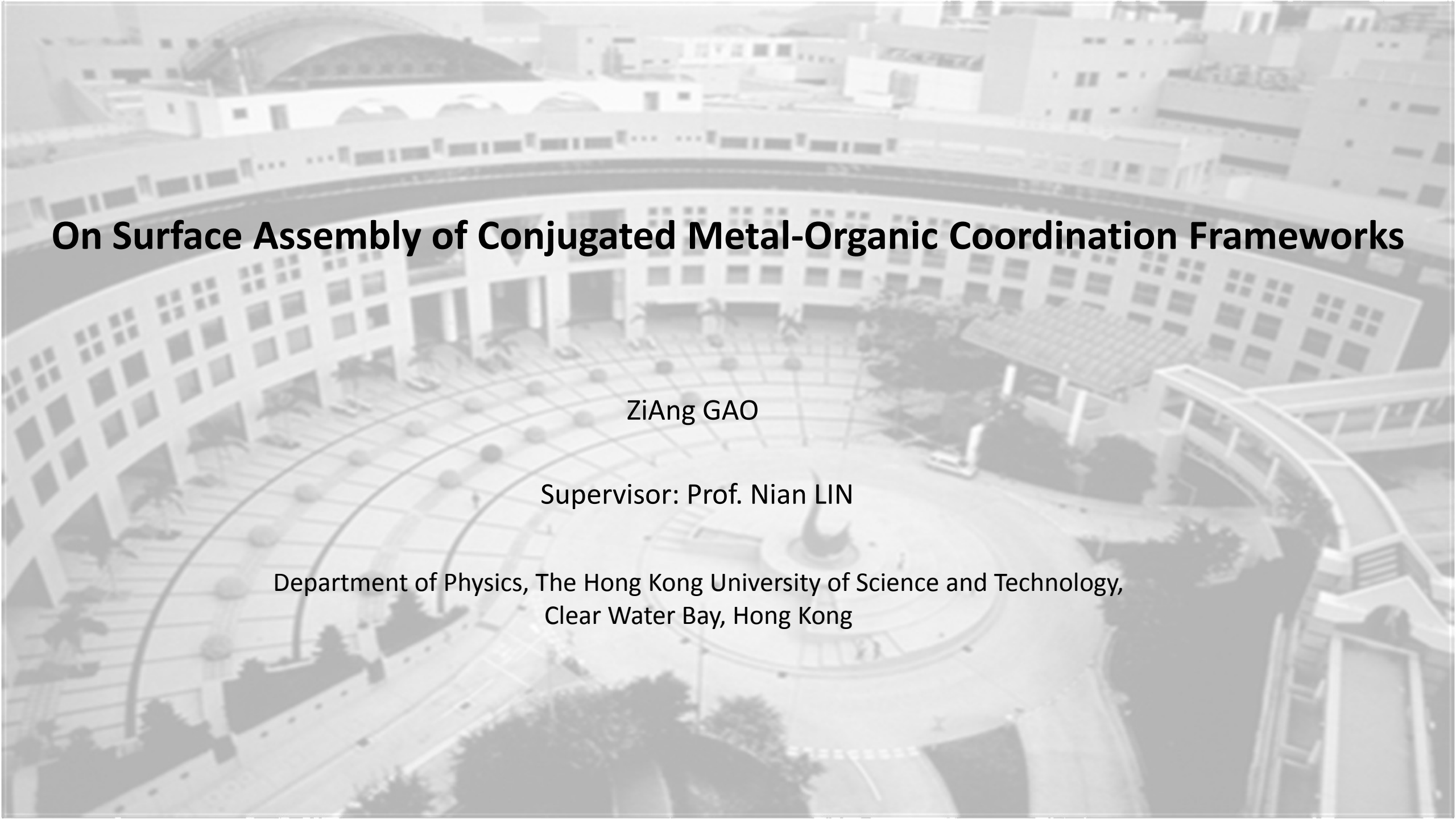

On Surface Assembly of Conjugated Metal-Organic Coordination Frameworks

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Clear Water Bay, Hong Kong

OUTLINE

Part 1 Introduction

- Self-assembly of 2D metal–organic coordination structures on surface
- 2D Organic Topological Insulators

Part 2 The coordination of Nickel, Palladium and Platinum with HATP on Ag(111)

- Experimental realization
- Conclusions

Part 3 Synthesis of $Ni_3(HITP)_2$ network with QSH effects on Au(111)

- Experimental realization
- Theoretical Results

OUTLINE

Part 4 Design and Synthesis of a Ferromagnetic Metal-Organic Framework, $Fe_3(HITP)_2$ with a Quantum Anomalous Hall Gap

- Theoretical Results
- Experimental realization
- Kondo effect

Part 5 Synthesis of $Ni_3(HAT)_2$, $Fe_3(HAT)_2$ network on Ag(111)

- Experimental realization
- Spin-flip

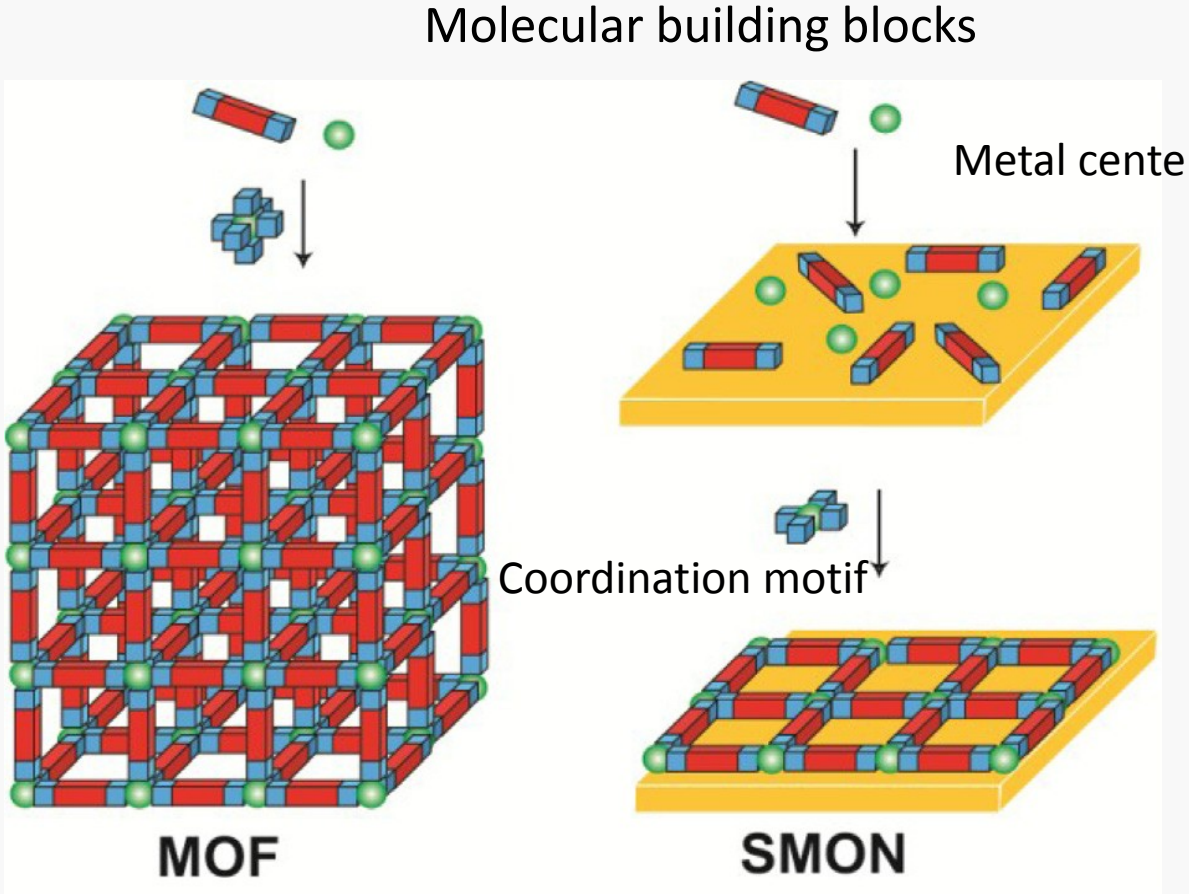
PART 01

Part 1 Introduction

- Self-assembly of 2D metal–organic coordination structures on surface
- 2D Organic Topological Insulator

From three-dimensional frameworks to two-dimensional networks

- Coordination chemistry
- Reversible, high directionality and selectivity.



Metal–Organic Frameworks (MOFs) **Surface-Confined Metal–Organic Networks (SMONs)**

Assembly protocol and mechanism of SMONs

Substrate:

Atomically flat, single crystals

Environment:

Ultra-high vacuum (UHV) reduces contaminations

solvent-free

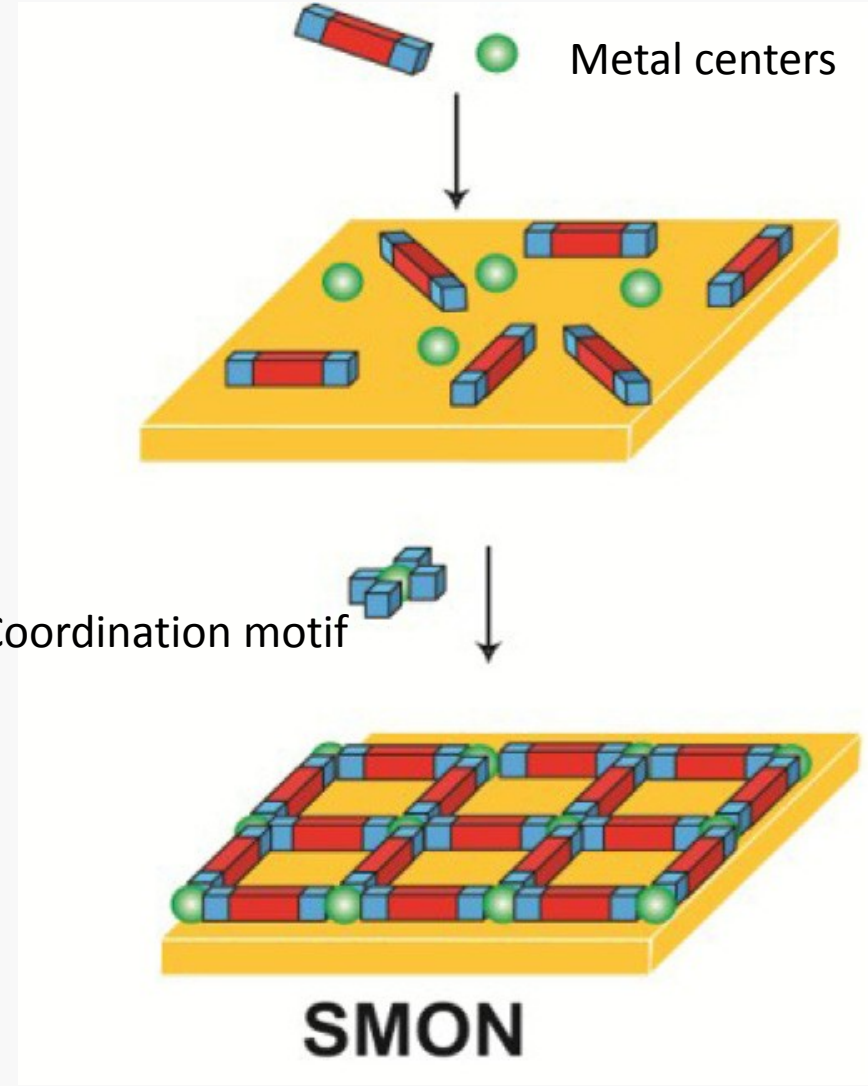
Parameters:

substrate temperature, evaporation rate or sequence,

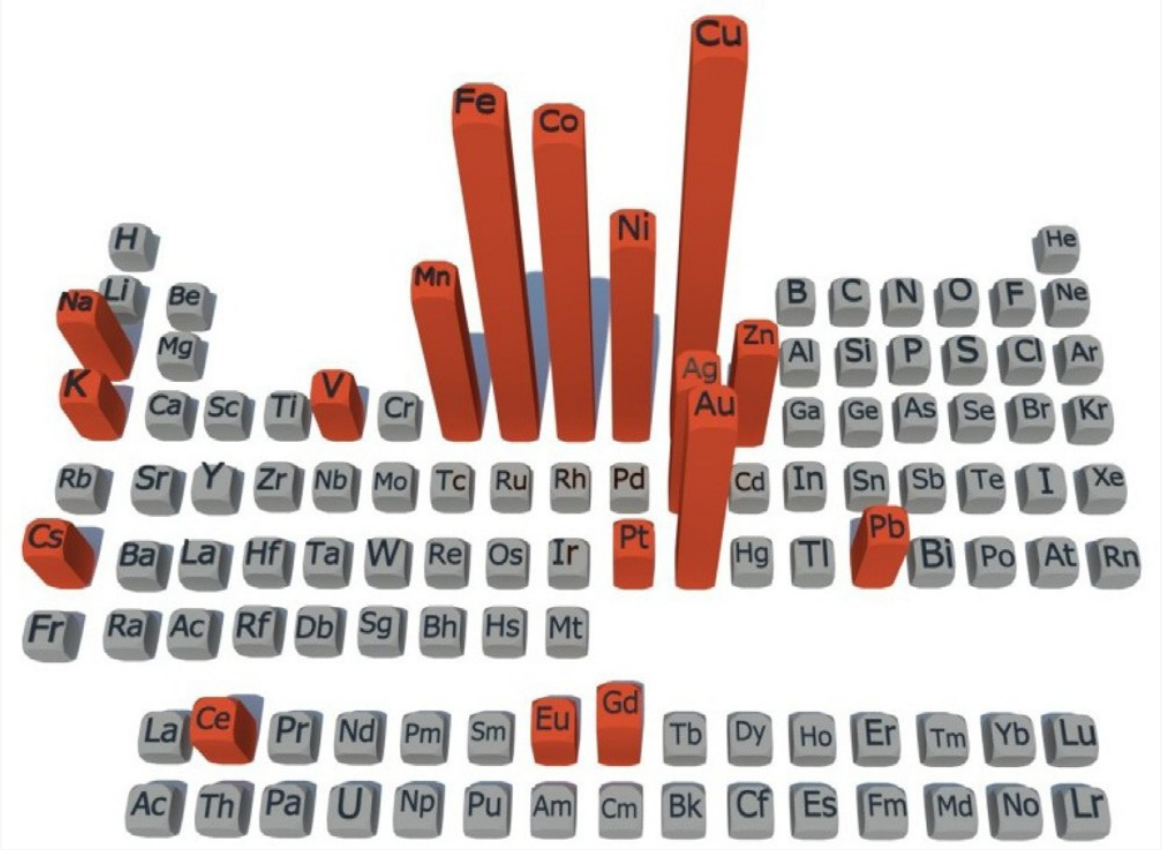
and surface concentrations of the adsorbates

Metal–molecule, inter-molecule and adsorbate–surface interactions to determine the structure of the SMONs

Molecular building blocks



Metal elements

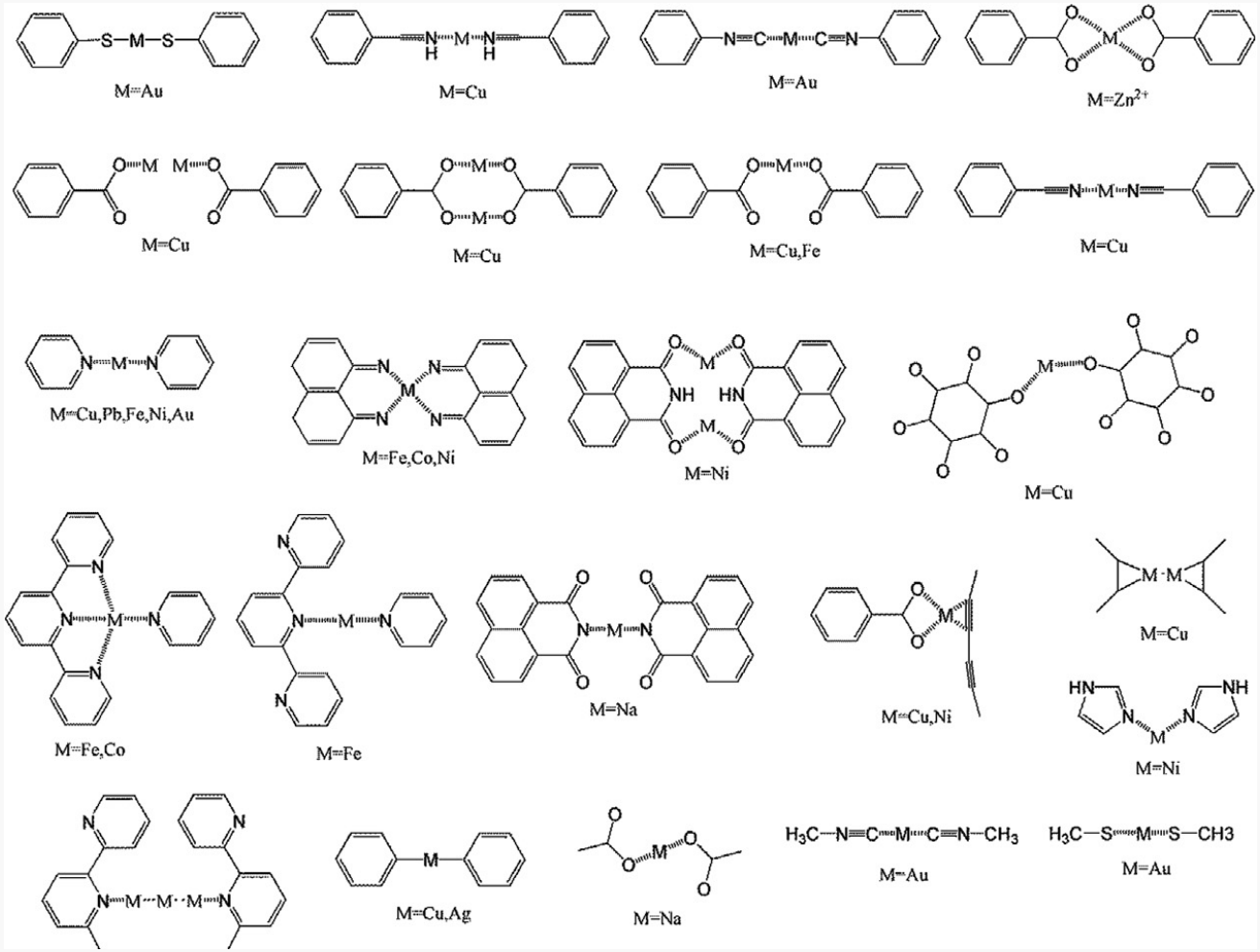


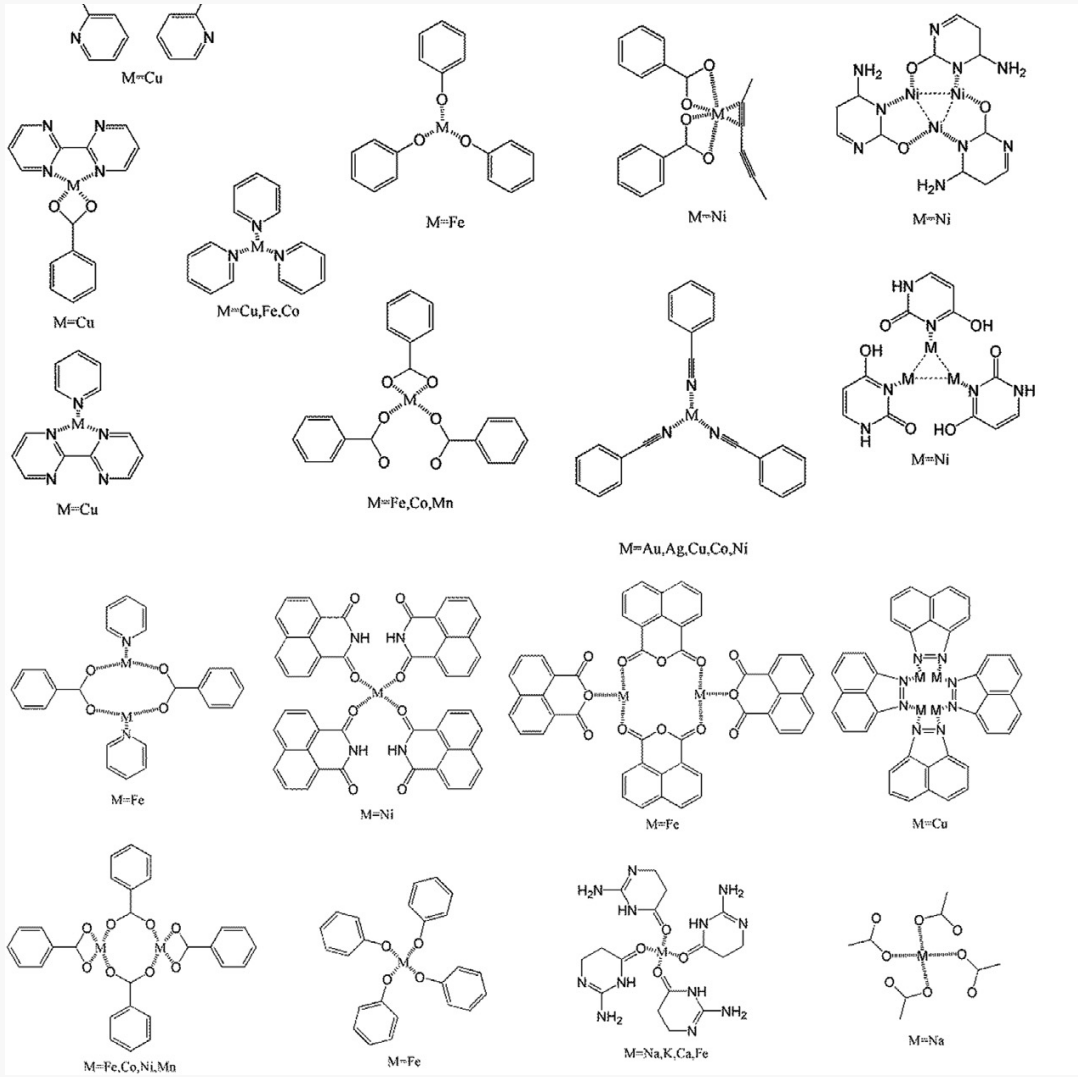
Metal elements used in SMONs.

The column heights indicate the number of SMON structures using this element.

Dong L, Gao Z A, Lin N. Progress in Surface Science, 2016, 91(3): 101-135.

Coordination motifs

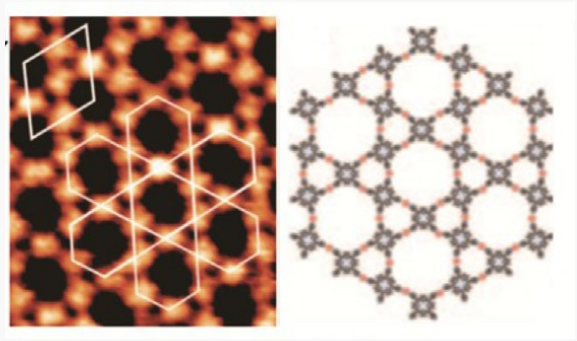




Different kinds of Coordination motifs

Dong L, Gao Z A, Lin N. Progress in Surface Science, 2016, 91(3): 101-135.

2D metal–organic coordination structures



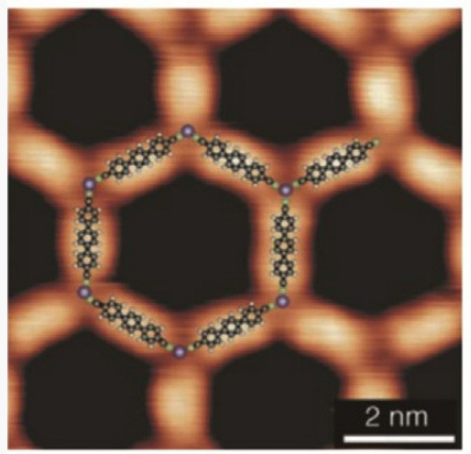
pyridyl and Au

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

SMONs

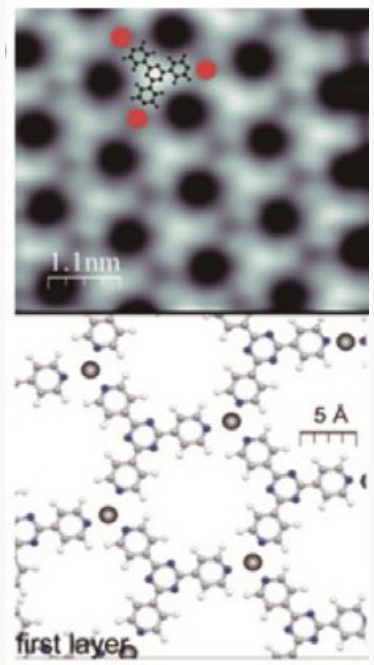
- Kagome lattices
- Hexagonal lattices
- Triangular lattices
- Square lattices
- Rectangular lattices

Co-$(CN)_3$



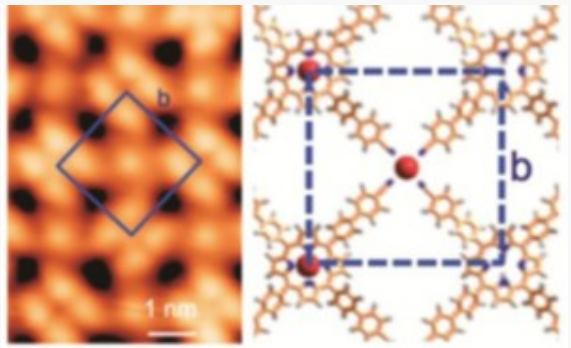
S. Stepanow, N. Lin, et al, Angew. Chem. 119 (2007) 724–727.

Fe-pyridyl$_3$



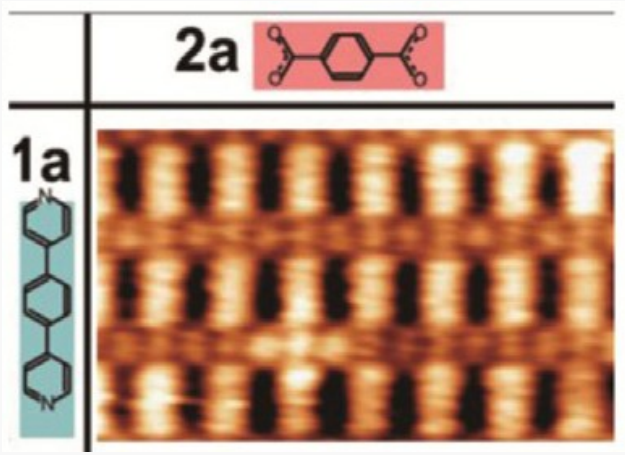
T.R. Umbach, et al, Phys. Rev. Lett. 109 (2012) 267207.

Co–CN_4

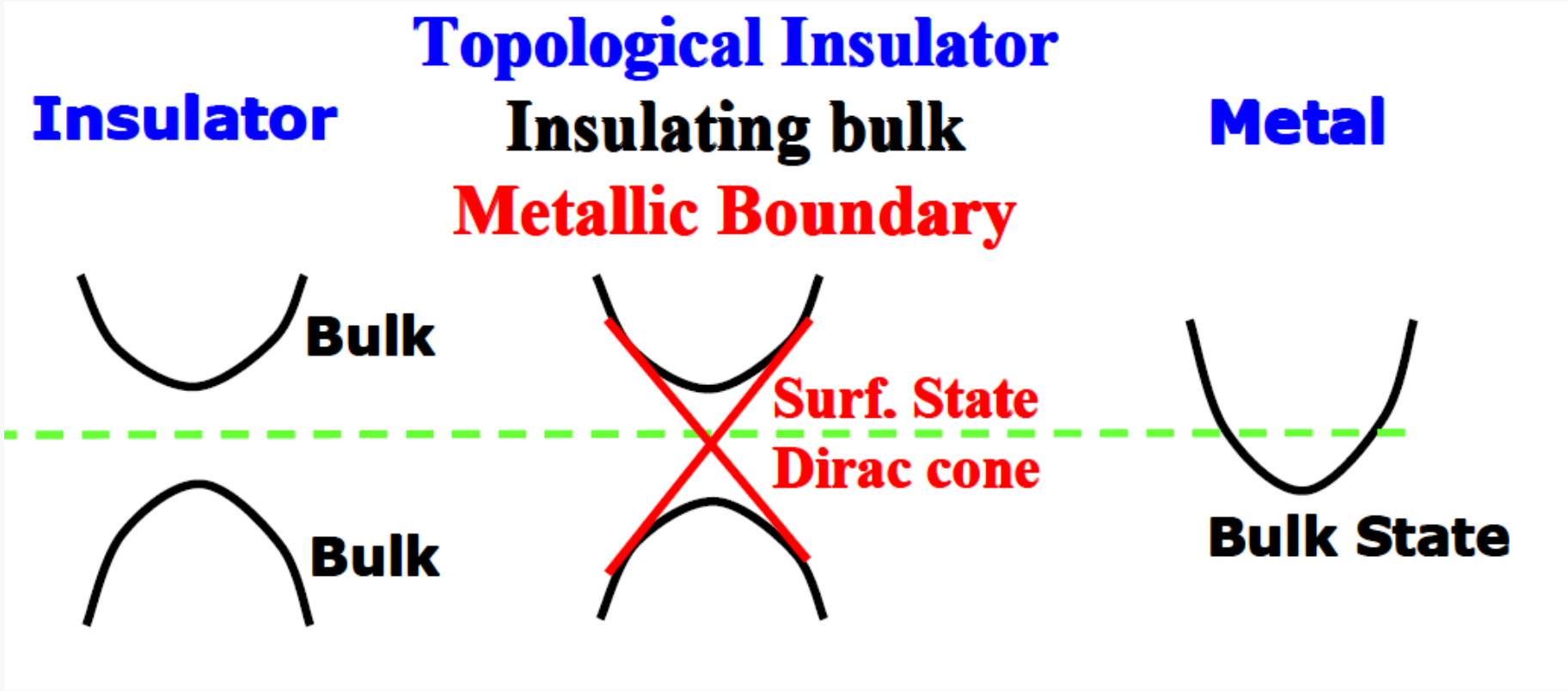


J.I. Urgel, et al, J. Am. Chem. Soc. 137 (2015) 2420–2423.

carboxylate and pyridyl with Fe



A. Langner, et al, PNAS 104 (2007) 17927–17930.

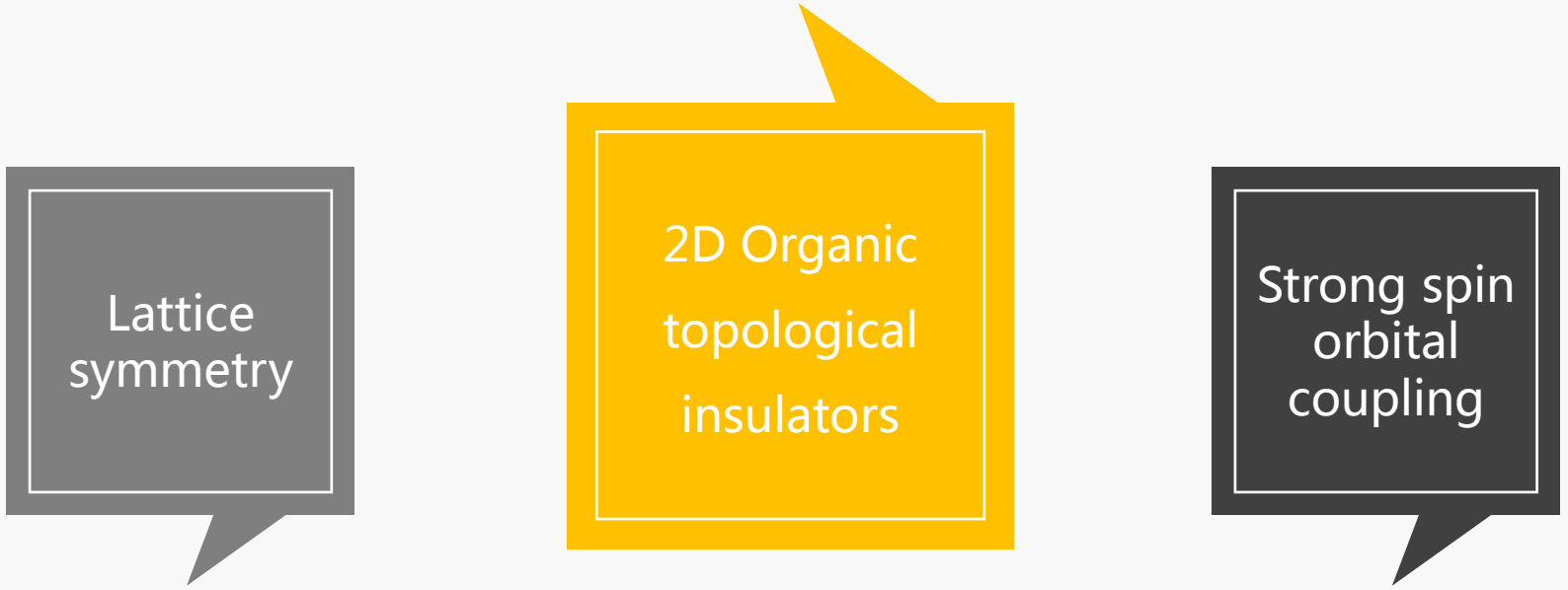


Nontrivial band structure topology

2D Organic Topological Insulator

To achieve 2D Organic topological insulators,

there are two key ingredients are essential.

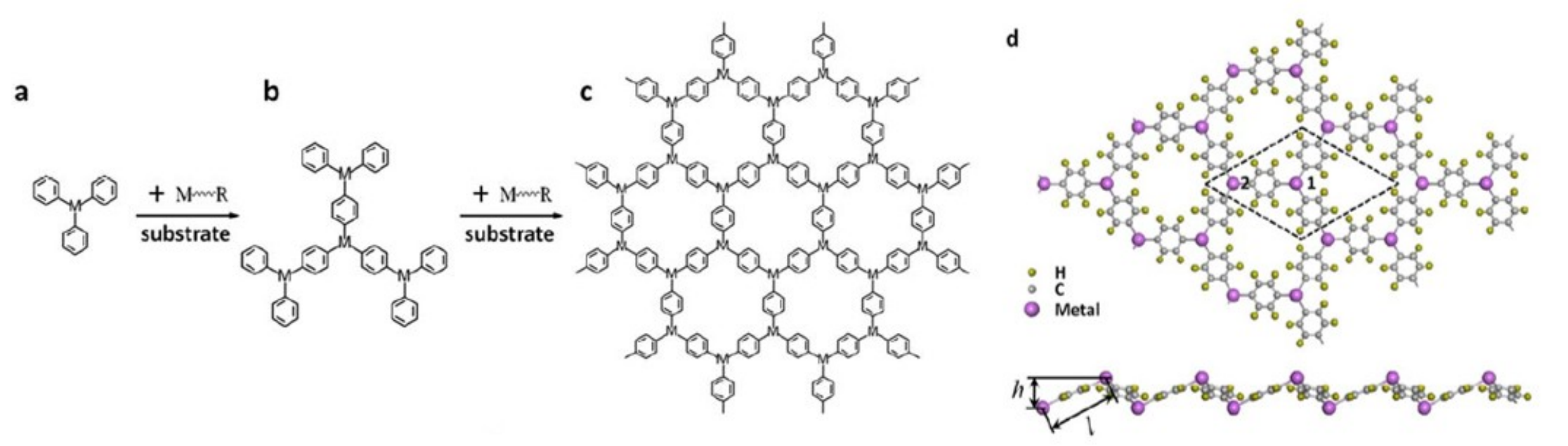


Hexagonal, Kagome lattice

Heavy metals contribute large gap

In general, organic counterparts of inorganic materials have the added advantages of **low cost**, **easy fabrication** and **mechanical flexibility**.

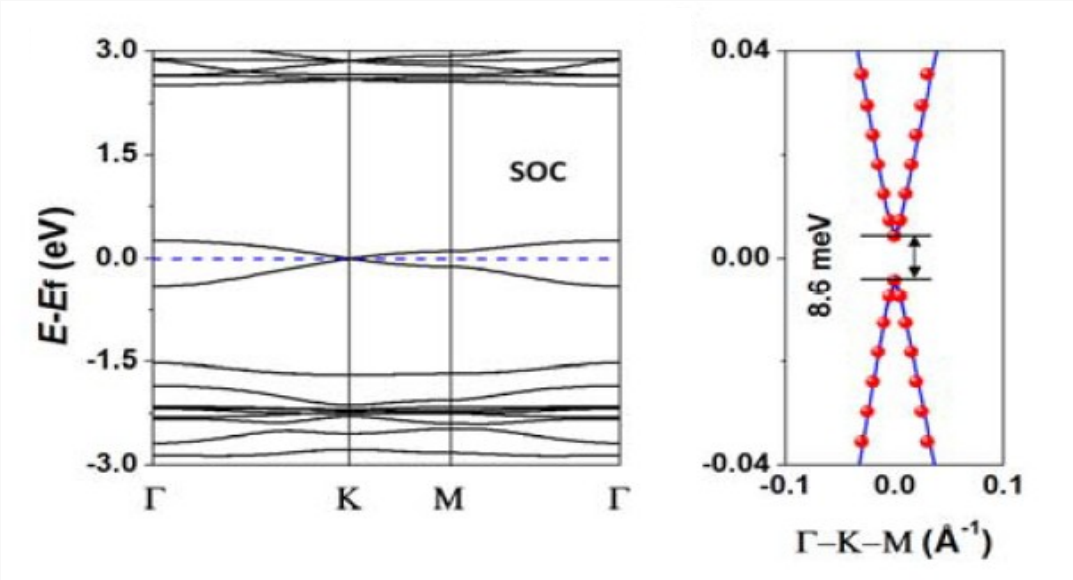
Hexagonal lattice

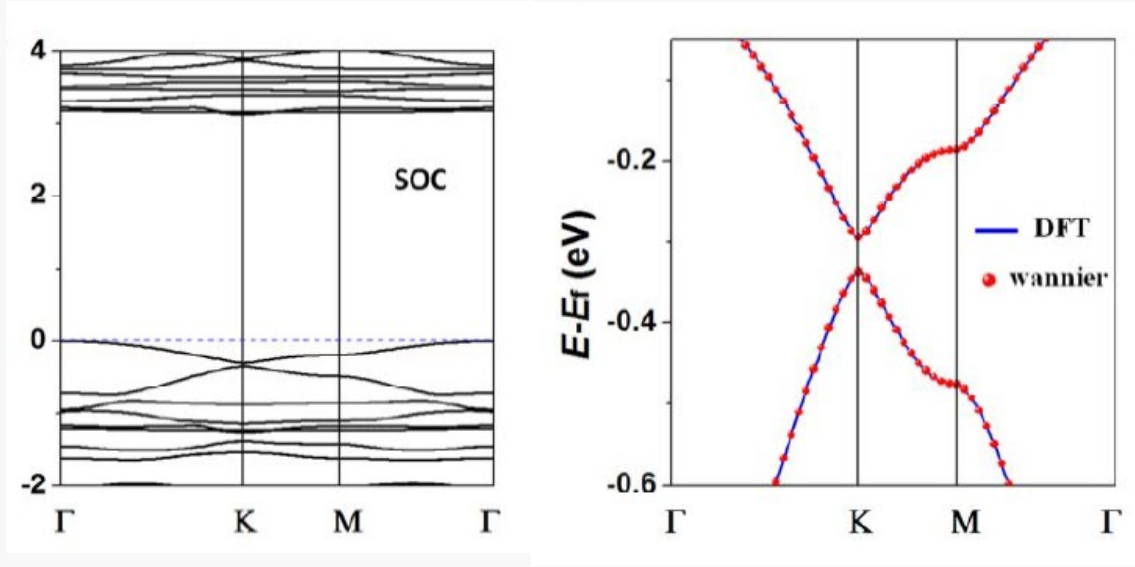


- **Spin Hall insulators, in organometallic lattices made of triphenyl-Pb [$Pb(C_6H_5)_3$] and triphenyl-Bi [$Bi(C_6H_5)_3$] molecules.**

Z. F. Wang, Z. Liu, and F. Liu, Nat. Commun. **4**, 1471 (2013).

Hexagonal lattice



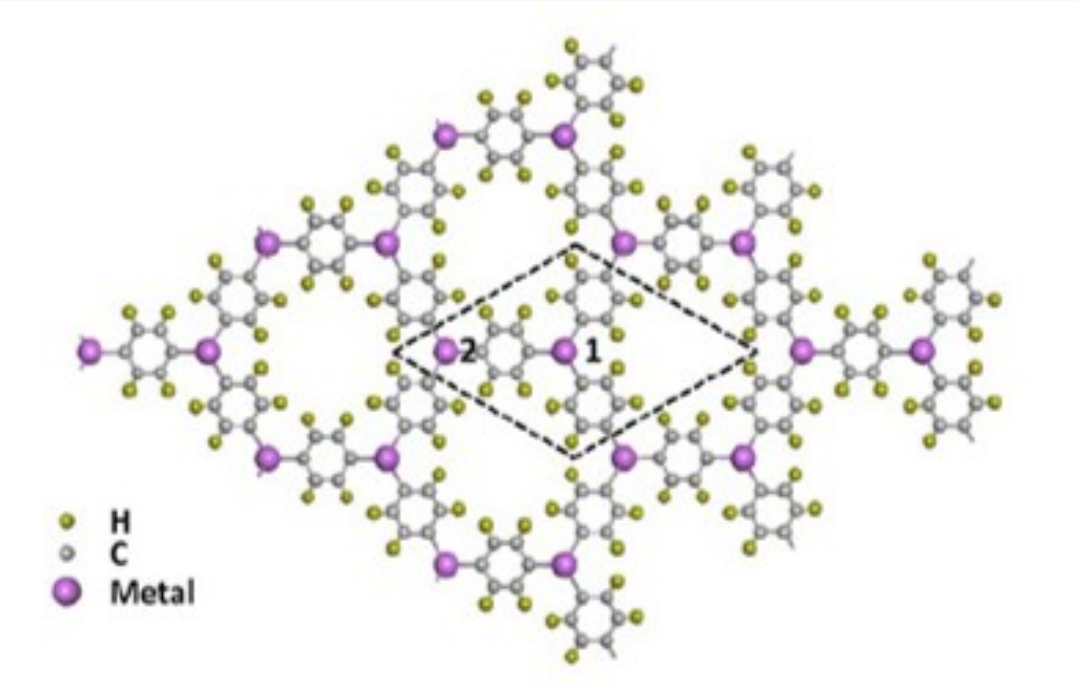


- The electronic band structure of triphenyl-Pb lattice displays a Dirac cone with a ~8.6 meV gap opens at the K point.

- The electronic band structure of triphenyl-Bi lattice displays a gap as large as ~43 meV .
  Fermi level is ~0.31 eV above the Dirac point

Z. F. Wang, Z. Liu, and F. Liu, Nat. Commun. **4**, 1471 (2013).

Hexagonal lattice



Hard to be realized

Pb	Mn	In
Quantum Spin Hall effect (QSH)	Quantum Anomalous Hall effect (QAH)	Flat Chern-band , ferromagnetism
~8.6 meV	~43 meV below Femi-level	

Z. F. Wang, Z. Liu, and F. Liu, Phys. Rev. Lett. **110**, 196801 (2013).
Z. Liu, Z. F. Wang, J. W. Mei, Y. S. Wu, and F. Liu, Phys. Rev. Lett. **110**, 106804 (2013).

Kagome lattice

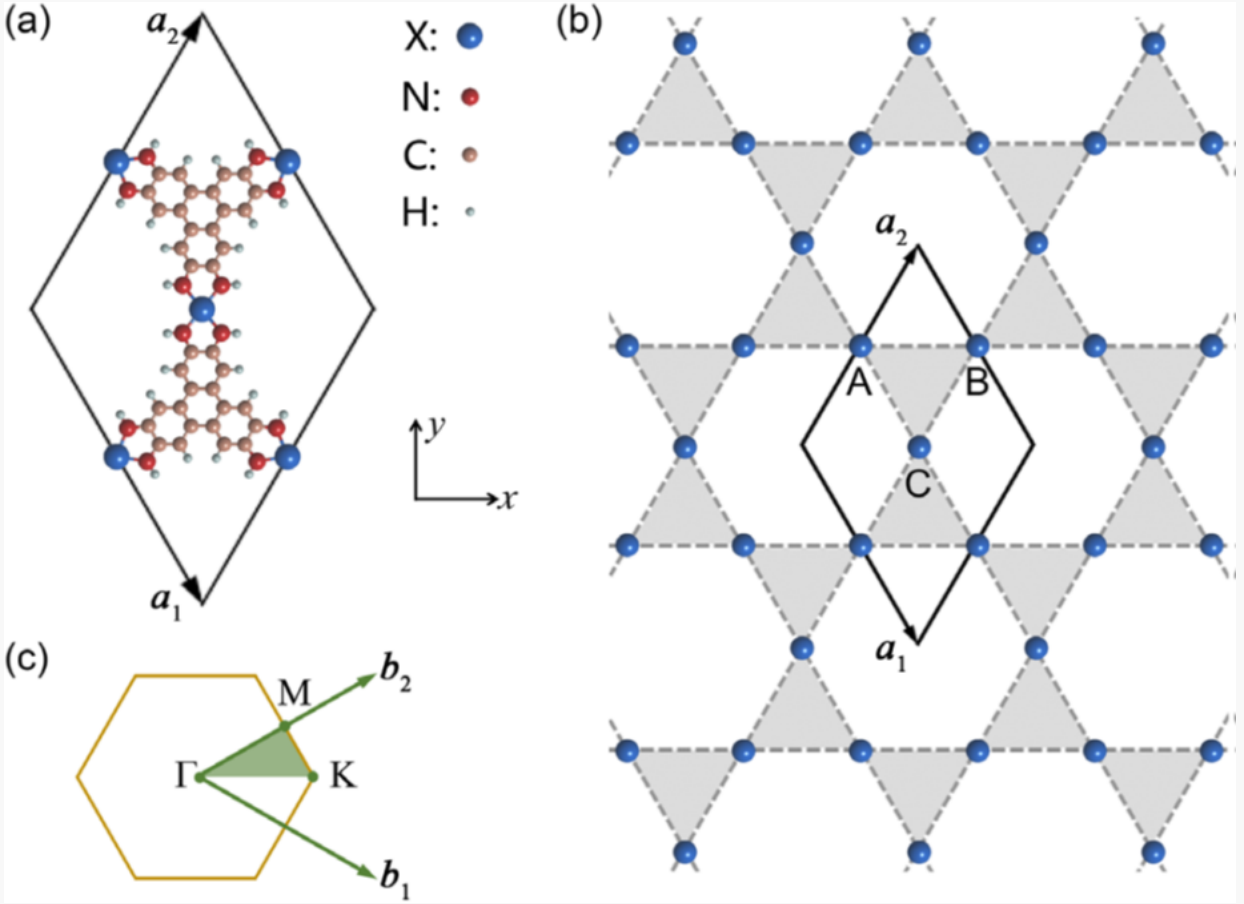
- The molecular linker consists of four benzene rings in triangle shape with six functional groups –NH_2, -OH, or –SH .

QAH： $Ta_3(C_{18}H_{12}O_6)_2$

$Ir_3(C_{18}H_{12}N_3O_3)_2$

$Pt_3(C_{18}H_{12}S_6)_2$

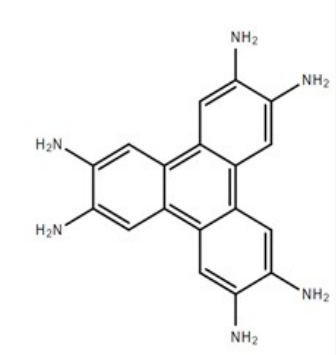
QSH： $Ni_3(C_{18}H_{12}N_6)_2$



L. Dong, Y. Kim, D. Er, A. M. Rappe, and V. B. Shenoy, Phys. Rev. Lett. **116**, 096601 (2016).
B. Zhao, J. Zhang, W. Feng, Y. Yao, and Z. Yang, Phys. Rev. B **90**, 201403 (2014).
X. Zhang, Z. Wang, M. Zhao, and F. Liu, Phys. Rev. B **93**, 165401 (2016).

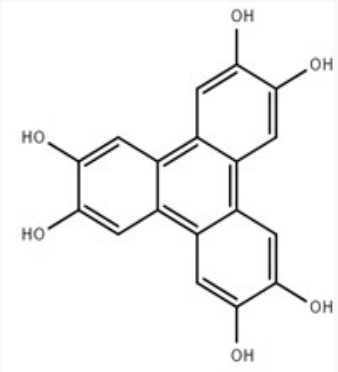
My work

HATP



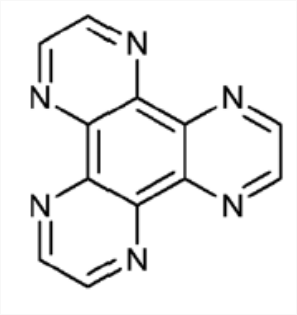
	Au (111)	Cu (111)	Ag (111)
Bare surface	Gas phase	Isolated molecules	Trimer honeycomb structure
Ni	Kagome structures	Isolated molecules	Kagome structures
Pt	Disordered structure	Isolated molecules	Disordered coordination structures
Pd	Disordered structure	Isolated molecules	Disordered coordination structures
Fe	Kagome structures		

HHTP



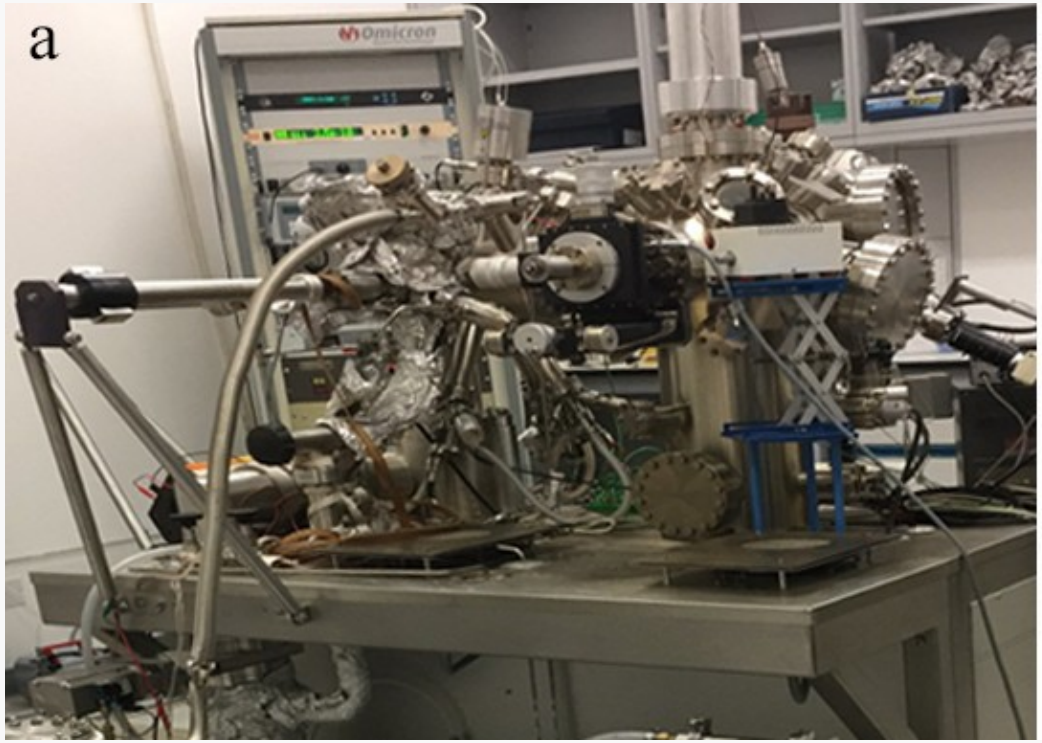
	Au (111)	Cu (111)	Ag (111)
Bare surface	Gas phase	Isolated molecules	Hydrogen bond, Triangle and Honeycomb networks
Ni	Close packed structure		
Cu	Close packed structure		
Pt	Close packed structure		Hydrogen bond structure
Pd	Close packed structure		Hydrogen bond structure
Fe	Close packed structure		Hydrogen bond disordered structure

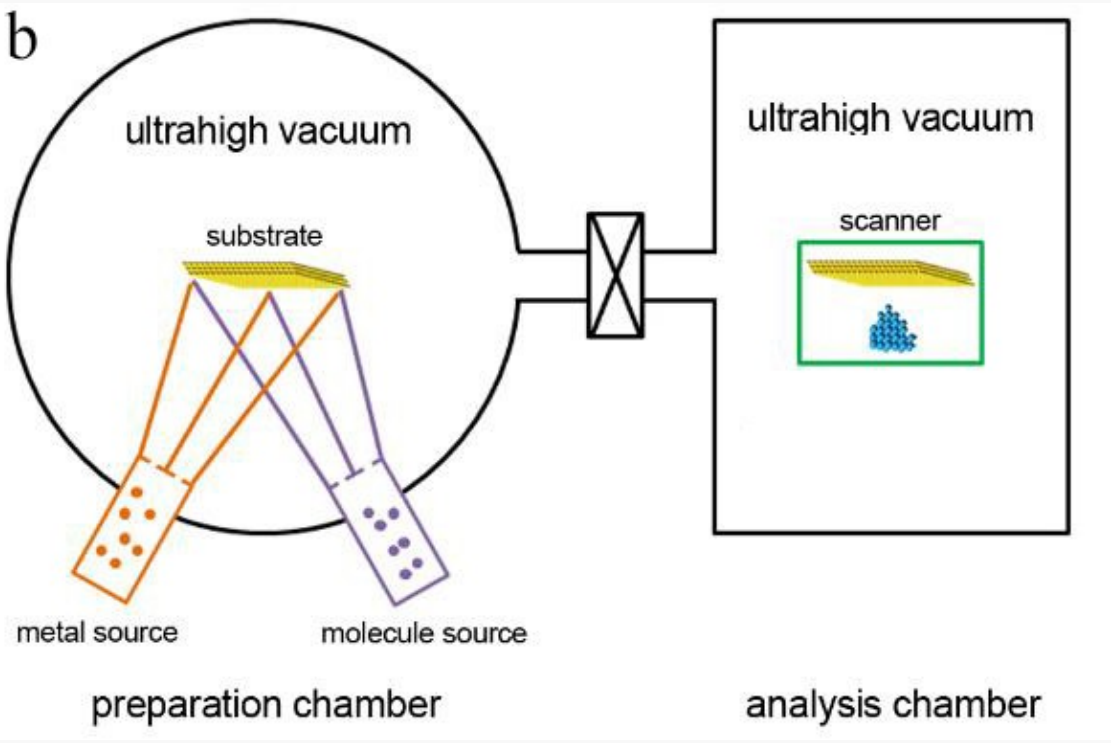
HAT



	Cu (111)	Ag (111)
Bare surface	Kagome structures	Hydrogen bond structures
Ni		Kagome structures
Fe		Kagome structures

Scanning Tunneling Spectroscopy (STM)





(a) An overview of STM equipment (Omicron nanotechnology).

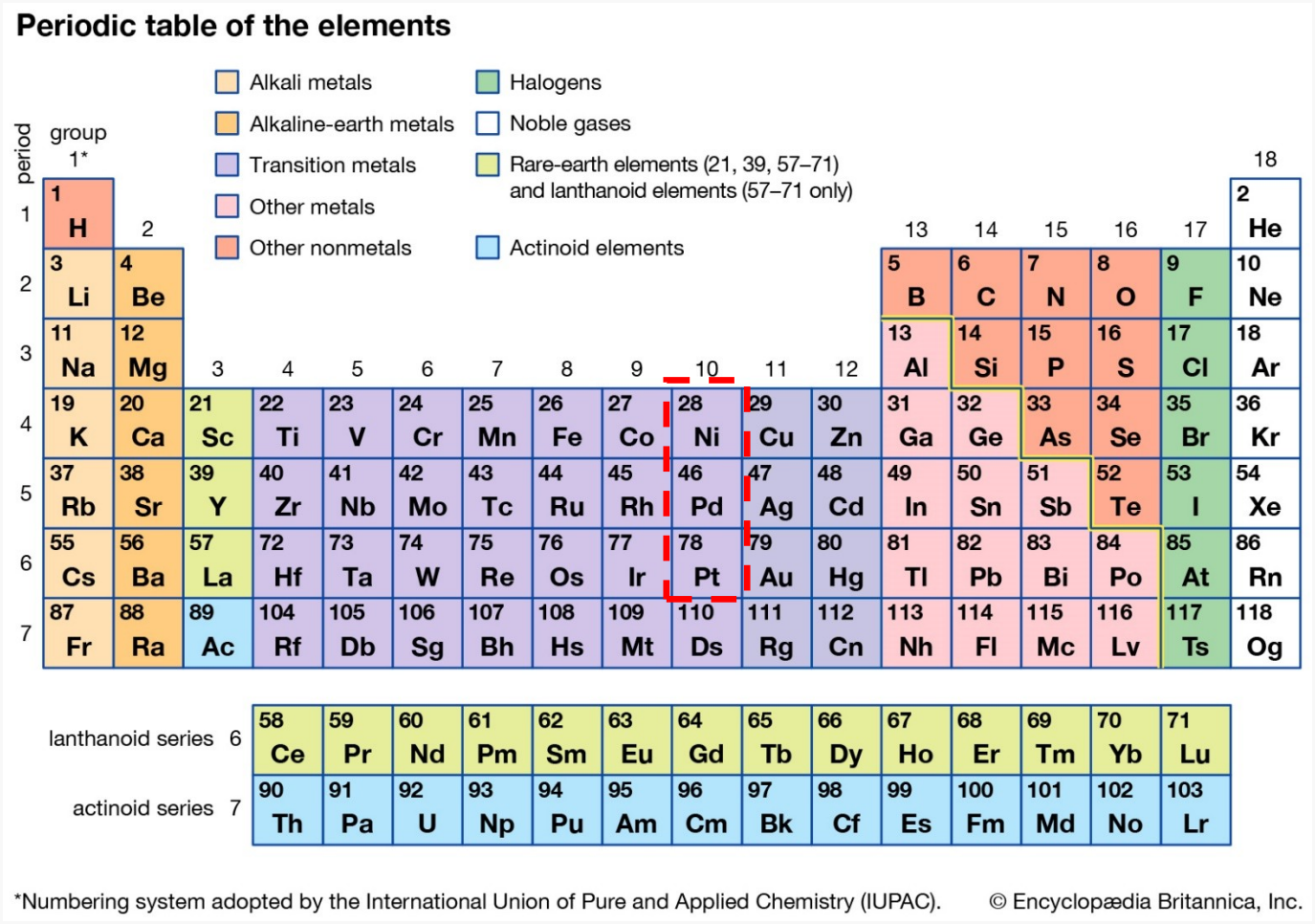
(b) A schematic diagram of this system: preparation chamber and analysis chamber

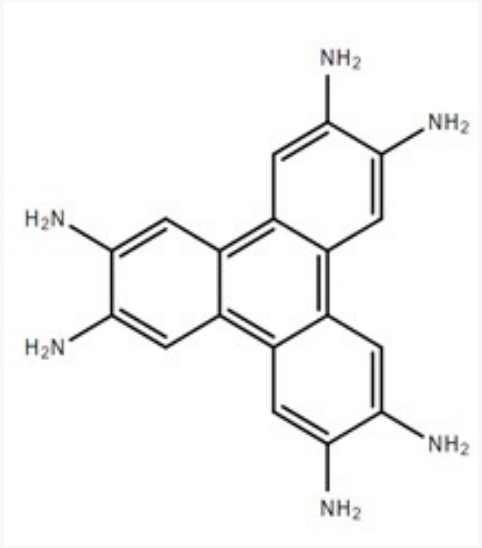
PART 02

Part 2 The coordination of Nickel, Palladium and Platinum with HATP on Ag(111)

- Experimental methods
- Results and discussion
- Conclusion

Experimental methods





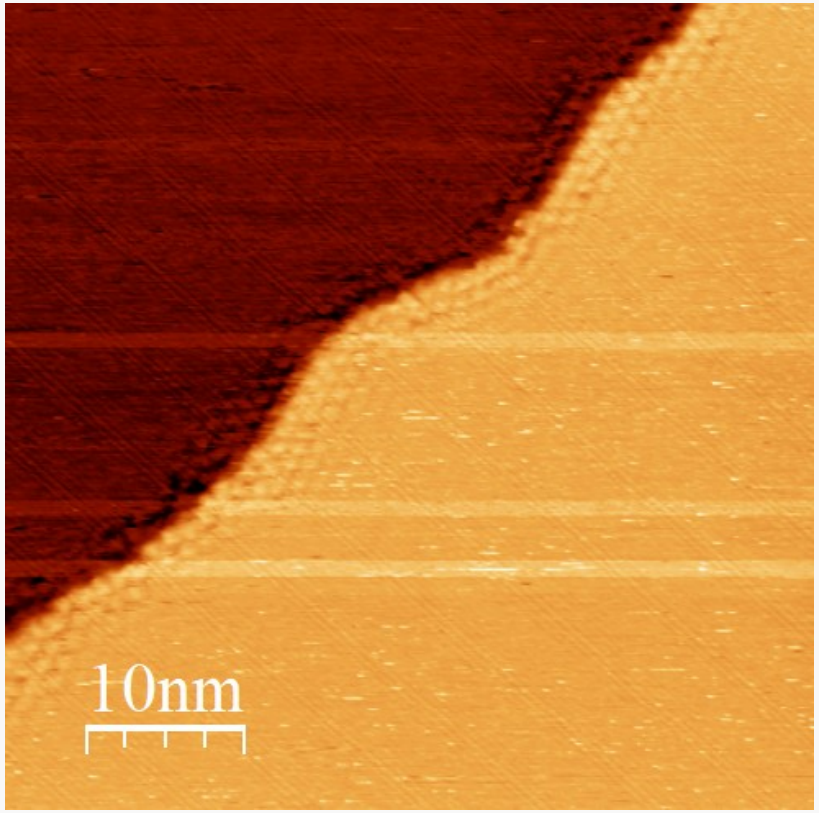
Chemical structures :

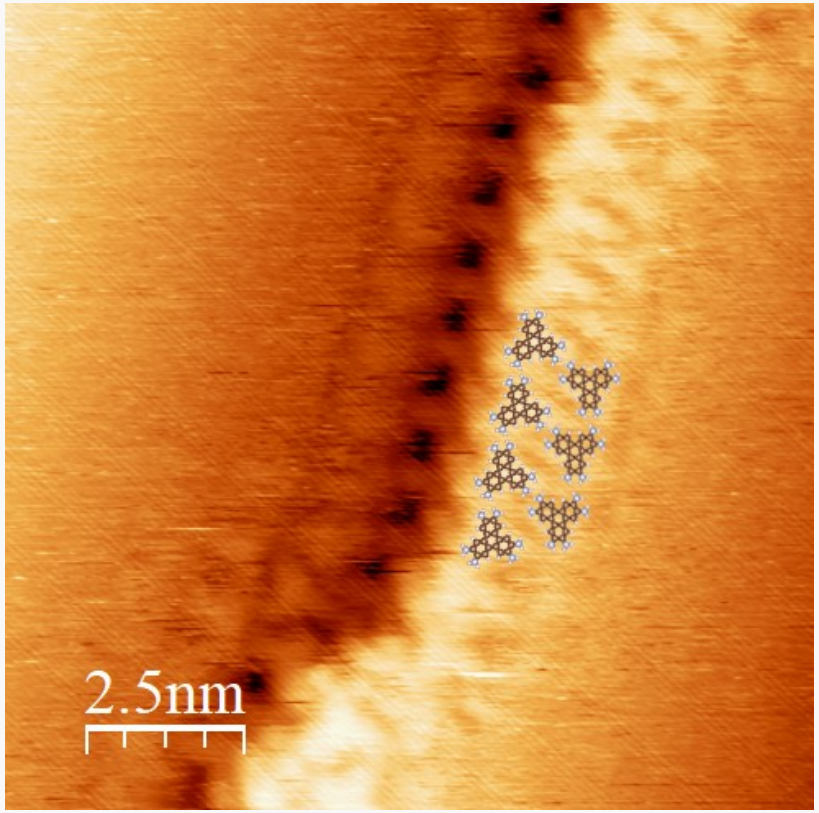
2,3,6,7,10,11-Hexaaminotriphenylene (HATP)

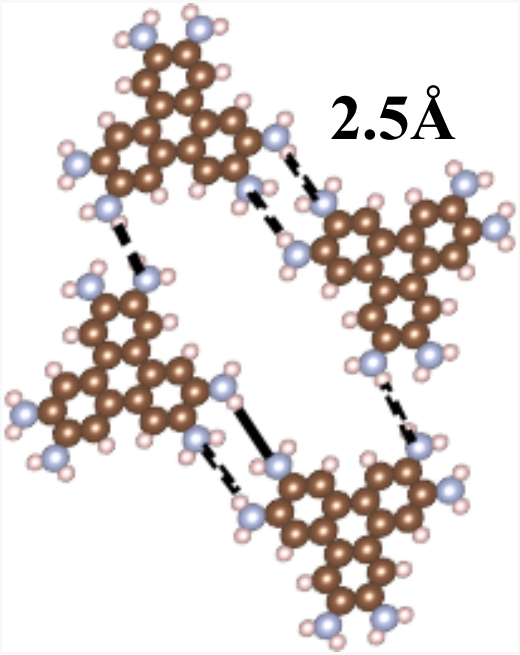
- UHV-STM;
- @RT;
- Ag(111);

https://www.britannica.com/science/periodic-table

HATP molecules

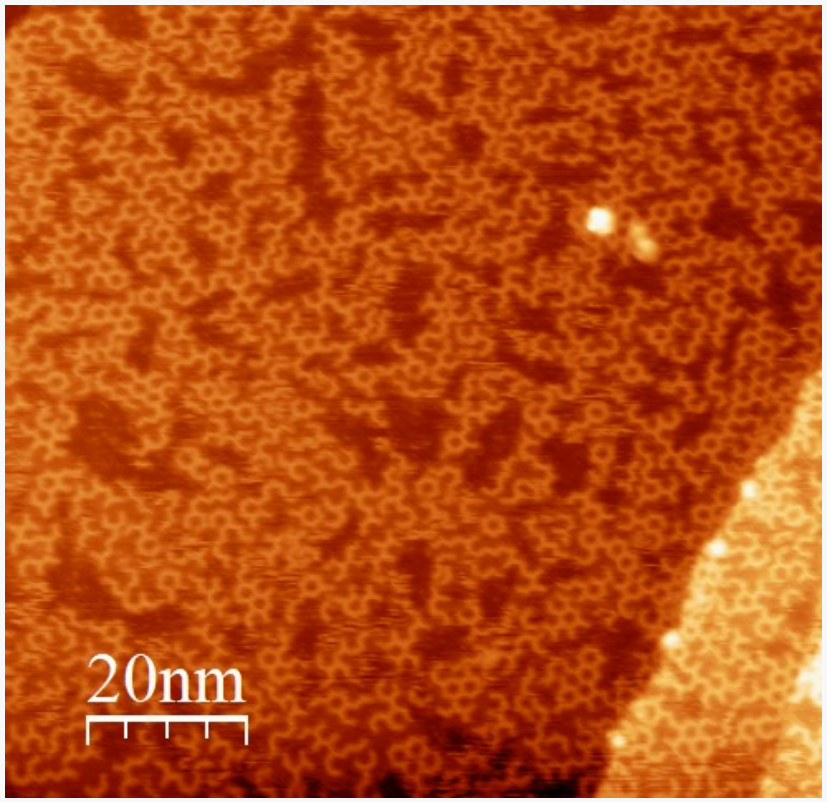


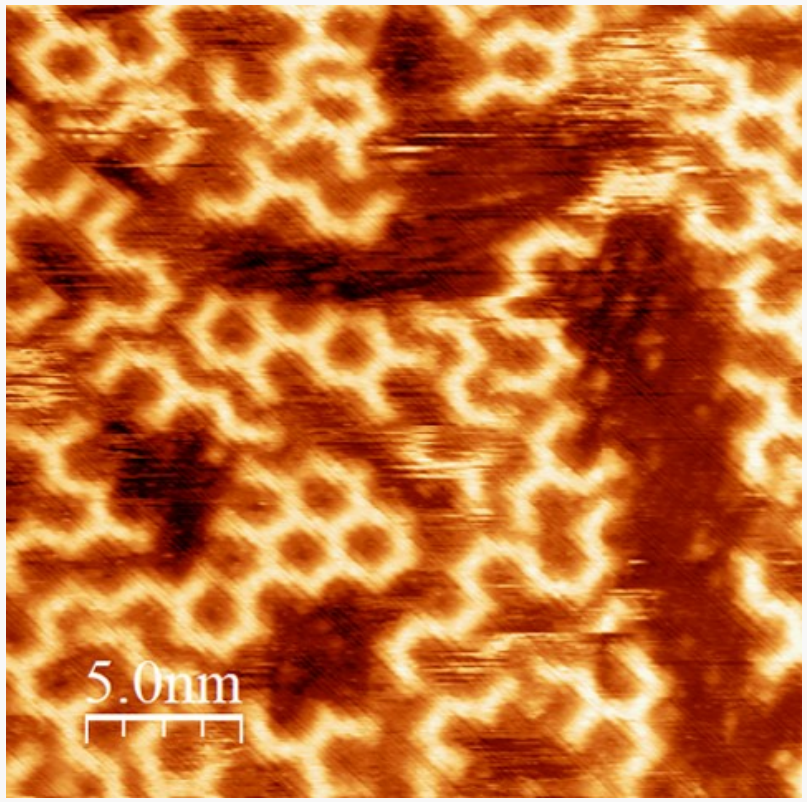


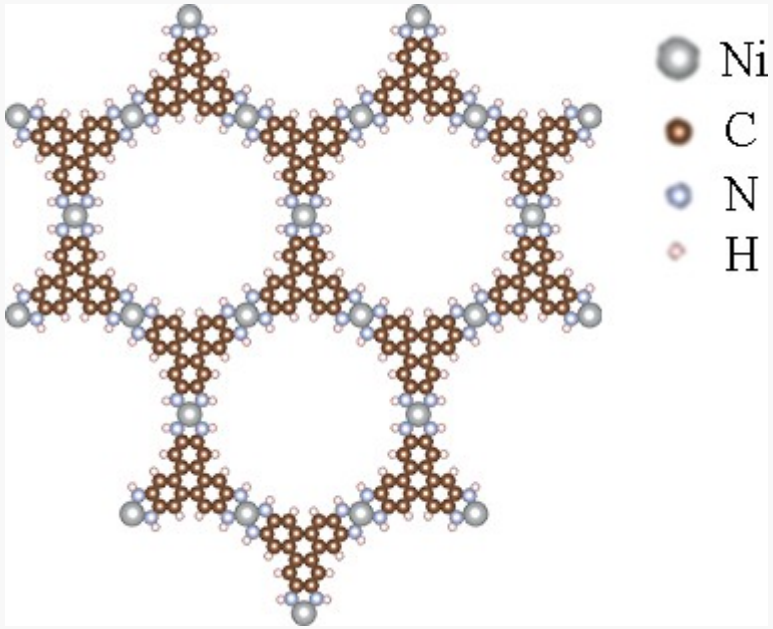


Only Deposit HATP molecules onto Ag(111) surface after annealing to 150℃

Ni







Hexagonal rings, Linked polymers

2,3,6,7,10,11-hexaiminotriphenylene (HITP)

Deposit HATP molecules and Ni onto Ag(111) surface after annealing to 250℃.

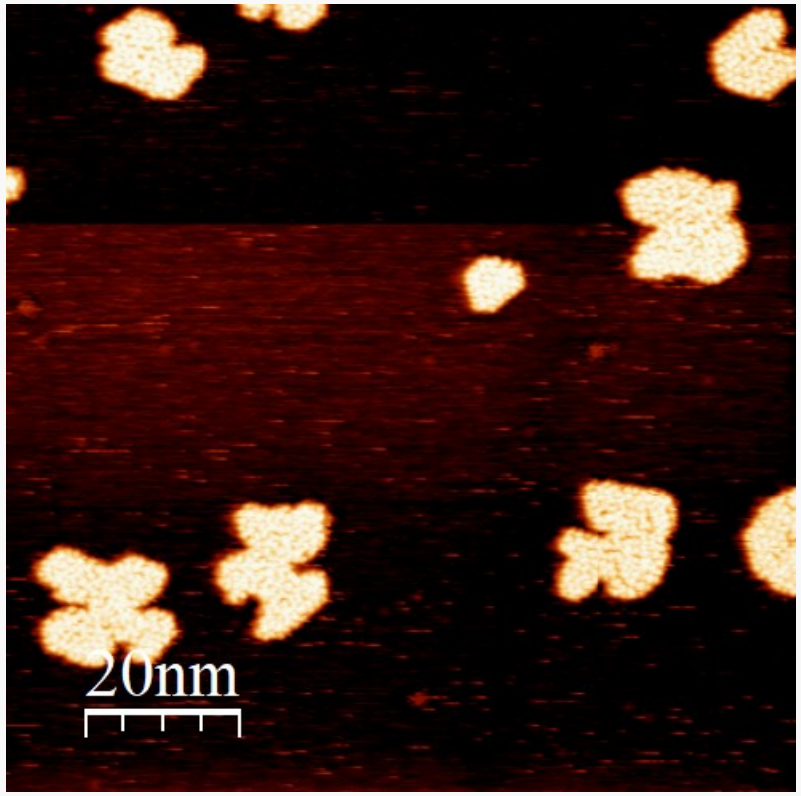
Honeycomb networks

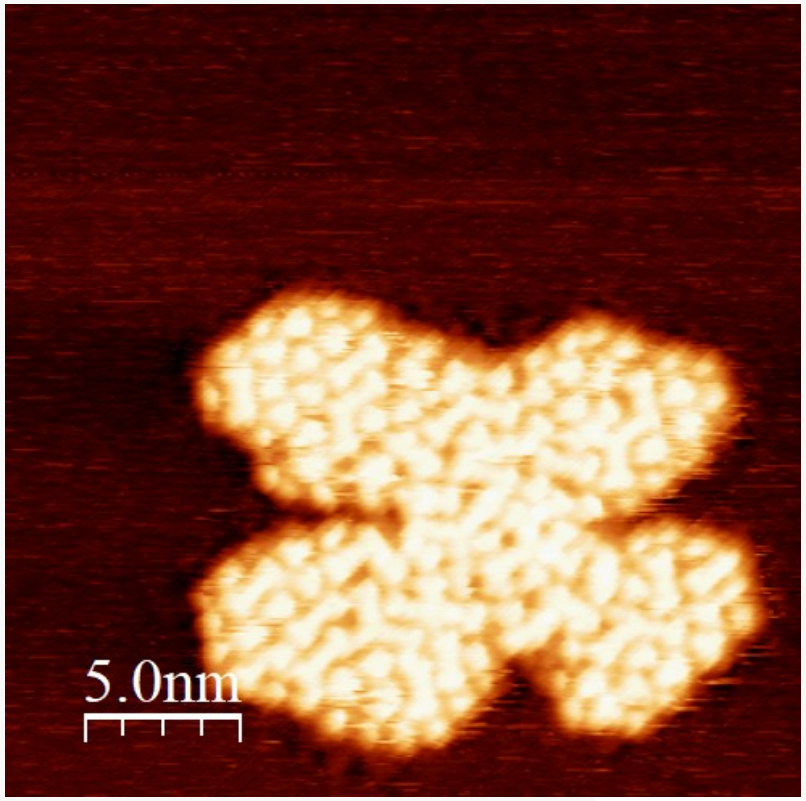
Lattice constant: 23Å

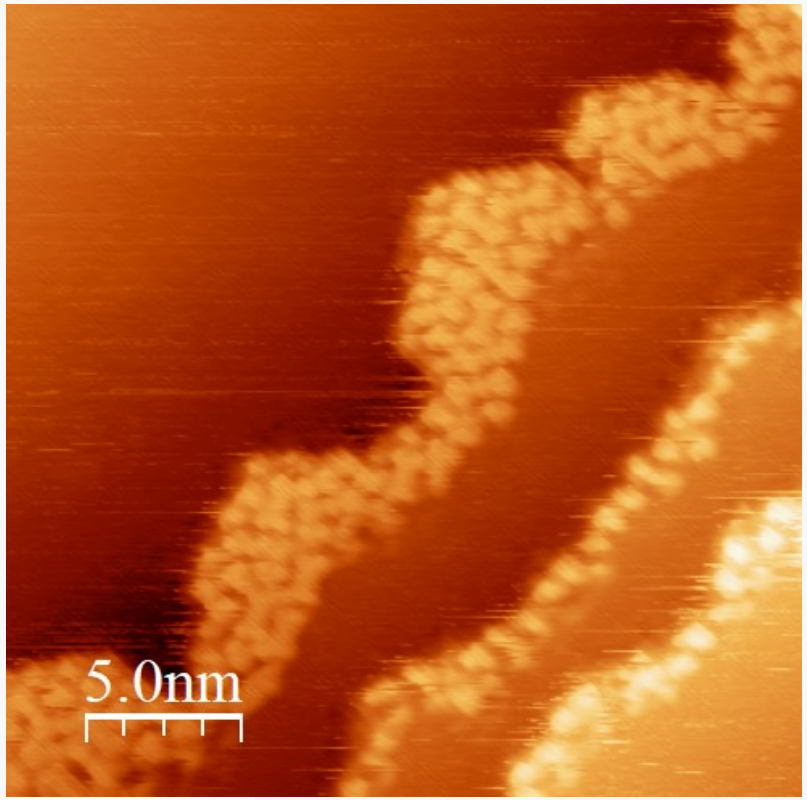
$Ni_3(HITP)_2$ network

Results and discussion

Pd



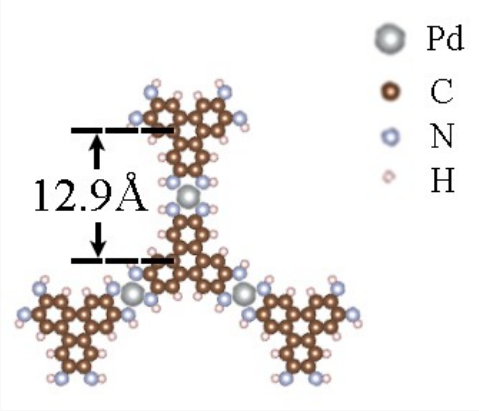




Deposit HATP molecules and Pd on Ag(111) surface at RT.

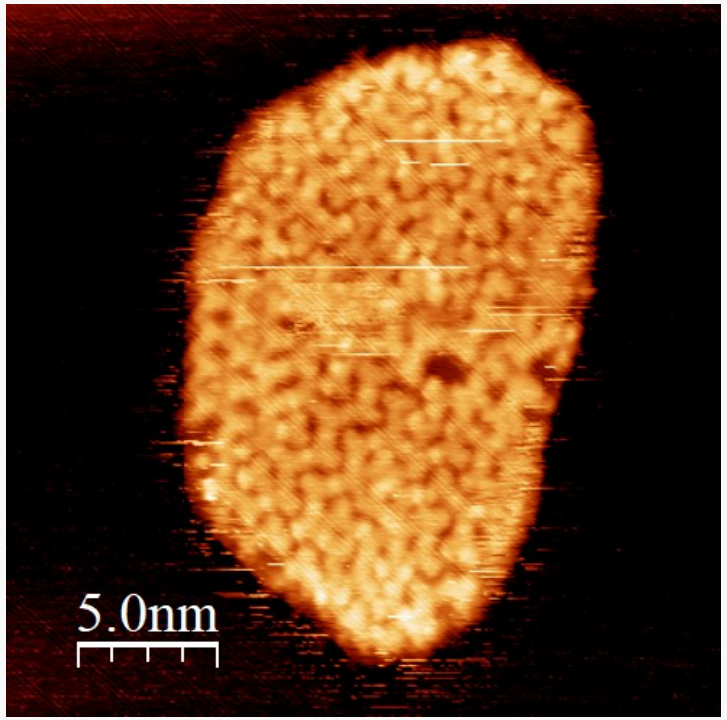
Flower lobes like Pd island

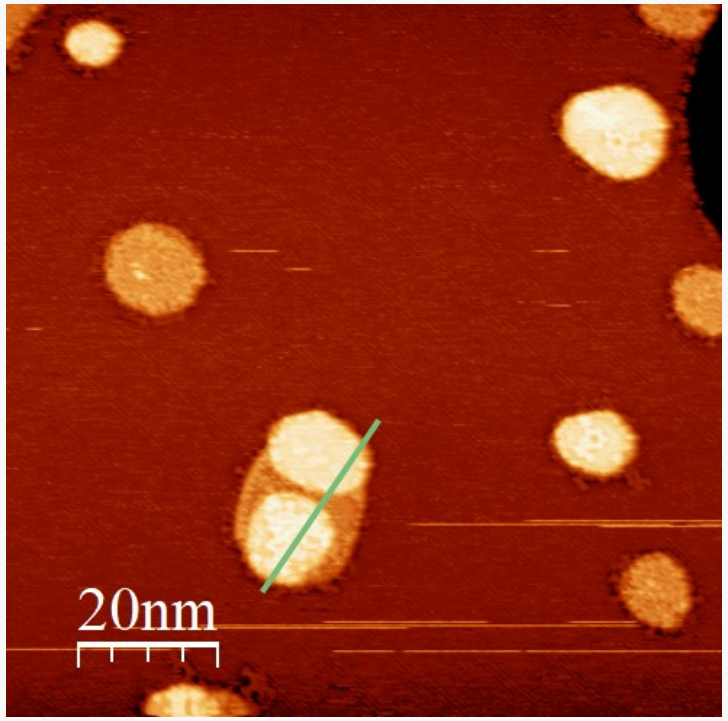
Linked polymers on Pd island

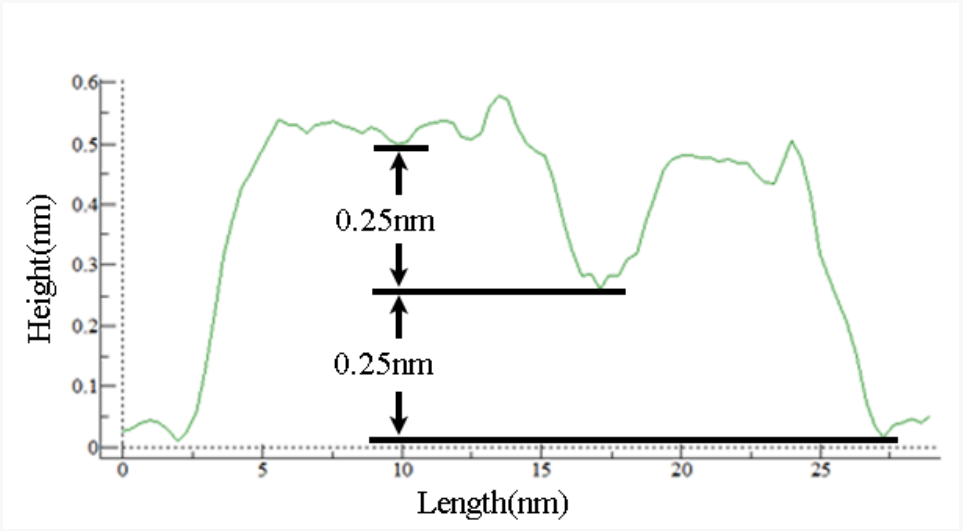


Results and discussion

Pd







Pd island turns into bilayer

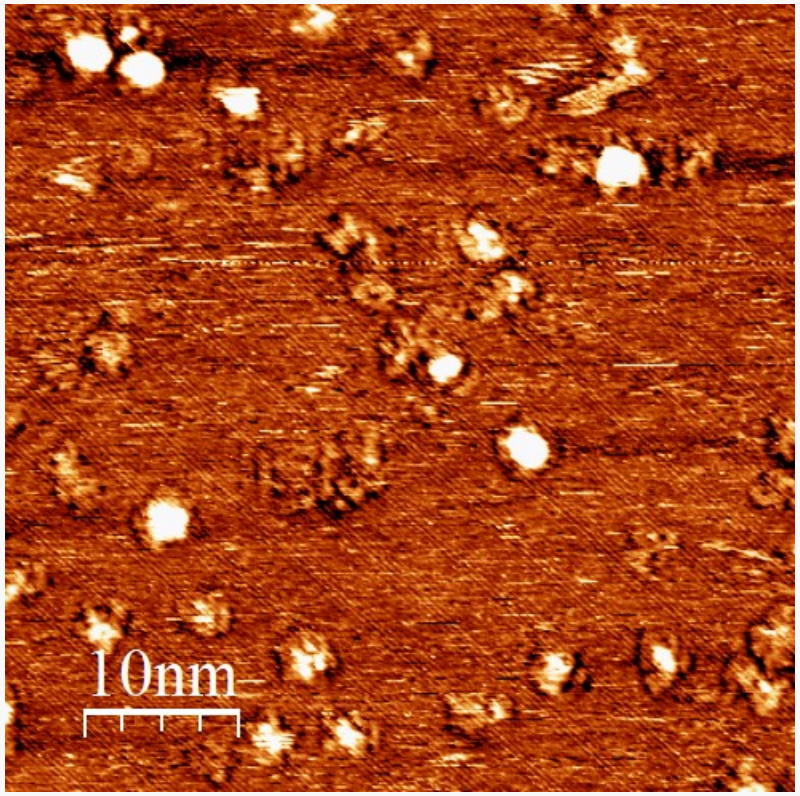
Annealing to 100 ℃.

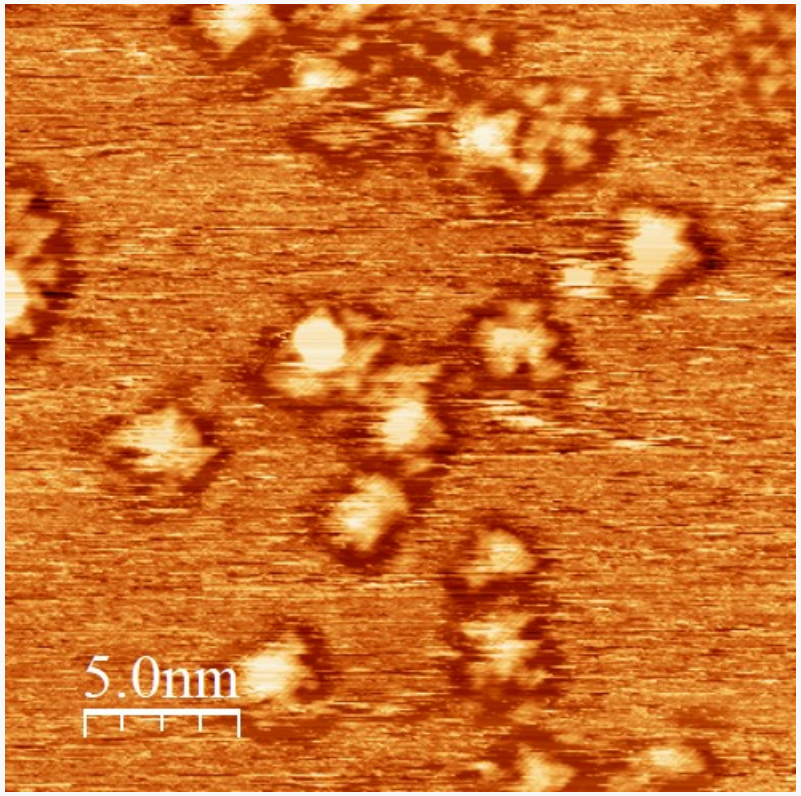
Round shape island

Annealing to 200 ℃.

Results and discussion

Pt

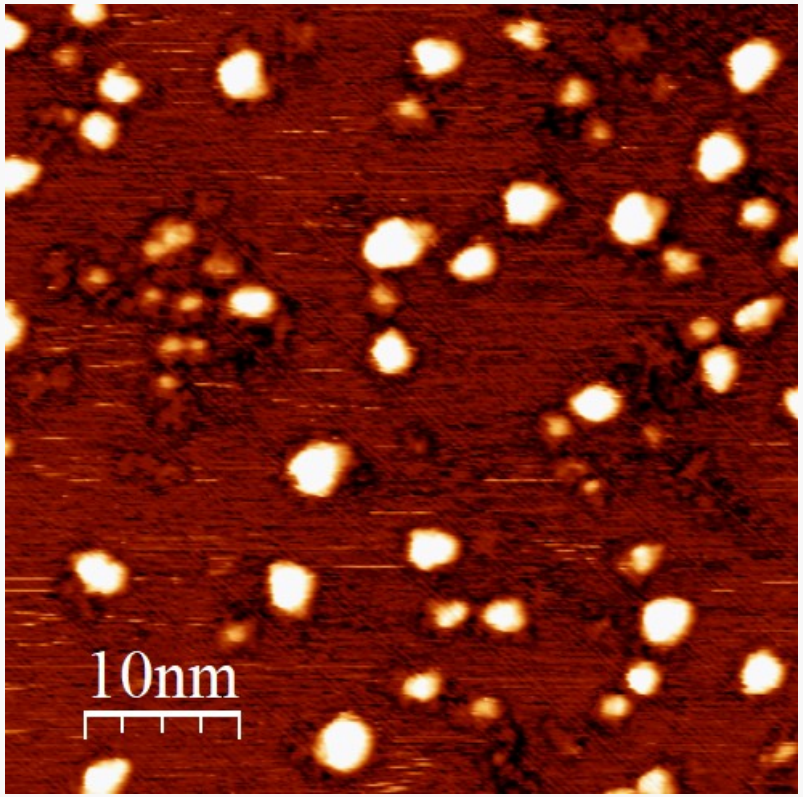


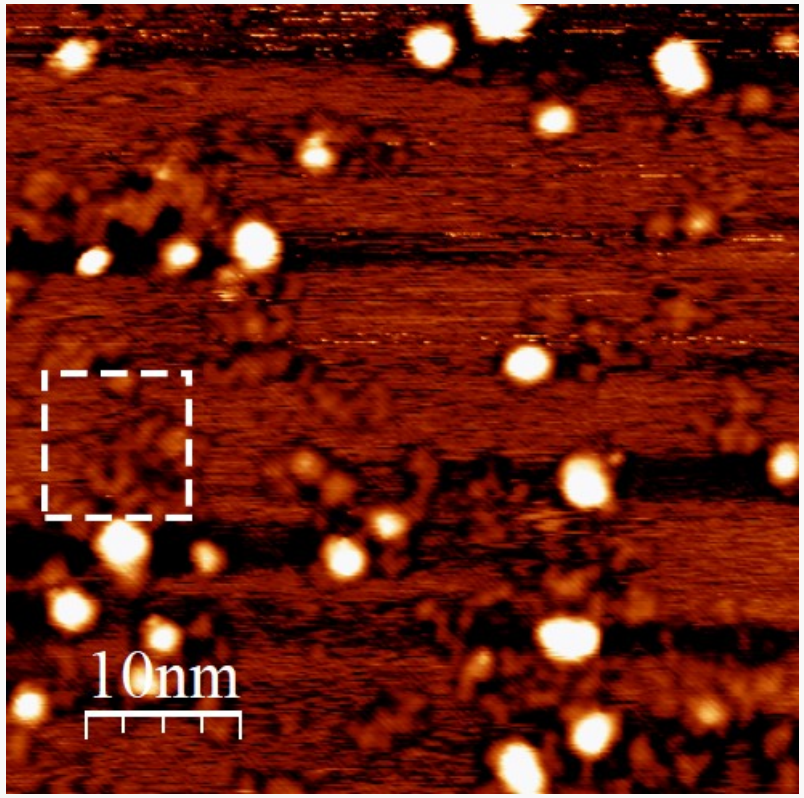


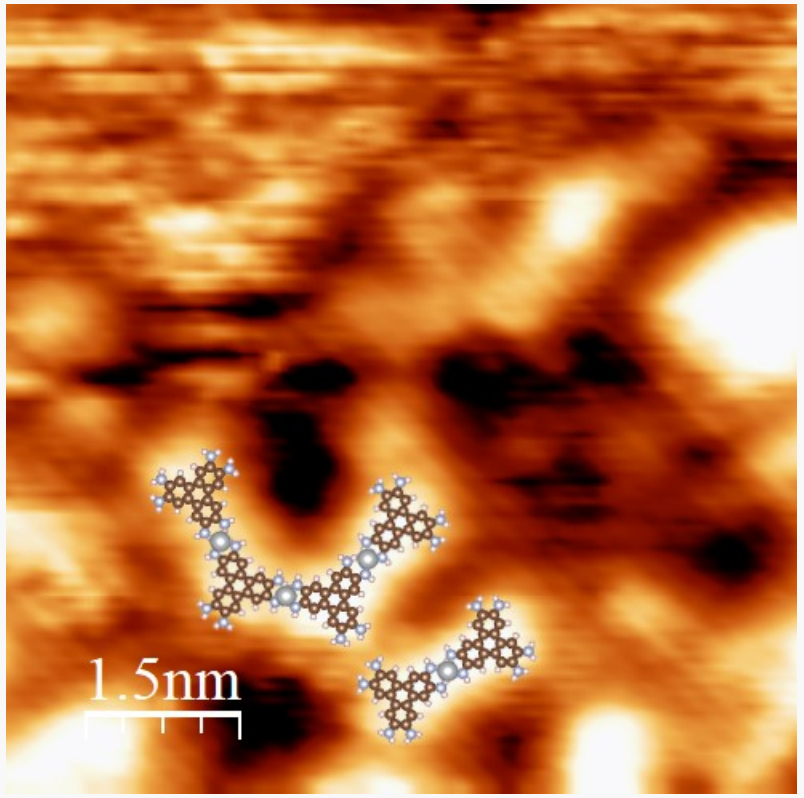
Deposit HATP molecules and Pt onto Ag(111) surface at RT.

Results and discussion

Pt



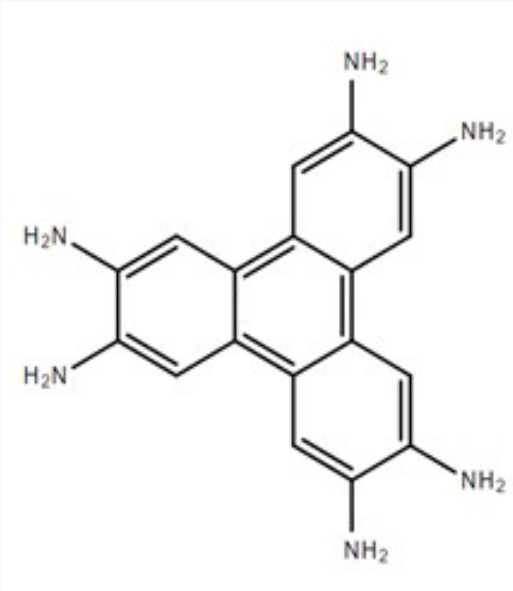




Annealing to 200℃

Conclusions

- The coordination of HITP-Pt, Pd, Ni can happened.
- Reducibility: Pt>Pd>Ni
- Ni: Metal organic network are observed.
- Pd: Linked polymers on Pd island.
- Pt: Detached all H on Ag(111) surface, disordered phases.



Chemical structures : HATP

Large domain of metal-organic network is not achieved on Ag(111).

PART 03

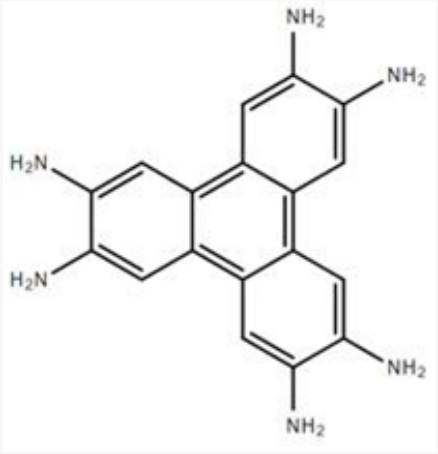
Part 3 Synthesis of $Ni_3(HITP)_2$ network with QSH effects on Au(111)

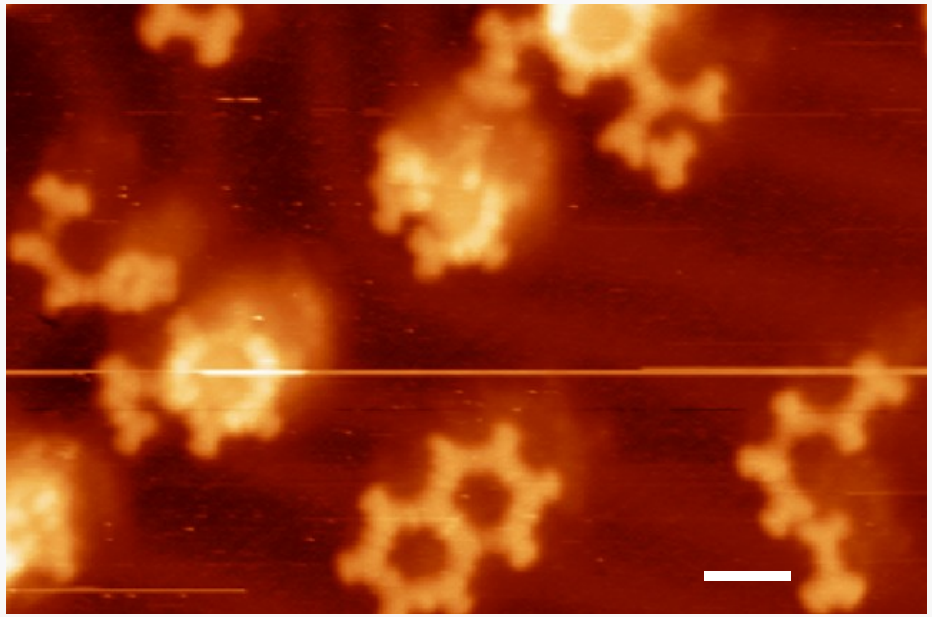
- Experimental methods
- DFT calculations
- Conclusion

Experiment

1. Depositing HATP on Au(111) surface: the molecules are in gas phase.
2. Depositing Ni onto the sample and annealing the sample to 100°C: hexagonal rings were observed.
3. Further annealing the sample to 250°C.

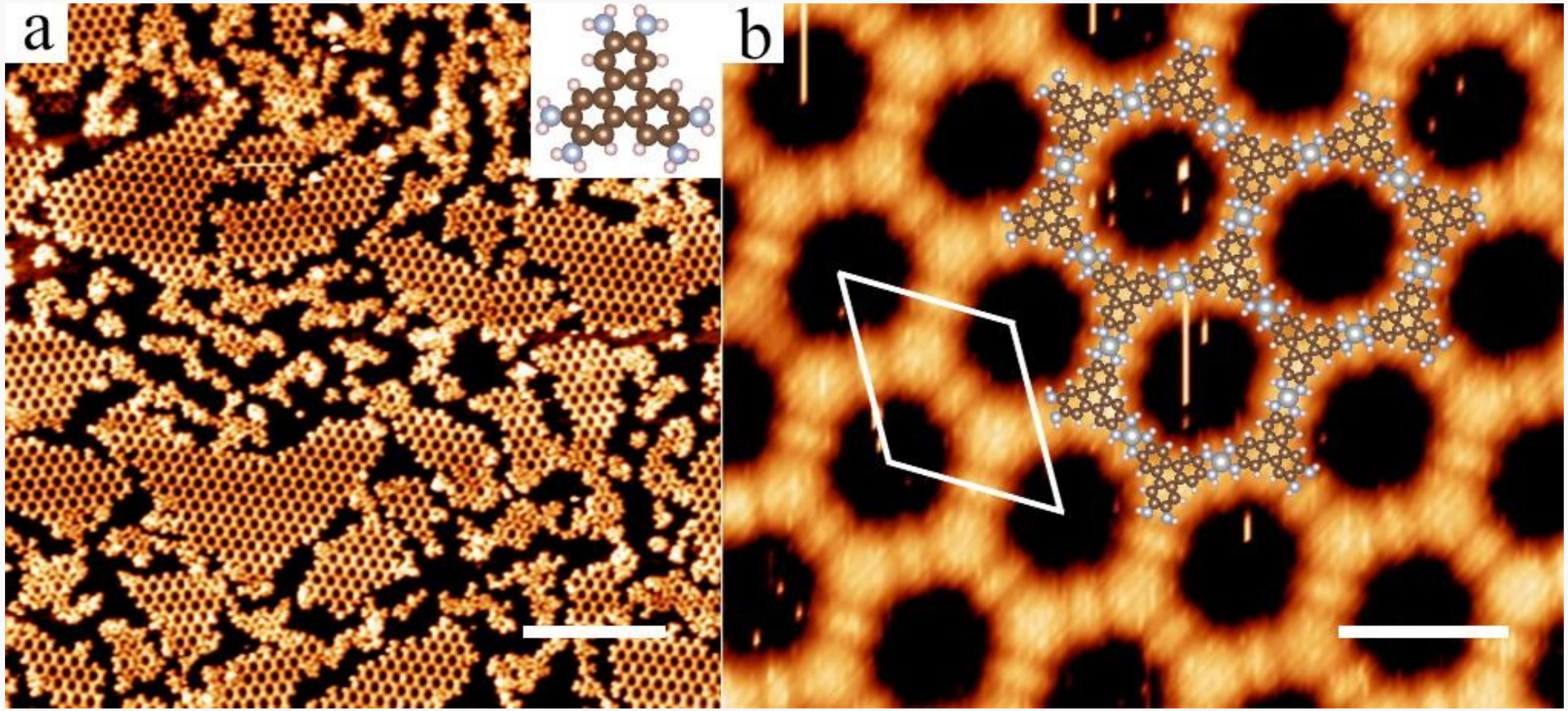
- UHV-STM;
- @RT;
- Au(111);





Scale bar: 2 nm

Experiment

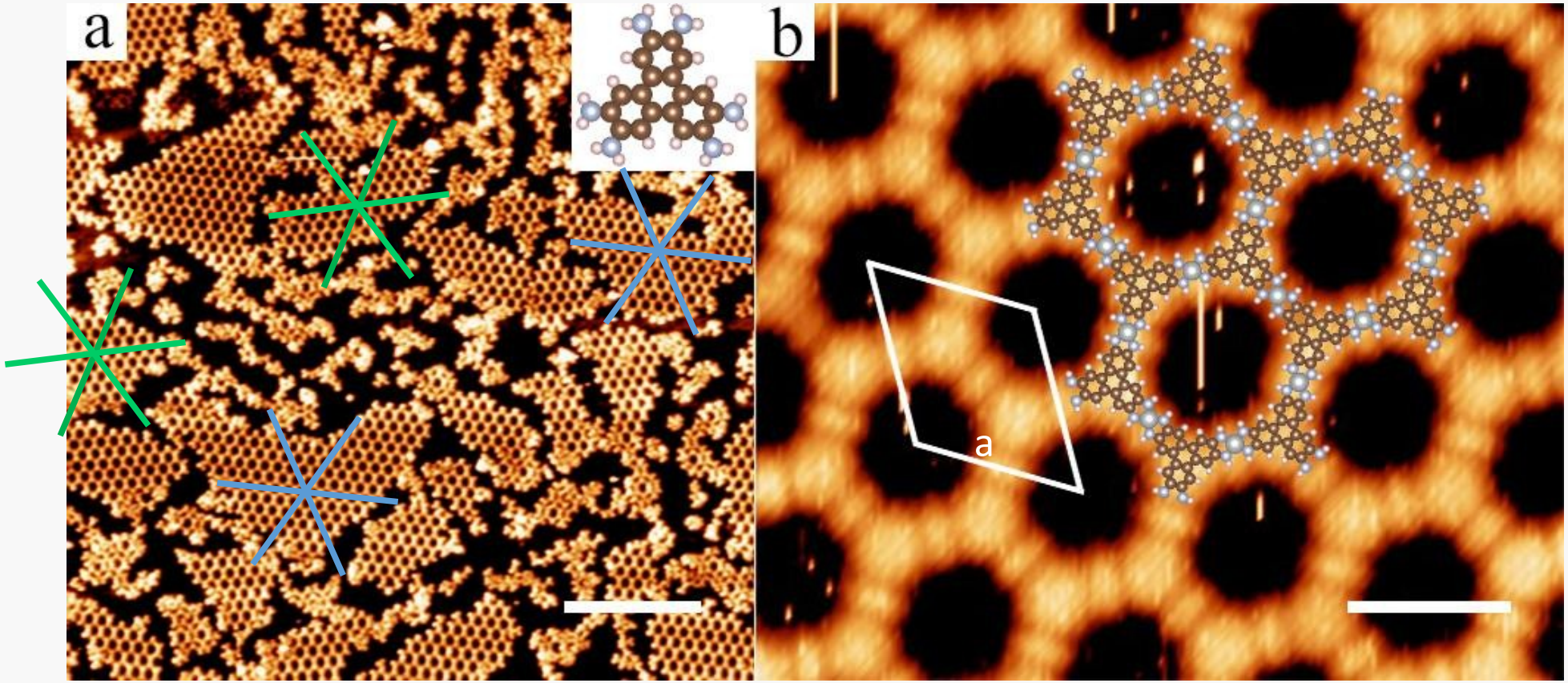


2,3,6,7,10,11-hexaiminotriphenylene (HITP)

Monolayer of $Ni_3(HITP)_2$ network self-assembled on Au(111). (a) An overview STM image. Scale bar: 20 nm. (b) A high-resolution STM image overlaid with a molecular model showing Ni atoms (large blue balls). Scale bar: 2 nm.

Gao Z A, Hsu C H, Liu J, et al. Nanoscale, 2019, 11(3): 878-881.

Experiment

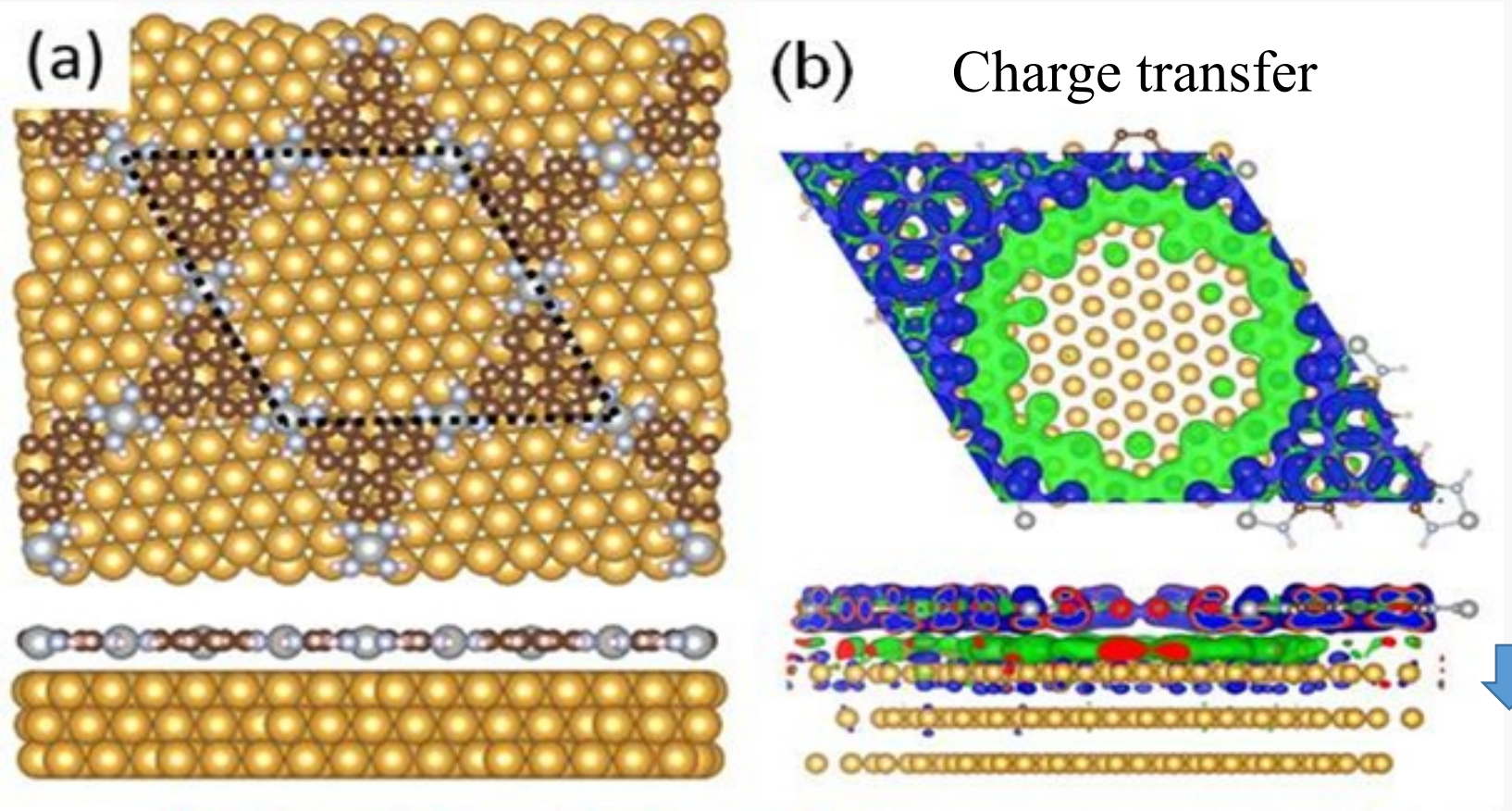


a=21.7 ± 0.2 Å

There exists two different lattice orientations with angles of ±6.5° mirrored with respect to the [01−1] direction of the Au(111) substrate.

Gao Z A, Hsu C H, Liu J, et al. Nanoscale, 2019, 11(3): 878-881.

Density-functional theory calculations



(b)Top and side views of charge transfer at an isosurface level of 2.87 × 10^{-4} e a^{-3} (a stands for Bohr radius). Green (blue) color represents charge accumulation (depletion), respectively.

3.460 Å

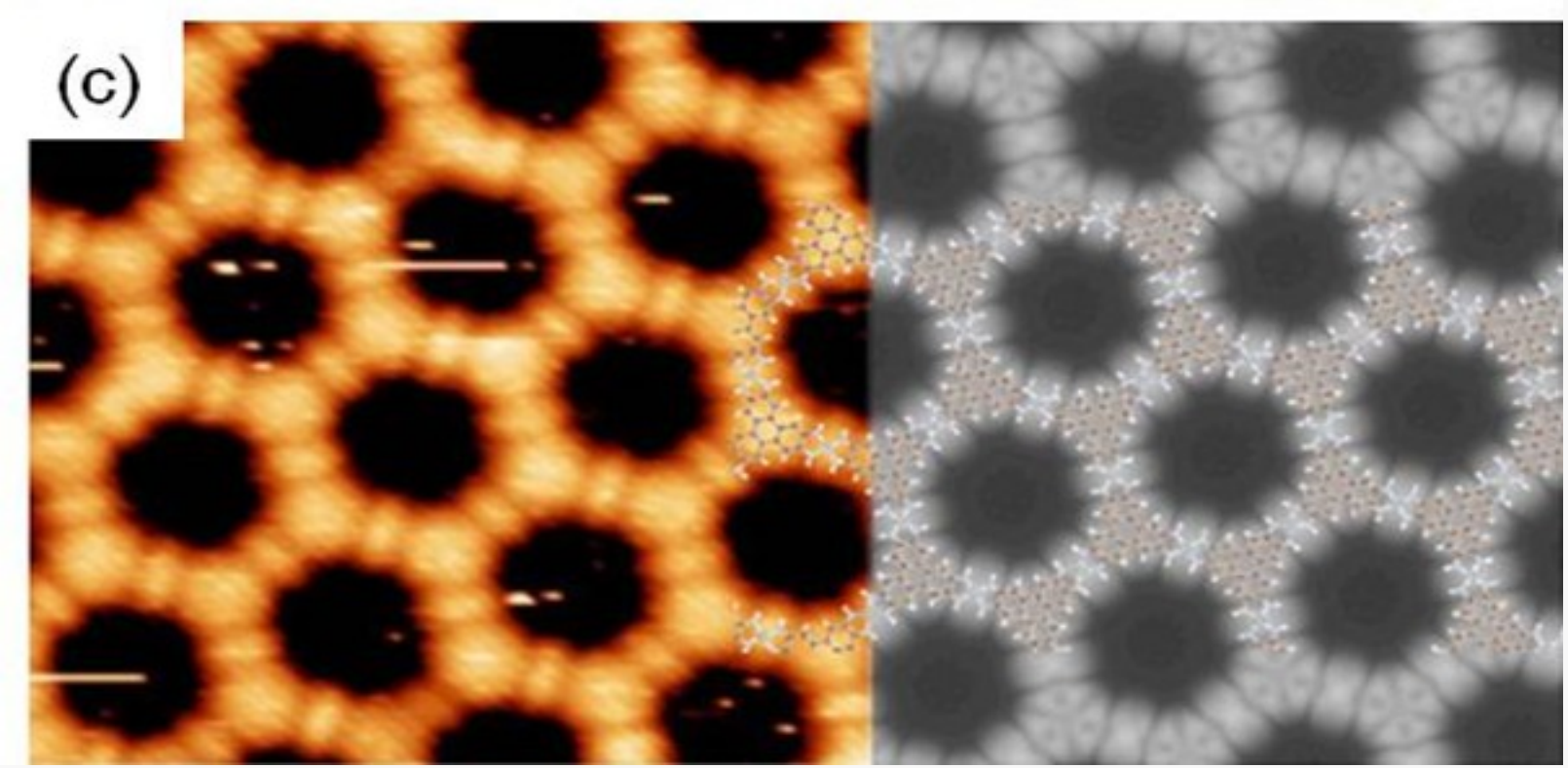
$Ni_3(HITP)_2$ network

The charge transfer per unit cell is 0.82e

calculation: a=21.89 Å, 6.587° mirrored with respect to the [01−1] direction

Gao Z A, Hsu C H, Liu J, et al. Nanoscale, 2019, 11(3): 878-881.

Density-functional theory calculations



Partial charge density

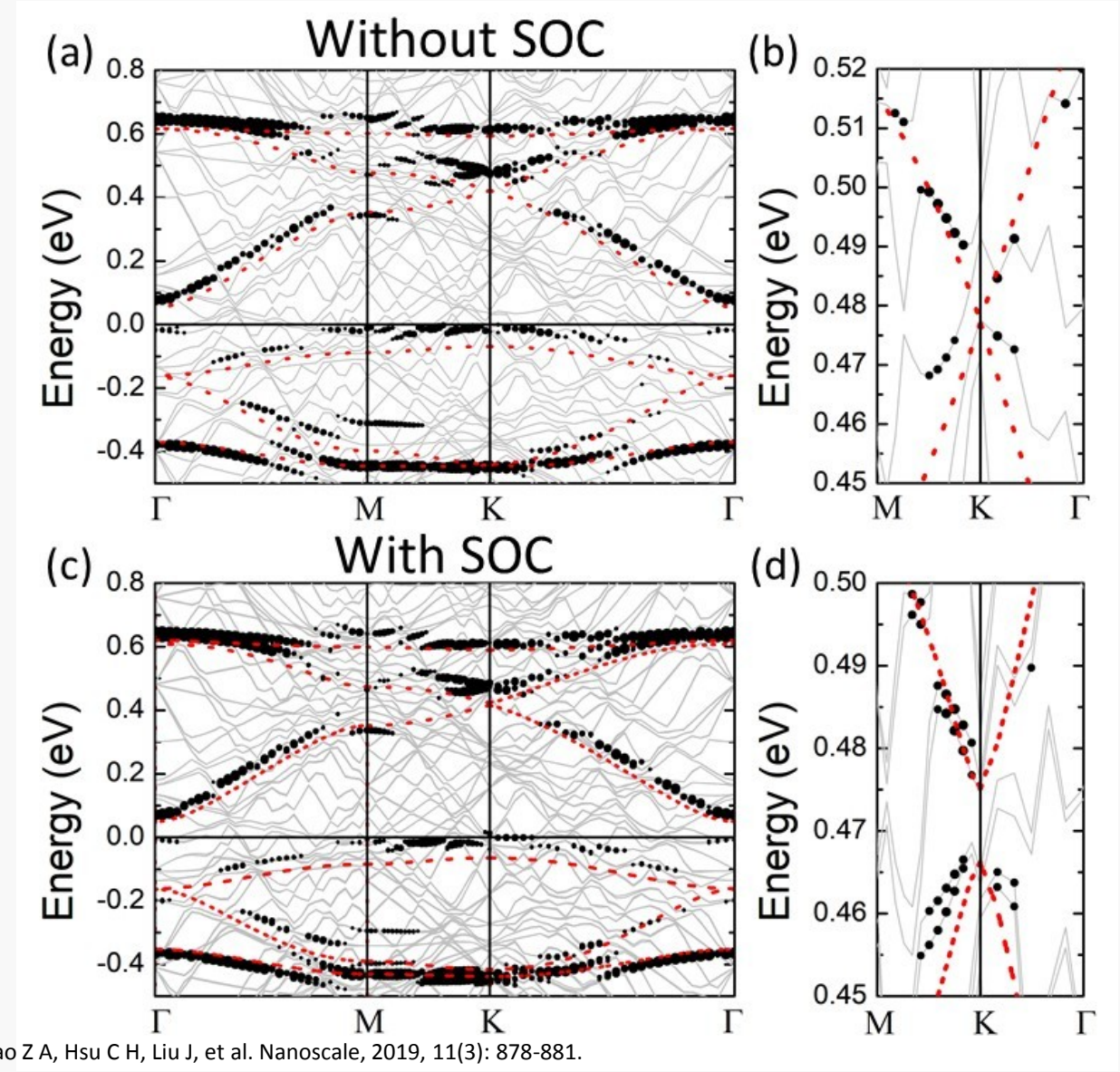
Experimental (left) and simulated (right) STM images. Scale bar: 2 nm.

$Ni_3(HITP)_2$ network

Gao Z A, Hsu C H, Liu J, et al. Nanoscale, 2019, 11(3): 878-881.

Density-functional theory calculations

Band Structure



Gao Z A, Hsu C H, Liu J, et al. Nanoscale, 2019, 11(3): 878-881.

Free standing
Gap=8meV

Black dots —— $Ni_3(HITP)_2$ network
Gray band —— Au(111) substrate

Red dots —— free standing $Ni_3(HITP)_2$ network

up-shifted by 51 meV for comparison.

The gap of the free-standing layer is preserved in the surface-adsorbed single layer.

Conclusions

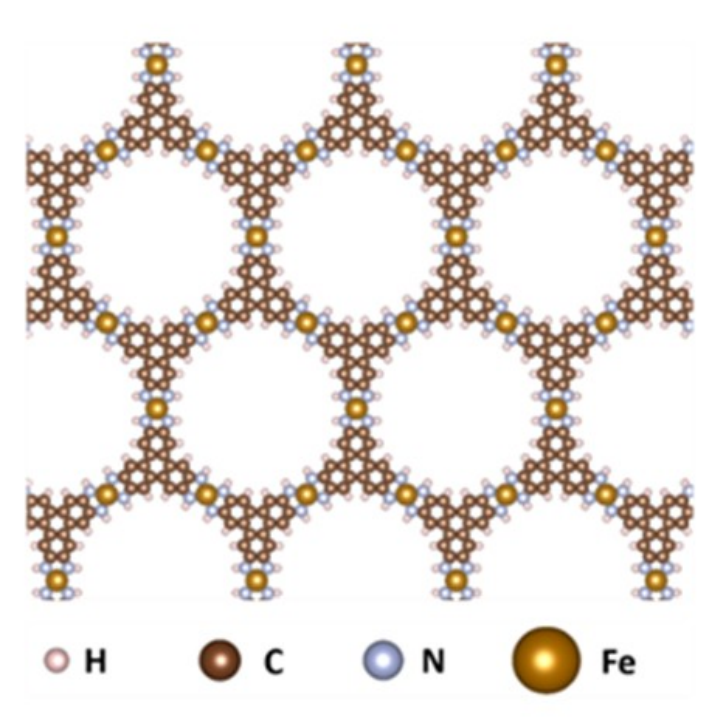
- Monolayer of two-dimensional $Ni_3(HITP)_2$ can be synthesized on Au(111) substrate.
- The density-functional theory (DFT) calculations with substrate indicates that its non-trivial topological gap is preserved.
- Due to strong background contribution of the Au substrate states, the topological gap cannot be resolved in tunneling spectroscopy measurements.

PART 04

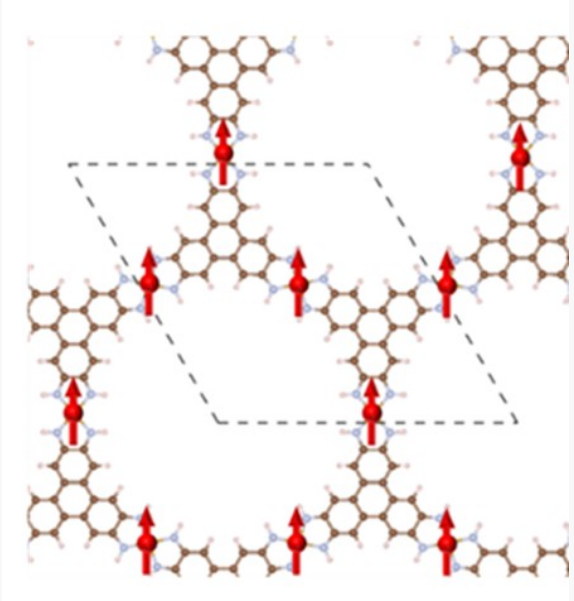
Part 4 Design and Synthesis of a Ferromagnetic Metal-Organic Framework, $Fe_3(HITP)_2$ with a Quantum Anomalous Hall Gap

- DFT calculations
- Experimental realization
- Conclusion

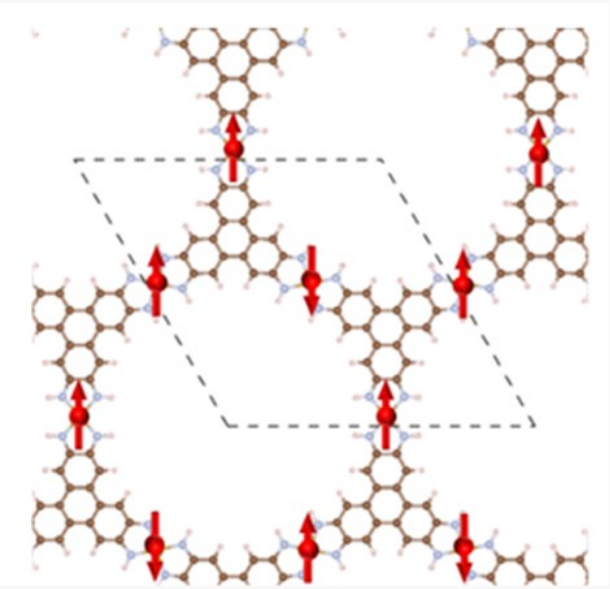
Density-functional theory calculations



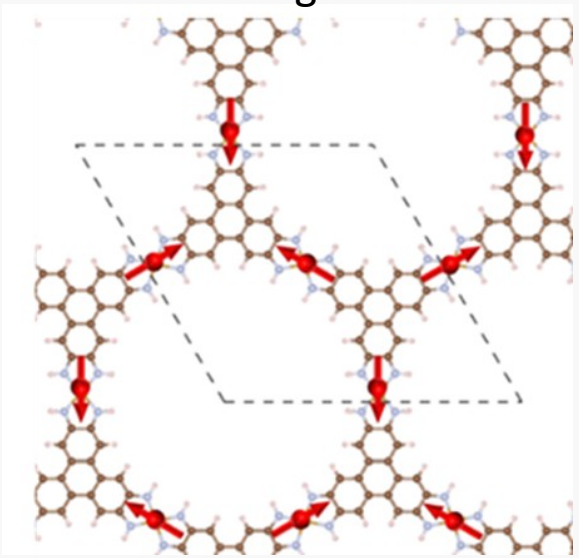
Ferromagnetic state



Ferrimagnetic state



Antiferromagnetic state



Lattice constant,

Experiment: 21.7 Å

Calculation: 22.08 Å

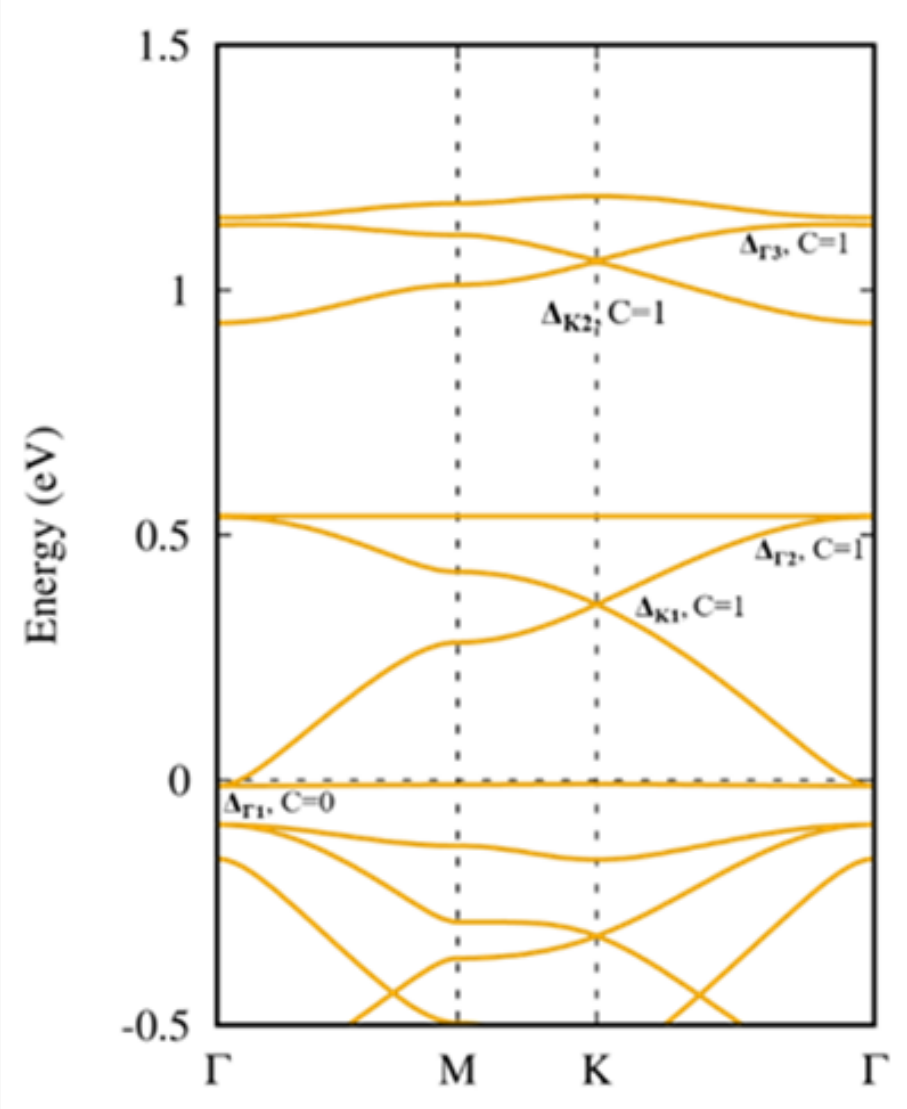
Ferromagnetic state:

Out-of-plane magnetic moment

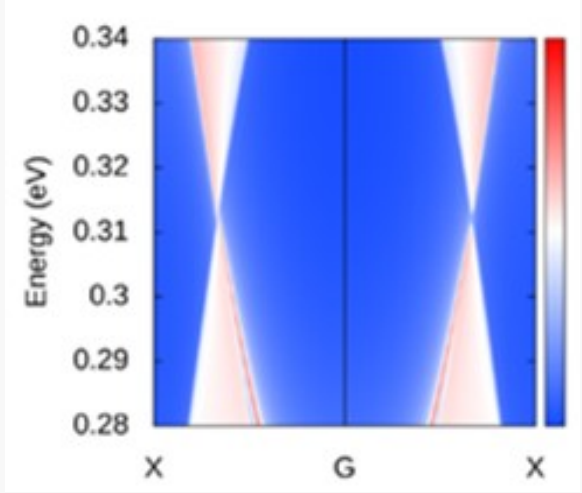
of 6 μB per cell

By Y. F. Gao

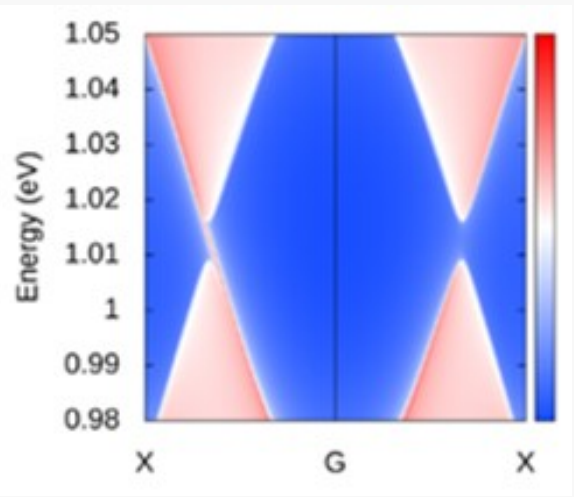
Density-functional theory calculations



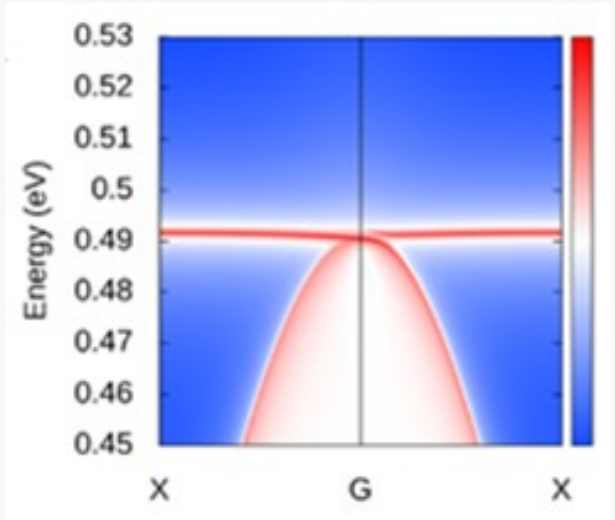
Wannier band structure



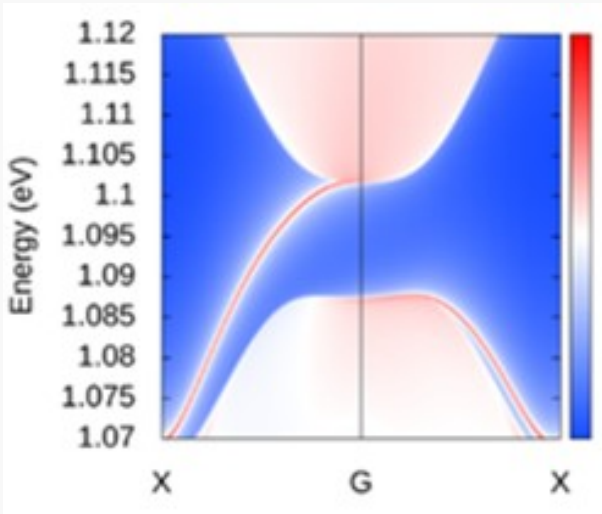
ΔK1 = 1.71 meV



ΔK2 = 7.02 meV



ΔΓ2 = 2.45 meV



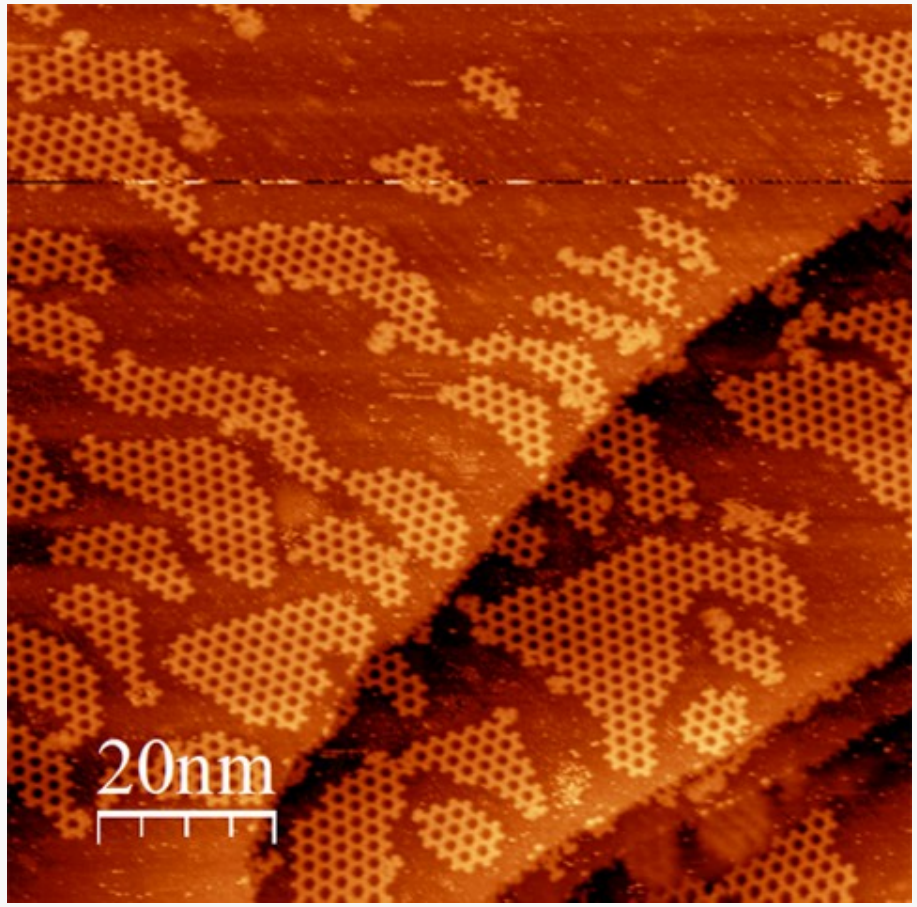
ΔΓ3 = 14.76 meV

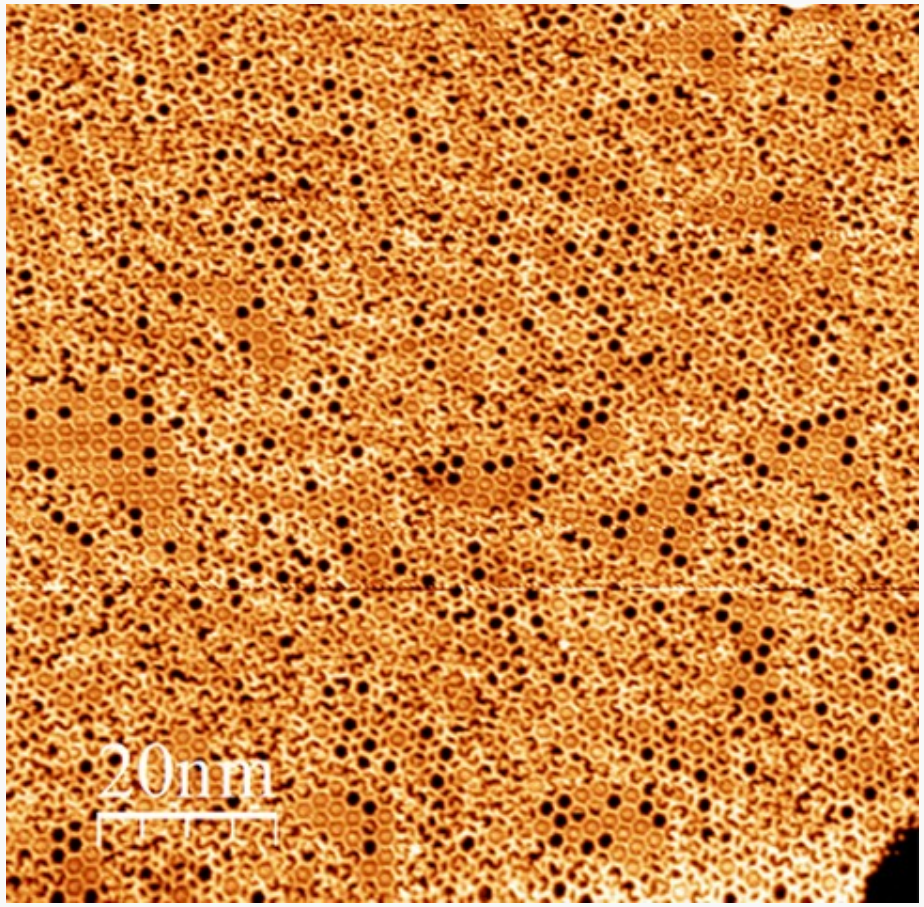
Chern numbers for bands, C=1 non-trivial

By Y. F. Gao

Experimental realization

Fe





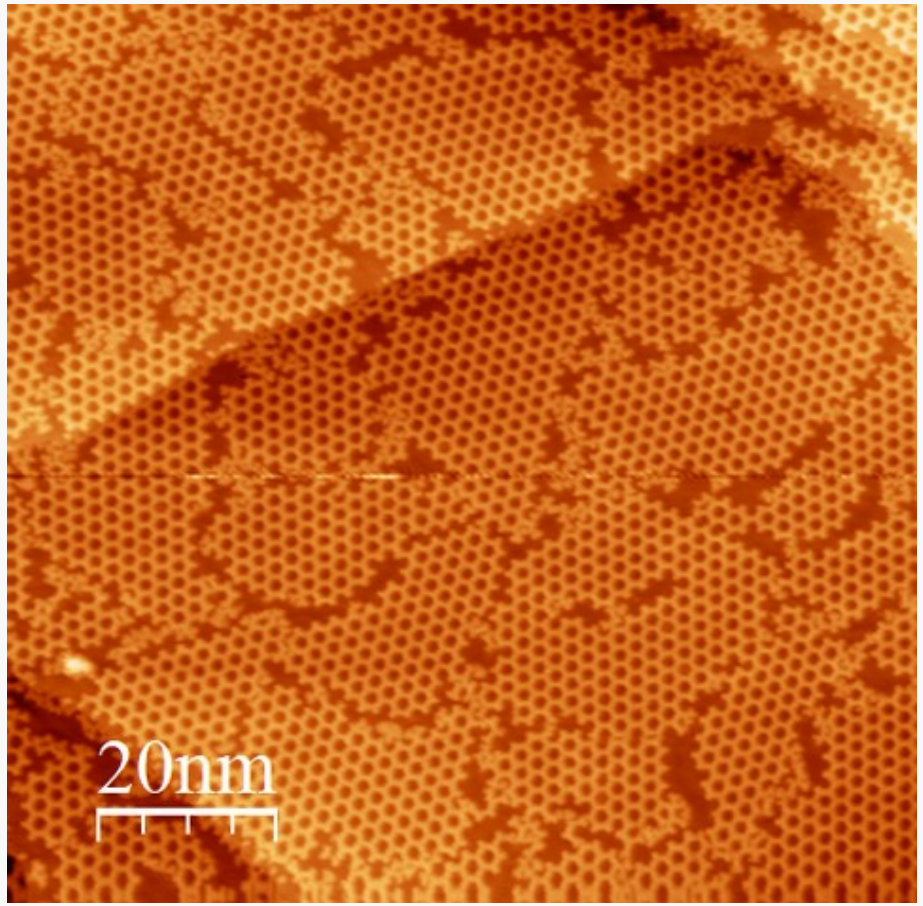
Low coverage

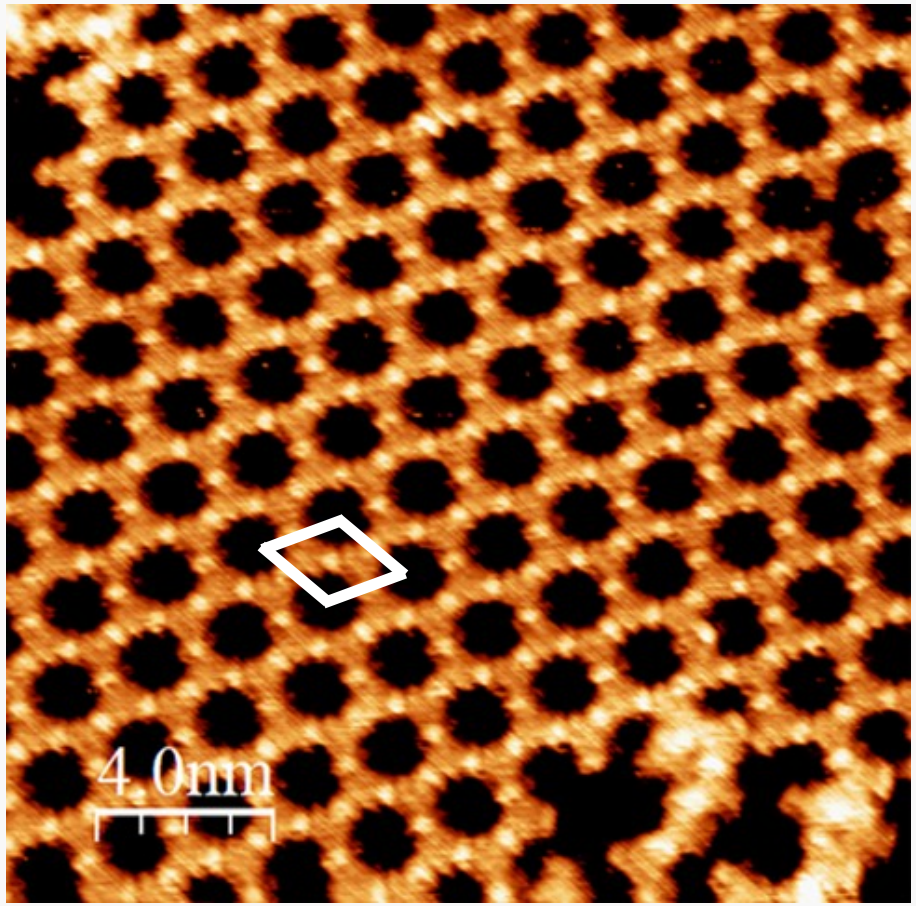
High coverage

Only Deposit HATP molecules and Fe onto Au(111) surface after annealing to 250℃

Experimental realization

Fe



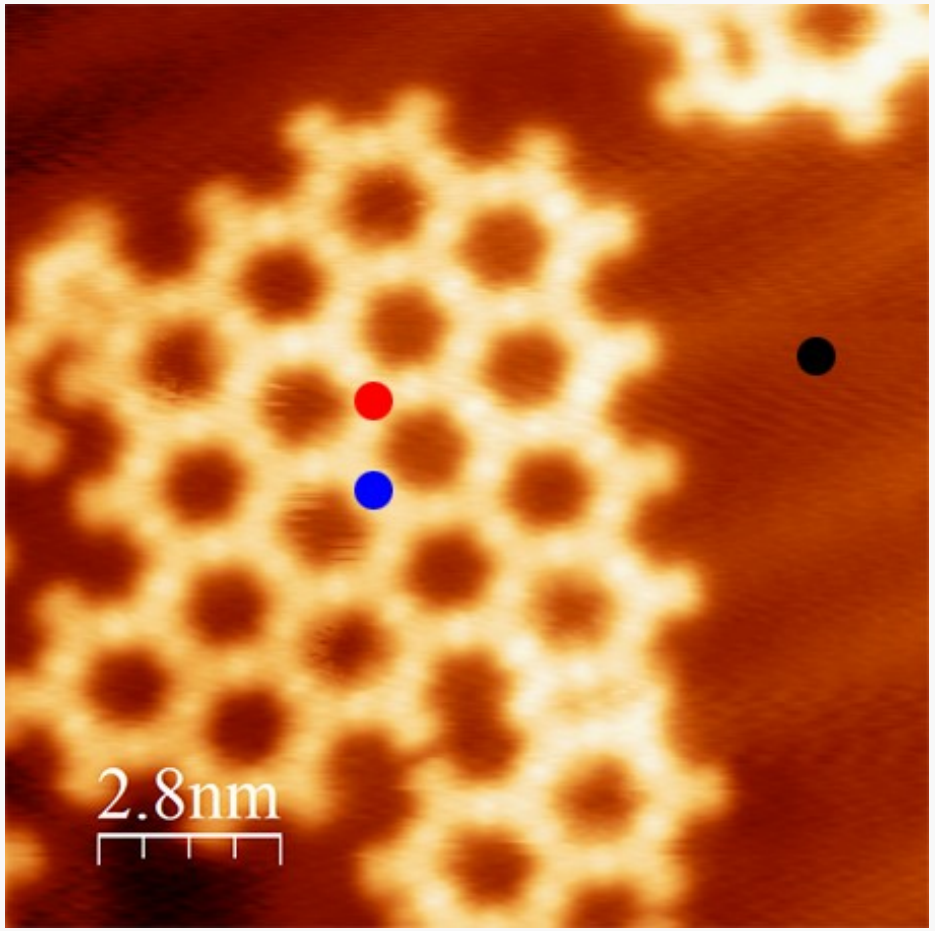


Lattice constant:

21.7±0.2 Å

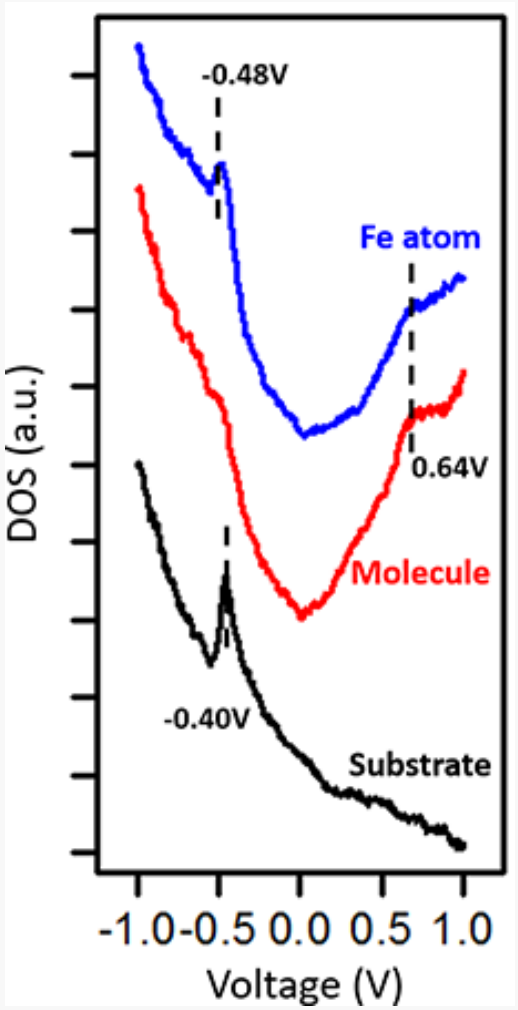
Deposit HATP molecules and Fe onto Au(111) surface after annealing to 250℃

Experimental realization



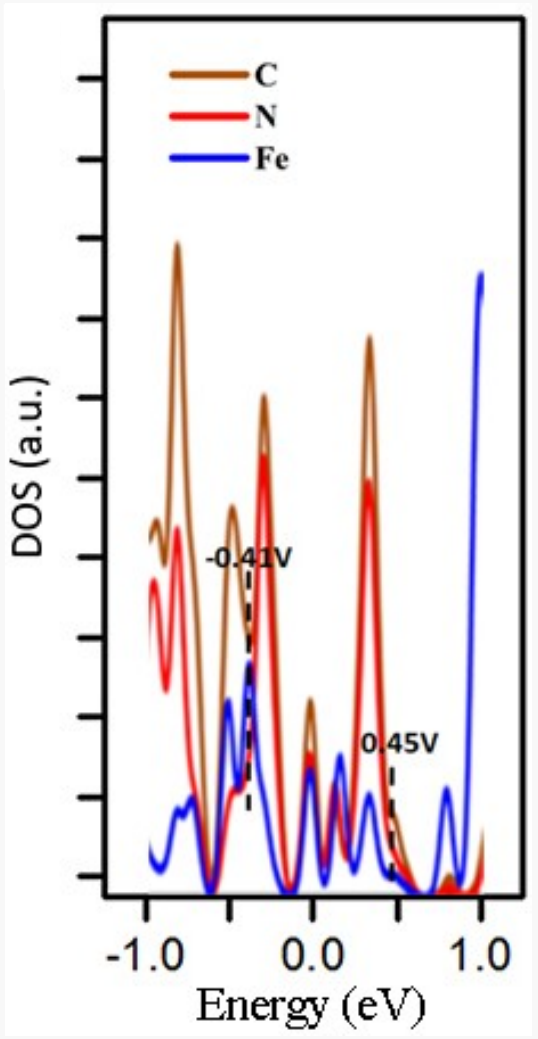
Large-range STS measurement of $Fe_3(HITP)_2$ network.

Experiment



The dI/dV spectra

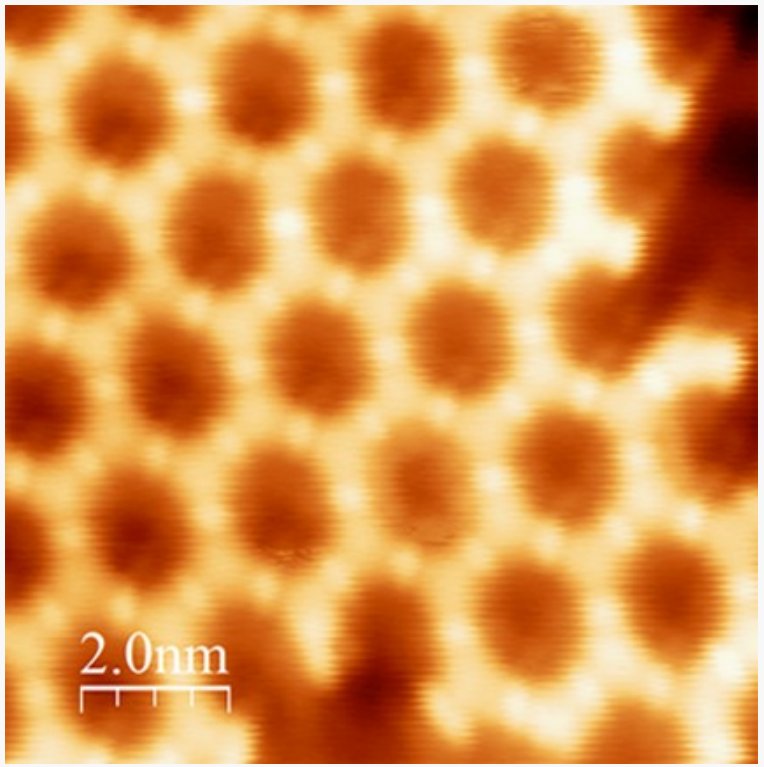
Calculation



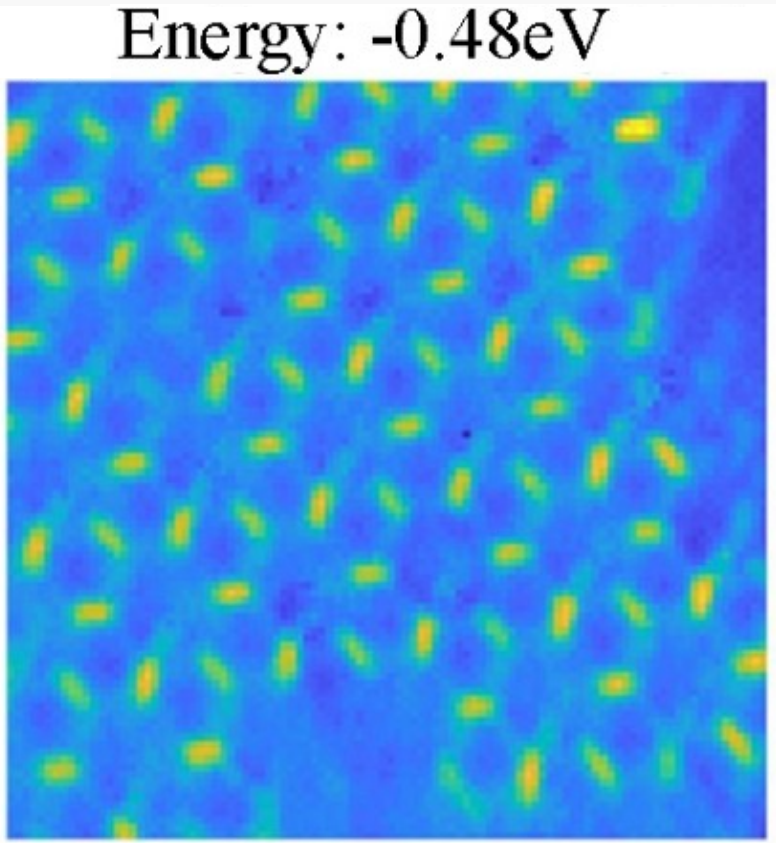
The calculated PDOS

By M. Q. Hua

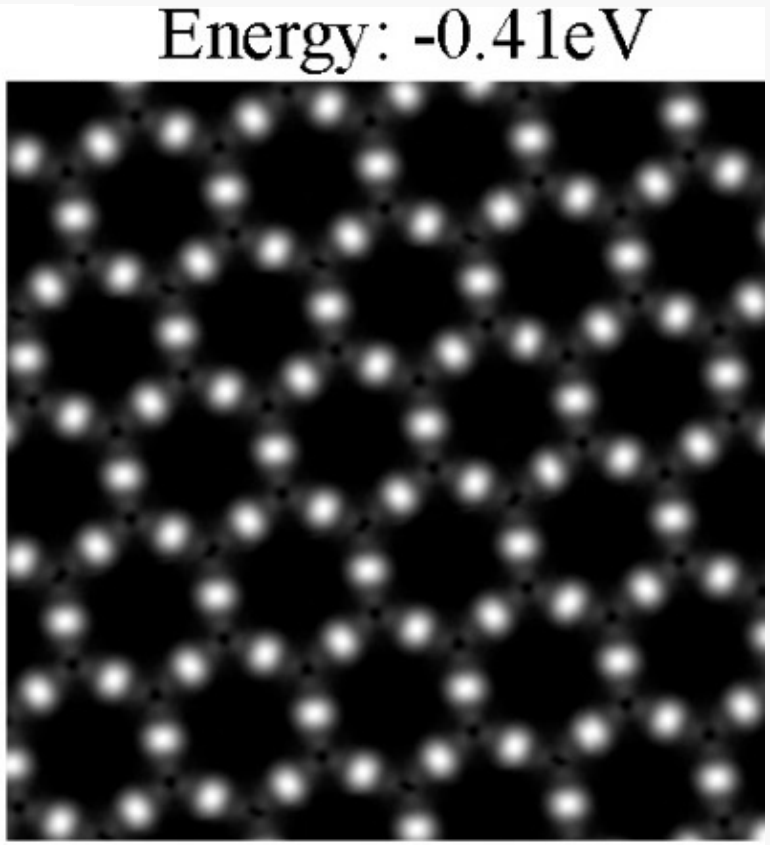
Experimental realization



STM image



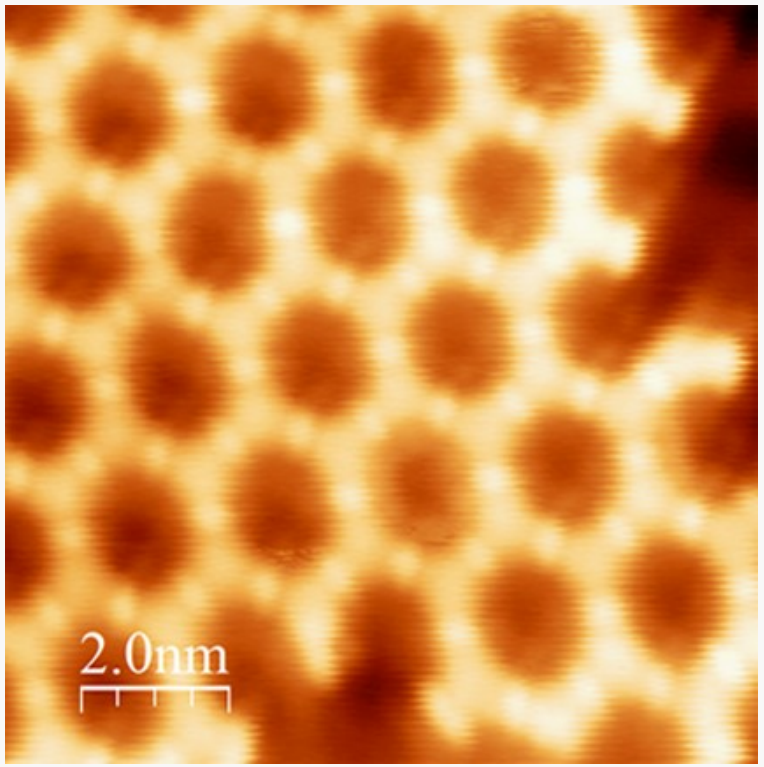
STS mapping measurement



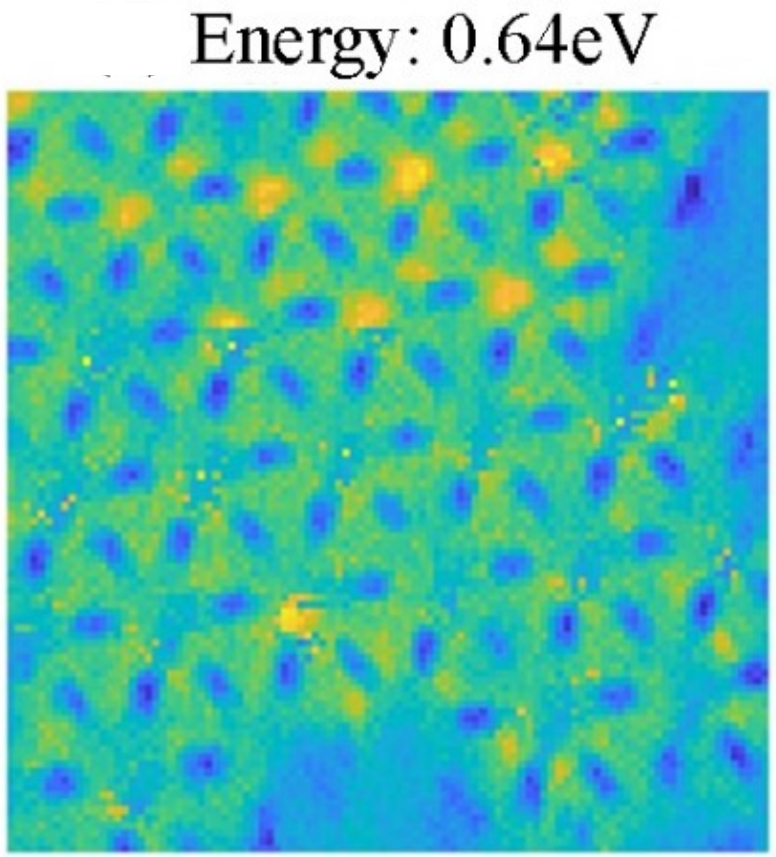
DFT calculation

By M. Q. Hua

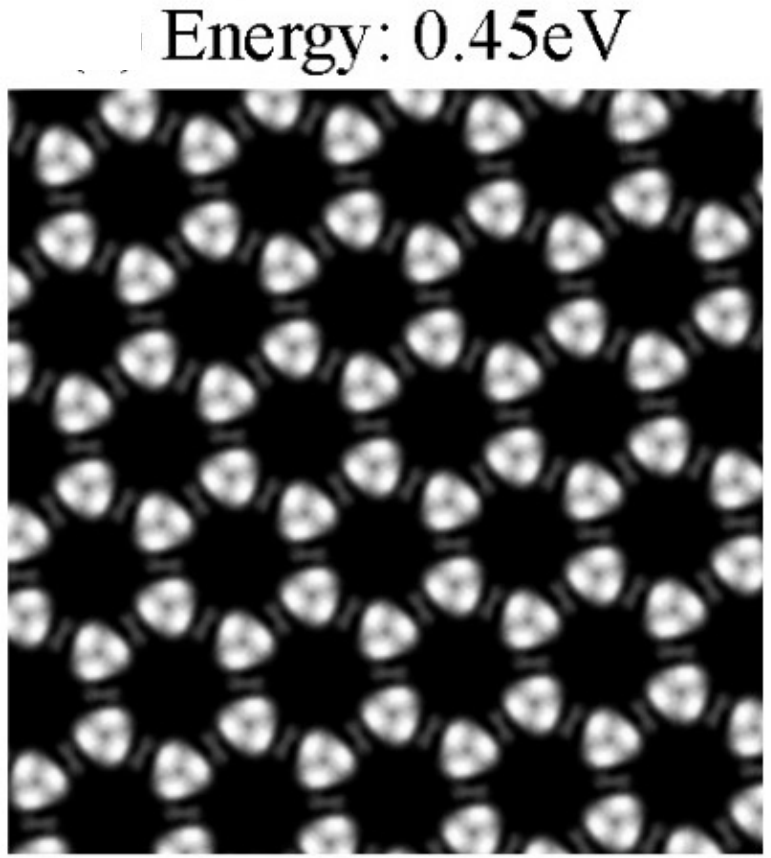
Experimental realization



STM image



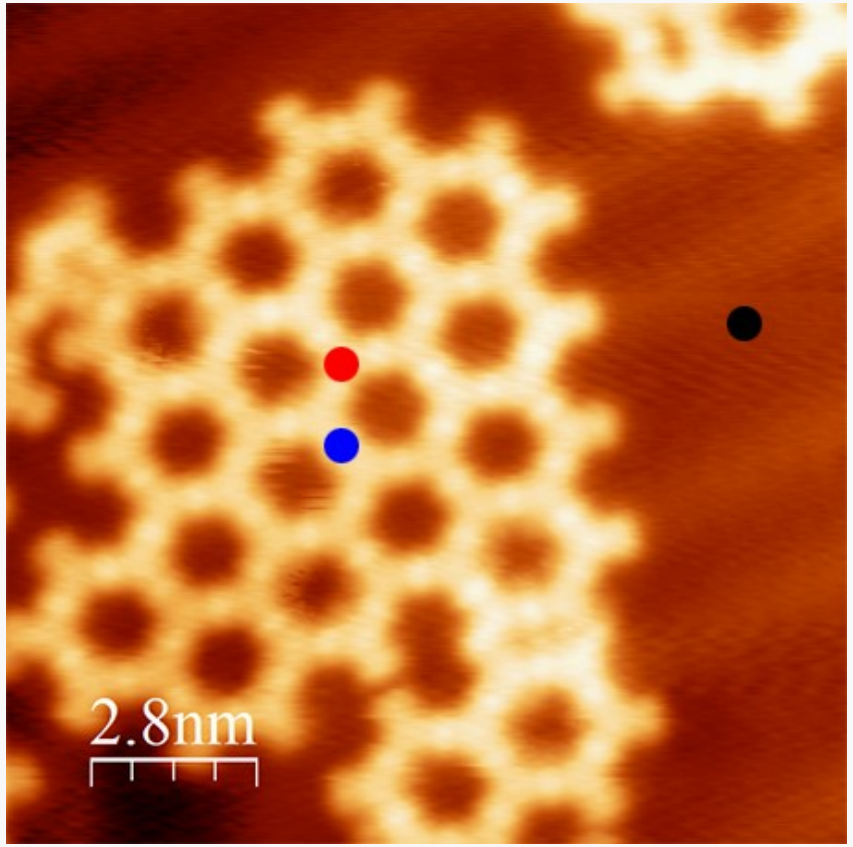
STS mapping measurement

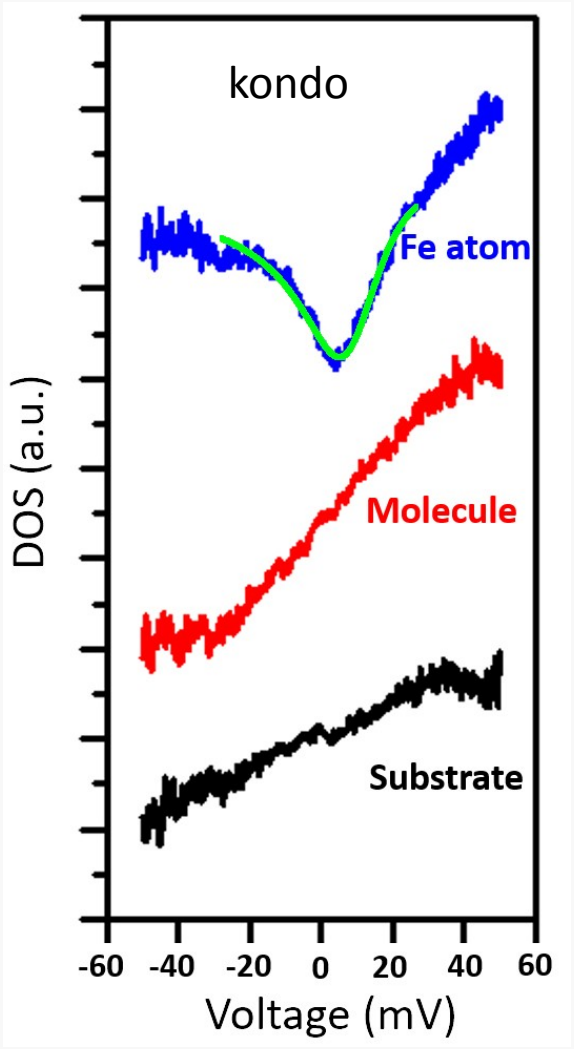


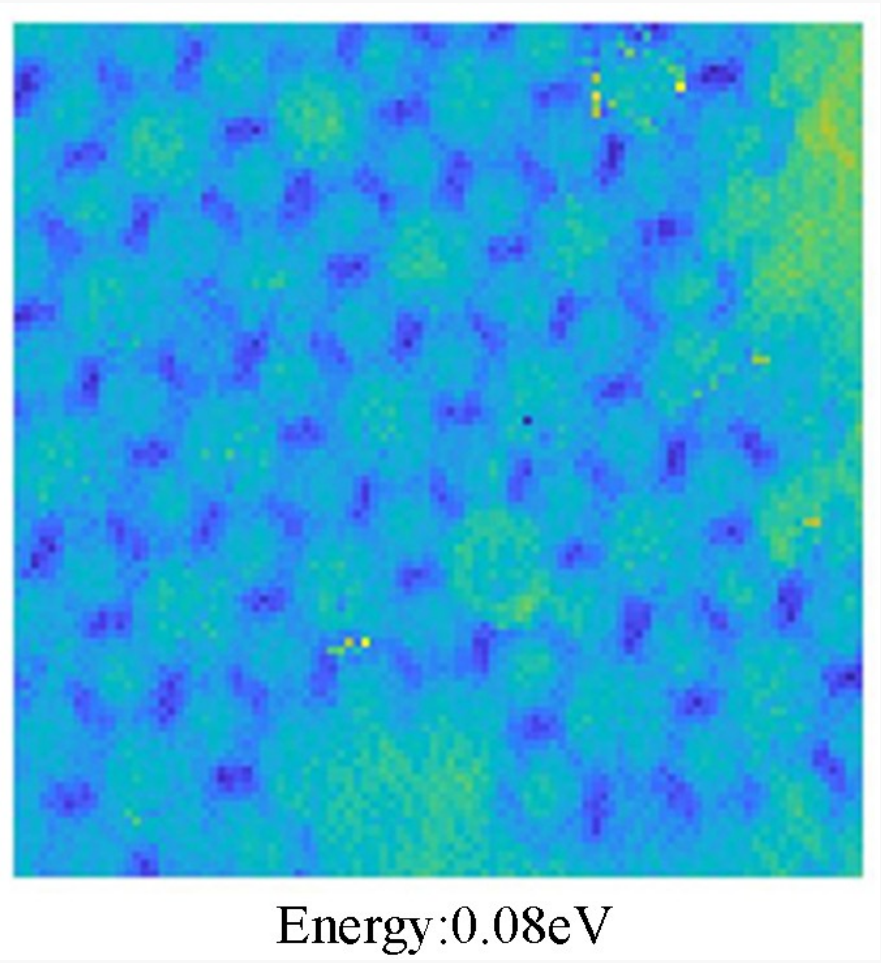
DFT calculation

By M. Q. Hua

Experimental realization



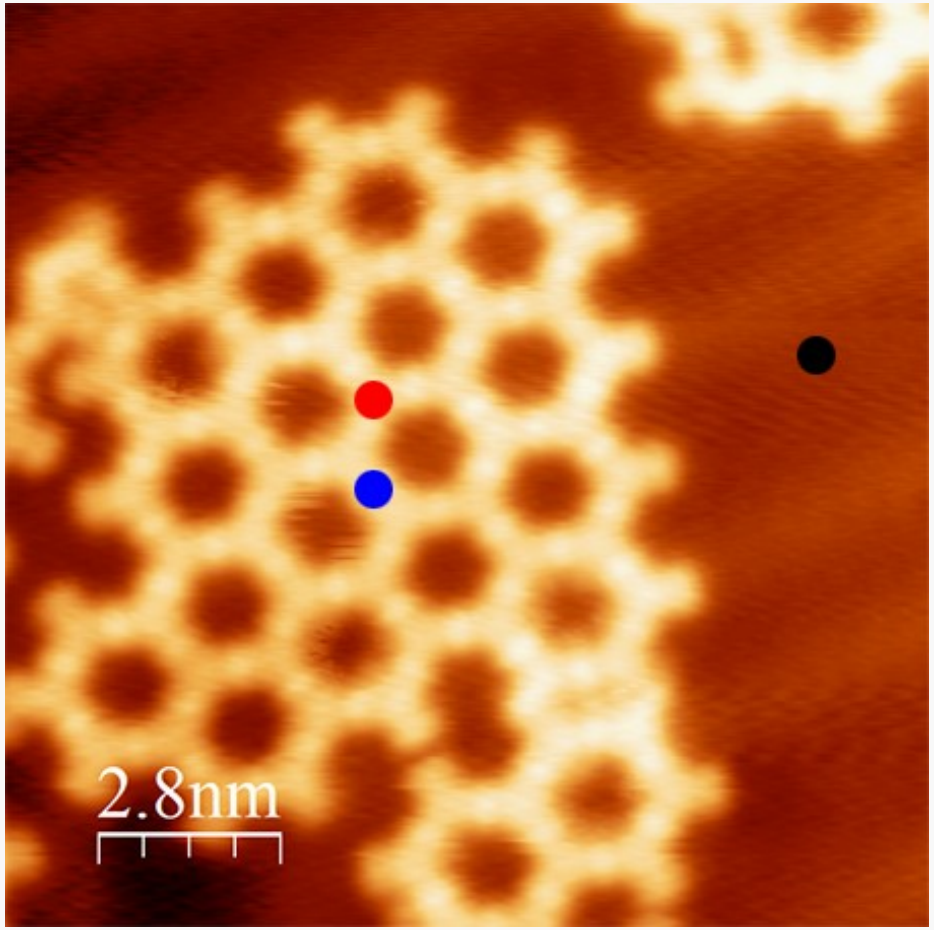


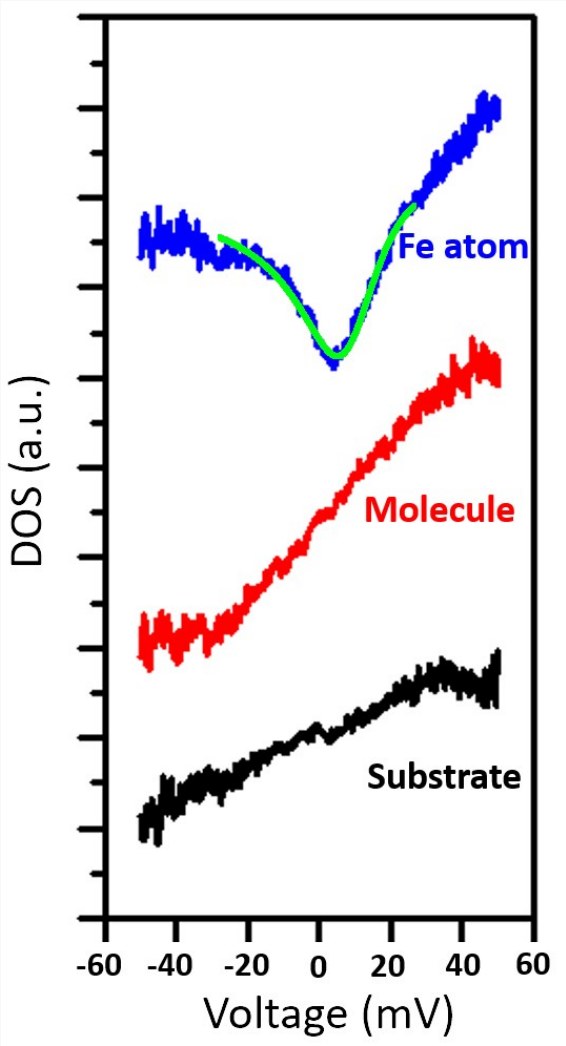


STS mapping measurement

Small-range STS measurement of $Fe_3(HITP)_2$ network.

Experimental realization





Fano function

$$\frac{dI}{dV} = A\frac{[q + (x - \epsilon_0)/\Gamma]^2}{1 + [(x - \epsilon_0)/\Gamma]^2} + B$$

$$\Gamma = k_B T_K = 12.19mV$$

$$T_K = 141.5K$$

Kondo temperature falls in the range of 133K–150 K

Small-range STS measurement of $Fe_3(HITP)_2$ network.

Summary

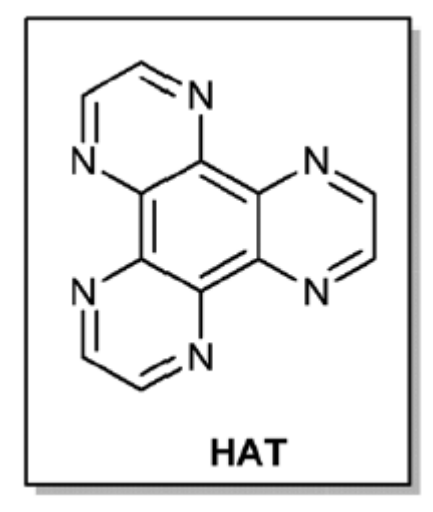
- Monolayer of two-dimensional $Fe_3(HITP)_2$ can be synthesized on Au(111) substrate.
- DFT calculations indicate $Fe_3(HITP)_2$ are Ferromagnetic.
- STS measurement shows a clear dip on Fe adatom resulting in the Kondo effect.
- The band structure shows four non-trivial gaps (largest: 14.76 meV), indicates that the system is a candidate of organic topological insulator with QAH effect.

PART 05

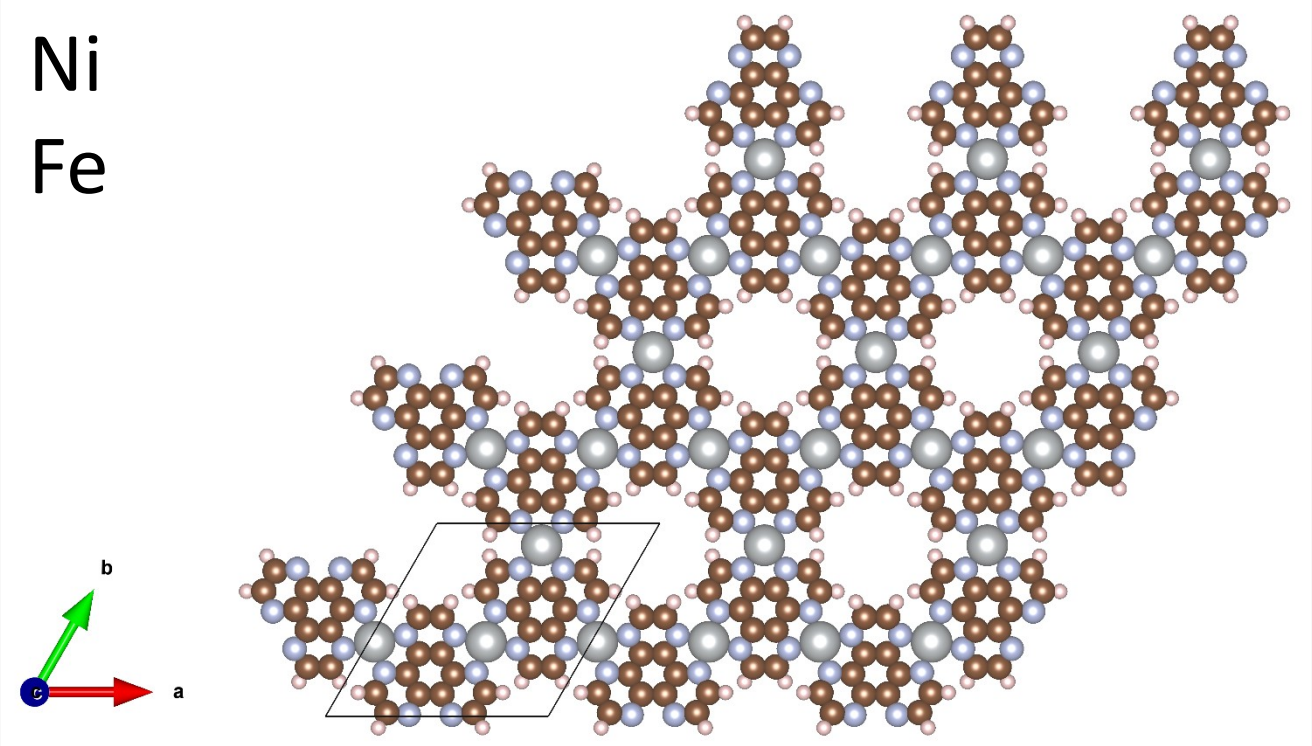
Part 5 Synthesis of $Ni_3(HAT)_2$, $Fe_3(HAT)_2$ network on Ag(111)

- Experimental realization
- Conclusion

Experimental realization



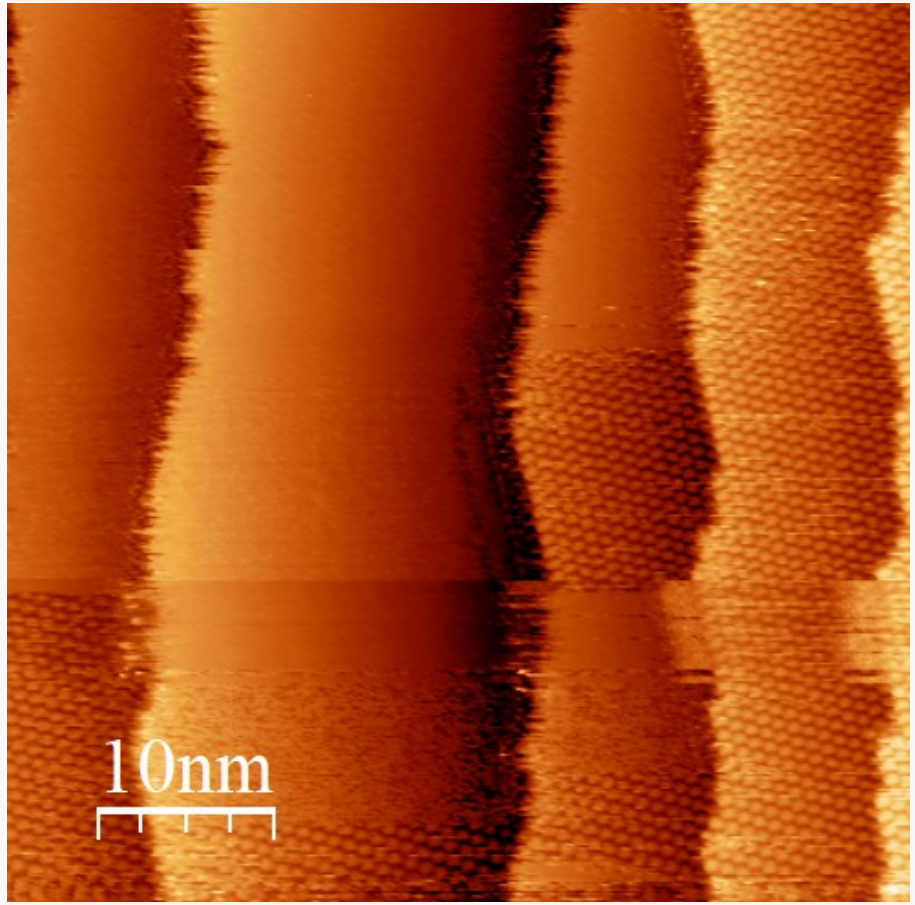
1,4,5,8,9,12-hexaazatriphenylene (HAT)



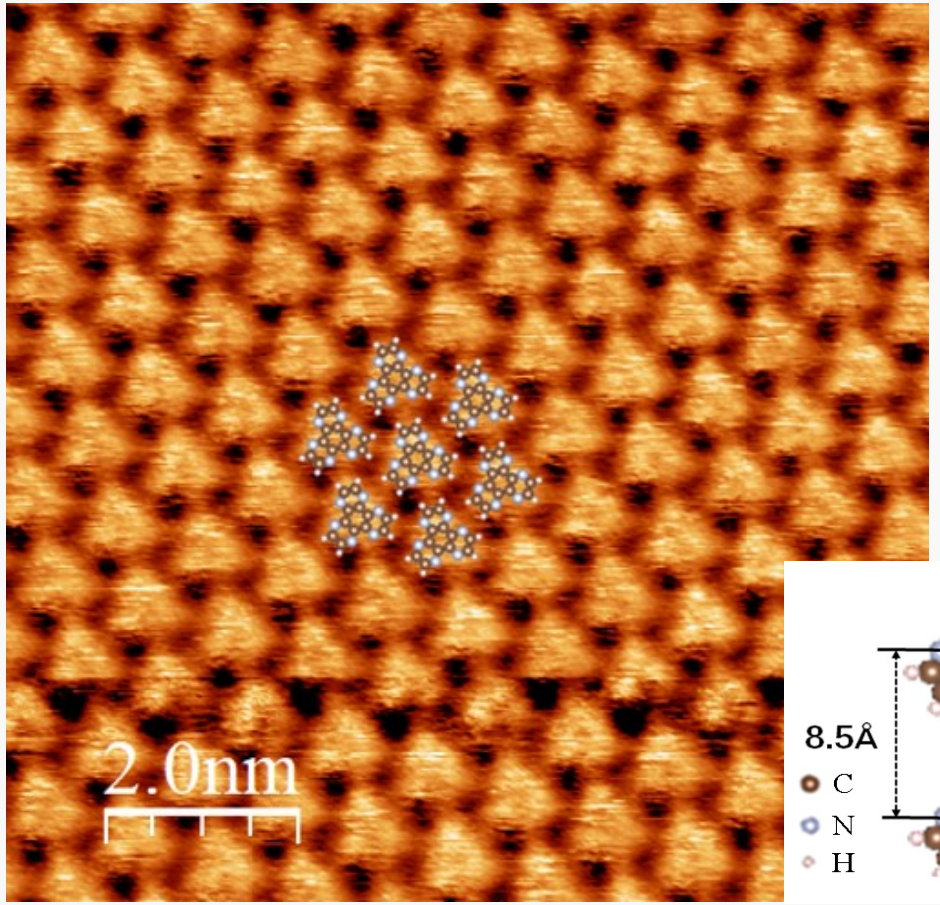
- UHV-STM;
- @RT;
- Ag(111);

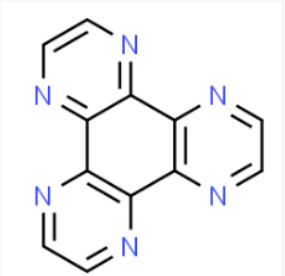
Segura J L, Juárez R, Ramos M, et al. Chemical Society Reviews, 2015, 44(19): 6850-6885.

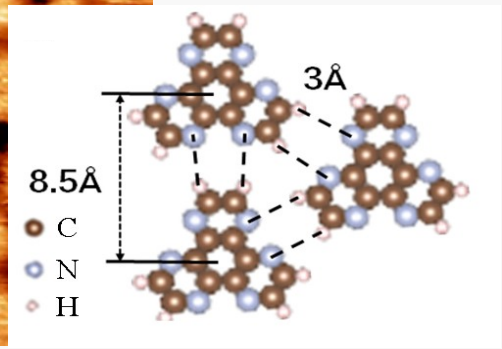
Experimental realization



HAT molecules



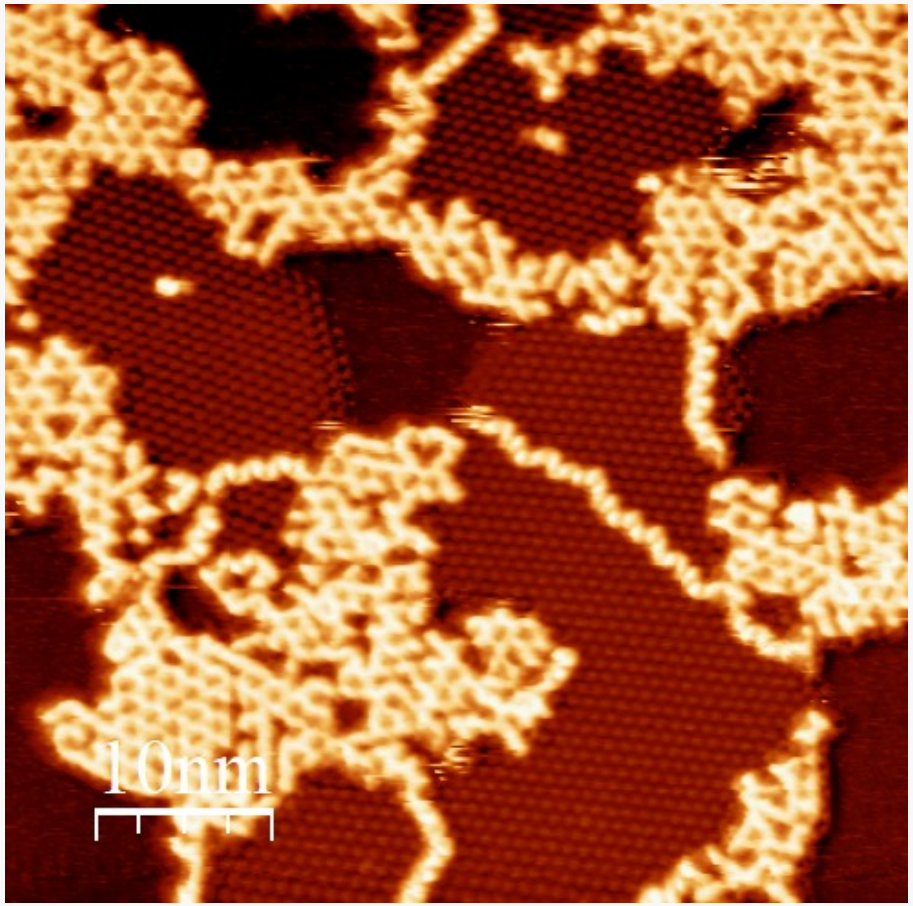


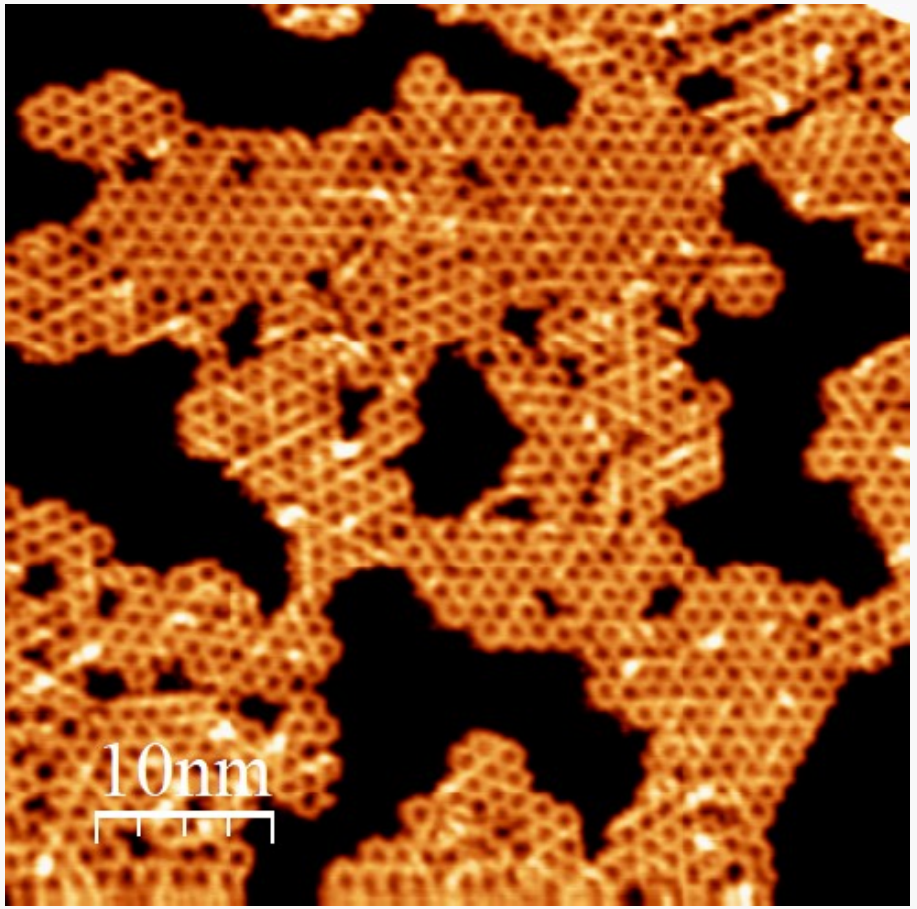


Only Deposit HATP molecules onto Ag(111) surface. Close packed molecules

Experimental realization

Ni





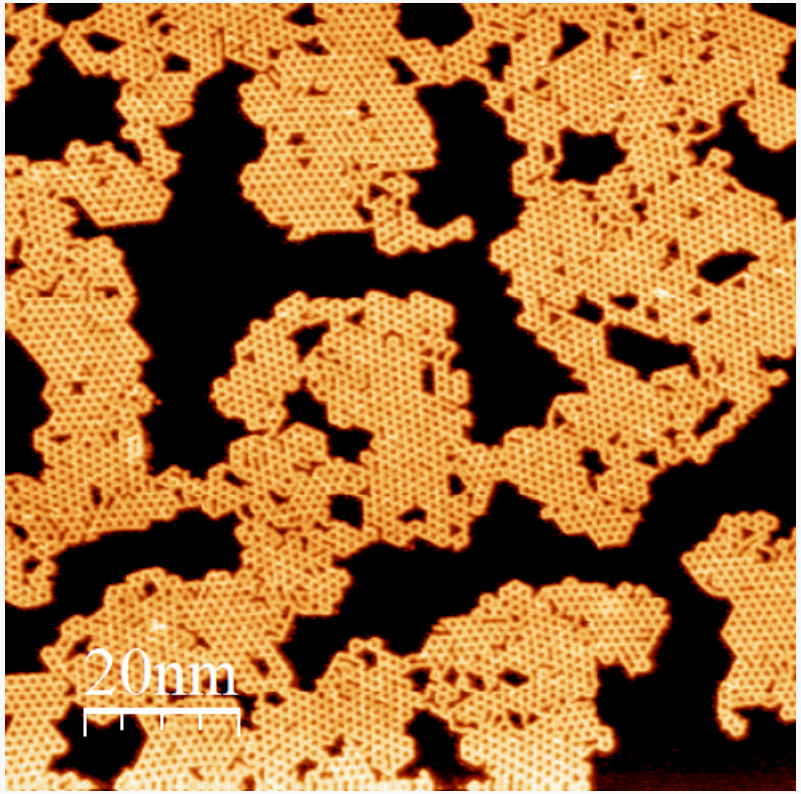
Deposit HAT molecules and Ni on Ag(111) substrate at RT.

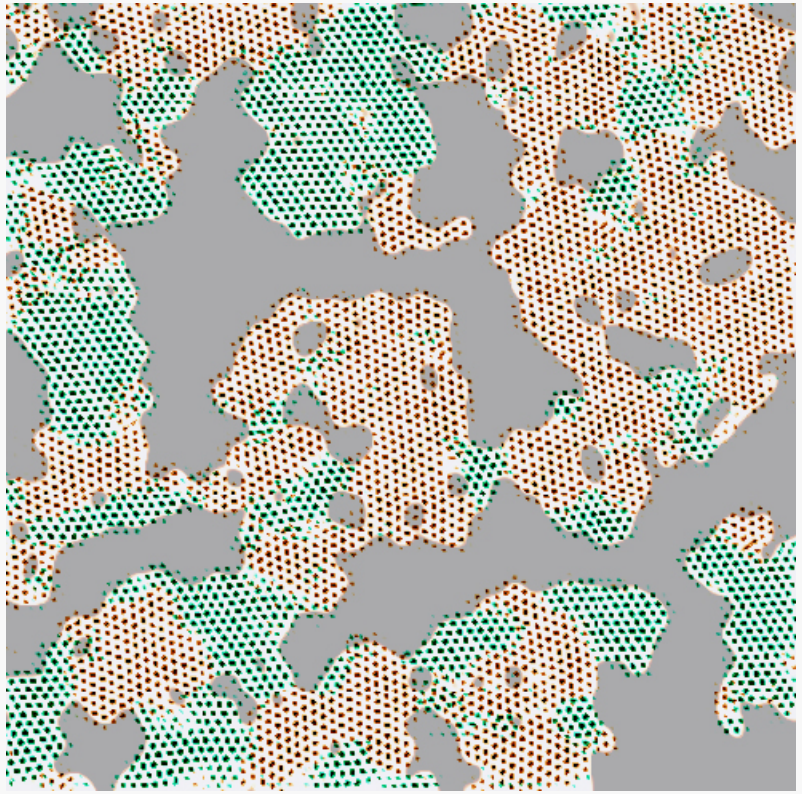
Annealing the sample to 150℃

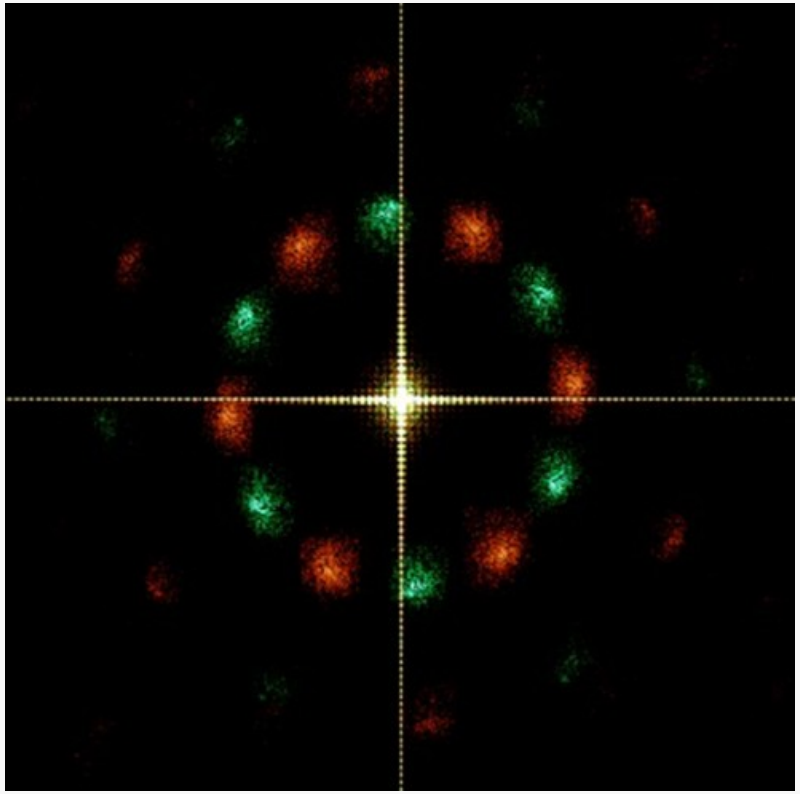
Experimental realization

Ni

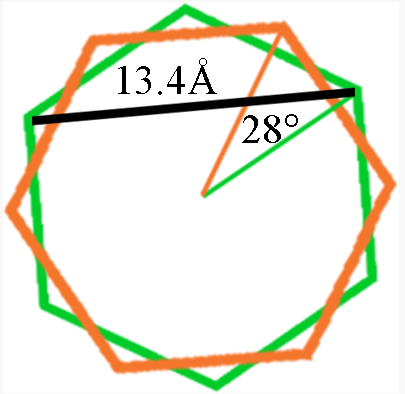
Fast Fourier Transformation (FFT)







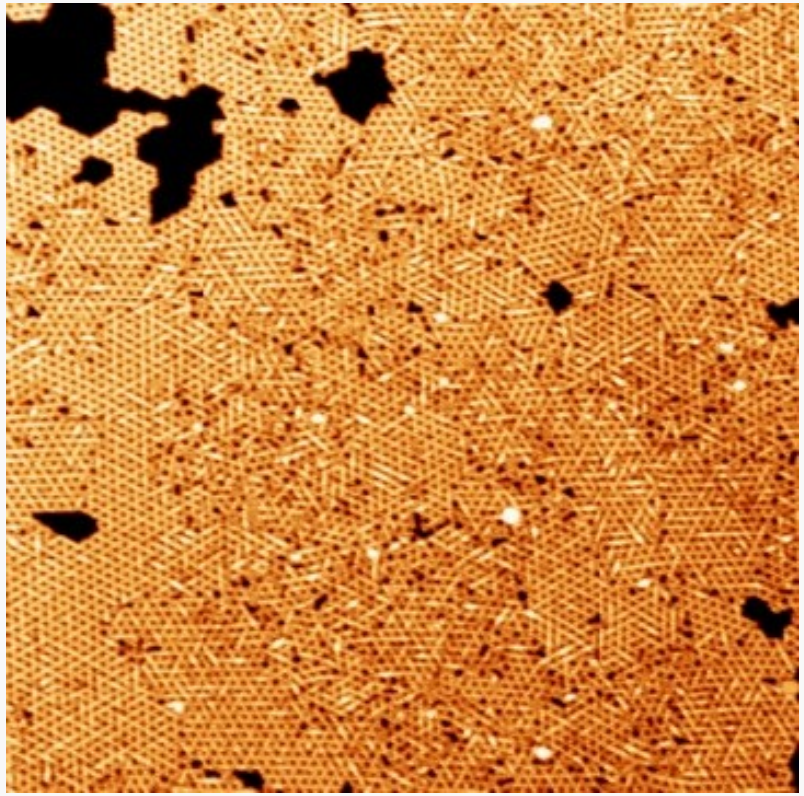
Submonolayer

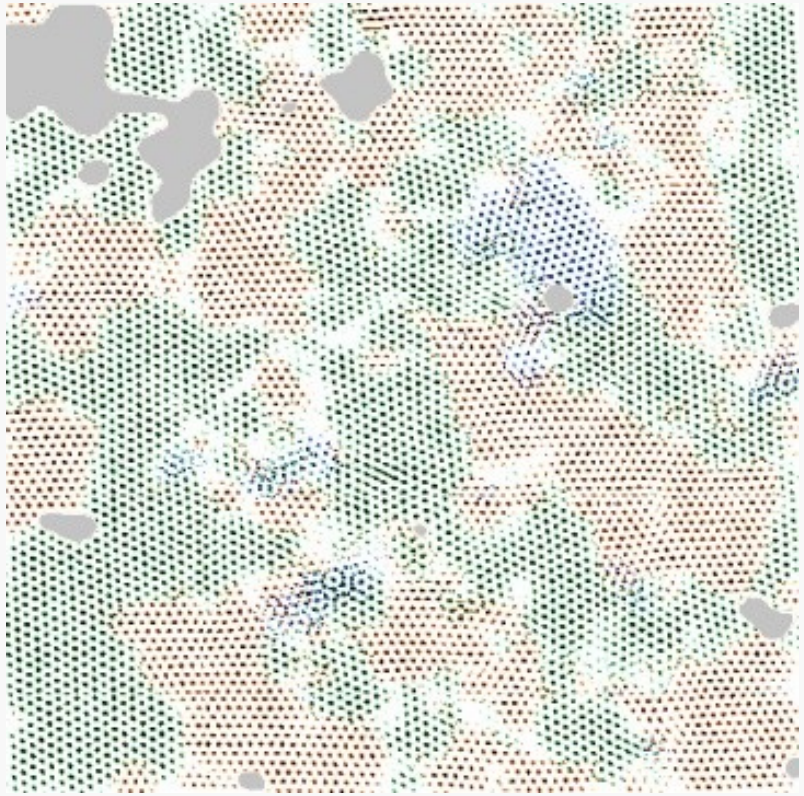


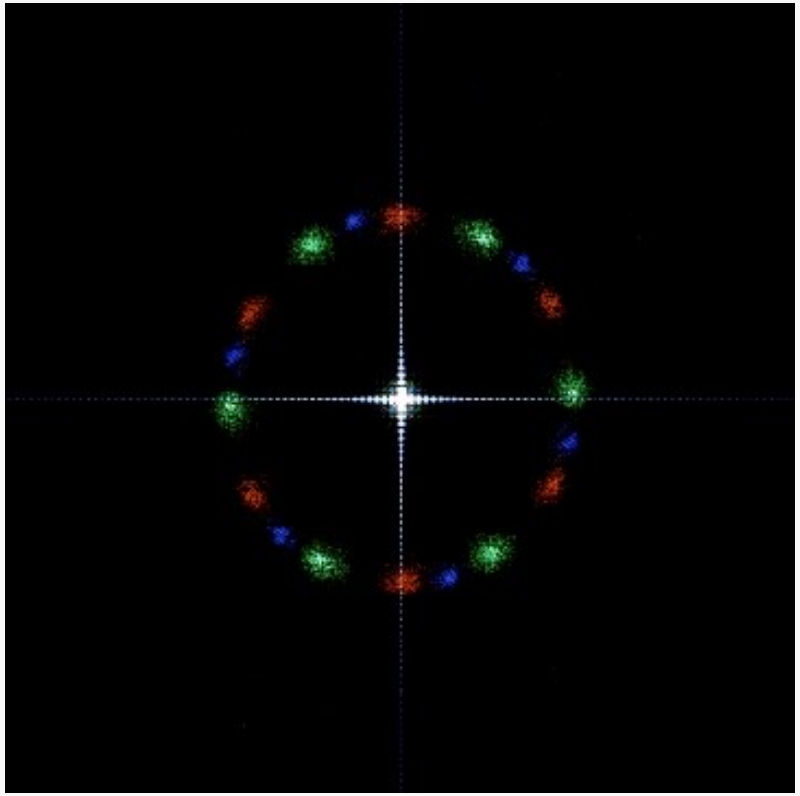
Experimental realization

Ni

Fast Fourier Transformation (FFT)

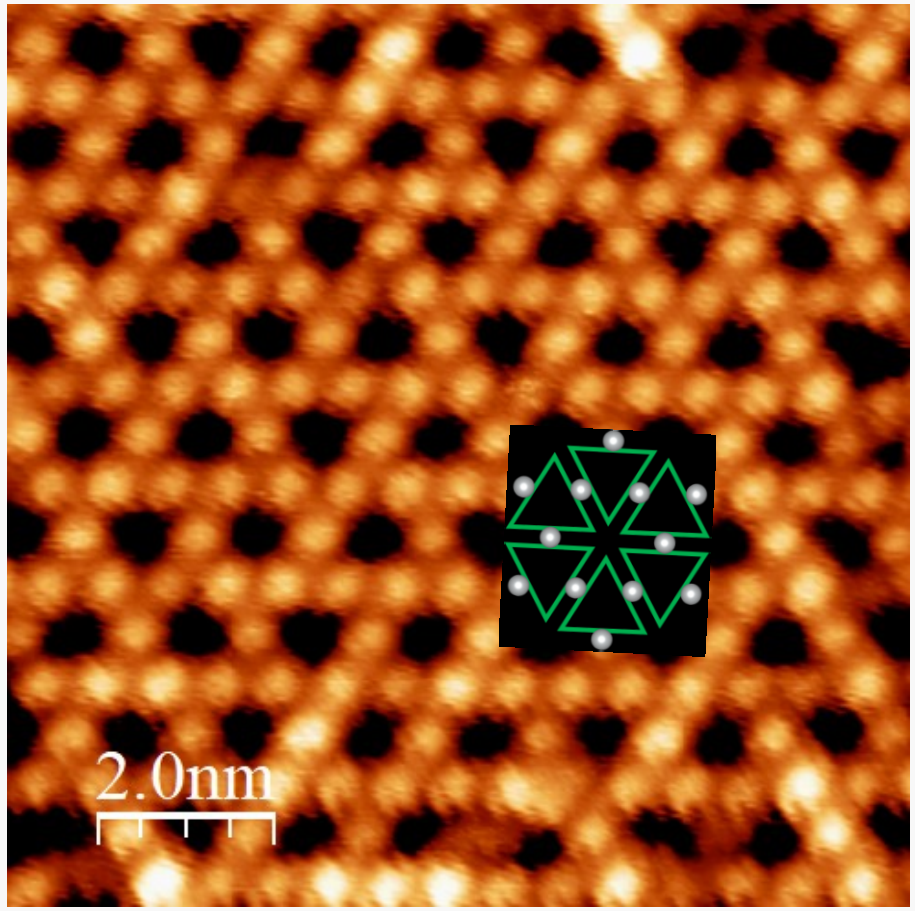






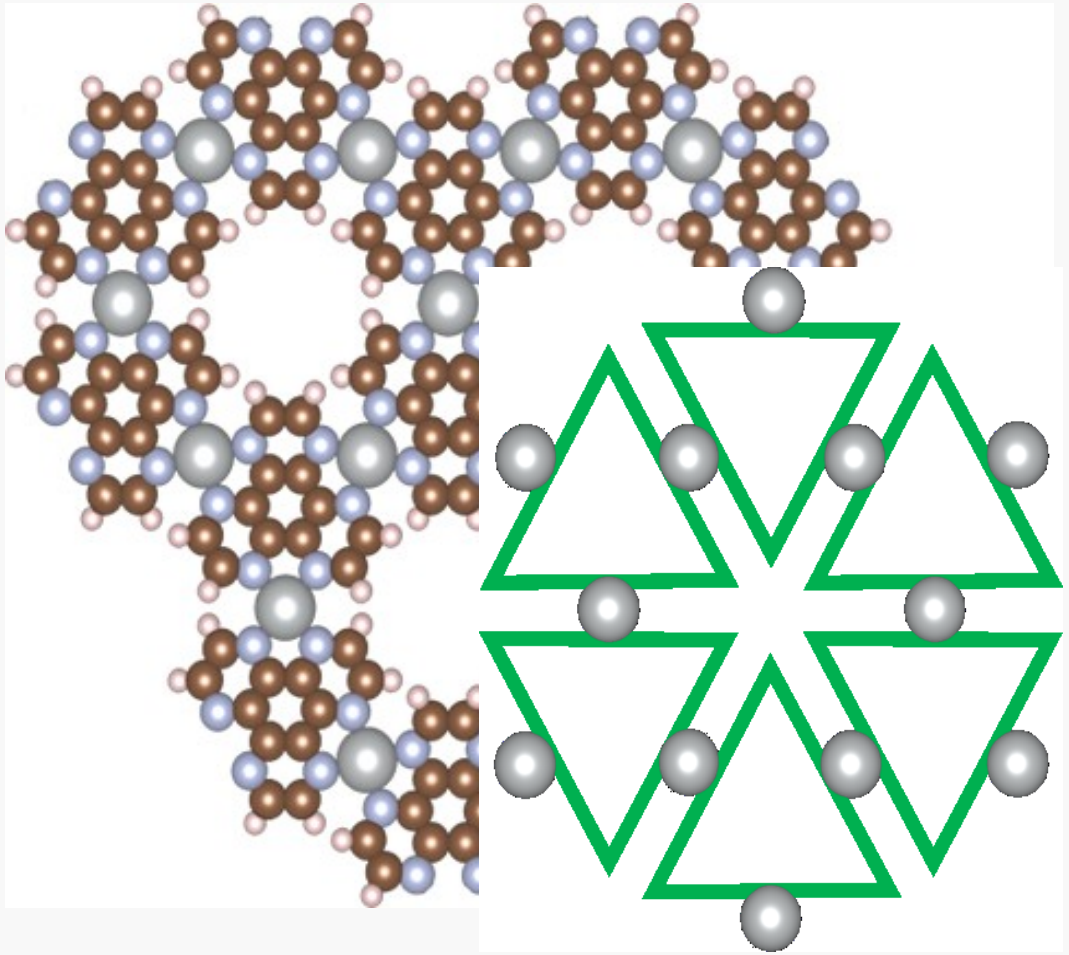
High coverage, monolayer

Experimental realization



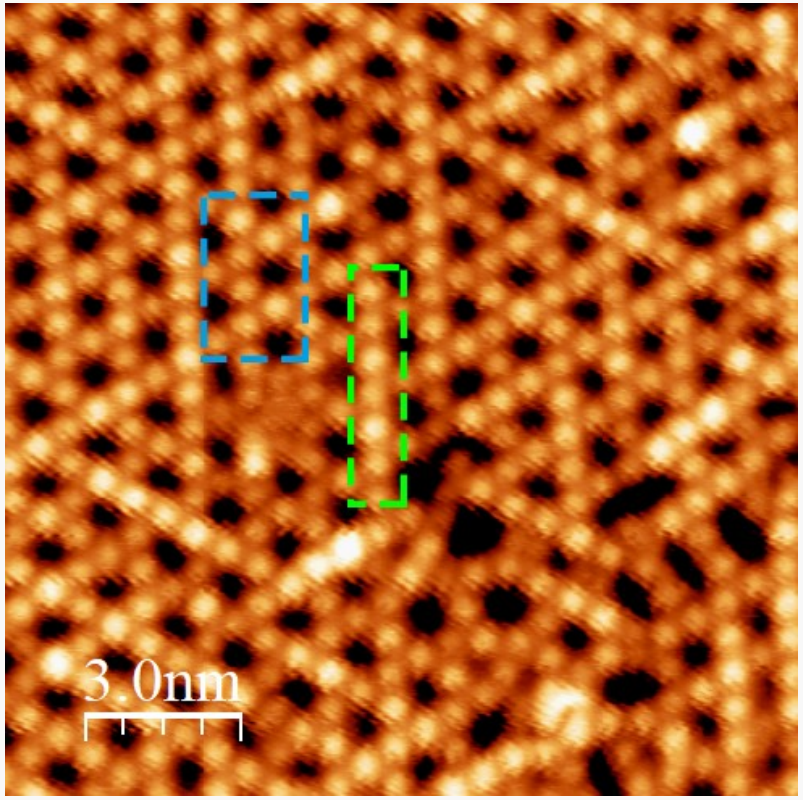
Annealing the sample to 200℃

Ni

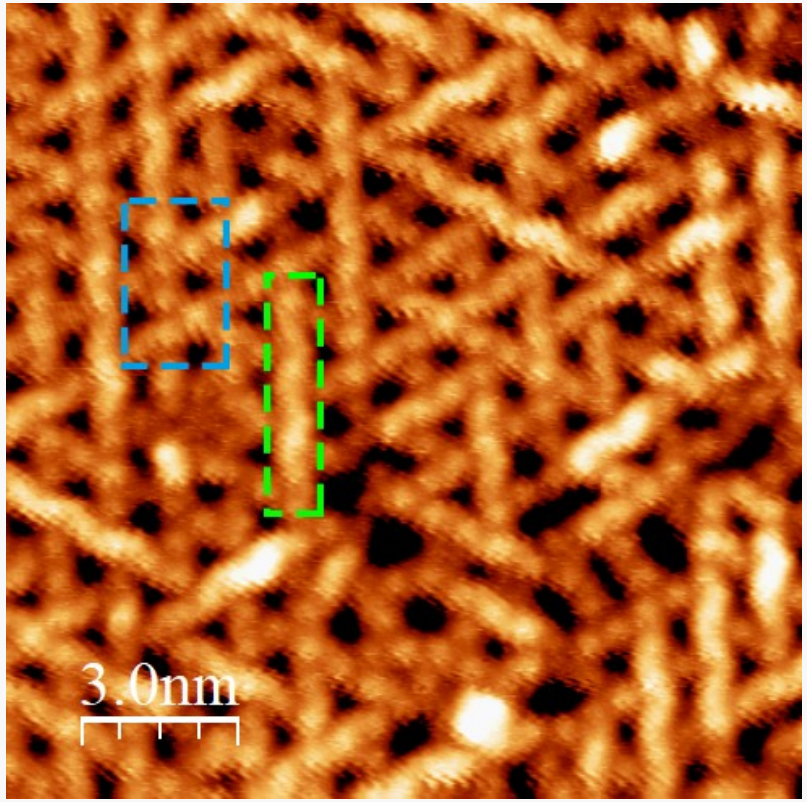


Lattice constant is 13.4Å

Ni



U=-1.6V, I=1.5nA



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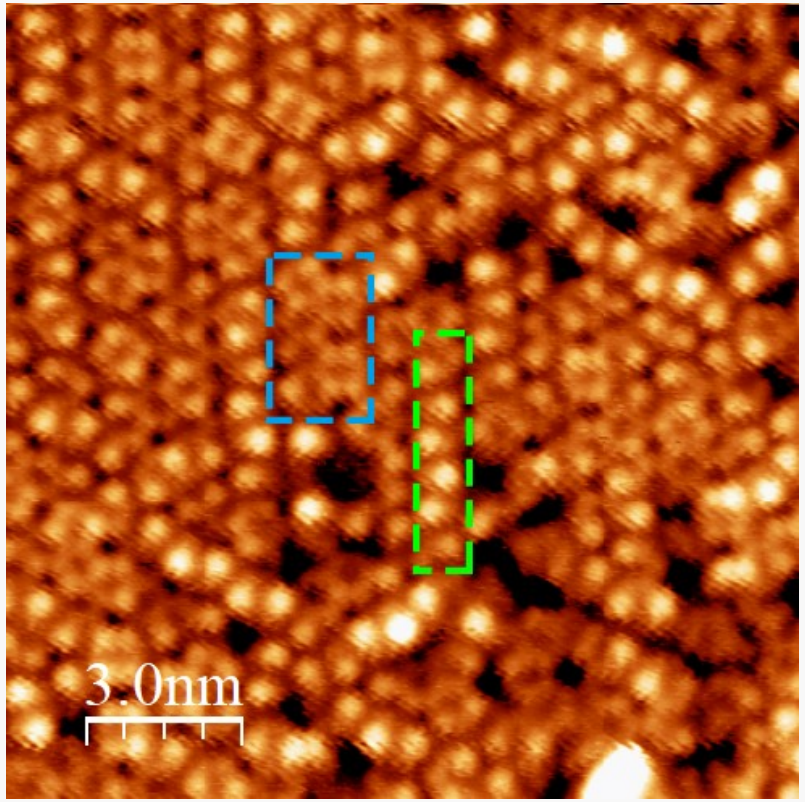
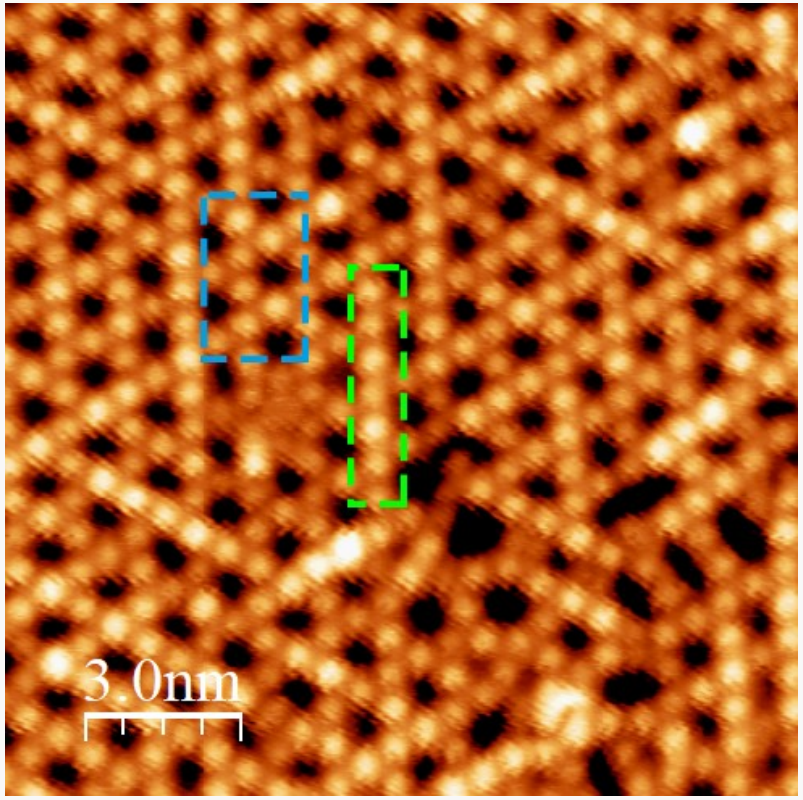


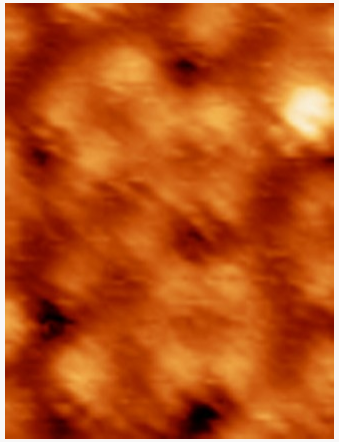
U=+1.6V, I=1.5nA

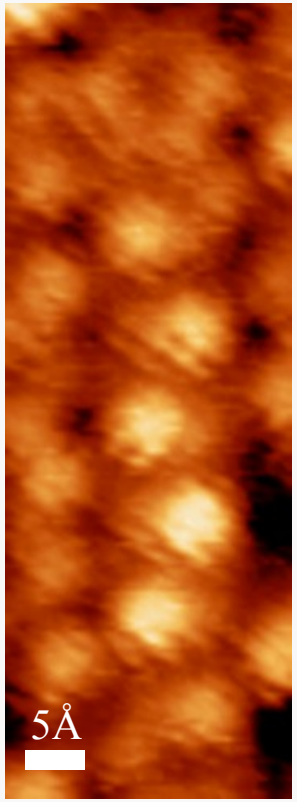
Same area, RT measurement

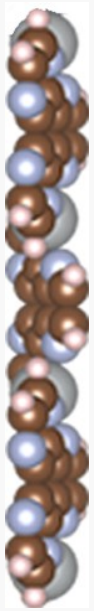
Experimental realization

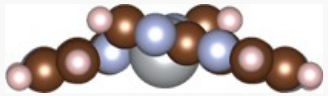
Ni

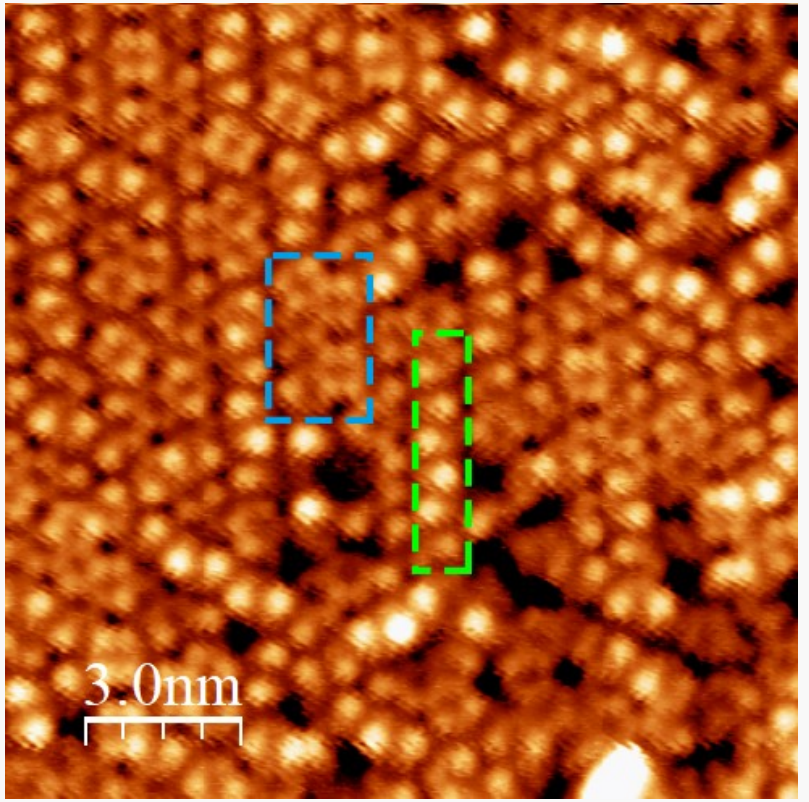












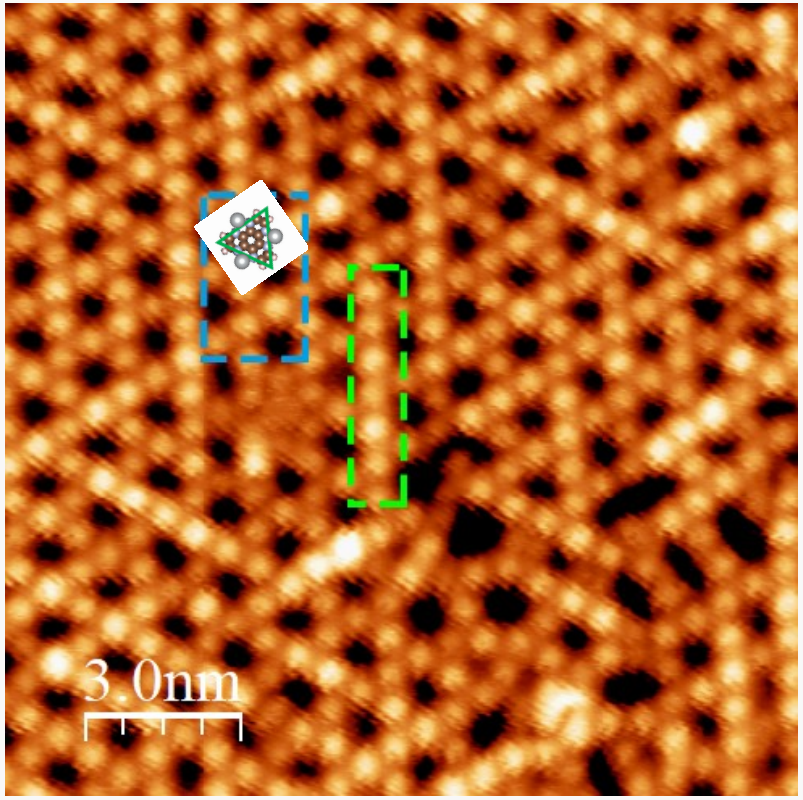
U=-1.6V, I=1.5nA

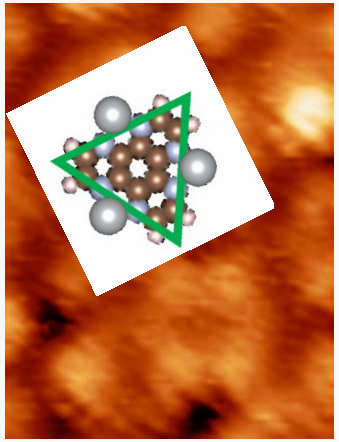
U=+1.6V, I=1.5nA

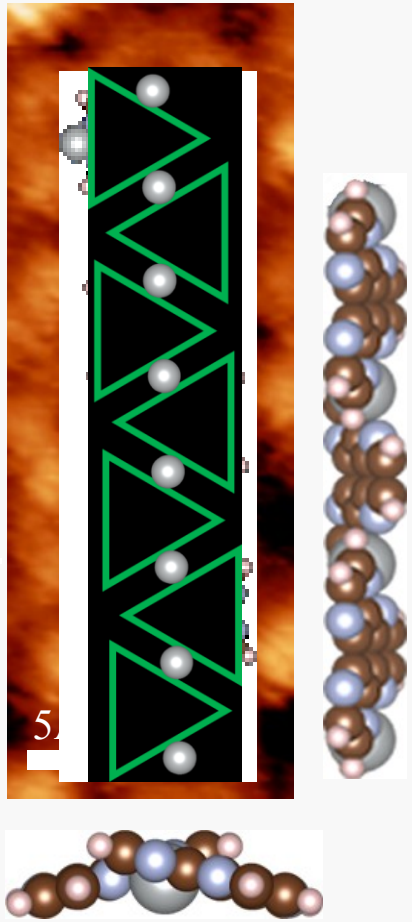
Same area, RT measurement

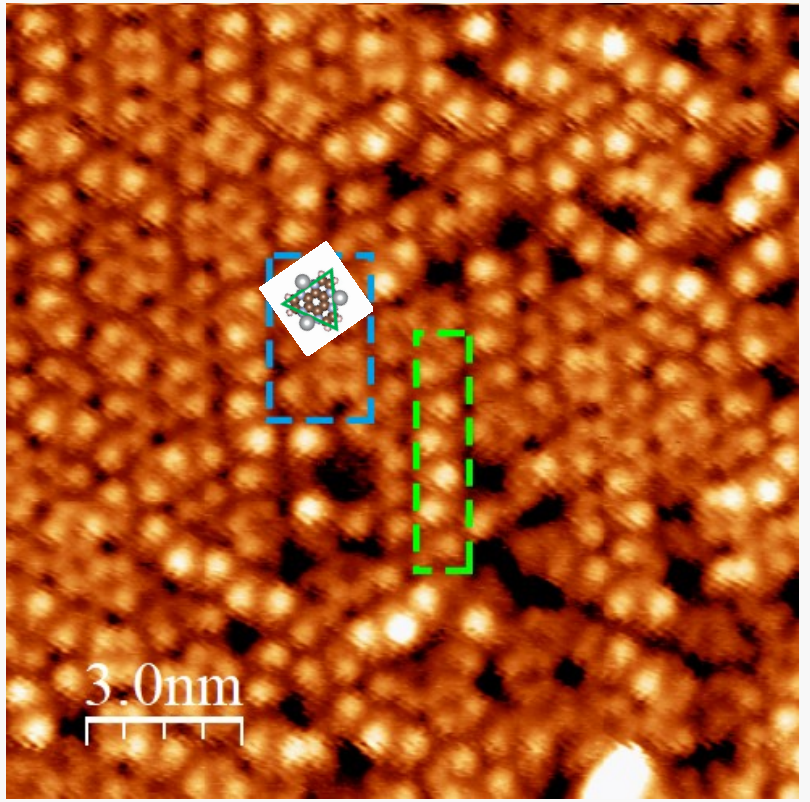
Experimental realization

Ni







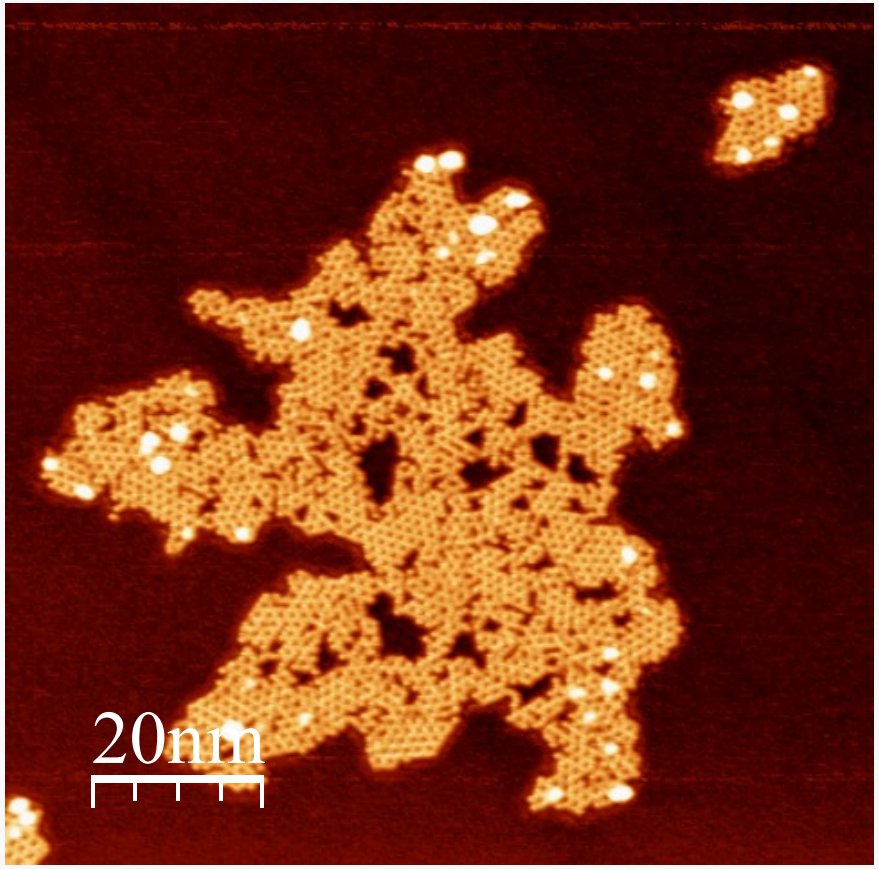


U=-1.6V, I=1.5nA

U=+1.6V, I=1.5nA

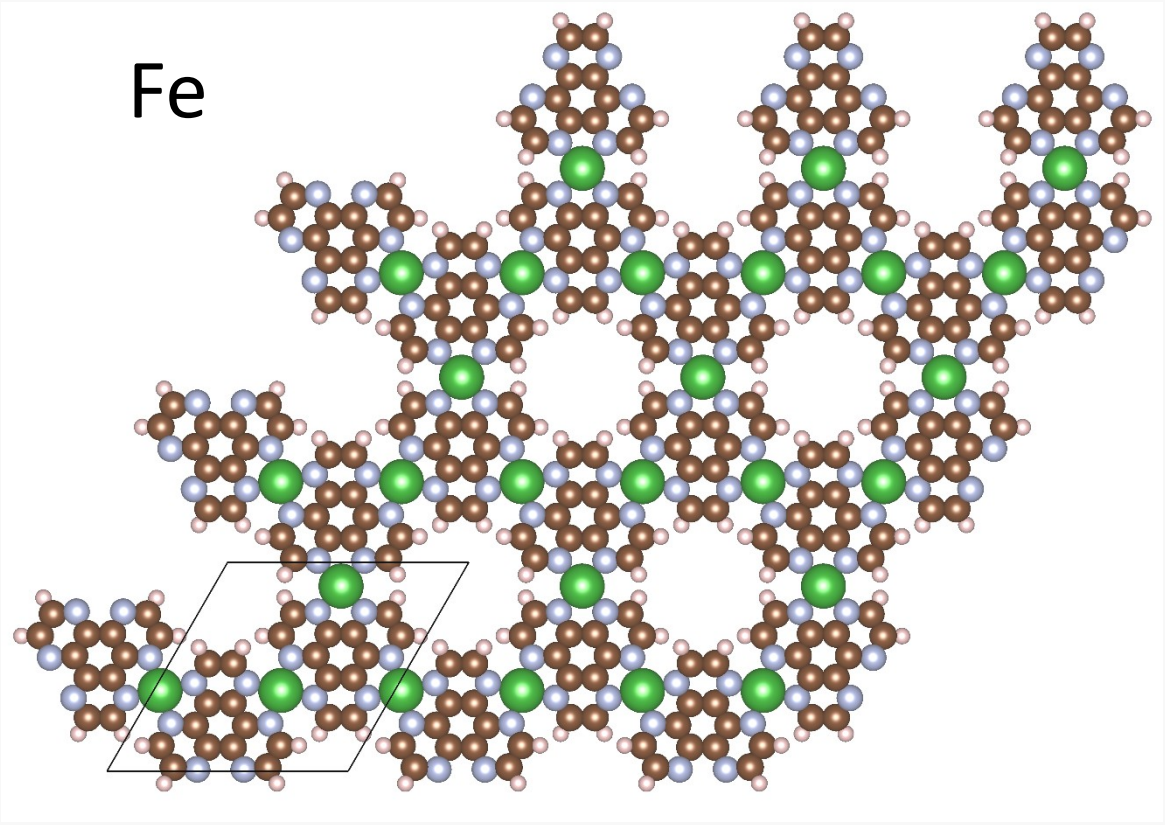
Same area, RT measurement

Experimental realization



Annealing the sample to 200℃

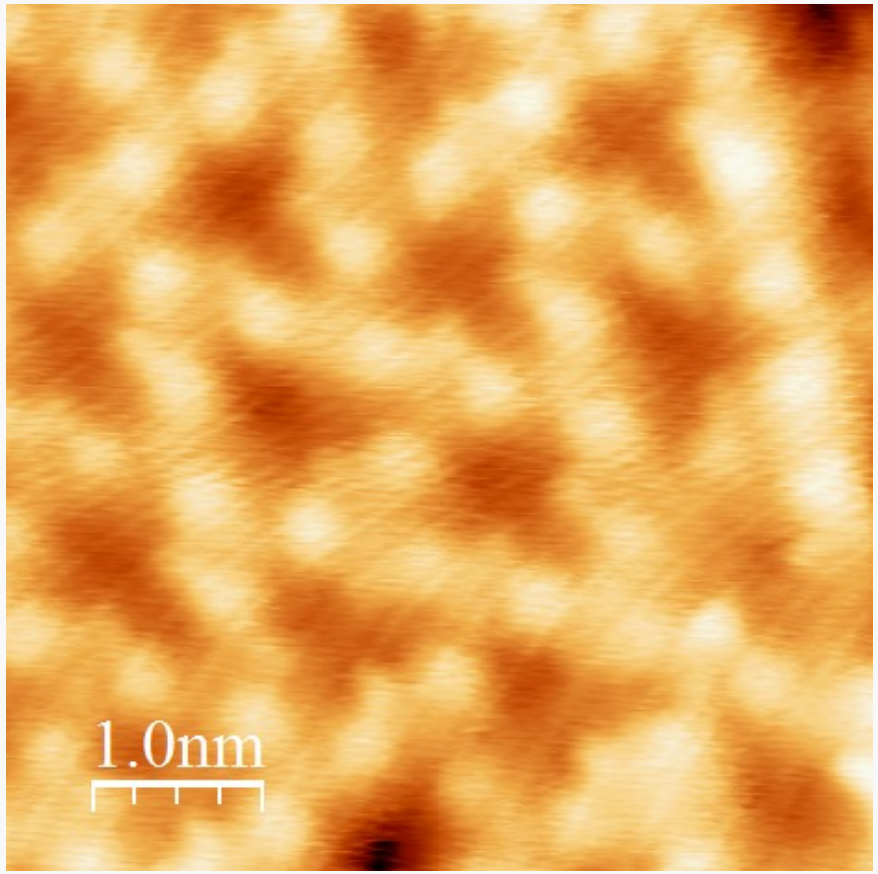
Fe

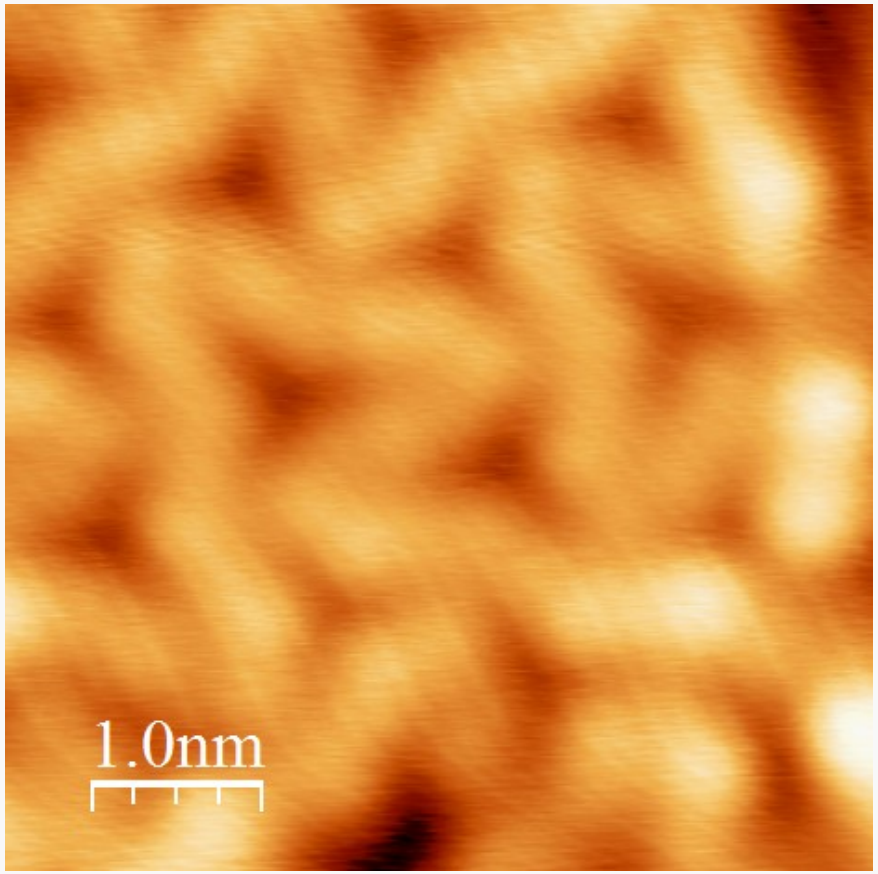


Lattice constant is 13.4Å

Experimental realization

Fe

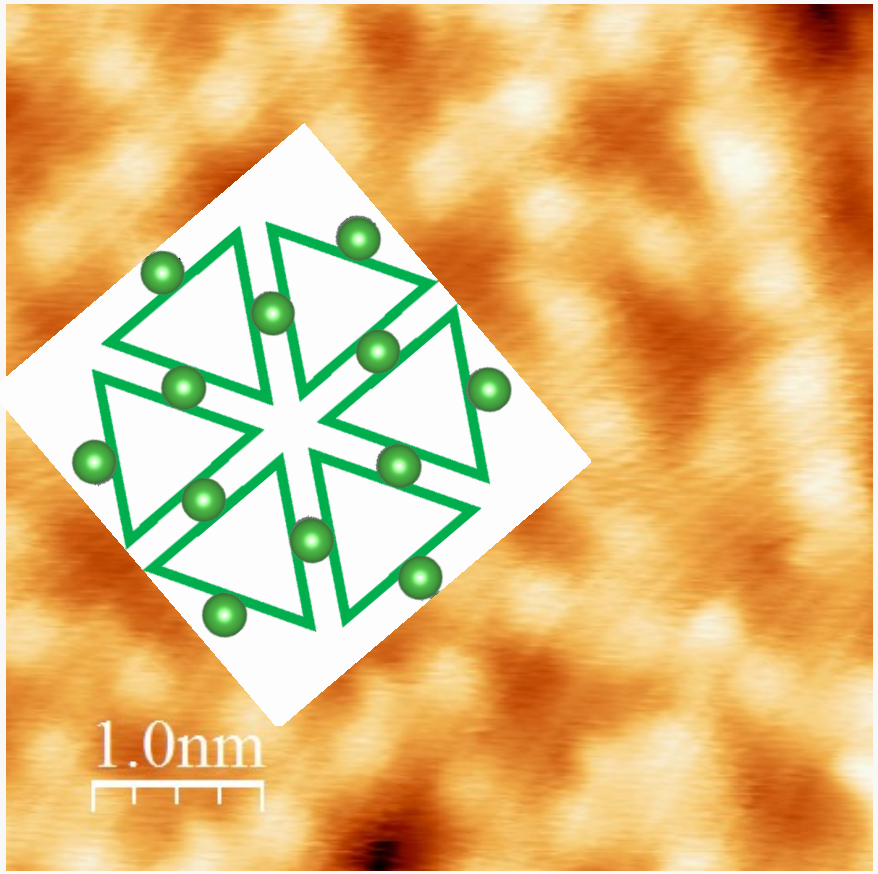


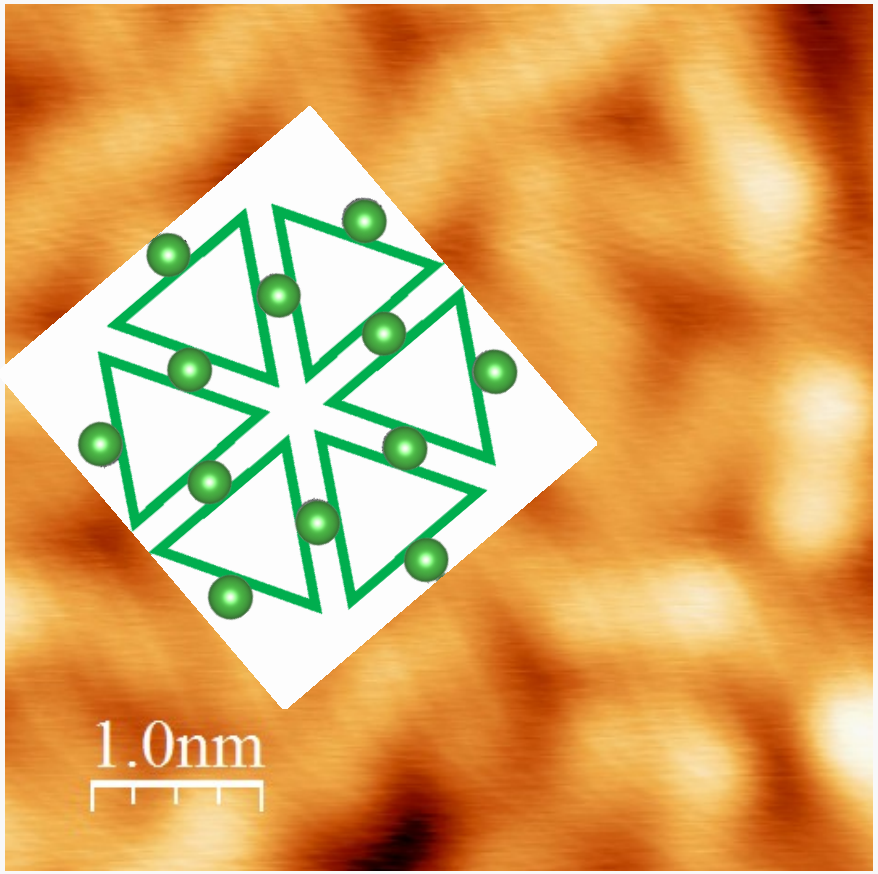


Acquired at 5K by LT-STM (M. Q. Hua)

Experimental realization

Fe





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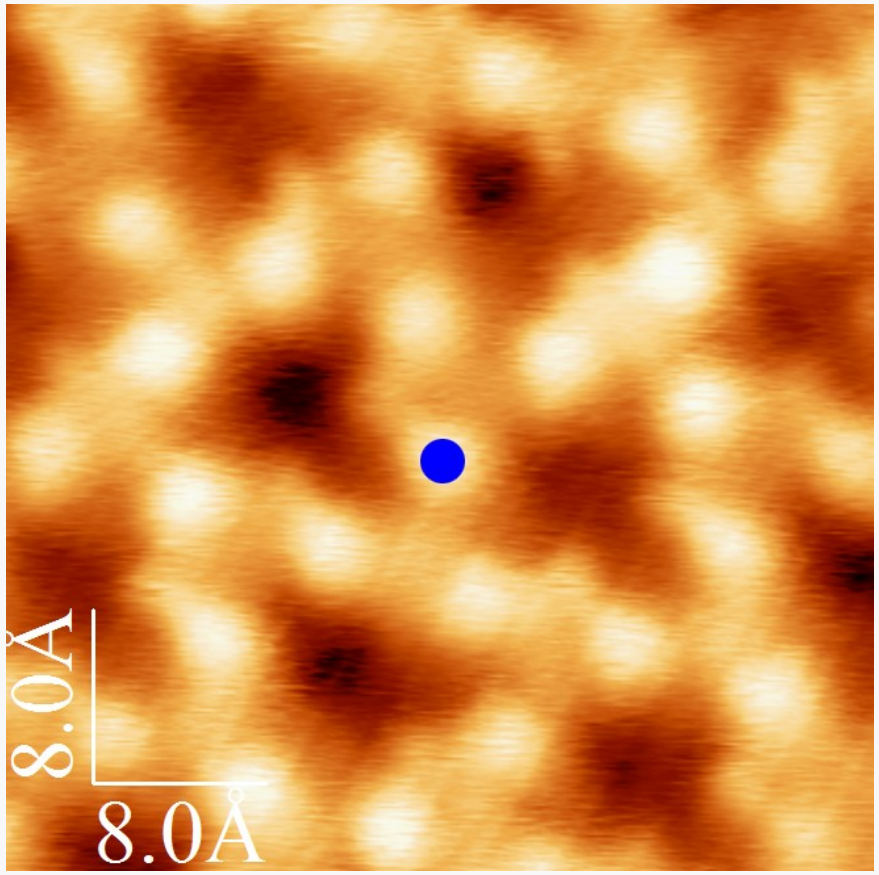
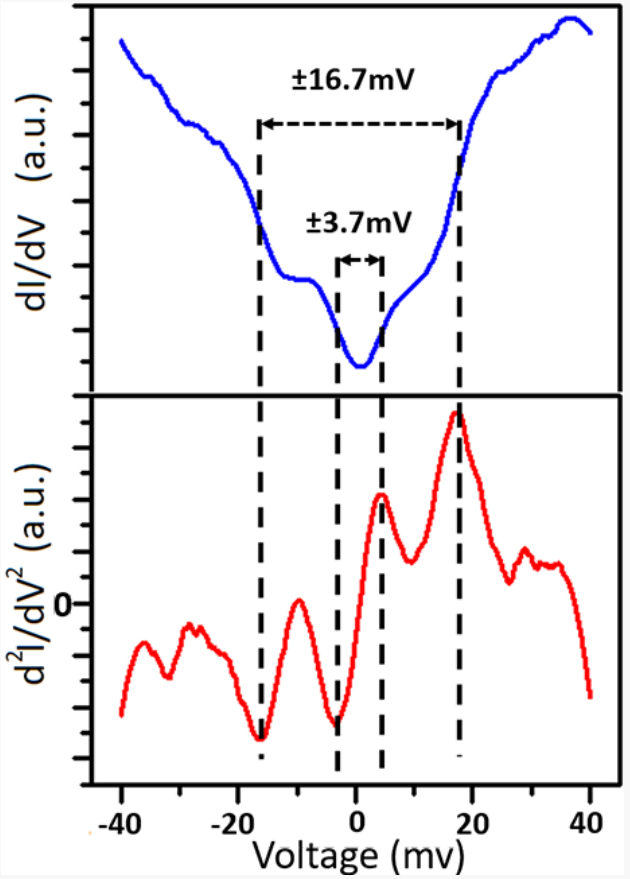
Experimental realization

Fe





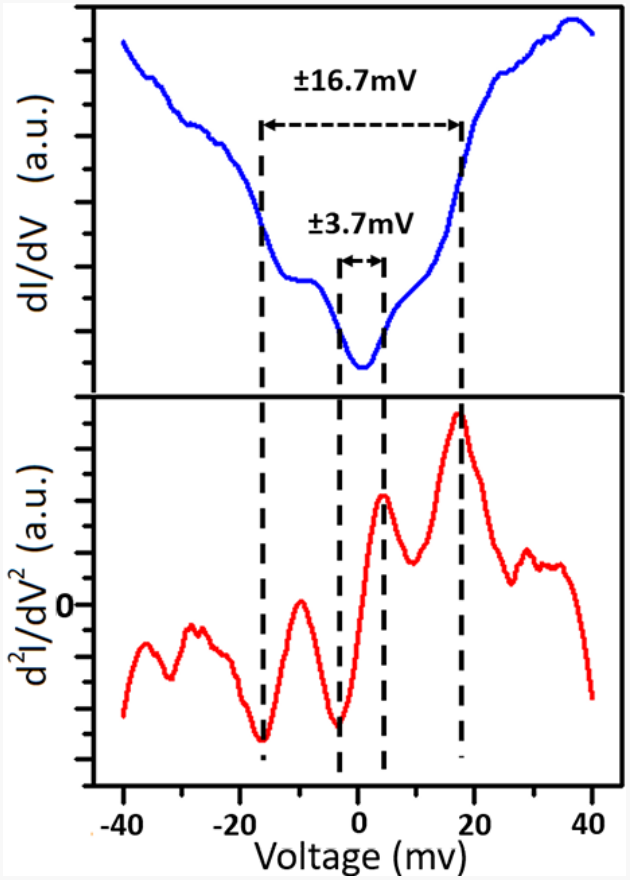
Energy splitting appears even in the absence of an external magnetic field, and thus it is called zero-field splitting (ZFS)

Small-range STS measurement at Fe.

Acquired at 5K by LT-STM

Experimental realization

Fe



Small-range STS measurement at Fe.

Zero-field splitting (ZFS)
spin Hamiltonian:

$|-1\rangle, |0\rangle, |+1\rangle$

$$H_{eff} = DS_z^2 + E(S_x^2 + S_y^2)$$

D is the axial ZFS constant to determine the magnetic anisotropy, E represents the rhombicity of the environment molecule, and Sx, Sy, and Sz are the spin operators

$|\Omega_+\rangle = D/3 + E$ $|\Omega_-\rangle = D/3 - E$ $|\Omega_0\rangle = -2D/3$

Two steps:

$\Delta E_1 = 2E$ $\Delta E_2 = -D + E$

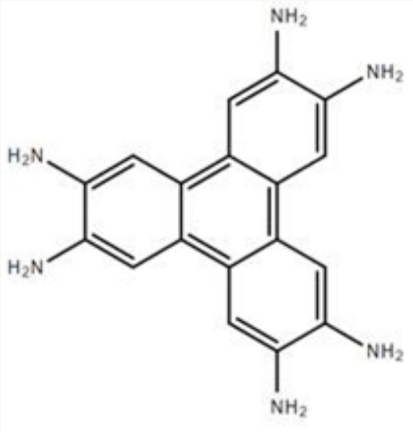
$\mathrm{E} = 1.85\mathrm{meV}$ $\mathrm{D} = -14.85\mathrm{meV}$

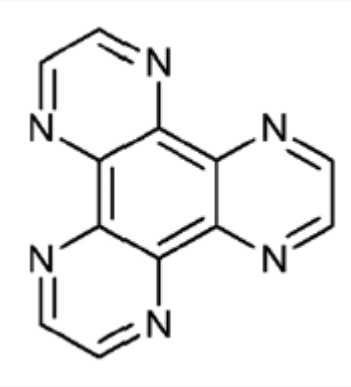
Summary

- Monolayer of two-dimensional $Ni_3(HAT)_2$, $Fe_3(HAT)_2$ can be synthesized on a Ag(111) substrate.
- The high-resolution STM image shows the non-planner structure.
- STS measurement shows a double-step feature on Fe adatom which is resulted from Spin-flip effect.

Conclusions

	$Ni_3(HITP)_2$	$Fe_3(HITP)_2$	$Ni_3(HAT)_2$	$Fe_3(HAT)_2$
Substrate	Au(111)	Au(111)	Ag(111)	Ag(111)
Annealing temperature	250°C	250°C	200°C	200°C
Lattice constant	21.7 Å	21.7 Å	13.4 Å	13.4 Å
Calculation	Quantum Spin Hall	Quantum Anomalous Hall, Ferromagnetic		
STS measurement		Kondo effect		Spin-flip effect





Acknowledgements

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Prof. Li HUANG

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- Mr. Xiaobo WANG
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- Prof. Michael Scott ALTMAN
- Prof. Yilong HAN
- Prof. Haibin SU

On Surface Assembly of Conjugated Metal-Organic Coordination Frameworks

THANKS

FOR YOUR WATCHING

HKUST ZiAng Gao

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