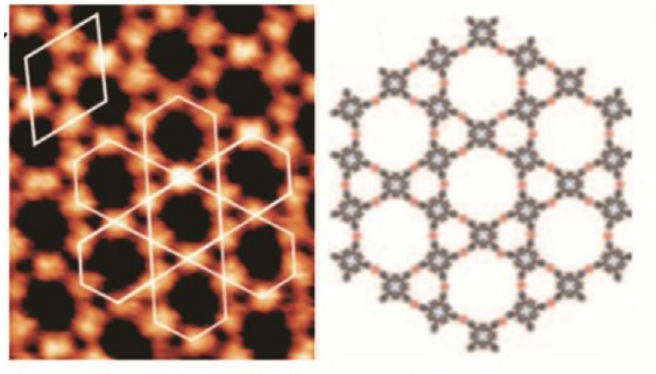
1. Introduction

2D metal-organic frameworks structures

- Component recognition
- Design structures

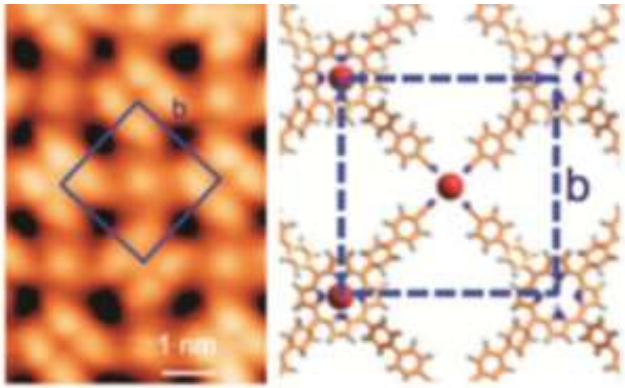


Kagome lattices



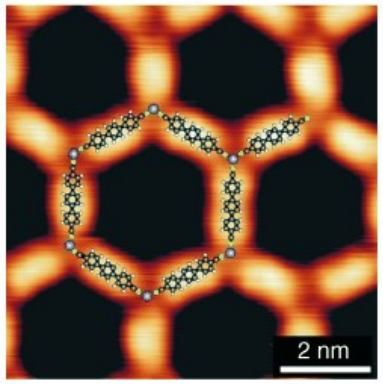
Z. Shi, N. Lin, J. Am. Chem. Soc. 131 (2009) 5376–5377.

Square lattices



J.I. Urgel, et al, J. Am. Chem. Soc. 137 (2015) 2420–2423.

Hexagonal lattices

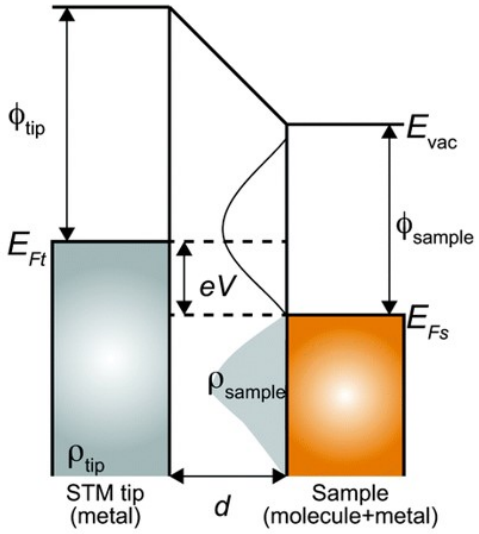


S. Stepanow, N. Lin, et al, Angew. Chem. 119 (2007) 724–727.

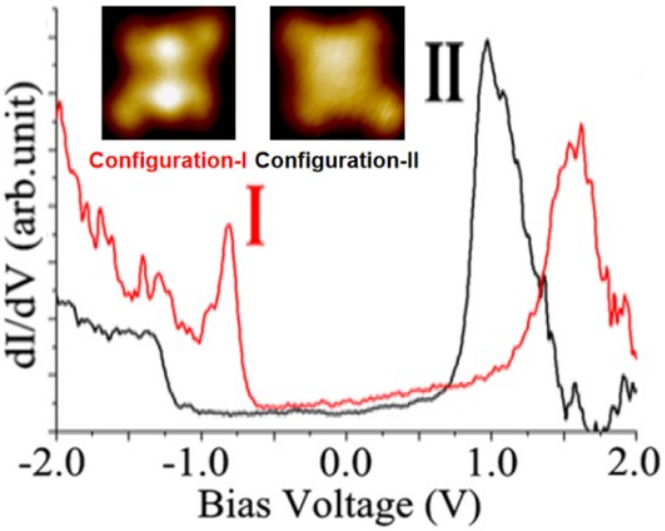
1. Introduction

Experimental techniques -- electronic properties

Electronic properties



S. Kano, T. Tada, and Y. J. C. S. R. Majima, 44, 970 (2015).



Q. Zhang et al., 8, 1241 (2017).

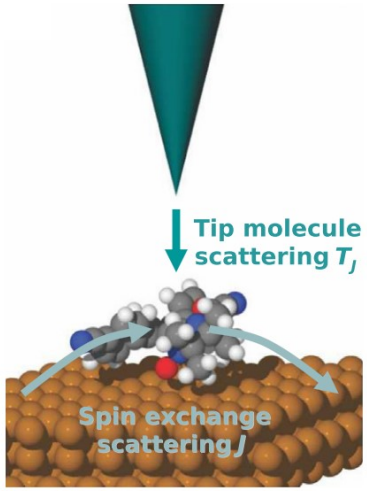
- Scanning Tunneling Spectroscopy (STS)
- Density of state (DOS)
- dI/dV spectra

- Configuration-I Peaks at -0.8 V, 1.6 V
- Configuration-II Peaks at -1.3 V, 1.0 V
- Br_2TPP molecules

1. Introduction

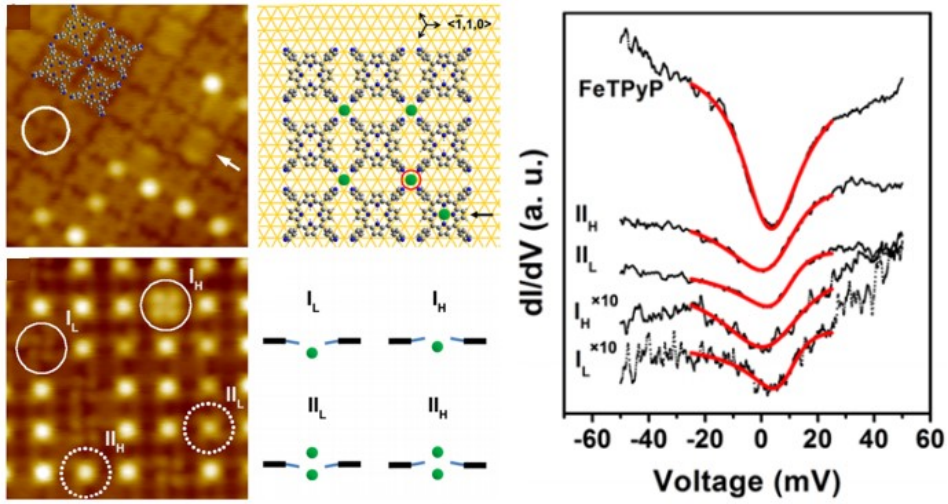
Experimental techniques -- magnetic properties

Kondo effect



M. J. P. i. s. s. Ternes, 92, 83 (2017).

- Scattering of localized spins with conduction electrons
- Kondo temperature T_K



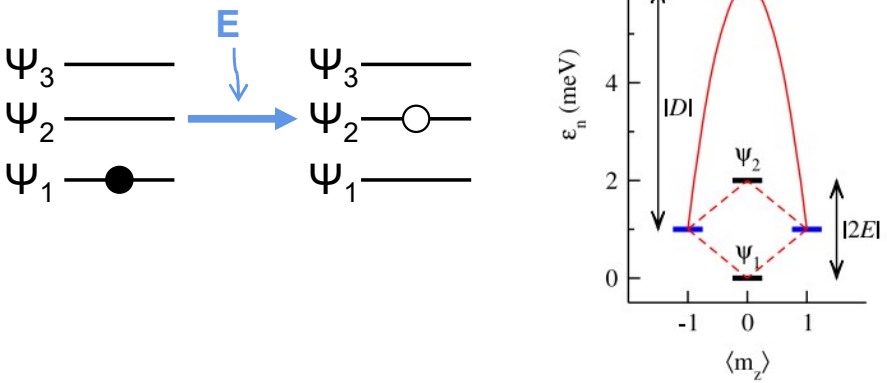
T. Lin, G. Kuang, W. Wang, and N. J. A. n. Lin, 8, 8310 (2014).

- Kondo resonance in STS spectra
- Fano function fitting
- Fe-TPyP 2D MOF

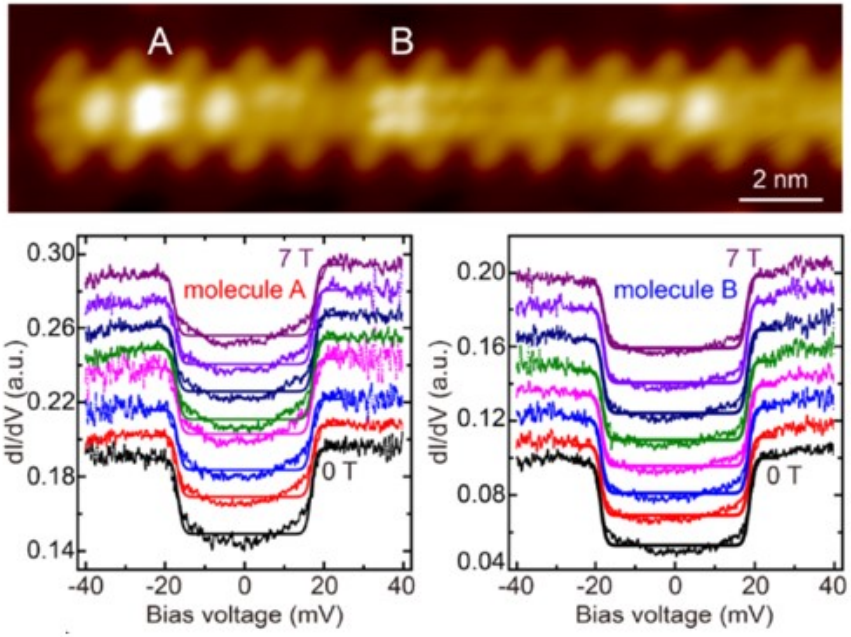
1. Introduction

Experimental techniques -- magnetic properties

Spin-flip excitation



M. J. N. J. o. P. Ternes, 17, 063016 (2015).



M. J. P. i. s. s. Ternes, 92, 83 (2017).

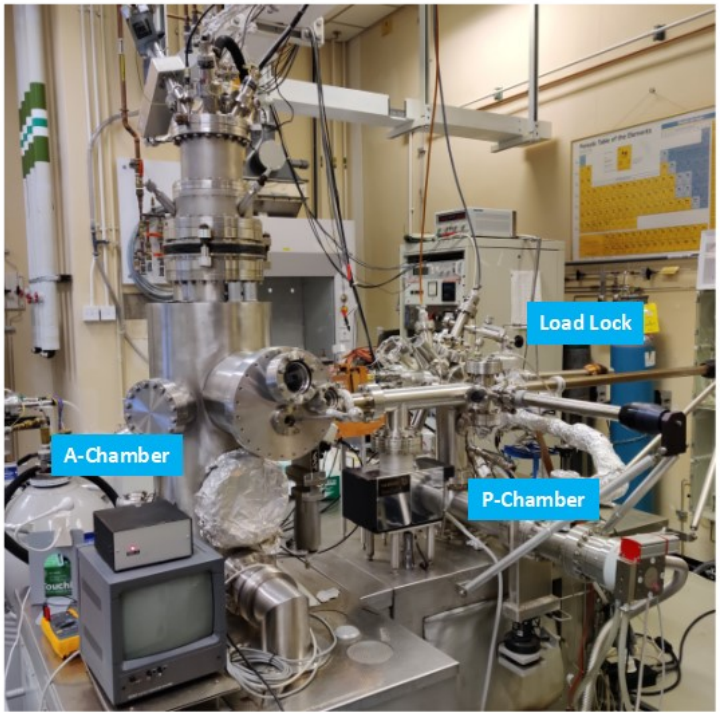
- Interaction of tunneling electrons with localized magnetic impurities (metal centers)
- Magnetic anisotropy or Spin-spin exchange coupling
- Spilt of the energy level

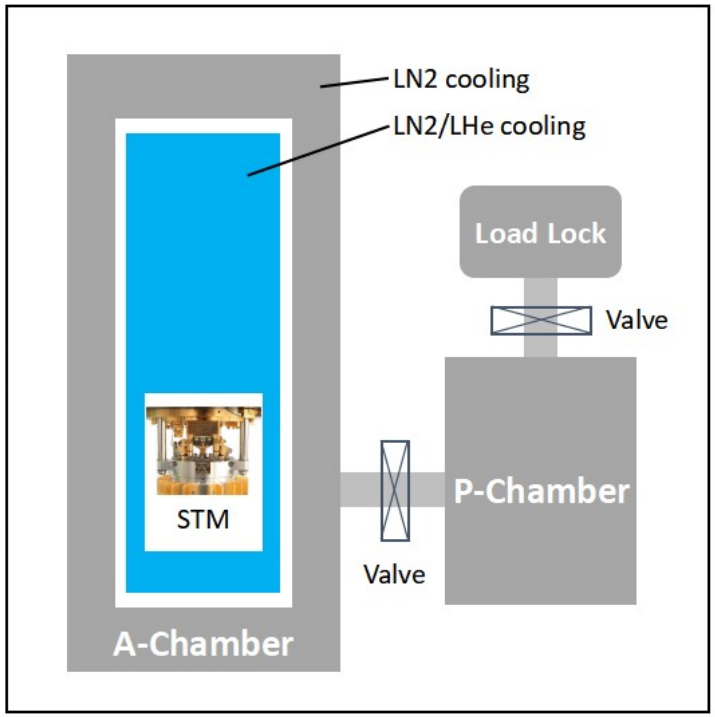
- Inelastic spin-flip excitations
- Step-like features
- Metal-organic chains

1. Introduction

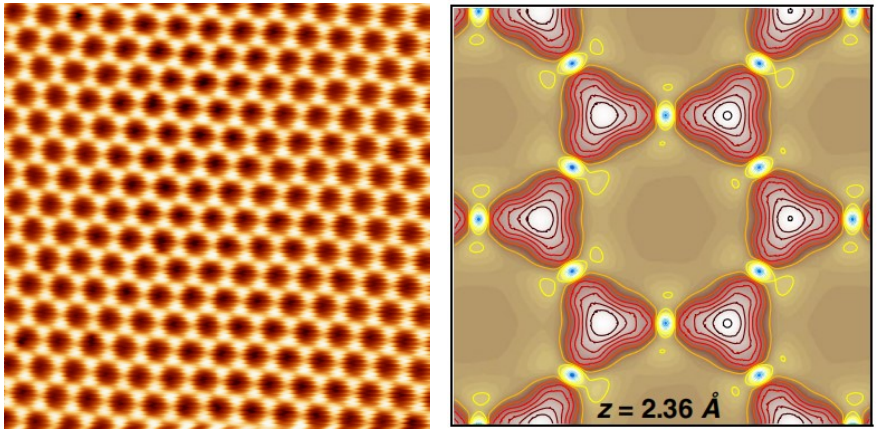
General set-up of STM

- Ultra-High Vacuum
- Low temperature
- Three chambers



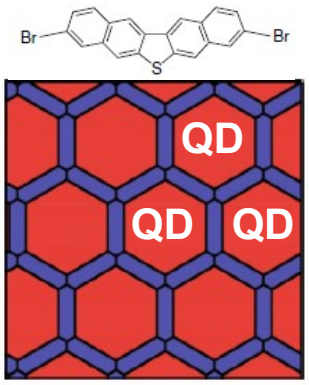


Part 2 Characterization of the electrostatic potential of Cu atoms embedded in metal-organic nanoporous networks

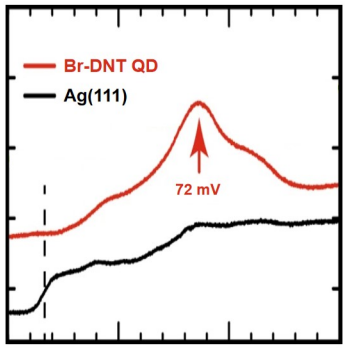


2. TPyB + Cu / Cu(111) MOFs

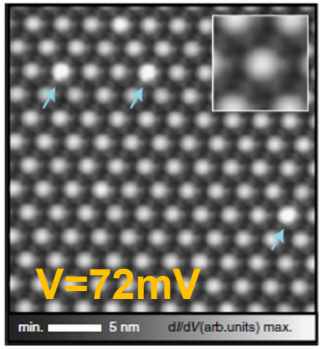
Introduction



Br-DNT
Halogen bond



STS spectra
V= 72 mV

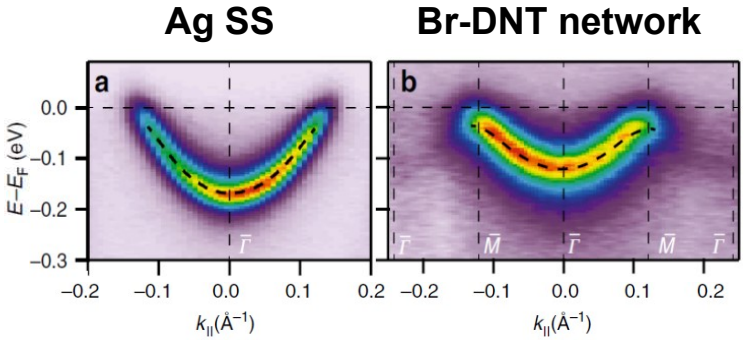


STS map
Confinement state

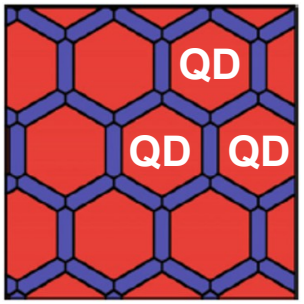
- Quantum Dot (QD)

  Confine electrons with discrete energy levels

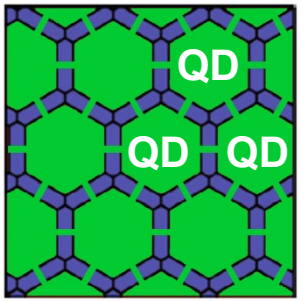
  Each pore acts as a QD



- QD weakly couped as shown by the flatten **band dispersion**



- Individual dots



- Coupling dots

I. Piquero-Zulaica et al., 8, 1 (2017).

2. TPyB + Cu / Cu(111) MOFs

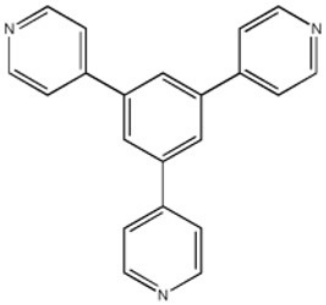
Sample preparation

- 1,3,5-tri(4-pyridyl)-benzene (TPyB)
- Cu(111) substrate

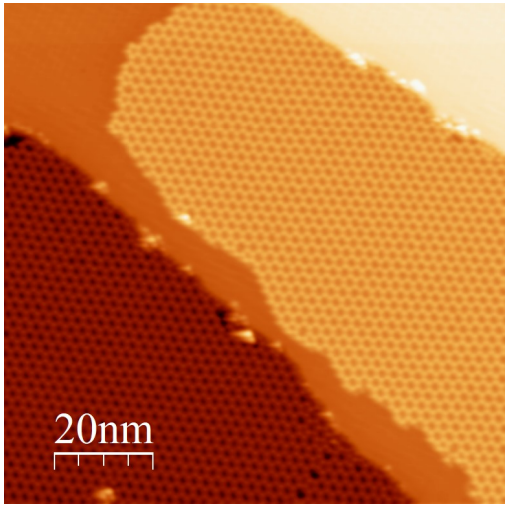
- Sample preparation
  - (1) Deposit TPyB on Cu(111) at RT
    [evaporate temperature: 480K]
  - (2) Anneal at 420K

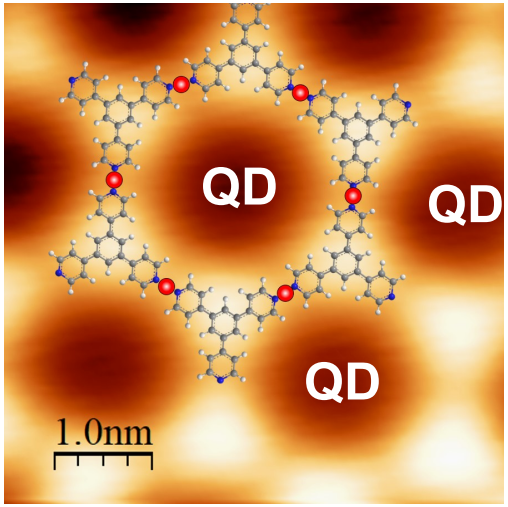
- Lattice constant: 2.65 nm

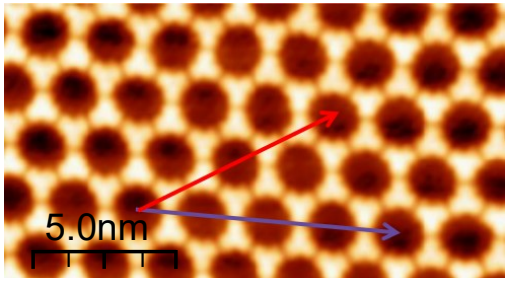
- apparent height at Cu & TPyB

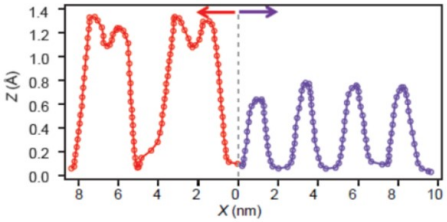


1,3,5-tri(4-pyridyl)-benzene
(TPyB)









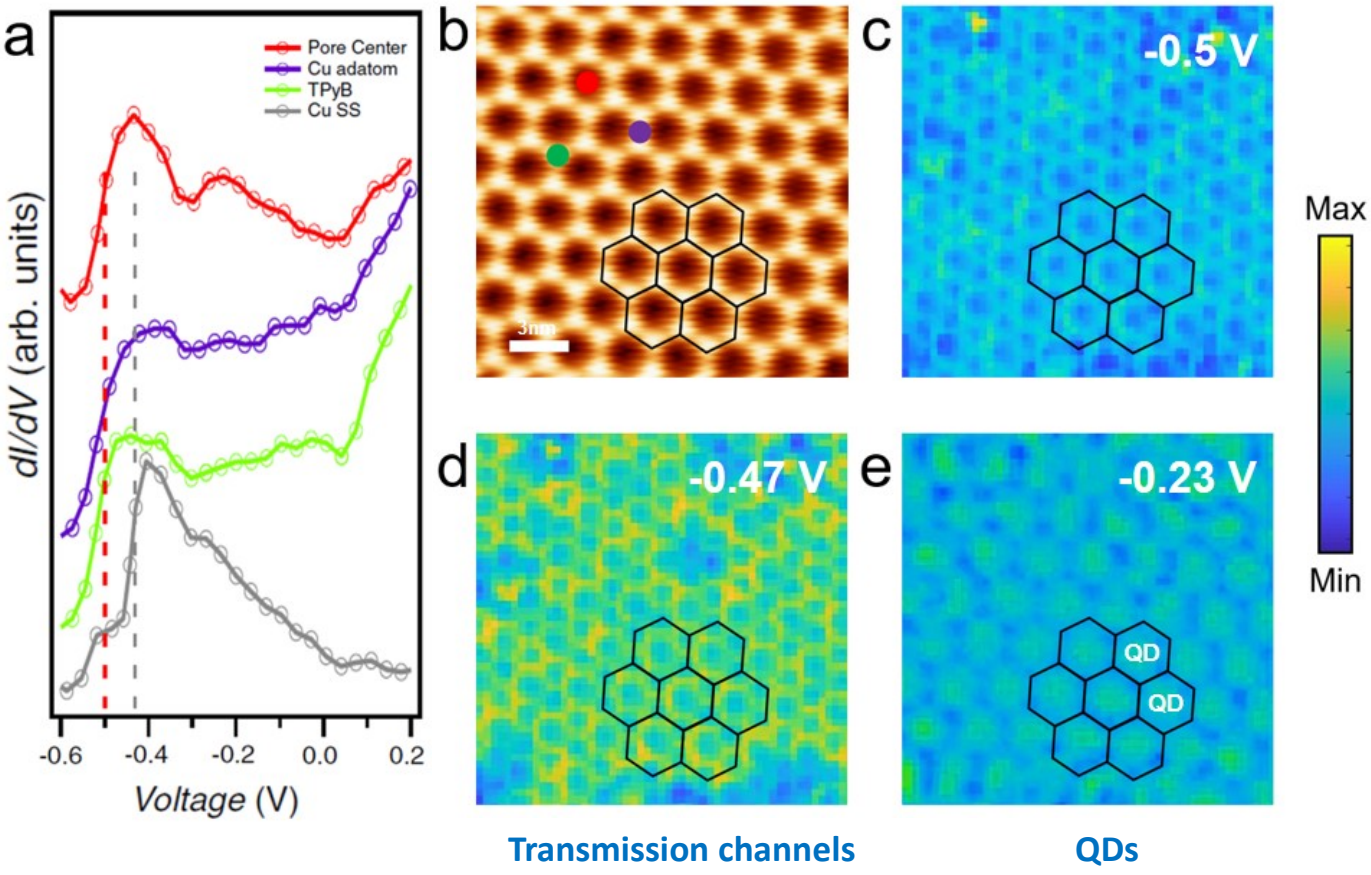
2. TPyB + Cu / Cu(111) MOFs

dI/dV spectra & grid-mode STS

- Red & gray dash lines
  onsets of the TPyB-Cu & Cu(111)
  −70 meV shift

- At the pore center (red line)
  weak confinement resonances
  peaking at -0.42 V, -0.23V and 0.2V

- dI/dV grid from -0.6V to -0.1V



2. TPyB + Cu / Cu(111) MOFs

Electron plane wave expansion (EPWE) simulations

EPWE simulation

- Model: two different scattering regions:

  Highly repulsive for molecules (V_{mol}=250 meV in **green**)

  Weakly repulsive for Cu atoms (V_{Cu}=50 meV in **purple**)

- Simulated line shapes

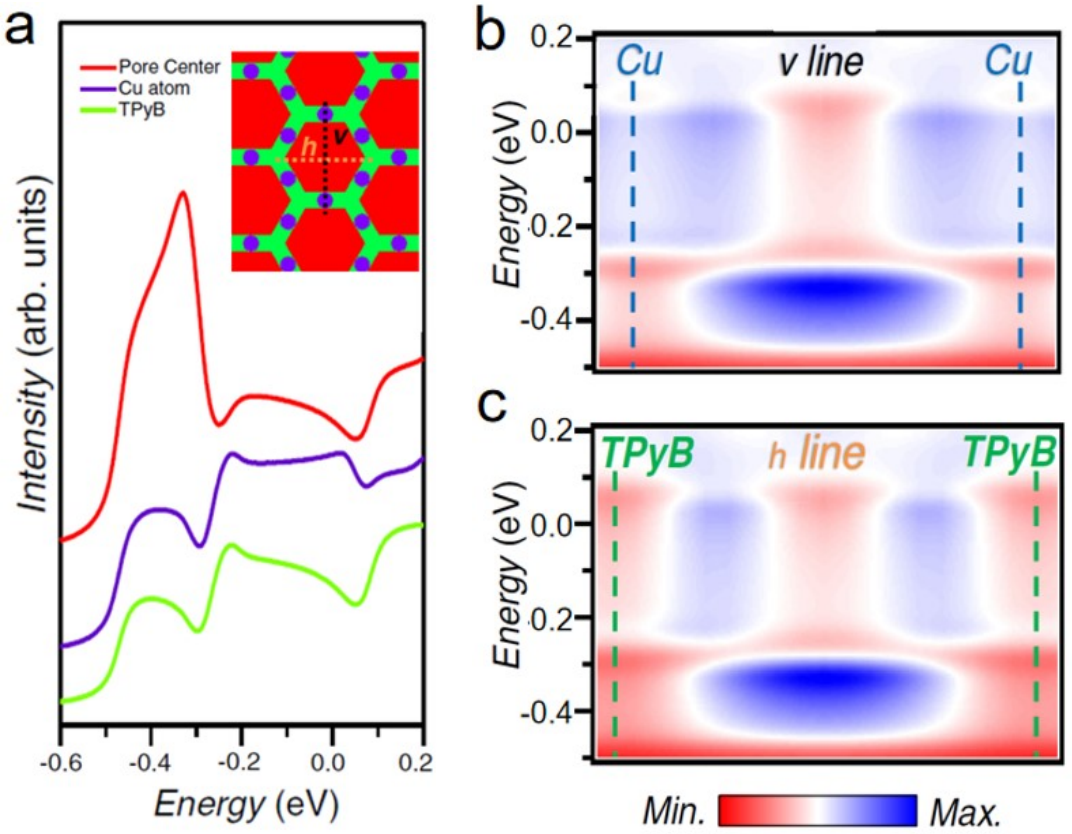
- EPWE simulate 1D linescans

  In both directions:

  First confined state is well trapped within the pore

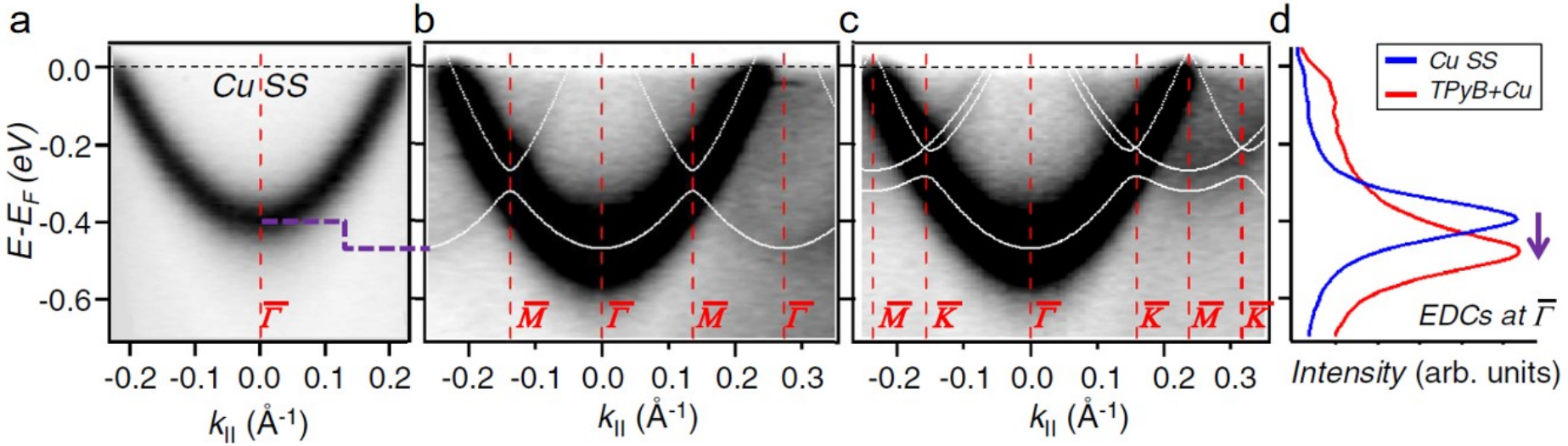
  In vertical direction:

  weaker barriers at Cu atoms



2. TPyB + Cu / Cu(111) MOFs

ARPES experimental datasets



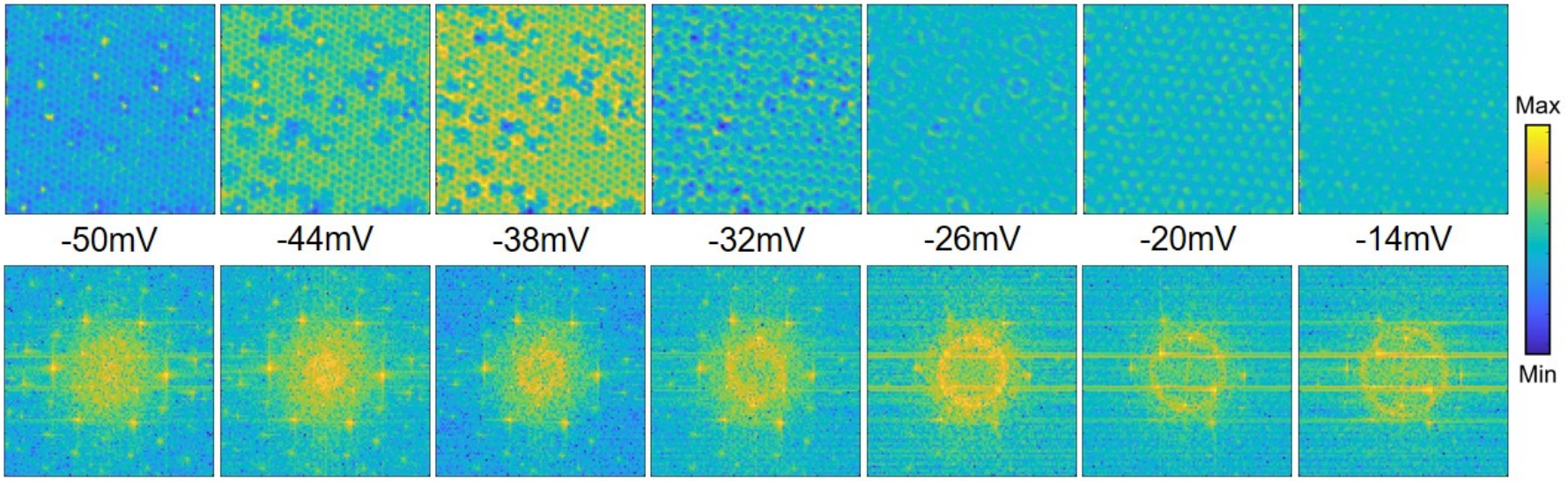
- Angle-resolved photoemission spectroscopy (ARPES) spectral density
  - (a) Pristine Cu(111) substrate
  - (b)(c) TPyB-Cu covered surface
- Overlaid white lines in (b) and (c) indicate EPWE band calculations

- A down-shift of the fundamental energy (Γ̄ point) of **−70** meV

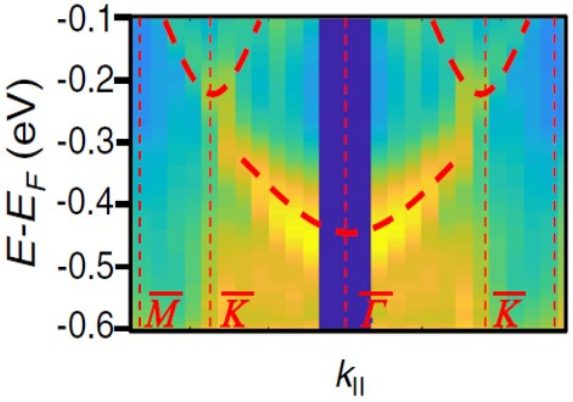
highly dispersive

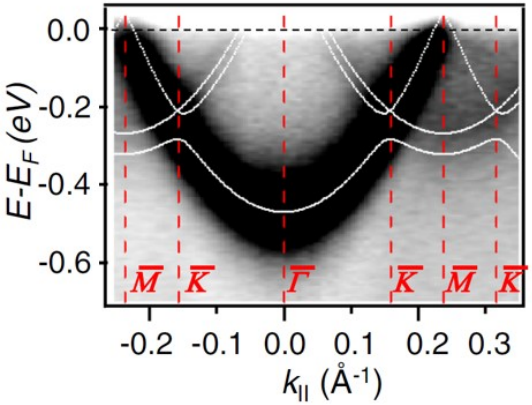
2. TPyB + Cu / Cu(111) MOFs

Grid-mode STS & power spectra functions



- Grid mode STS from -0.6V to -0.1V
- Fourier-transformed to density of states maps
- Power spectra functions

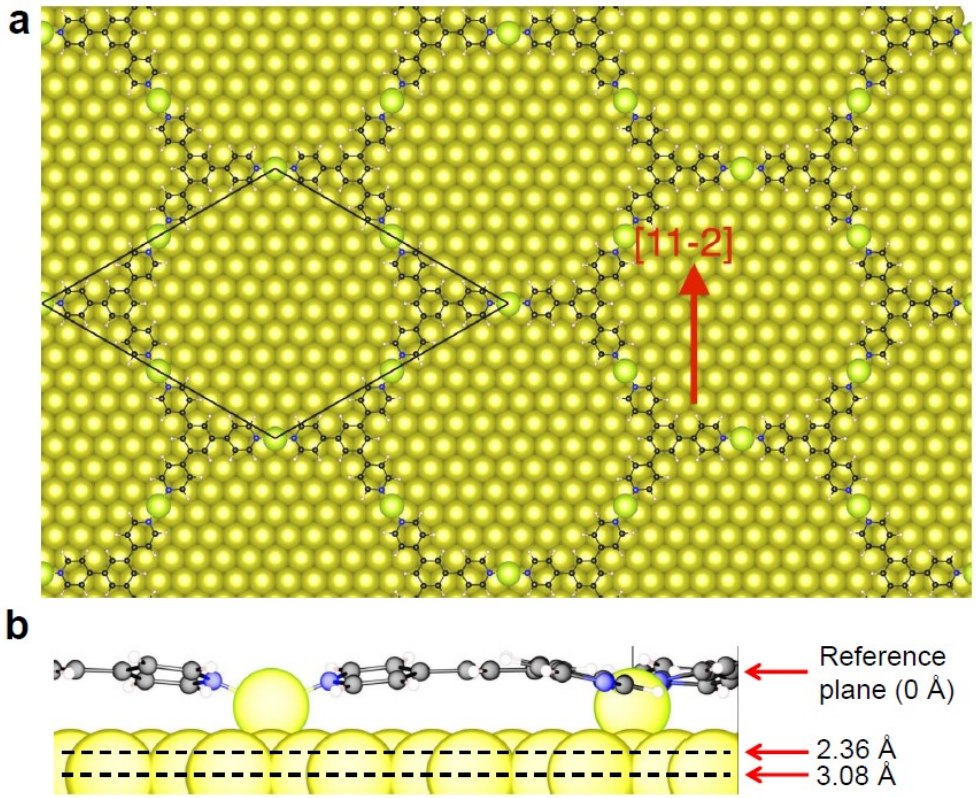




2. TPyB + Cu / Cu(111) MOFs

DFT calculations

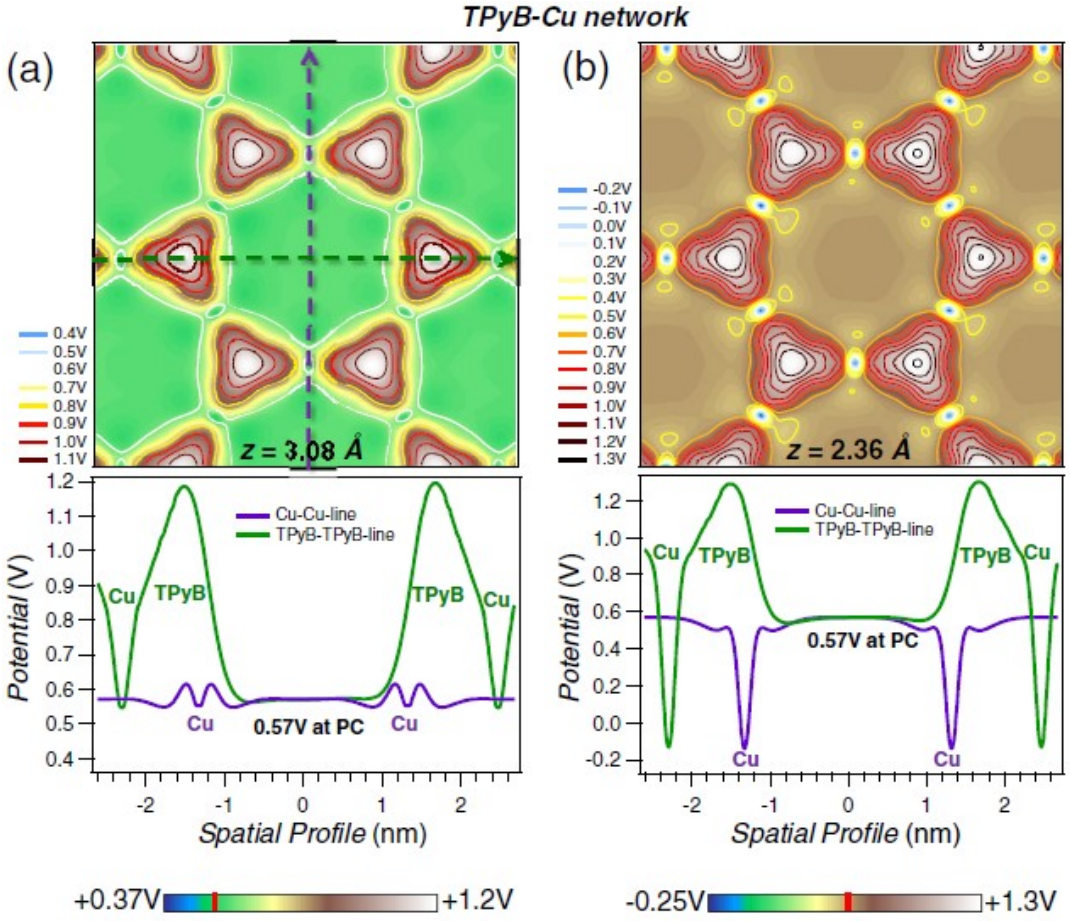
- DFT top view & side view of TPyB-Cu MOF
- Cu(111) SS has its largest probability density close to the substrate's last layer
- Two positions used for the electrostatic potential maps (ESP)



2. TPyB + Cu / Cu(111) MOFs

Electrostatic potential (ESP) maps from DFT calculations

- Consistant with EPWE simulation
- Heterogeneous scattering potential
  - Strong repulsive at TPyB
  - Weak repulsive at Cu
- Cu position
  - the outer rim is weakly repulsive
  - reverses its character towards its center
- Cu atoms act like effective transmission channels

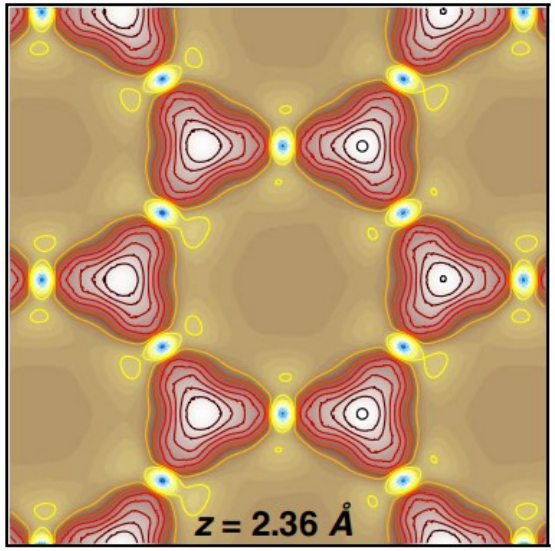


2. TPyB + Cu / Cu(111) MOFs

Conclusion

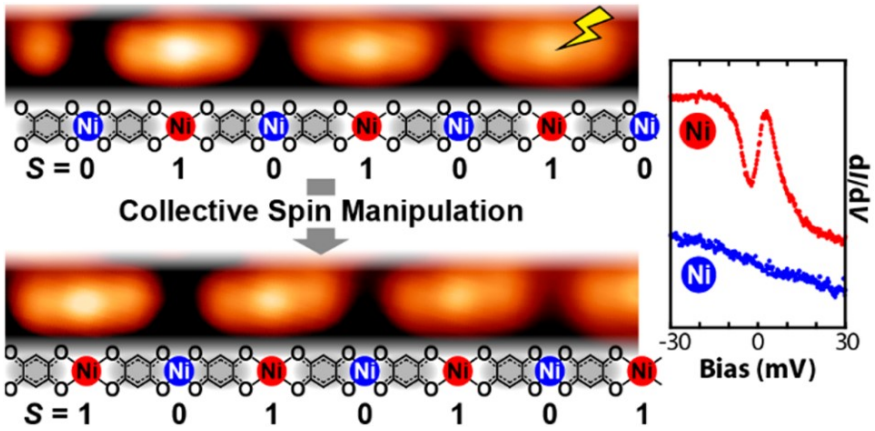
- The on-surface synthesis of TPyB-Cu MOFs, which create QD arrys in the 2D pores.

- Cu adatoms act like efficient transmission channels between adjacent QDs that yields significant interdot coupling.



Cu atoms act like transmission channels

Part 3 Collective Spin Manipulation in Antiferroelastic Spin-Crossover Metallo-Supramolecular Chains

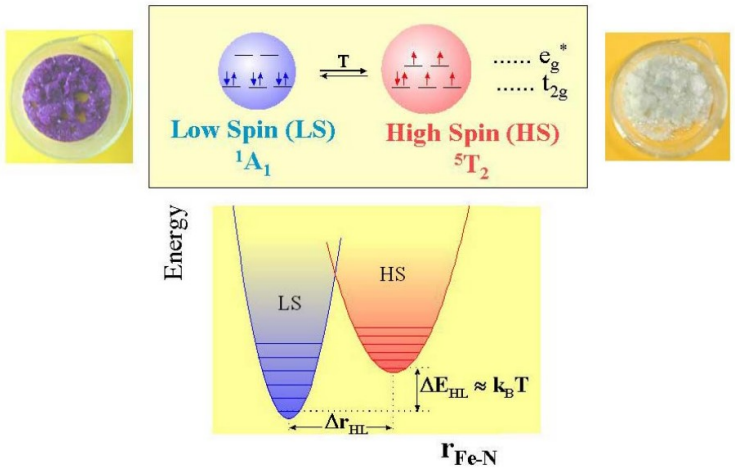


3. THB + Ni / Au(111) Coordination Chains

Introduction

- Spin-crossover (SCO) complexes

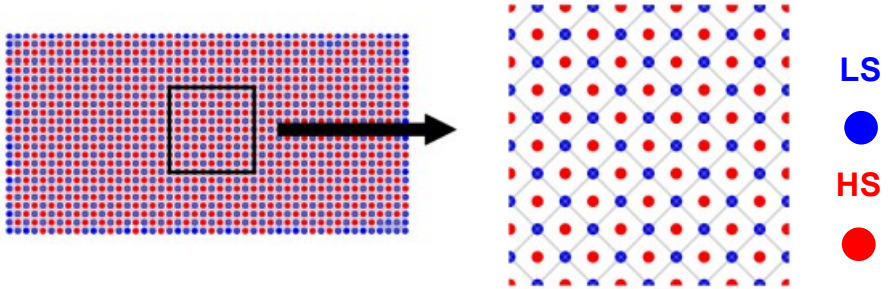
  Coordination compounds containing transition metal centers that exhibit switchable spin-state bistability.



P. Gütlich and Y. Garcia, in Journal of Physics: Conference Series (IOP Publishing, 2010), p. 012001.

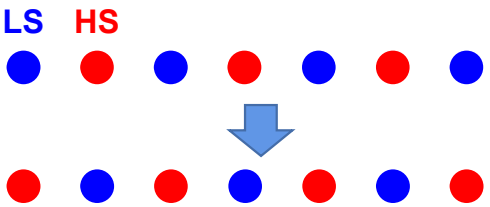
- Antiferroelastic SCO

  Neighboring SCO sites are in different spin states



M. Paez-Espejo, M. Sy, and K. J. J. o. t. A. C. S. Boukheddaden, 138, 3202 (2016).

- How to observe Antiferroelastic SCO



3. THB + Ni / Au(111) Coordination Chains

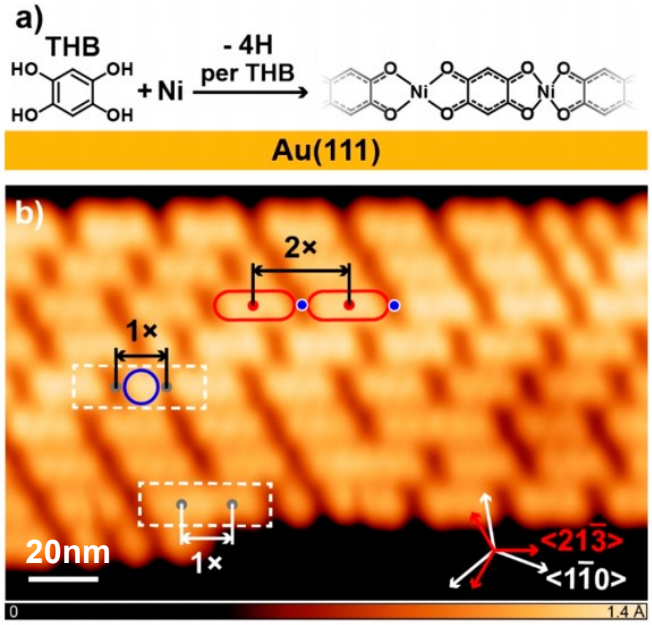
Sample preparation

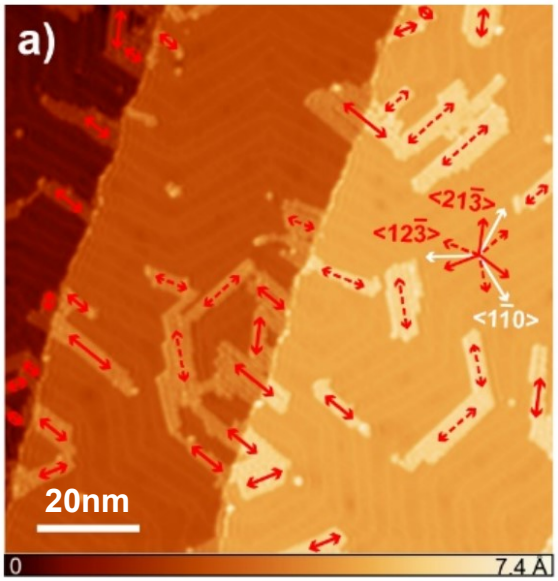
- Tetrahydroxybenzene (THB)
- Au(111) substrate

- Sample preparation
  - (1) Deposit THB on Au(111) at RT
    [evaporate temperature: 335K]
  - (2) Dose Ni atoms on sample
  - (3) Anneal at 500K

- Six orientations
  <1-10> <21-3>

- Dimers (red loops) & monomers (blue circle)





3. THB + Ni / Au(111) Coordination Chains

Structure characterization

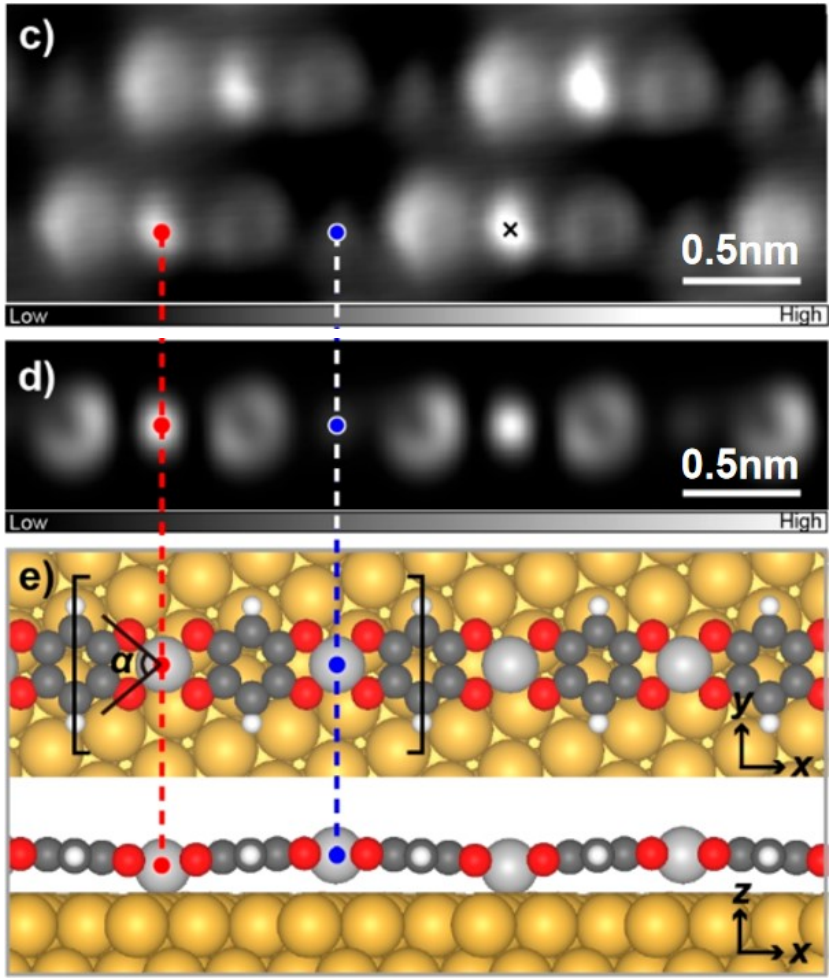
- **(c) Constant-height mode**
  (V = 3 mV, I = 4.81 nA)
  Donut-shaped protrusions
  Small brighter dot (red dot)
  Darker dot (blue dot)

- **(d) DFT-simulated STM image**

V = 50 mV, in constant-height mode

- **DFT calculations optimized model**

Unit cell: [2 molecules + 2 Ni] ***(2 × unit cell)***
Ni atoms --- hollow sites of Au(111) substrate
Ni-Ni separation: calculation --- 7.62 Å
experiment --- 7.6 Å



3. THB + Ni / Au(111) Coordination Chains

Structure characterization

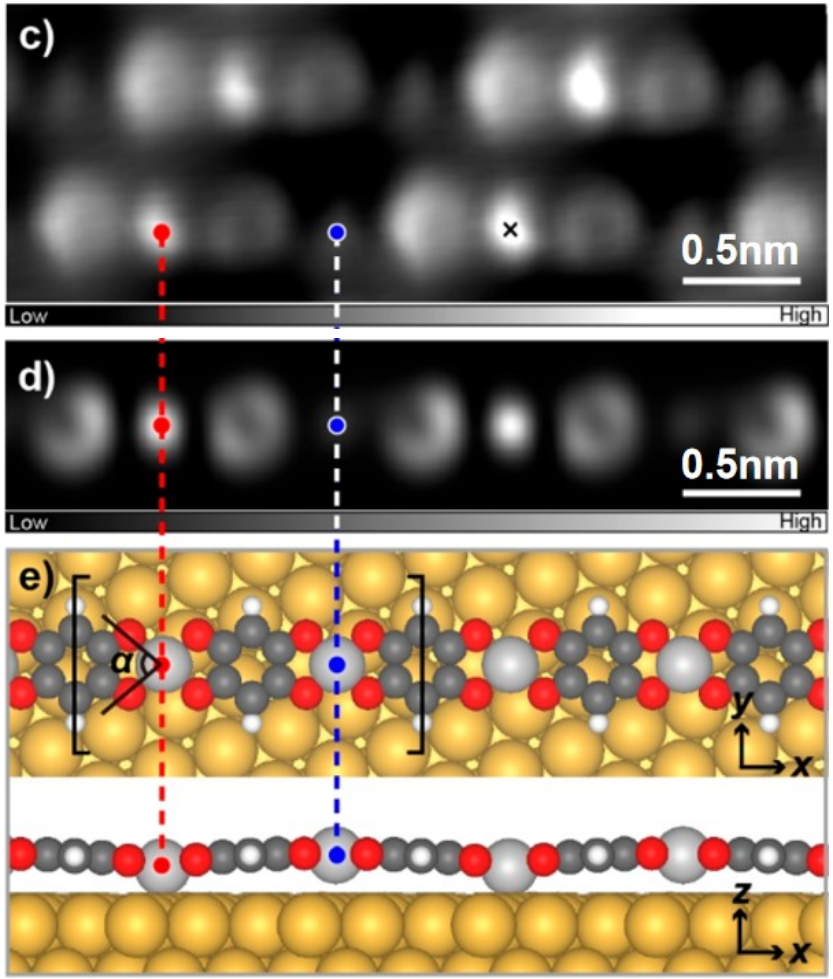
- **Two inequivalent Ni atoms:**

  Type 1 Ni: longer Ni−O bonds (2.00 Å) (red dot)

  smaller Ni−substrate distance (2.54 Å)

  Type 2 Ni: shorter Ni−O bonds (1.85 Å) (blue dot)

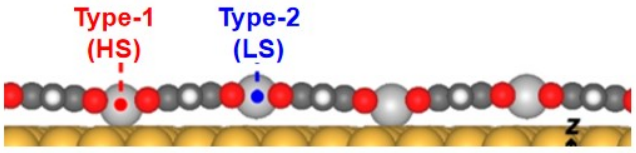
  larger Ni−substrate distance (3.07 Å)

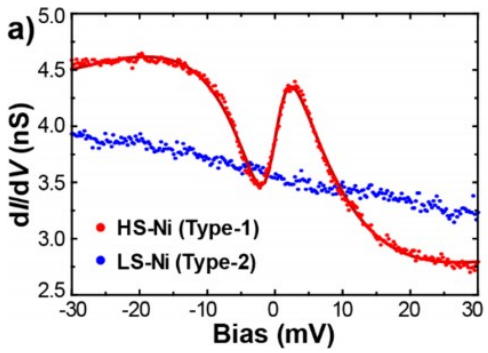


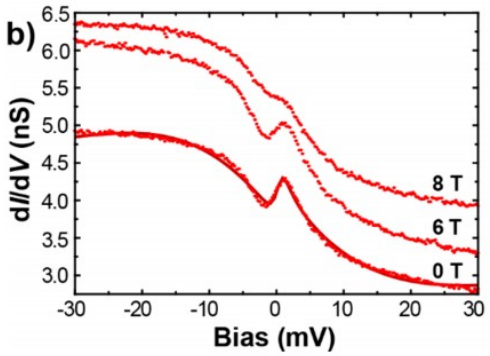
3. THB + Ni / Au(111) Coordination Chains

Spin States of the Ni Atoms

- **dI/dV spectra at two types Ni atoms**







- **Type-2**
  Featureless around 0 bias
- **Type-1**
  Kondo resonance

- **Type-1**
  Kondo effect measured in external magnetic field
  Fano fitting -- dark red line

- **DFT-calculated spin-polarized projected density of state**

  - **Ni, 3d orbitals**

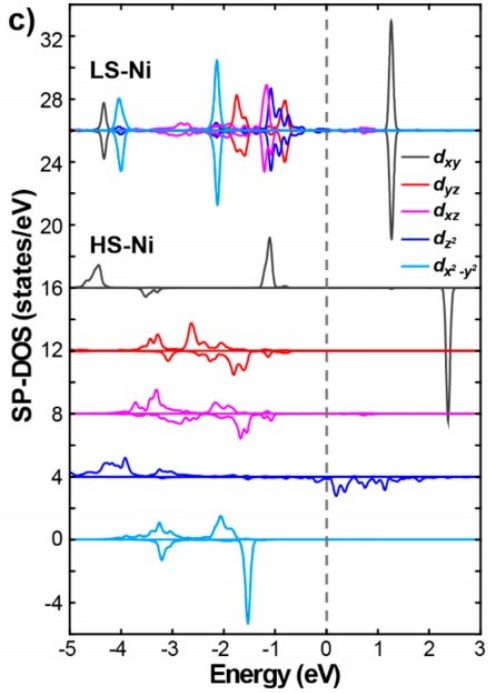
Type-2 S=0

Type-1 S=1

d_{xy}, d_{z2}

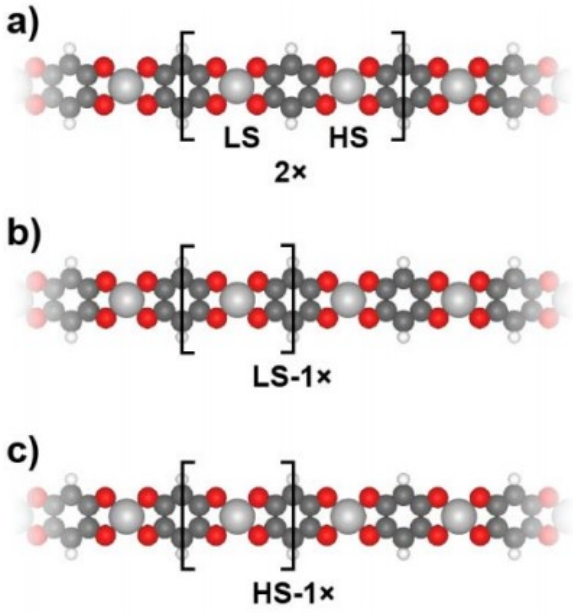
Magnetic moment: 1.59 μB

- **Antiferoelastic**

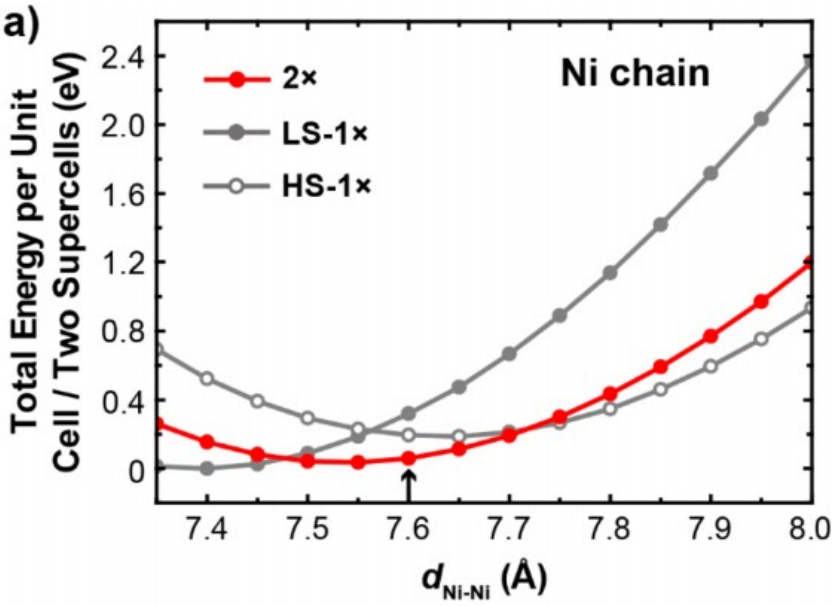


3. THB + Ni / Au(111) Coordination Chains

Antiferroelastic Phase of the Ni-Coordinated Chains



- Optimized free-standing models of the Ni chain



- Total energies per unit cell

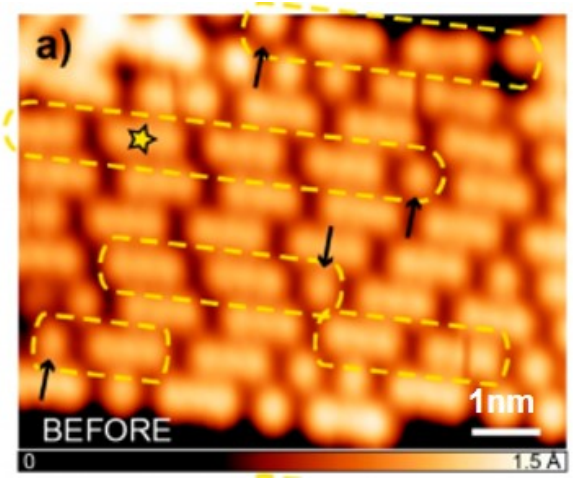
  d_{Ni-Ni} = 7.6 Å

  Substrate confine state

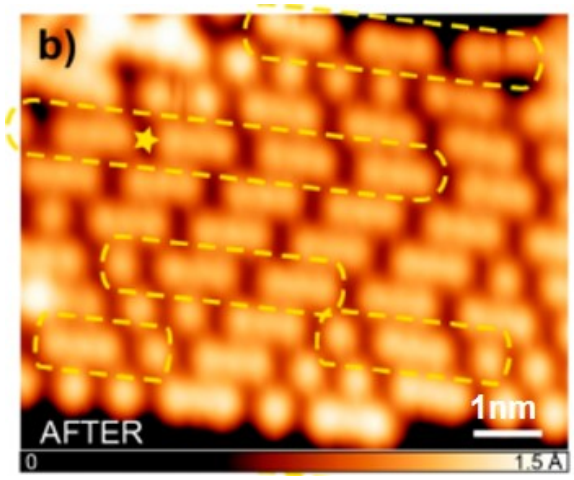
3. THB + Ni / Au(111) Coordination Chains

Collective Spin Manipulations in Ni-Coordinated Chains

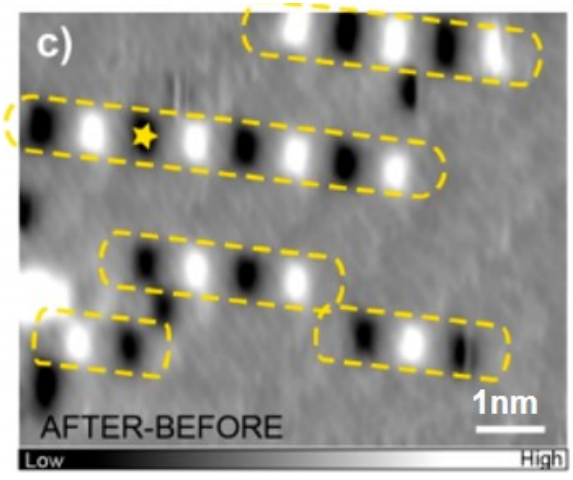
multiple chain manipulation



(a) Before voltage pulse



(b) After voltage pulse



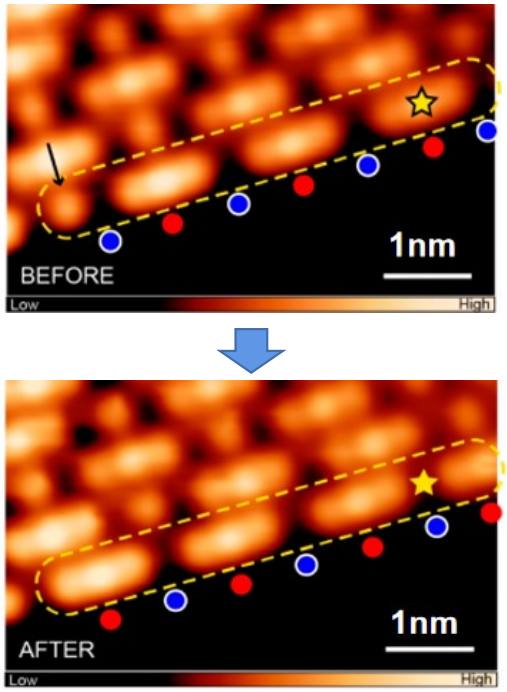
(c) Subtracting (a) from (b)

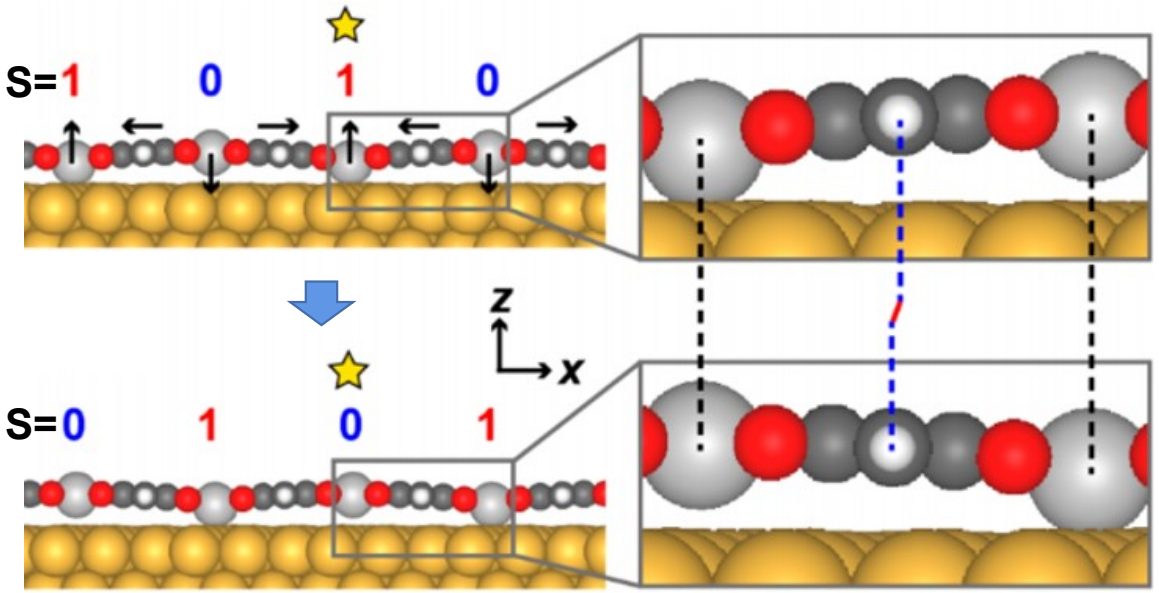
- Applying -4V pulse at Ni (yellow star position)
  Switched Ni atoms
  Chains are highlighted by the yellow dashed frames

- White position
  LS to HS switching
- Black position
  HS to LS switching

3. THB + Ni / Au(111) Coordination Chains

Mechanism of the Collective Spin-State Switching in Ni-Coordinated Chains





- 80 mV bias voltage pulse
- single chain manipulation

  Red dots --- HS - Ni

  Blue dots --- LS - Ni

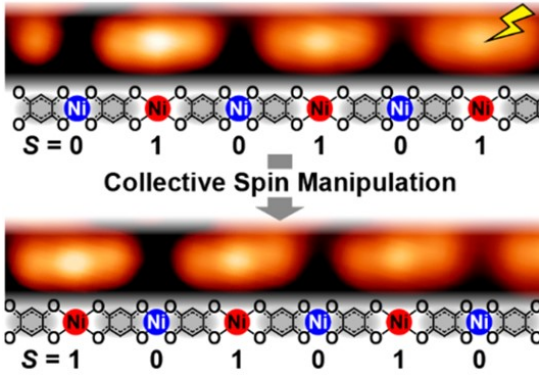
- Ni : lateral position no change vertical position shifted
- Molecules: titled & shifted
- Collective conversions --- domino-like process

3. THB + Ni / Au(111) Coordination Chains

Conclusion

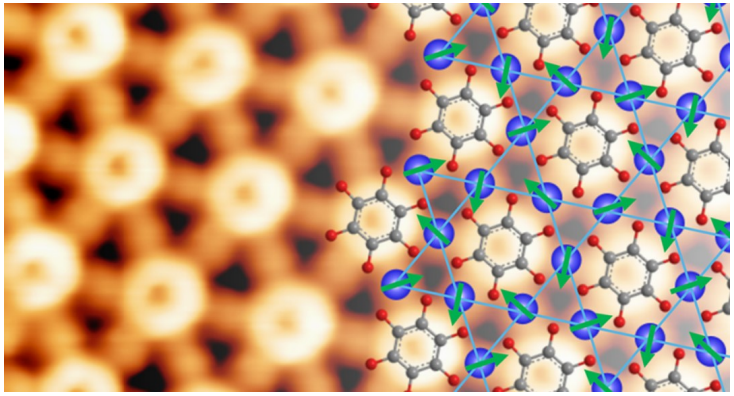
- The on-surface synthesis of the 1D antiferroelastic coordination chains (LS=0 HS=1)

- The spin states of the Ni atoms in the same coordination chain are found to switch collectively upon the local tip-excitation, resulting in the collective spin manipulation through a domino-like dynamic magneto-structural relaxation process



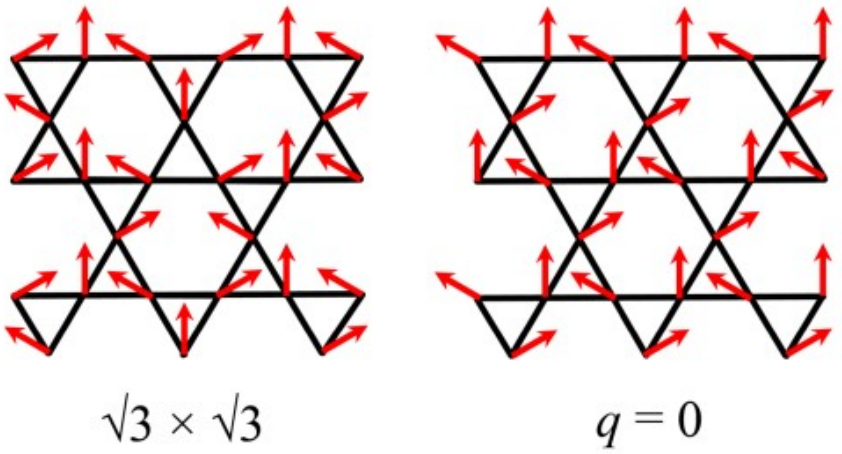
Collective Spin Manipulations in antiferroelastic Coordination chains

Part 4 Design and Characterization of an Antiferromagnetic Kagome Lattice in a Two-Dimensional Metal-Organic Framework



4. BHO + Fe / Au(111) MOFs

Introduction



D. J. F. o. P. Farnell, 14 (2019).

- Kagome lattice
- Kagome antiferromagnet (KAF)

Quantum spin liquid (QSL) states

- No long-range magnetic order
- Highly degenerated ground states
  - q = 0 state
  - q = $\sqrt{3} \times \sqrt{3}$ state

◆ 2D metal–organic frameworks
Kagome structure

4. BHO + Fe / Au(111) MOFs

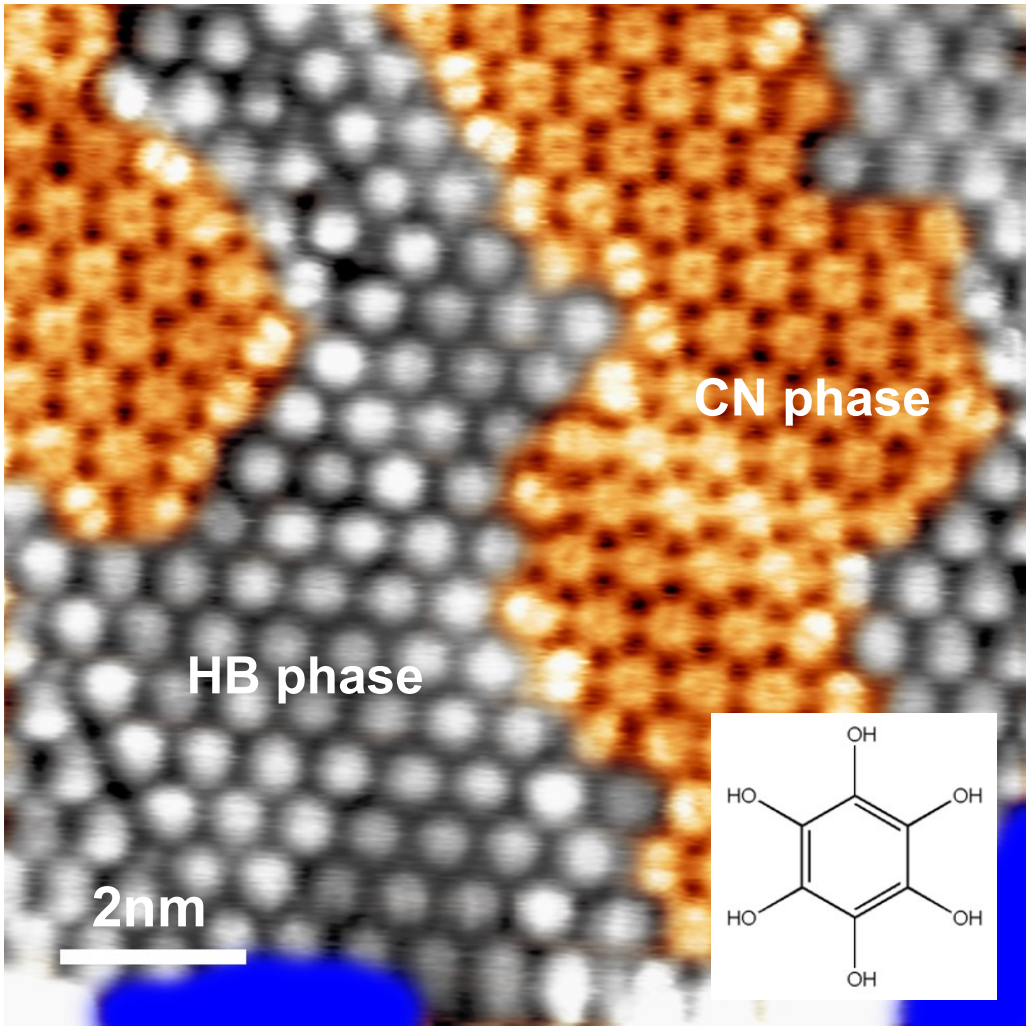
Sample preparation

- Benzene-1,2,3,4,5,6-hexaol (BHO)
- Au(111) substrate

- Hydrogen-bond (HB) phase
- Coordination network (CN) phase

- Sample preparation
  - HB phase: Deposit BHO on Au(111) at RT
    [evaporate temperature: 400K]
  - CN phase: (1) Dose Fe on HB phase
    (2) Anneal at 450K

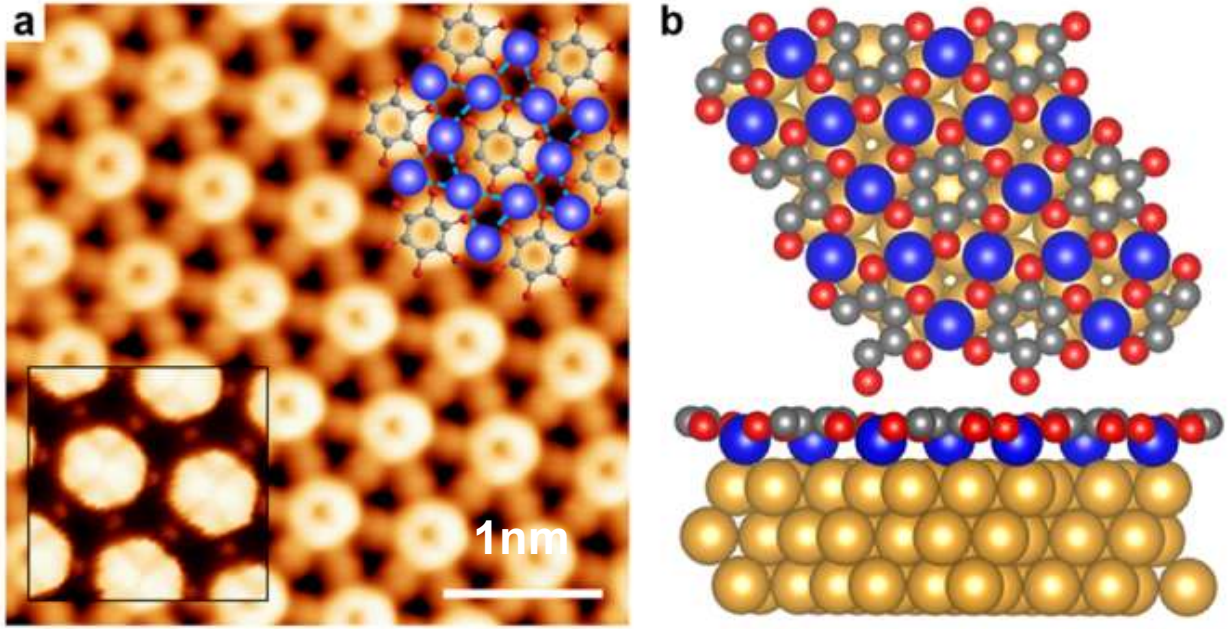
- Lattice constant
  - HB phase: 7.5 Å
  - CN phase: 7.6 Å



4. BHO + Fe / Au(111) MOFs

CN phase structure characterization

- **XPS results -- Fe^{2+}**
- Inset: constant-height mode STM (V = 10 mV, I = 1 nA, T = 2.6 K)
- Kagome lattice of Fe atoms
- DFT calculation obtained structure on Au(111)
  Lattice constant: 7.65 Å



4. BHO + Fe / Au(111) MOFs

Magnetic properties of Fe embedded in CN Phase

- DFT Spin-polarized analysis

  High-spin state --- S=2

  Magnetic moment --- 3.6 μB

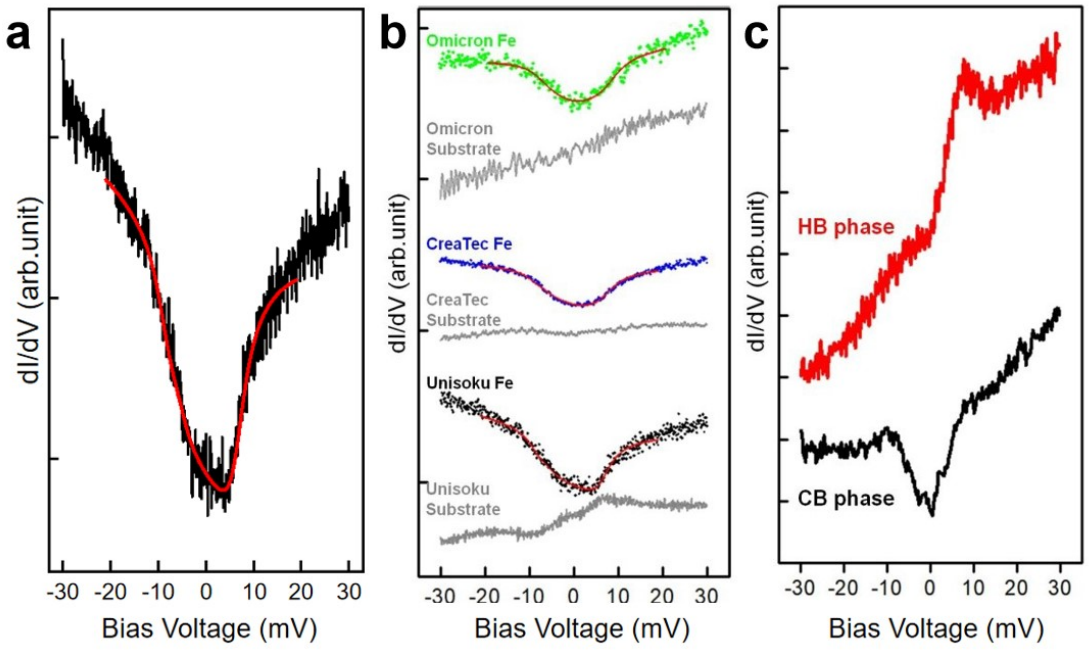
- Tunneling spectroscopy measurements at low-temperature

  Two steps at ±6 meV

  Spin excitation features

  Fitting magnetic anisotropy D = 6meV

  easy-plane



STS spectra

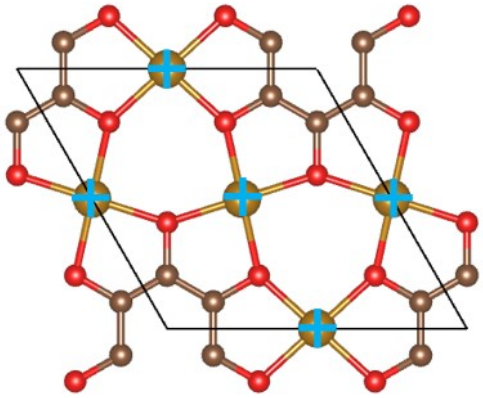
Spectra in 3 STMs

HB phase:
No feature

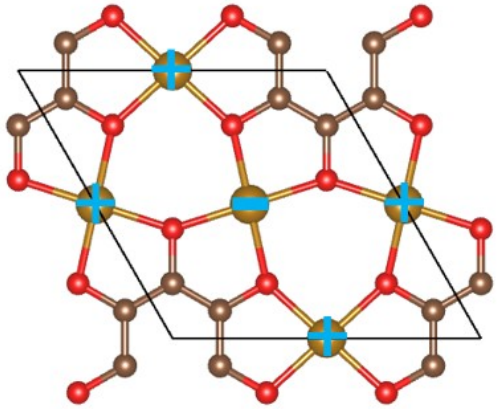
4. BHO + Fe / Au(111) MOFs

DFT-calculated lowest-energy configurations

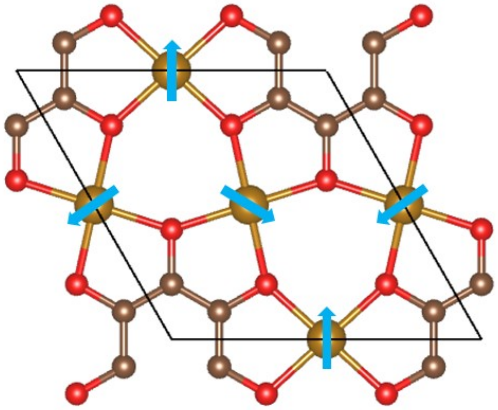
Various magnetic configurations



Out-of-plane ferromagnetic



Out-of-plane ferrimagnetic



In-plane antiferromagnetic

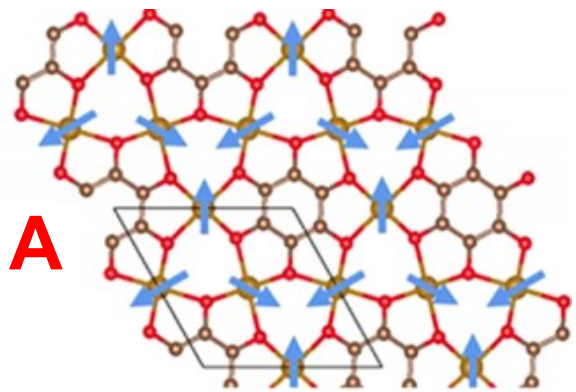
Lowest-energy configuration:

In-plane antiferromagnetic (AF) coupled magnetic moments

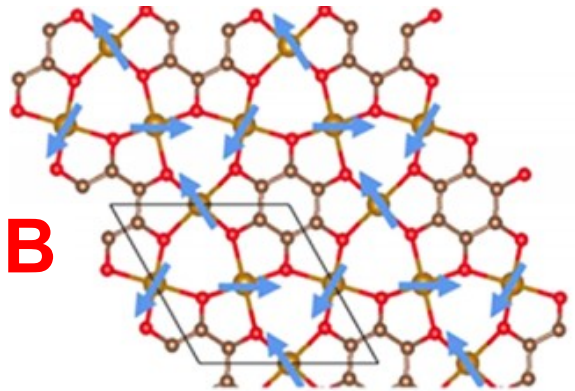
4. BHO + Fe / Au(111) MOFs

DFT-calculated lowest-energy configurations

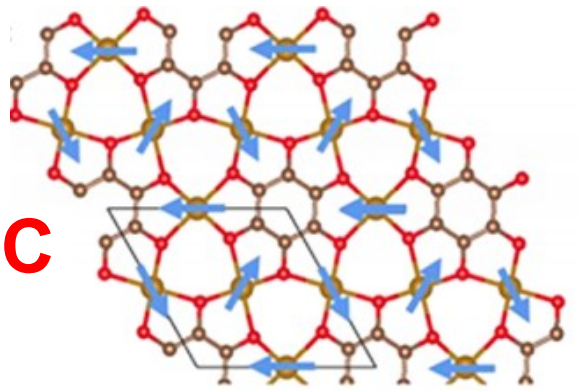
Three lowest-energy in-plane AF states



-161.72032 / -159.80840 eV



-161.72037 / -159.80875 eV



-161.72032 / -159.80942 eV

- Energy difference of three configurations ~1 meV

  A, B and C are **degenerate states**

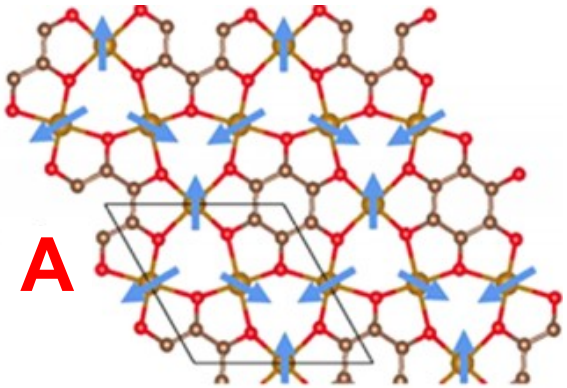
- Nearest-neighboring coupling J1=5.8 meV

ΔE_{tot} (meV)	with sub.	without sub.
A	0.00	0.00
B	-0.05	-0.35
C	0.00	-1.02

4. BHO + Fe / Au(111) MOFs

DFT-calculated lowest-energy configurations

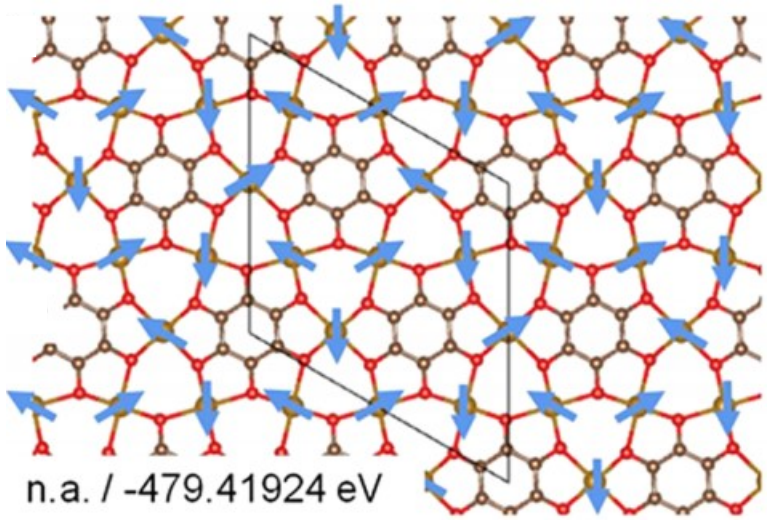
Next-nearest neighboring coupling J2



-161.72032 / -159.80840 eV

Triple unit cell

D



n.a. / -479.41924 eV

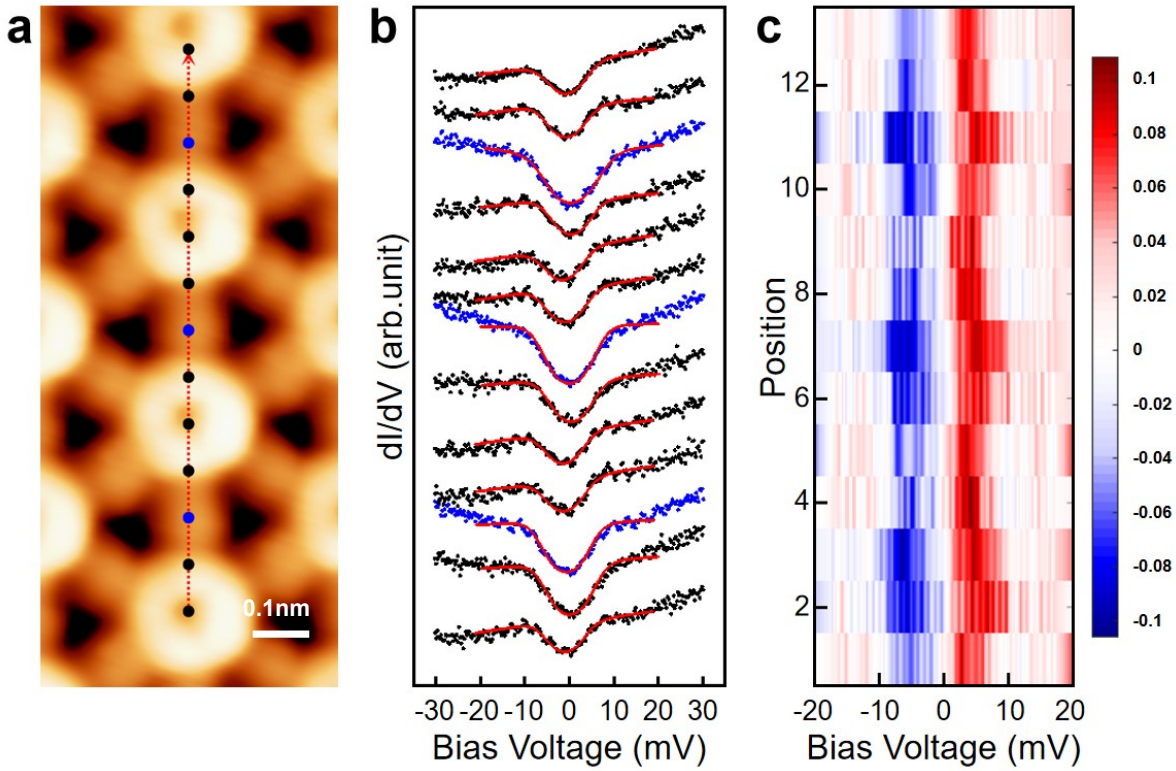
- J1=5.8 meV， J2=0.06 meV
- Total energy difference between A(B or C) and D/3 less than 1 meV
- Next-nearest neighboring interaction can be neglected

Highly degenerated ground states

4. BHO + Fe / Au(111) MOFs

STS Characterisation of CN Phase

- Spatially resolved differential conductance spectra
- Step signal is stronger at the Fe atoms
- Same excitation energy observed at Fe atoms and BHO molecules
- Spin excitation --- global effect

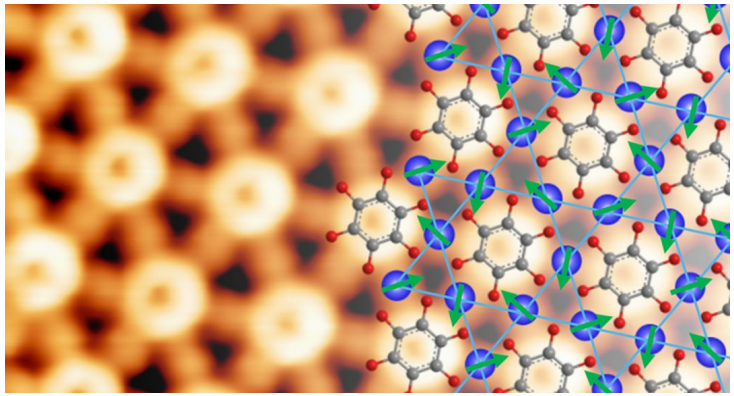


- **Second derivatives**

4. BHO + Fe / Au(111) MOFs

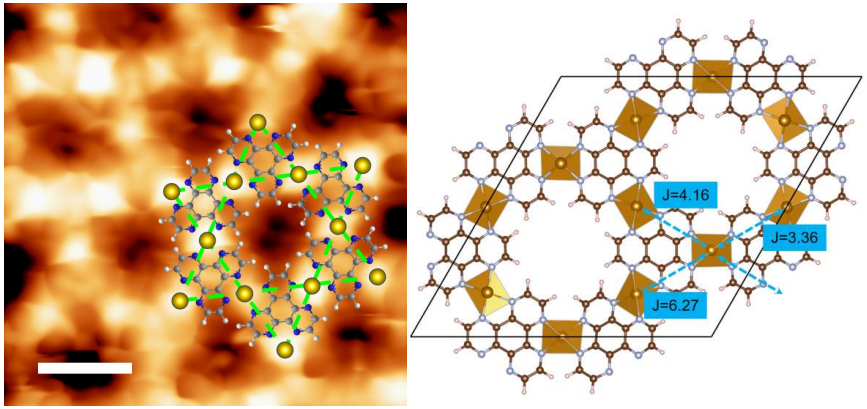
Conclusion

- Synthesize a single-layer 2D MOF and resolve the atomic structure of the Kagome Fe(II) lattice
- First-principles calculations show that the ground state of this system is highly degenerated containing antiferromagnetic coupled in-plane S = 2 spins.
- The BHO-Fe MOF exhibits a global spin excitation, which likely indicates a spin gap.



Highly degenerated antiferromagnetic ground states

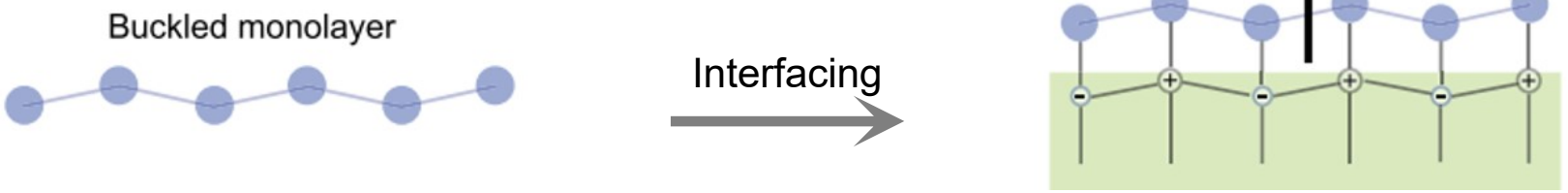
Part 5 Characterization of spin excitation in a Two-Dimensional Metal-Organic Network



5. HAT + Fe / Ag(111) MOFs

Introduction

Buckled structure



- The geometry of a free-standing buckled monolayer
- Interface-induced potential gradient through the monolayer when growing it on a substrate

- An effective way of tuning spin-orbit splitting in low-dimensional materials
- 2D MOF with a buckled structure

M. Chen and F. J. N. S. R. Liu, 8, nwaa241 (2021)

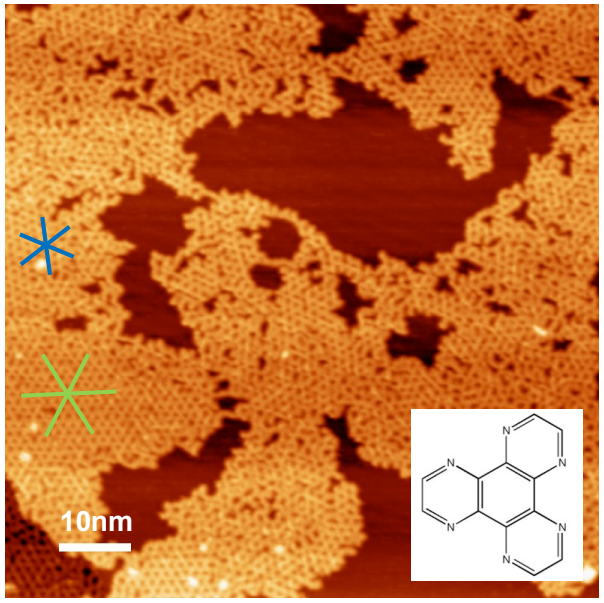
5. HAT + Fe / Ag(111) MOFs

Sample preparation

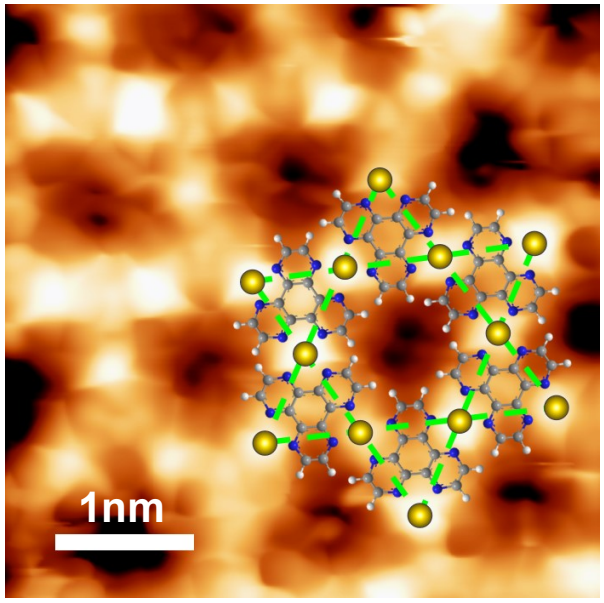
- 1,4,5,8,9,12-Hexaazatriphenylene (HAT)
- Ag(111) substrate

- Sample preparation
  - (1) Deposit HAT on Ag(111) at RT
    [evaporate temperature: 470K]
  - (2) Dose Fe atoms on sample
  - (3) Anneal at 470K

- Lattice constant: 1.38 nm



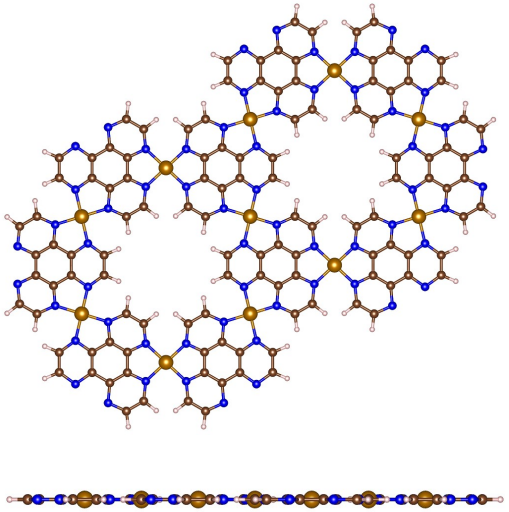
Two lattice orientations: 26°



Fe atoms: Kagome lattice

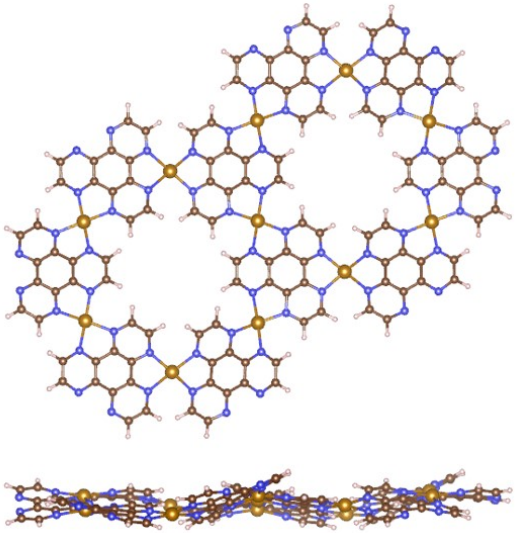
5. HAT + Fe / Ag(111) MOFs

DFT calculations



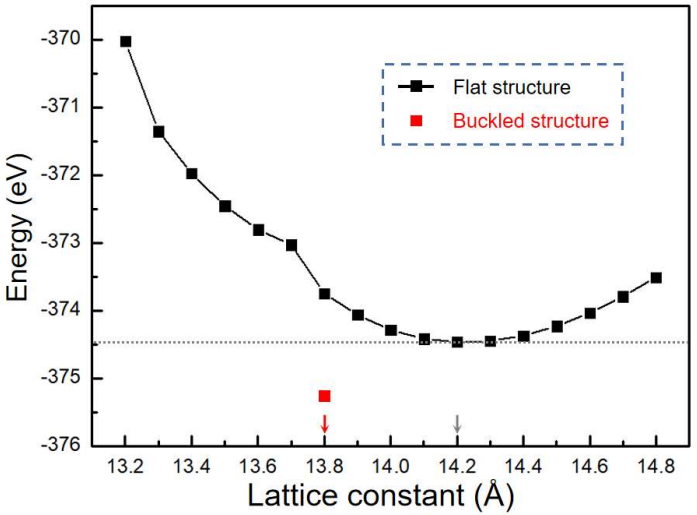
Flat structure

- Close distance between the hydrogen atoms
- Strong steric hindrance



Buckled structure

- HAT molecular backbones tilt up to 30°

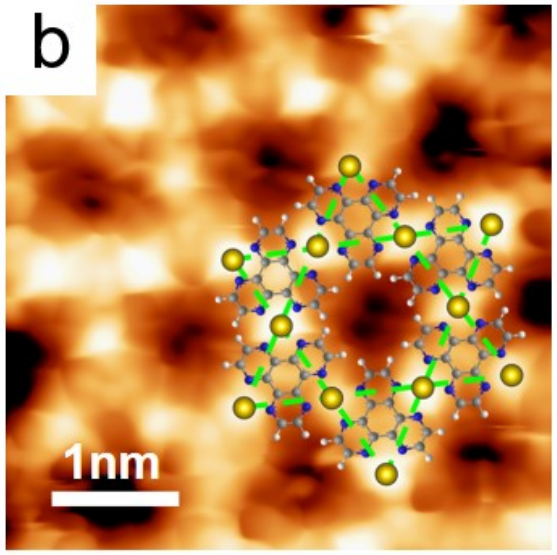


Total energy for $Fe_3(HAT)_2$

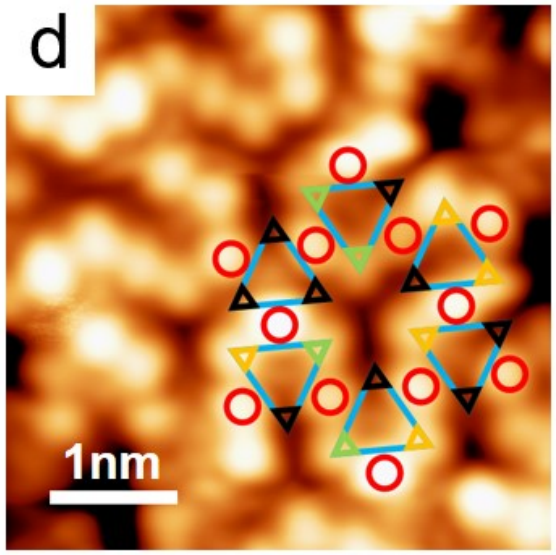
- Minimum energy:
  13.8A -- buckled structure

5. HAT + Fe / Ag(111) MOFs

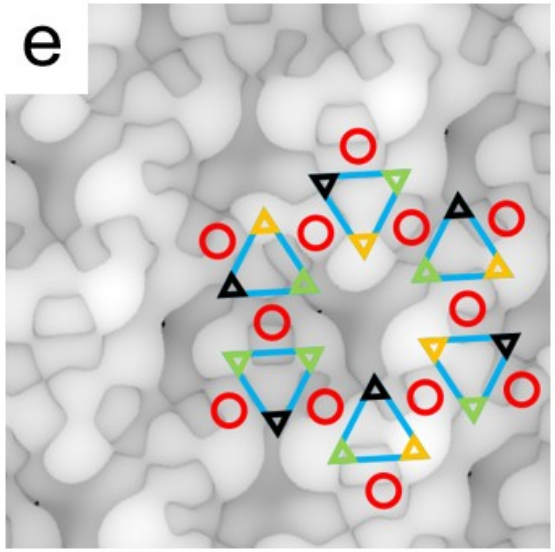
Structure characterization



STM image (V=-40 mV, I=1nA)



STM image (V=-200 mV, I=1nA)



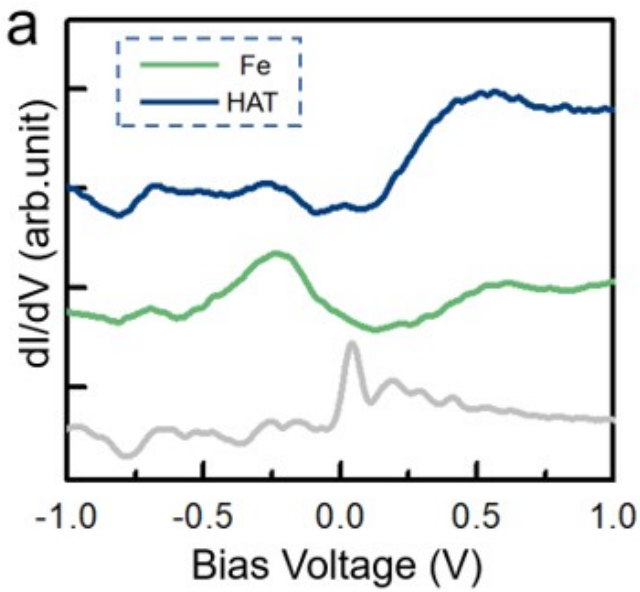
DFT simulated image

- (b),(d) --- Same area

- Fe atoms --- red circles
- HAT molecules --- blue triangles
  - bright corners (orange)
  - dimer corners (green)
  - dark corners (**black**)

5. HAT + Fe / Ag(111) MOFs

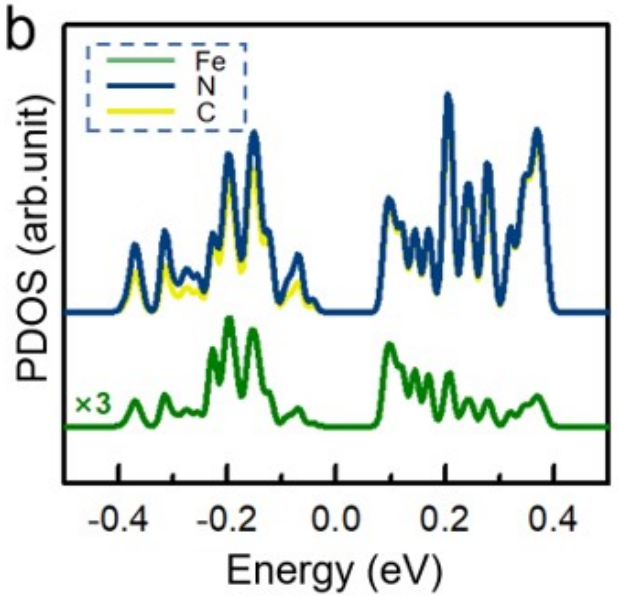
Electronic structure



- **STS dI/dV spectra**

Fe : -0.24V 0.5V

HAT: -0.25V 0.48V



- **DFT-calculated projected densities of states**

A gap between -0.1V and 0.1V

States of Fe overlapped with C and N

------Orbitals highly hybridized

5. HAT + Fe / Ag(111) MOFs

Magnetic properties

- Double-step structure symmetric about V=0

  Step edges: ±3.6 mV & ±16 mV

  Spin-flip excitation resonance

- Spin Hamiltonian

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

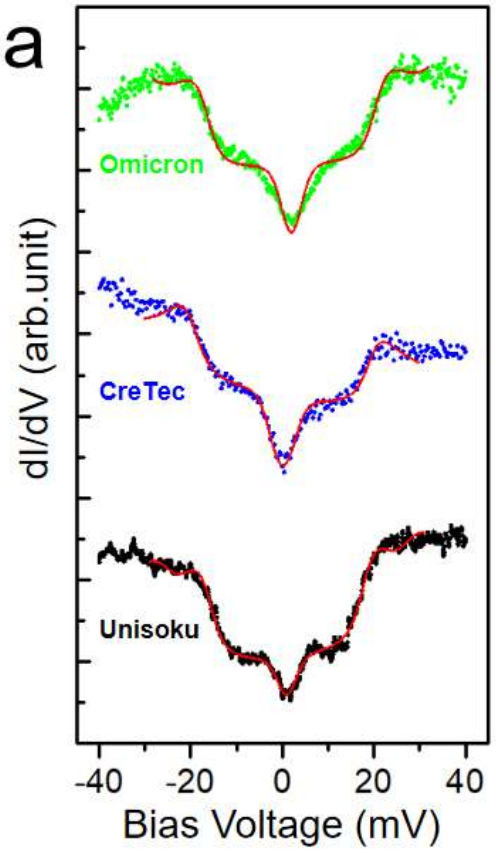
$$H_S = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g\mu\vec{B} \cdot \vec{S}$$

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

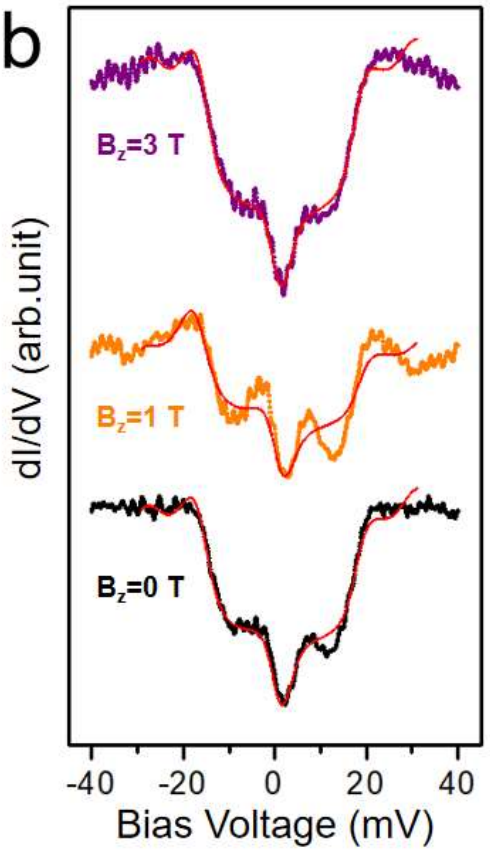
  Fitting of the experimental data shows a large magnetic anisotropy: D=6 meV

- DFT calculations

  S=2 MAE: 0.06 meV J≠0



STS spectra in three STMs

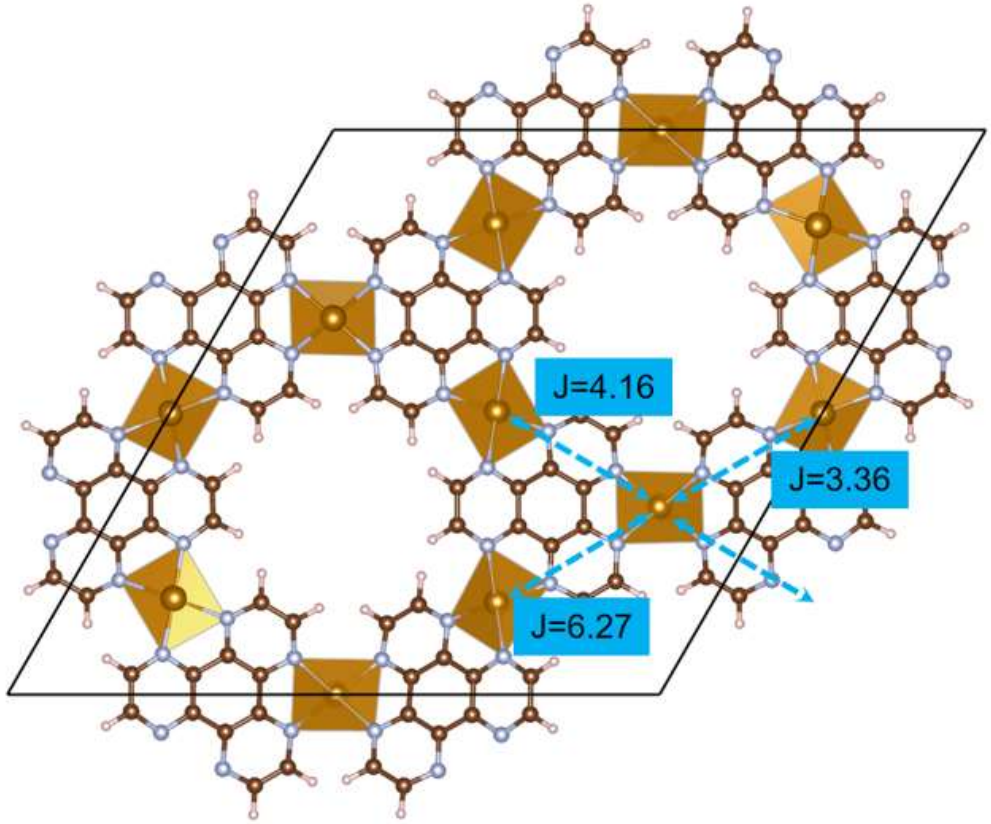


STS spectra on external B

5. HAT + Fe / Ag(111) MOFs

Magnetic properties

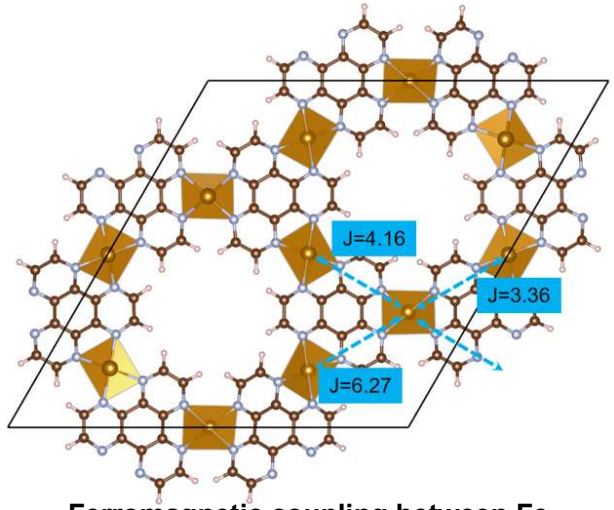
- Ferromagnetic ground state
- NN coupling J: 3.36 ~ 6.27 meV
- **The spin excitation is originated from spin-spin exchange coupling instead of MAE**



5. HAT + Fe / Ag(111) MOFs

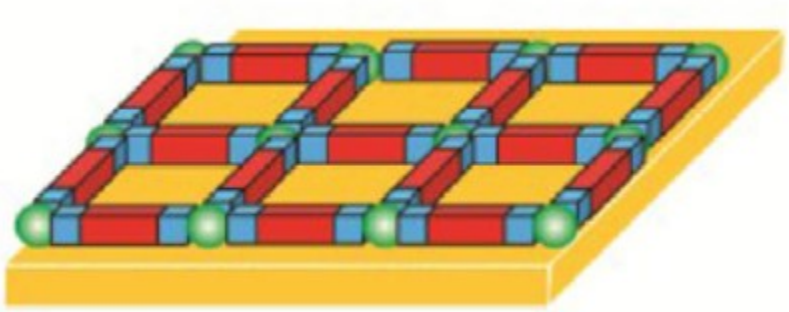
Conclusion

- The whole $Fe_3(HAT)_2$ network structure buckled due to the relatively small lattice constant and the strong steric hinderance from hydrogen atoms.
- STS spectra show spin excitations features on the coordinated Fe atoms.
- The experimental observed large spin excitation is originated from spin-spin exchange coupling instead of MAE.



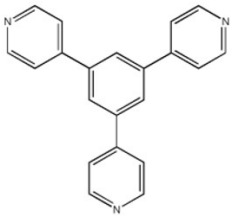
Ferromagnetic coupling between Fe

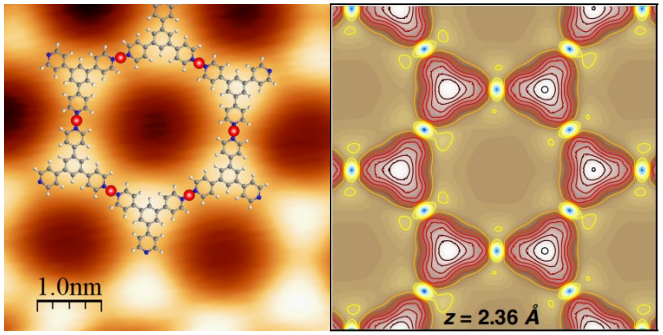
Part 6 Summary and perspectives



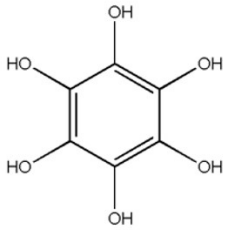
6. Summary and perspectives

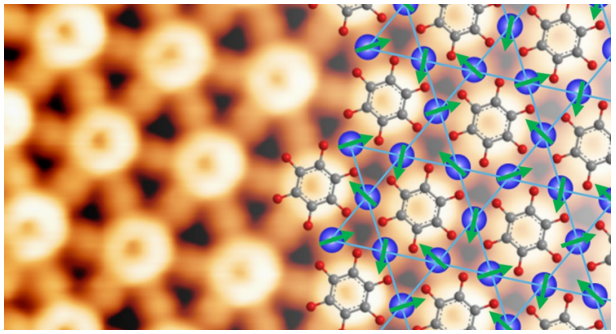
Metal-organic structures on metal surfaces



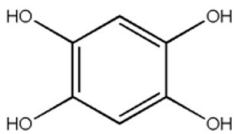


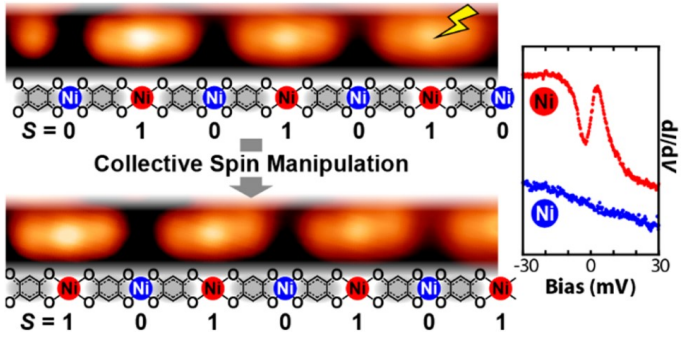
- TPyB + Cu / Cu(111) MOFs



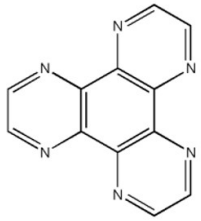


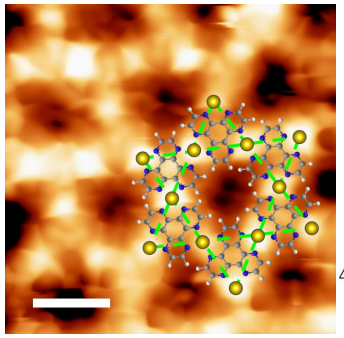
- BHO + Fe / Au(111) MOFs

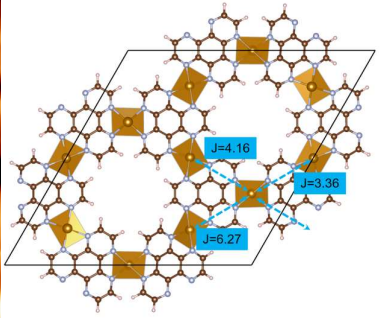




- THB + Ni / Au(111) Coordination Chains







- HAT + Fe / Ag(111) MOFs

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Collaborators:

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- Dr. Behnam Azizi (DFT)
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- Prof. Li Huang (DFT)
- Dr. Yifan Gao (DFT)
- Prof. Junfa Zhu (STM)
- Prof. Wei ZHAO (XPS)
- Prof. Hu Xu (DFT)
- Dr. Bowen Xia (DFT)

Thesis Examination Committee:

- Prof. Minhua Shao (*Chairman*)
- Prof. Yilong Han
- Prof. Iam Keong Sou
- Prof. Zhengtang Luo
- Prof. Wei Xu
- Prof. Nian Lin (*Supervisor*)

Colleagues:

- Dr. En Li
- Dr. Jing Liu
- Dr. Ran Zhang
- Dr. Ziang Gao
- Dr. Bowen Xia
- Dr. Yifan Gao
- Mr. Xiaobo Wang
- Mr. Songyu Mo
- Mr. Chengkun Lv
- Mr. Chengyi Chen

Thanks for your watching !

Muqing HUA

Supervisor: Prof. Nian LIN

Department of Physics
The Hong Kong University of Science and Technology