Synthesis and Characterization of Two-Dimensional Conjugated Metal-Organic Frameworks Self-Assembled on Metallic and Transition-Metal Dichalcogenides Surfaces

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Physics, HKUST

OUTLINE

Part 1 Introduction

Part 2 Synthesis of Single-Layer Two-Dimensional Metal-Organic Frameworks **$M_3(HAT)_2$** (M= **Ni**, **Fe**, **Co**, HAT=1,4,5,8,9,12-Hexaazatriphenylene) Using an **On-Surface Reaction**

Part 3 **Templated Growth** of Two-Dimensional Conjugated Metal-Organic Frameworks **Cu-HAT** on **Cu(111), Au(111)** and **MoS_2** Substrates

Part 4 Self-Assembly of Two-Dimensional Conjugated Metal-Organic Frameworks **$M_3(HAT)_2$** (M=Ni, Co) on a **MoS_2** Surface

Part 5 Summary and Perspectives

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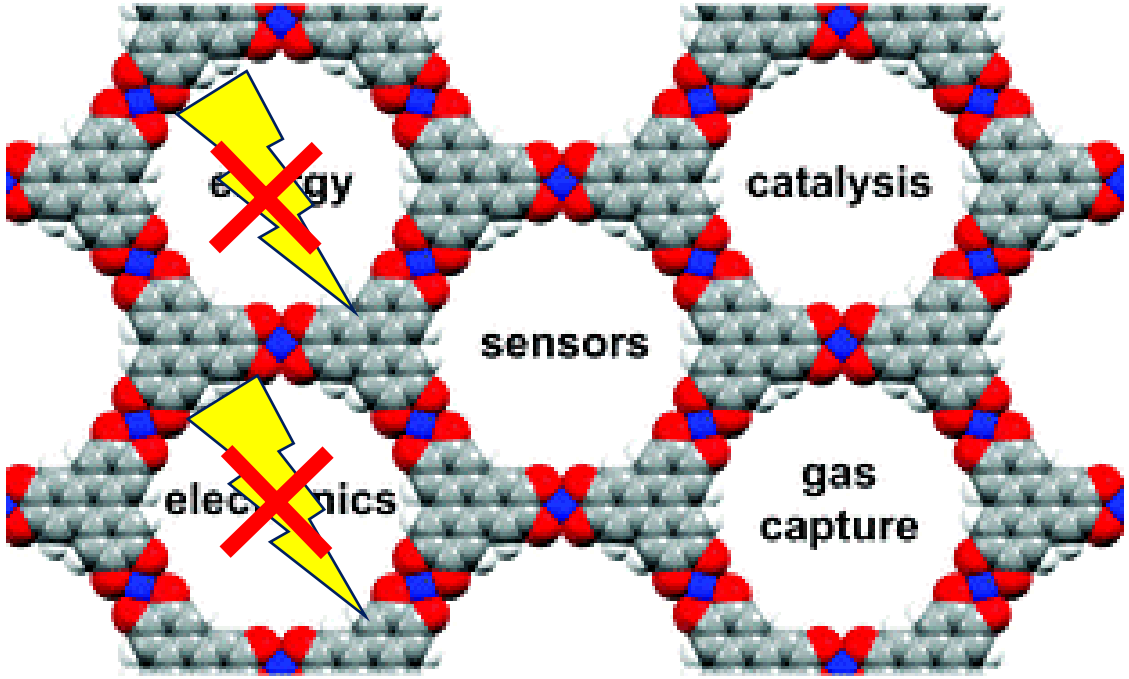
Part 5 Summary and Perspectives

PART 01

Introduction

- 2D conjugated metal-organic frameworks (c-MOFs)
- Experimental method: on-surface synthesis and scanning tunneling microscopy (STM)



Overview of 2D conjugated metal-organic frameworks (c-MOFs)

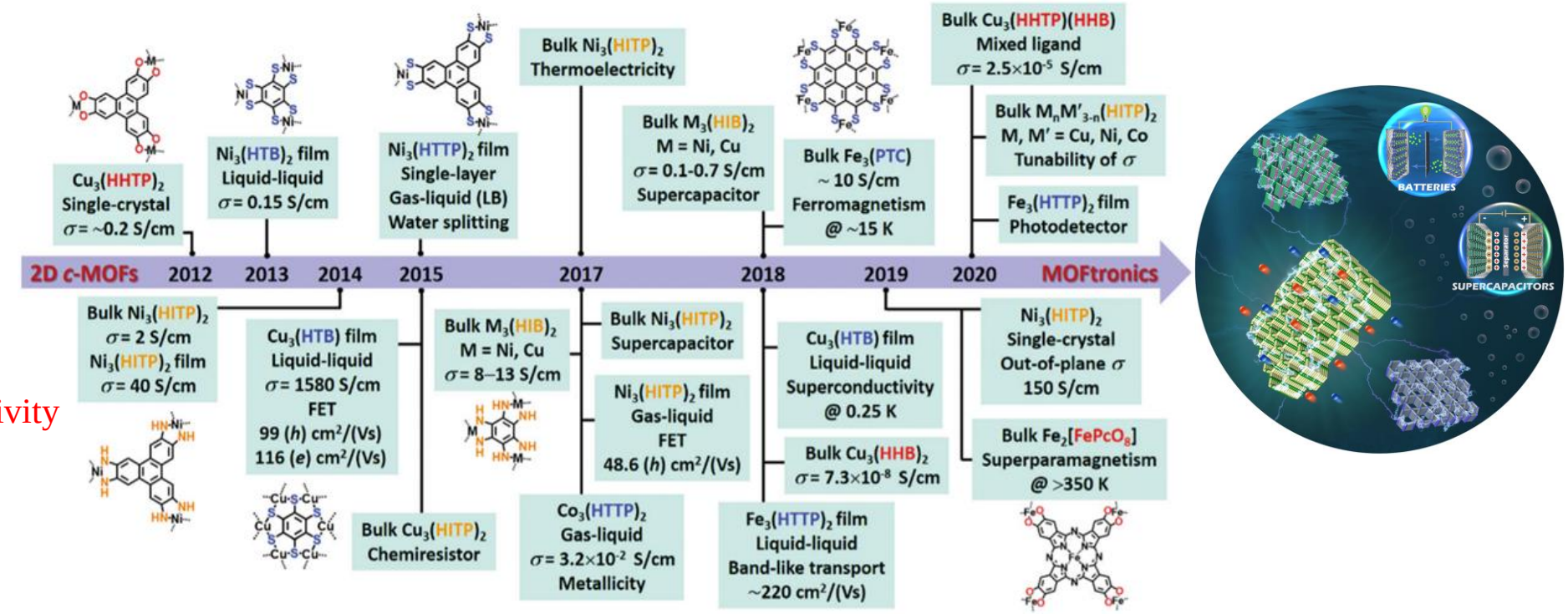
Characteristics

Traditional:
- Tunable porosity
- Versatile structures
- Well-defined active sites

Unique:
- High stability
- Electrochemical activity
- Photoactivity
- Tailorable band gaps
- Superior electrical conductivity
- Ferromagnetic ordering
- Topological state

Applications

- Optoelectronics
- Spintronics
- Batteries
- Supercapacitors



Synthesis timeline of 2D conjugated metal-organic frameworks

X. L. Feng, et al. *Chem. Soc. Rev.*, **2021**, 50, 27642793

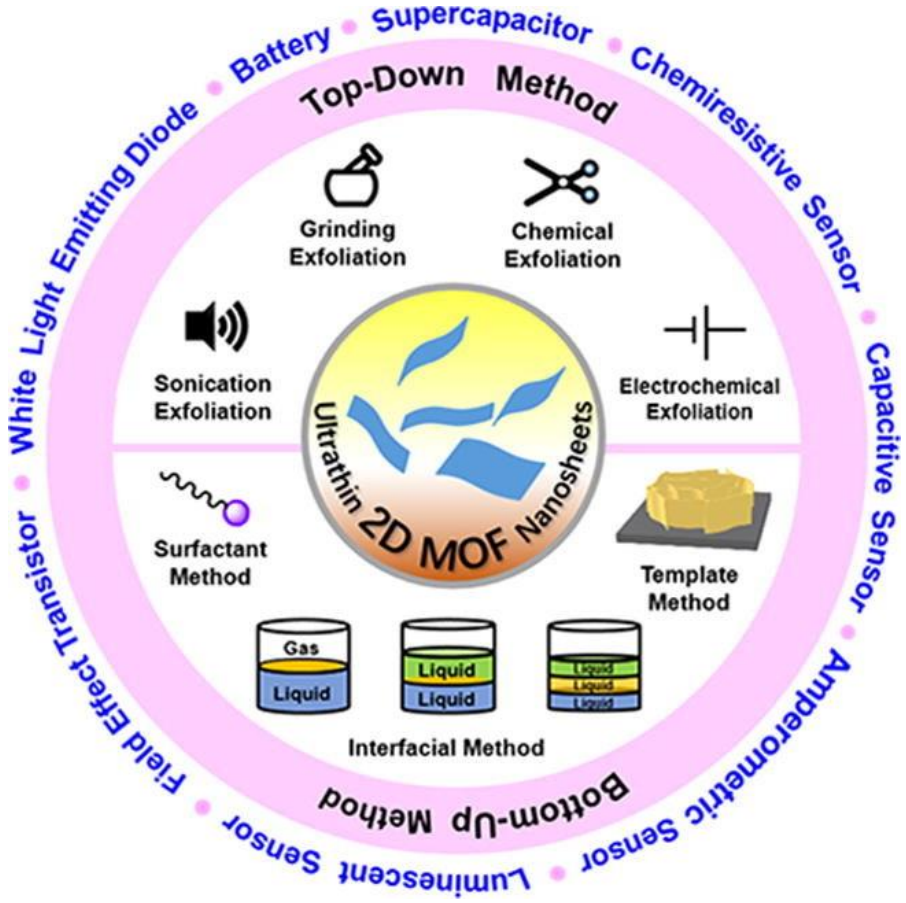
Synthetic strategies of 2D c-MOFs

Top-down exfoliation

- Sonication assisted liquid exfoliation
- Solvent-induced exfoliation
- Freeze-thaw cycling exfoliation
- Li-intercalation method
- Chemical exfoliation

Bottom-up assembly

- Hydro-/Solvothermal synthesis
- Wet-interface-assisted fabrication
- Diffusion-mediated growth
- **On-surface coordination self-assembly method**



Top-down and bottom-up approaches to 2D MOFs synthesis

C. Wang, et al. *Chin. J. Chem.*, **2018**, 36, 754.

W. Huang, et al. *Coordin. Chem. Rev.*, **2018**, 377, 44.

On-surface coordination self-assembly method

Substrate

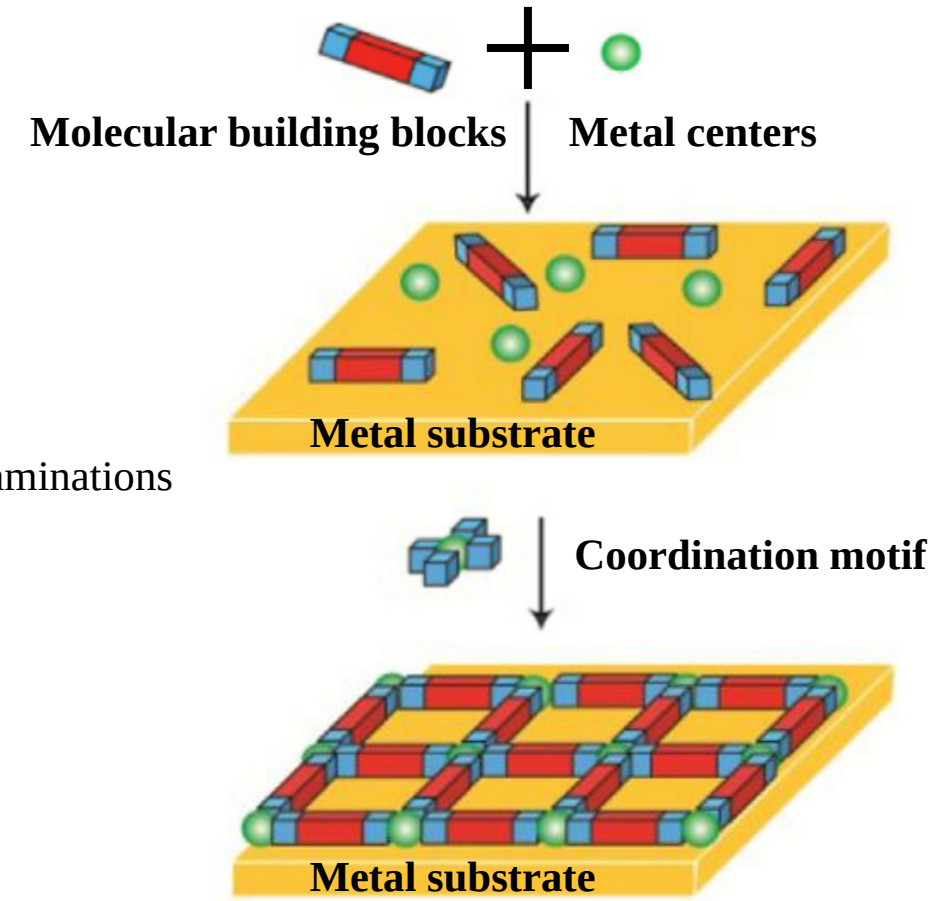
- Atomically flat
- Single crystals
- 2D materials

Environment

- Ultra-high vacuum (UHV) reduces contaminations
- Solvent-free

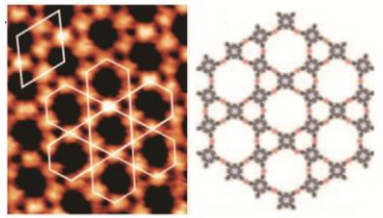
Parameters

- Substrate temperature
- Evaporation rate or sequence
- Surface concentrations of the adsorbates



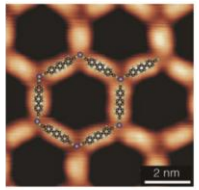
Surface-confined metal–organic networks

Kagome lattice



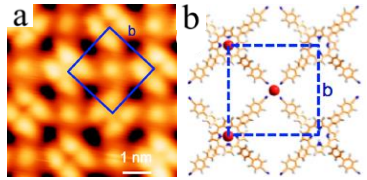
N. Lin, et al. *J. Am. Chem. Soc.*, **2009**, 131, 5376.

Honeycomb lattice



N. Lin, et al, *Angew. Chem.*, **2007**, 119, 724.

Square lattice

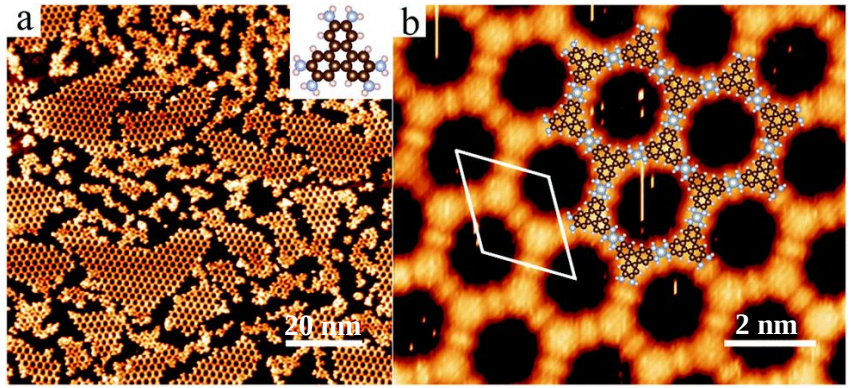


W. Auwärter, et al. *J. Am. Chem. Soc.*, **2015**, 137, 2420.

N. Lin, et al. *Prog. Surf. Sci.*, **2016**, 91(3), 101.

Review: 2D c-MOFs grown on metallic substrates

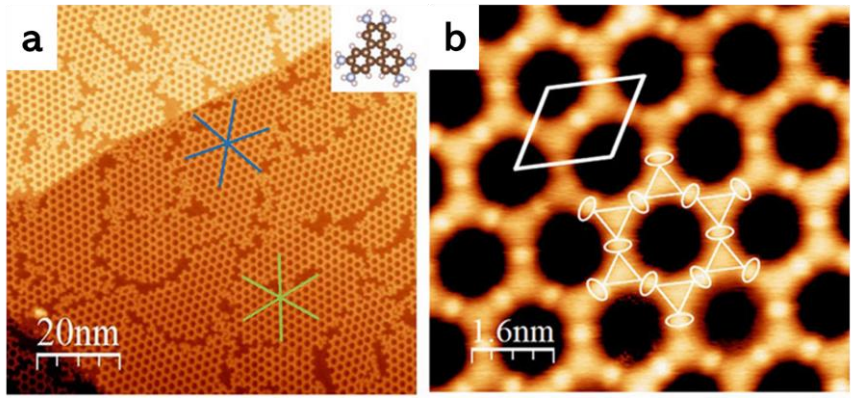
1



Z. Gao, et al. *Nanoscale*, **2019**, 11, 878–881.

$Ni_3(HITP)_2$ on Au(111)

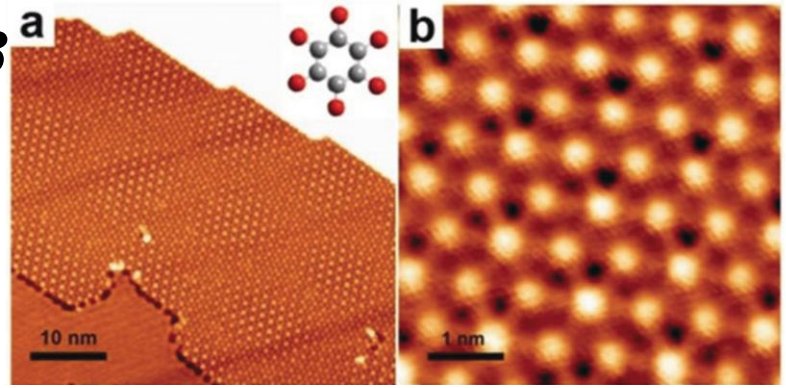
2



Z. Gao, et al. *J. Phys. Chem. C*, **2020**, 124, 27017.

$Fe_3(HITP)_2$ on Au(111)

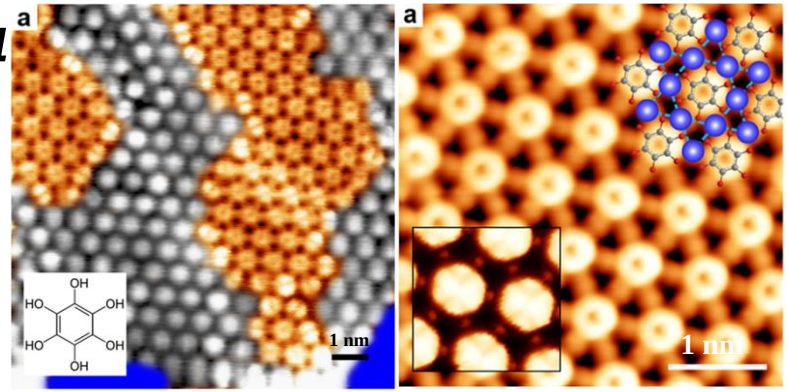
3



R. Zhang, et al. *Angew. Chem.*, **2020**, 132, 2691.

$Cu_3(BHO_{-6H})$ on Cu(111)

4

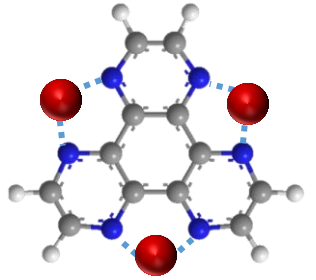


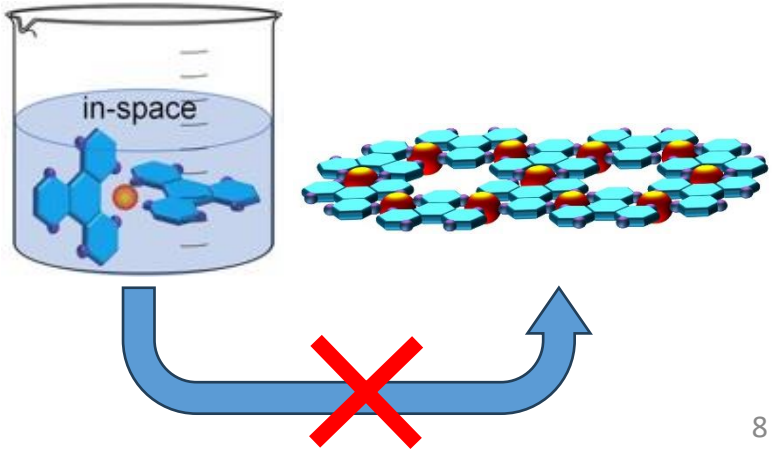
M. Hua, et al. *J. Phys. Chem. Lett.*, **2021**, 12, 3733.

$Fe_3(BHO_{-6H})$ on Au(111)

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

- Small size;
- Electron-deficient;
- A rigid planar conjugated structure;
- Three bipyridine side groups:
  strong metal-organic bond;
  no dehydrogenation reaction.





Scanning Tunneling Microscopy (STM)

Ultra-high vacuum (UHV)

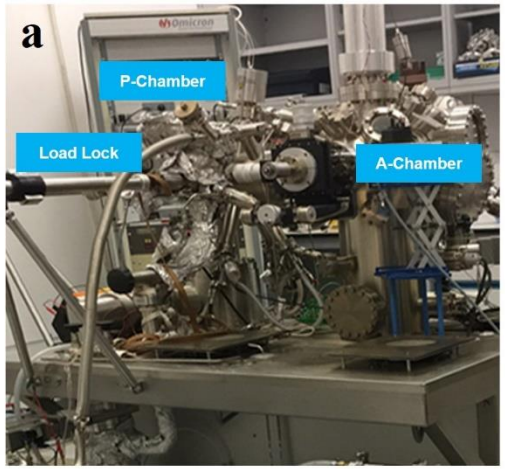
- $1 \times 10\text{^}(-9)\ mbar$
- ion pump, turbo pump, dry scroll pump

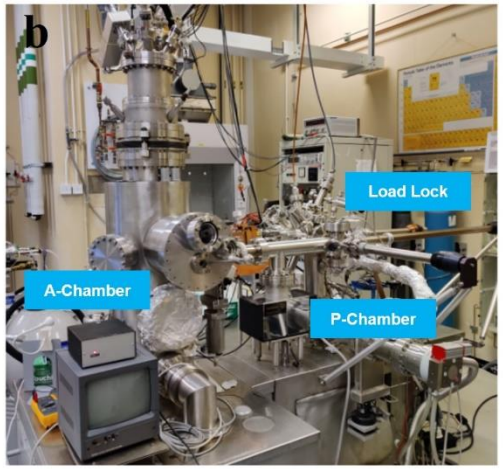
Two systems

- Variable-temperature (VT) system:
  room temperature (RT);
- Low-temperature (LT) system:
  LN_2 (77K); LHe (5K).

Sample preparation

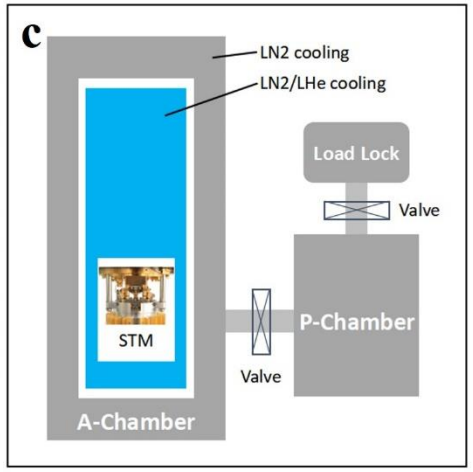
- Cleaning procedure:
  Single-crystal metals: sputtering and annealing;
  Bulk MoS_2: mechanical exfoliation and annealing.
- Molecule deposition: heating crucible with a filament.
- Metal deposition:
  for Fe, Co: electron beam deposition;
  for Ni, Cu: heating metal-wrapped filaments.

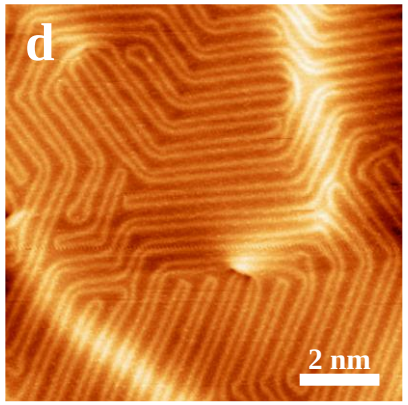


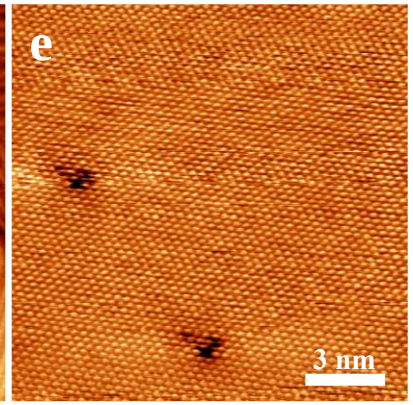


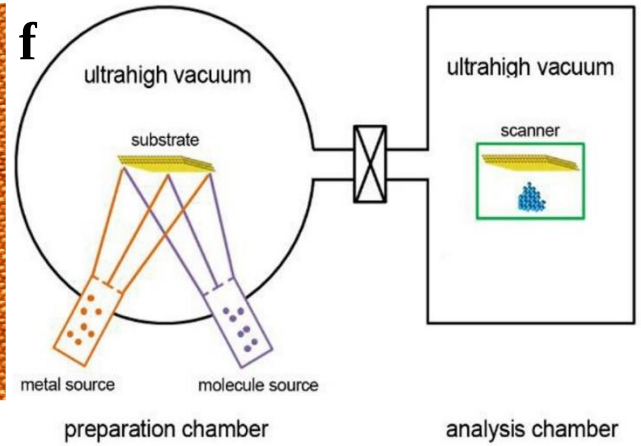
VT-STM

LT-STM









Clean Au(111) surface

Clean MoS_2 surface

Sample preparation

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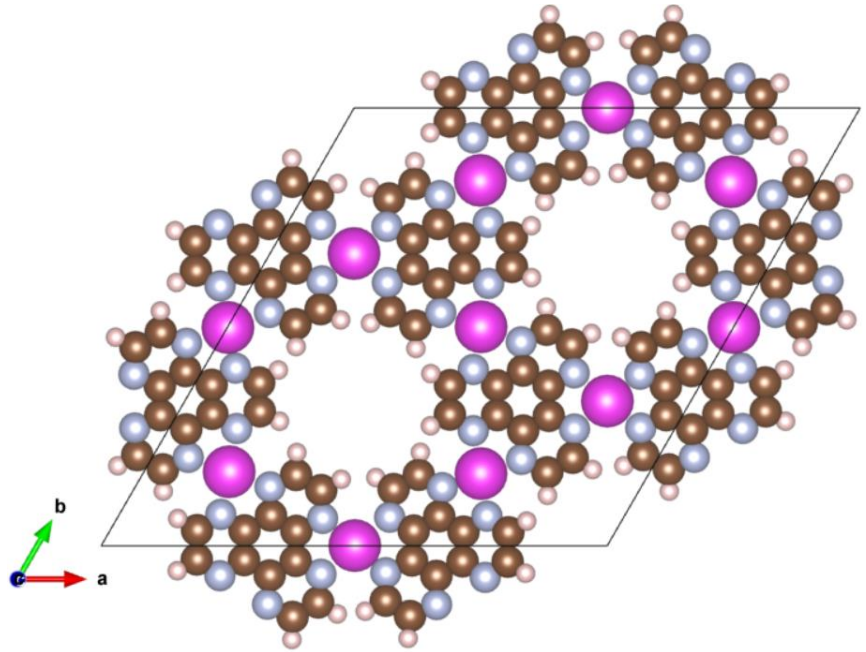
Part 5 Summary and Perspectives

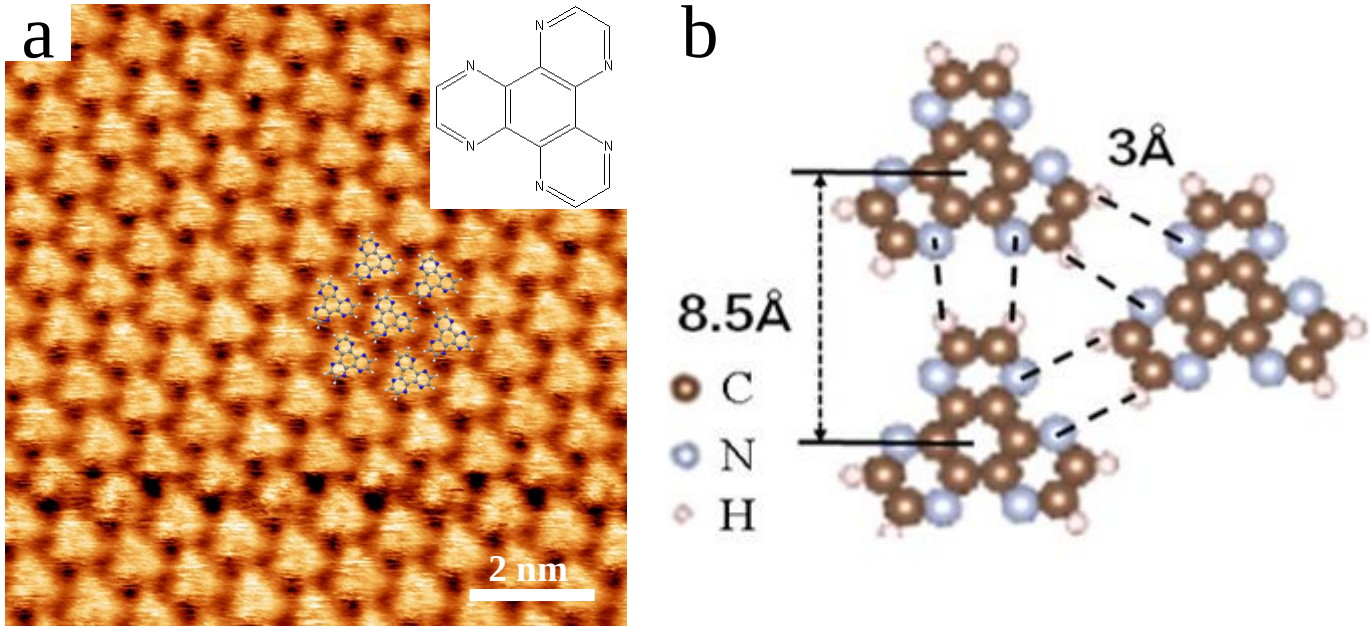
PART 02

Synthesis of Single-Layer Two-Dimensional Metal-Organic Frameworks $M_3(HAT)_2$ (M=**Ni**, **Fe**, **Co**, HAT=1,4,5,8,9,12-hexaazatriphenylene) Using an **On-Surface Reaction**

- **HAT** molecules self-assembled on metallic substrates
- $Ni_3(HAT)_2$ c-MOFs self-assembled on **Ag(111)**, **Au(111)** substrates
- $Fe_3(HAT)_2$ c-MOF self-assembled on **Ag(111)** substrate
- $Co_3(HAT)_2$ c-MOF self-assembled on **Au(111)** substrate



Close-packed molecular islands of HAT molecules self-assembled on Ag(111) substrate

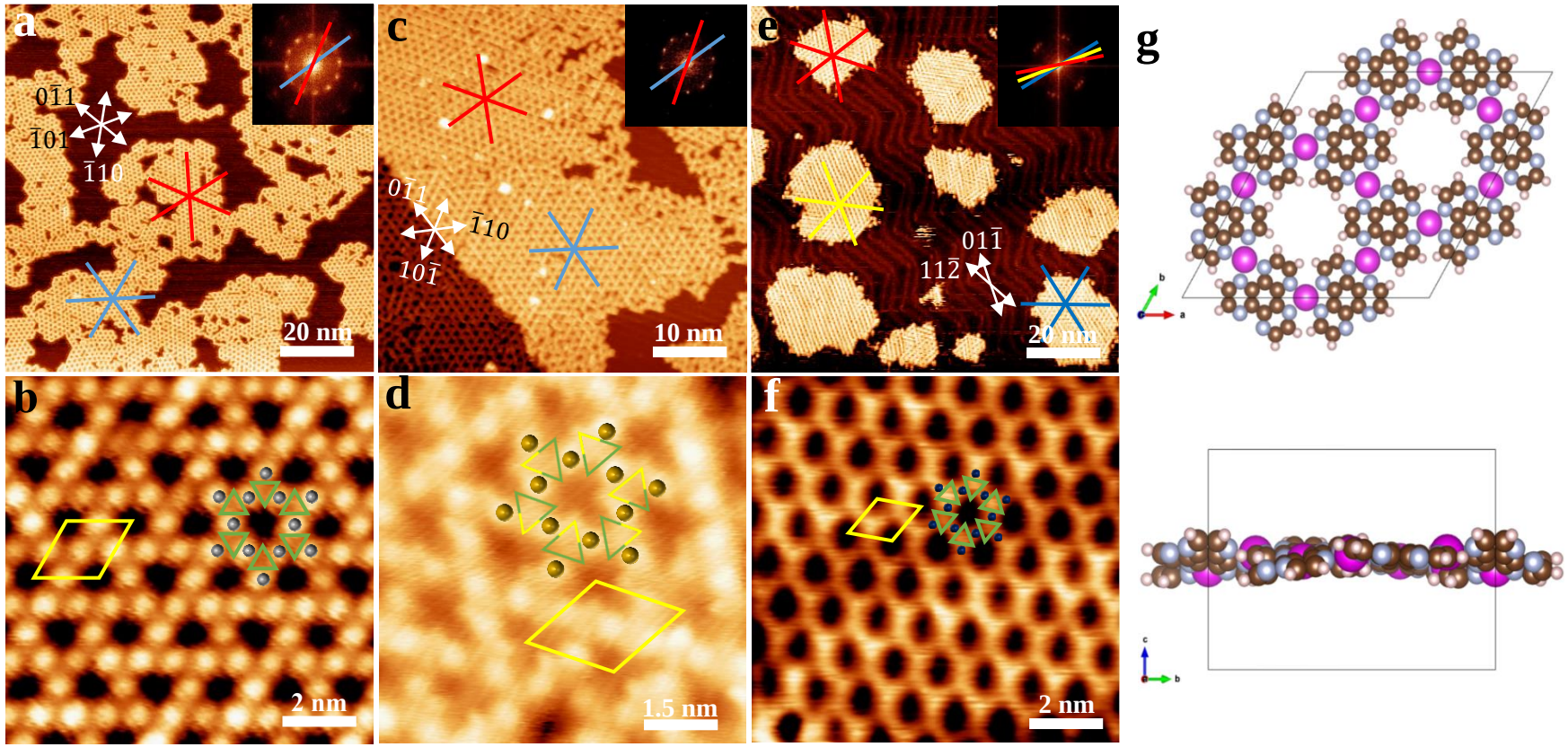


Close-packed HAT molecular islands on Ag(111) substrates

Close-packed HAT molecular islands

- A triangular lattice
- Lattice constant: 8.5 Å
- C-N length: 3 Å

2D $M_3(HAT)_2$ c-MOFs self-assembled on Ag(111) and Au(111) substrates (M=Ni, Fe, Co)

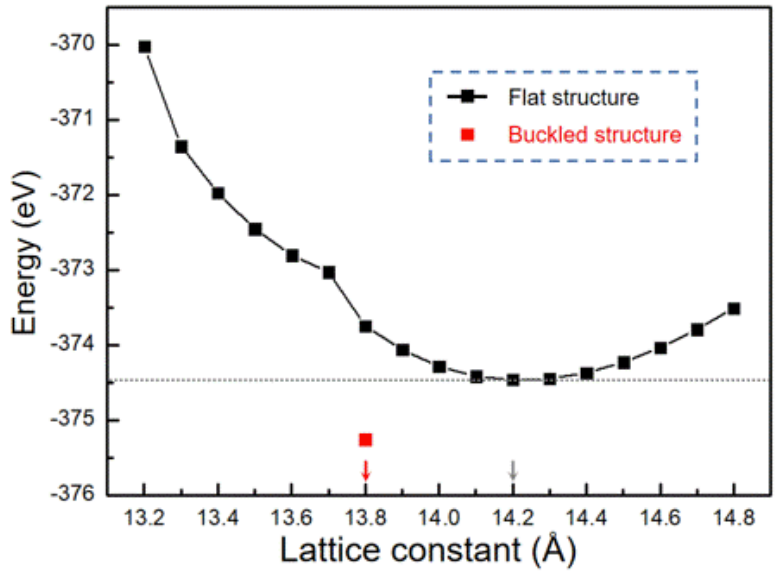


M-HAT 2D c-MOFs

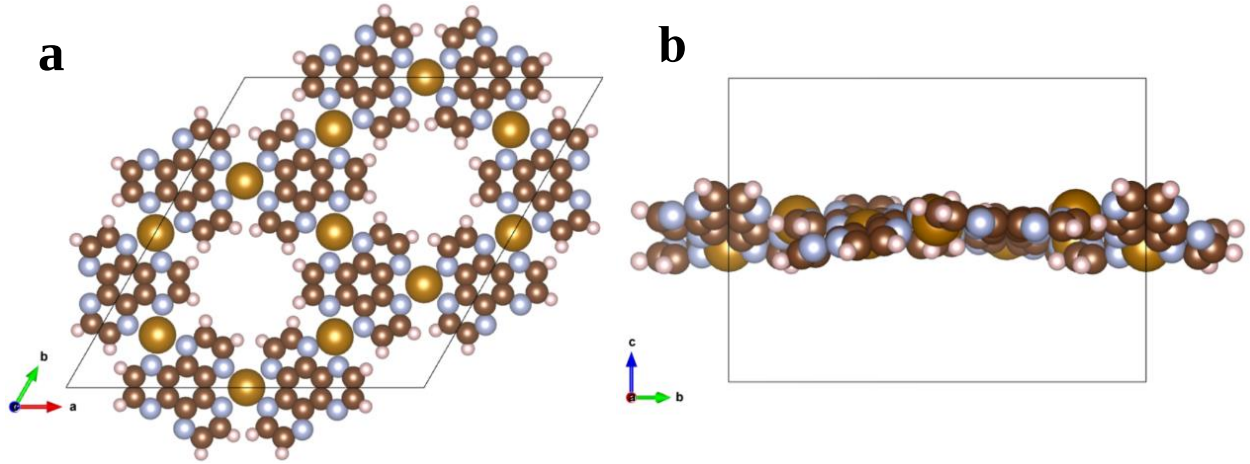
- Porous hexagonal networks: $M_3(HAT)_2$
- Honeycomb lattice (HAT);
  Kagome lattice (Ni, Fe, Co);

- Lattice constant: Ni-HAT: 13.9±0.1Å (13.81Å);
  Fe-HAT: 13.8±0.2Å;
  Co-HAT: 13.7±0.1Å;
- Side view of DFT model: buckled structure.

DFT-calculated 2D c-MOF $Fe_3(HAT)_2$ framework



DFT-calculated total energy of freestanding $Fe_3(HAT)_2$ framework



DFT-simulated model of freestanding $Fe_3(HAT)_2$ framework

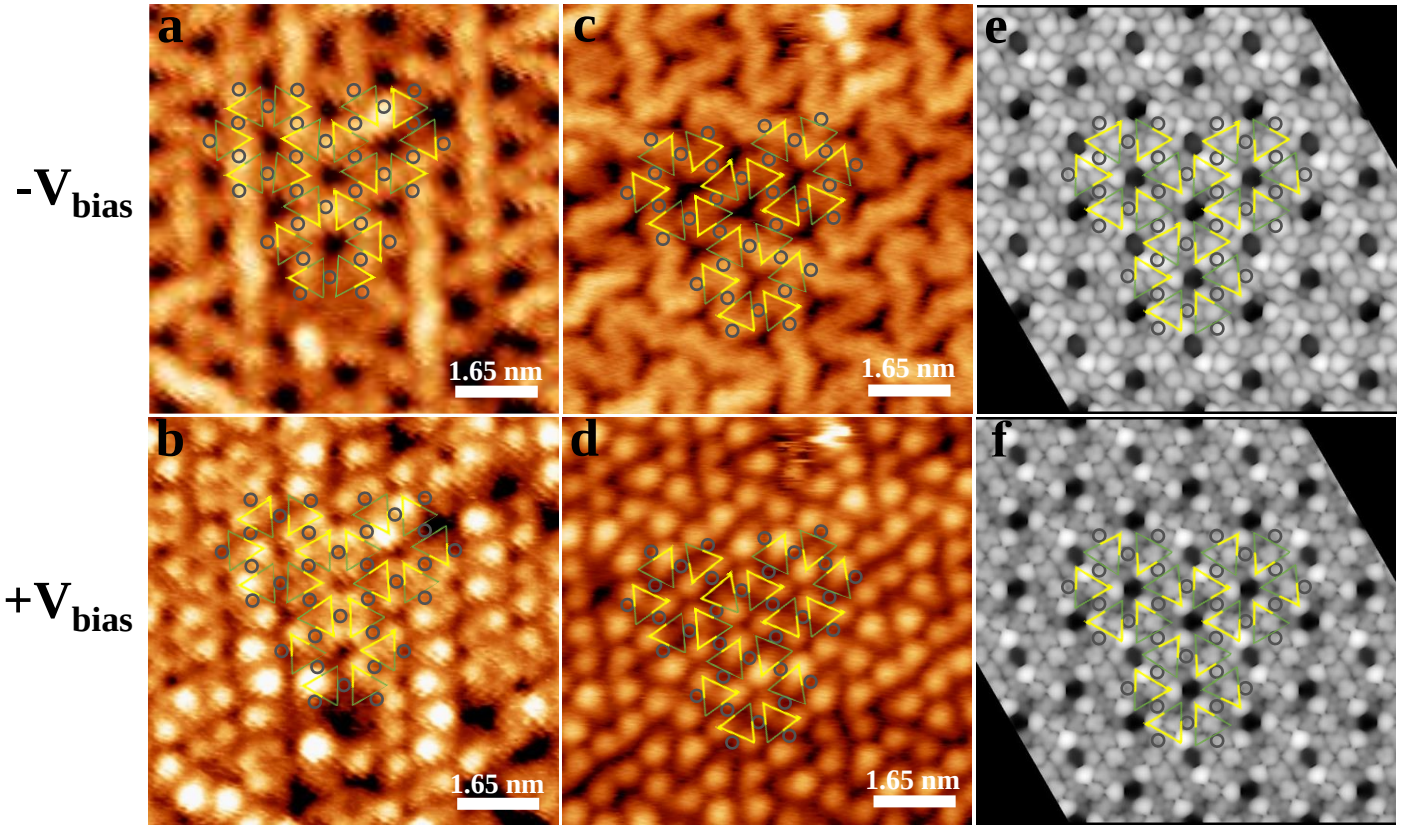
DFT-calculated total energy

- Flat structure (black square):
  minimum at 14.2 Å; 0.7 eV higher at 13.8 Å;
- Buckled structures: 13.8 Å (red square), stable;
  1.2 eV below 14.2 Å (flat), 1.9 eV below 13.8 Å (flat).

DFT-simulated model

- Buckled structure;
- Asymmetric appearance of HAT: tilted 25˚;
- Lattice constant: 13.81 Å;
- Fe-N bond: 2.037–2.156 Å;
- Inter-molecular steric hindrance:
  enlarged distance between neighboring hydrogen atoms

2D c-MOF $Ni_3(HAT)_2$ frameworks self-assembled on Ag(111) and Au(111) substrates

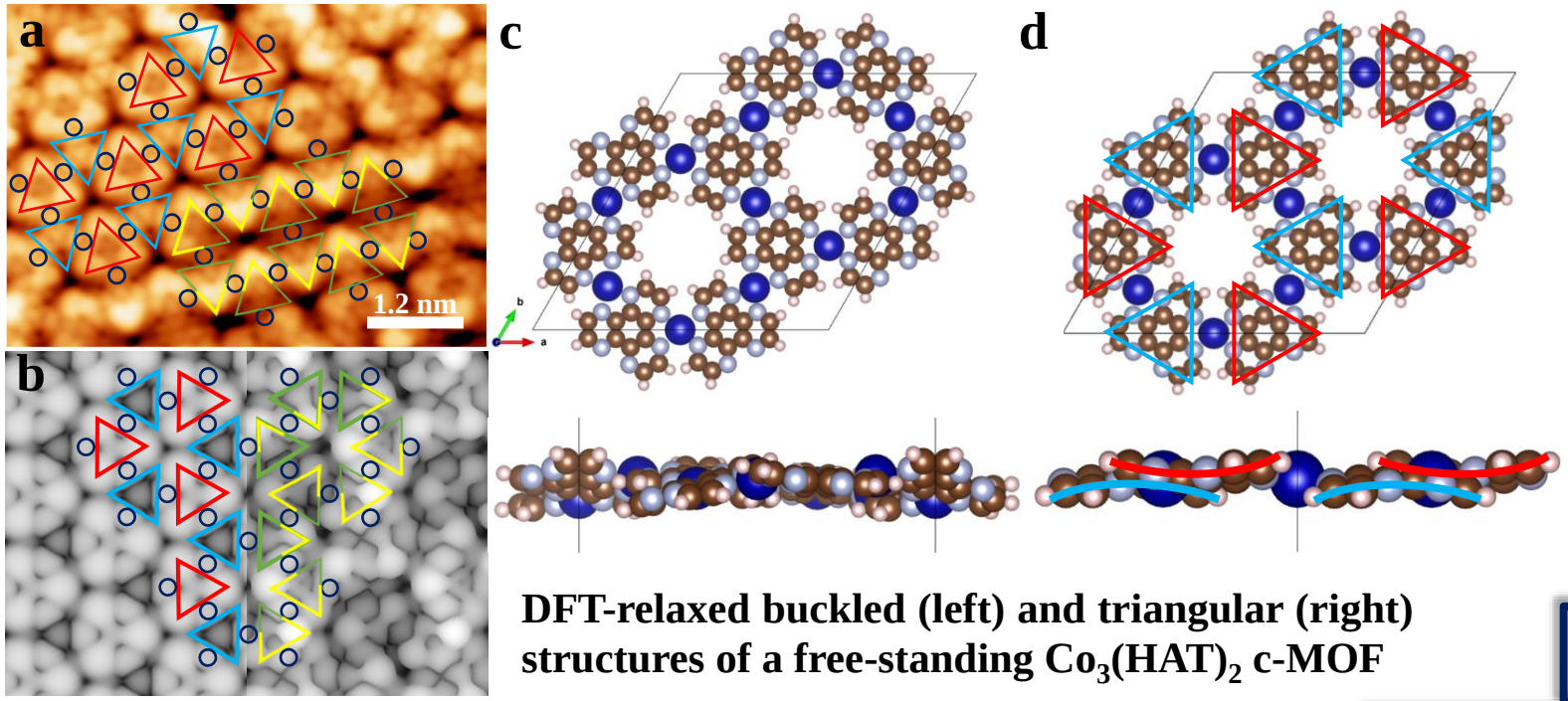


$Ni_3(HAT)_2$ framework on Ag(111) and Au(111) substrates

In-situ STM images with different bias

- Non-periodical features; buckled;
- Negative bias: cross-linked zigzag chains;
- Positive bias: dotted chains and the “three-leaf” patterns.

2D c-MOF $Co_3(HAT)_2$ framework self-assembled on Au(111) substrate

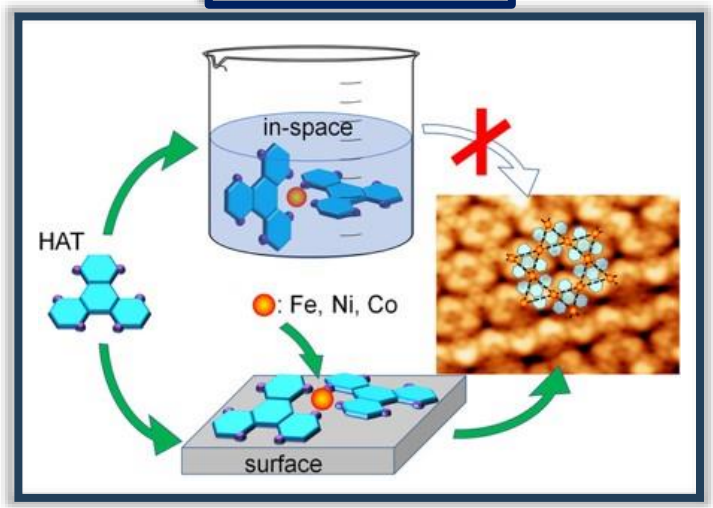


DFT-relaxed buckled (left) and triangular (right) structures of a free-standing $Co_3(HAT)_2$ c-MOF

Co-HAT network

- Two phases: zig-zag chains; bow-shape and dome-shape HAT;
- Zig-zag chains (lowest total energy); tilted with an angle of 25˚;
- Lattice constant: 13.81 Å; Co-N bond: 1.978 Å–2.176 Å
- Ordered triangular phase: metastable
  1.17 eV higher than the zig-zag chains;
  3.66 eV lower than the flat structure.

Summary



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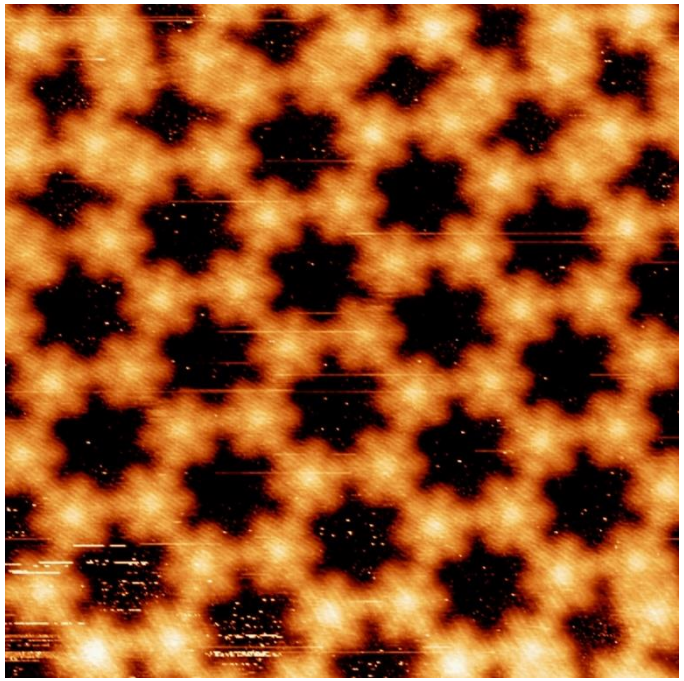
Part 5 Summary and Perspectives

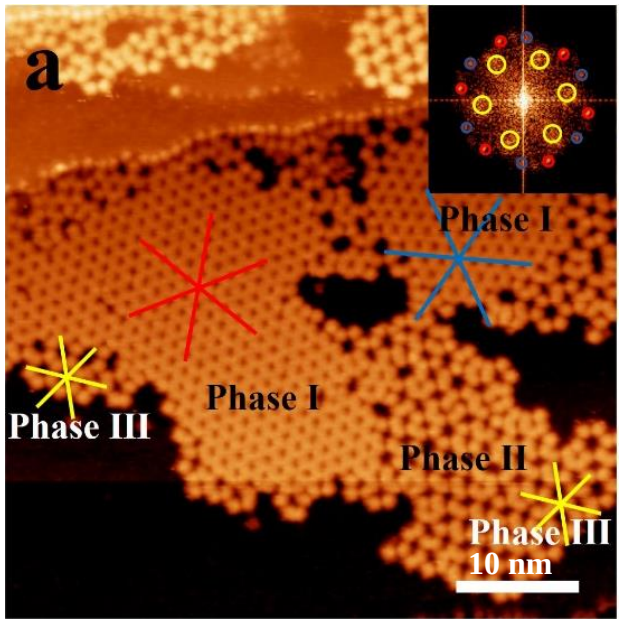
PART 03

Templated Growth of Two-Dimensional Conjugated Metal-Organic Frameworks **Cu-HAT** on **Cu(111)**, **Au(111)** and **MoS_2** Substrates

- Cu-HAT coordination structures grown on **Cu(111)** substrate at **room temperature**
- Cu-HAT coordination structures on **Cu(111)** substrate after annealing treatment at **423 K**
- Cu_3HAT_2 framework assembled on **Au(111)** substrate
- Cu_3HAT_2 framework self-assembled on bulk **MoS_2** substrate

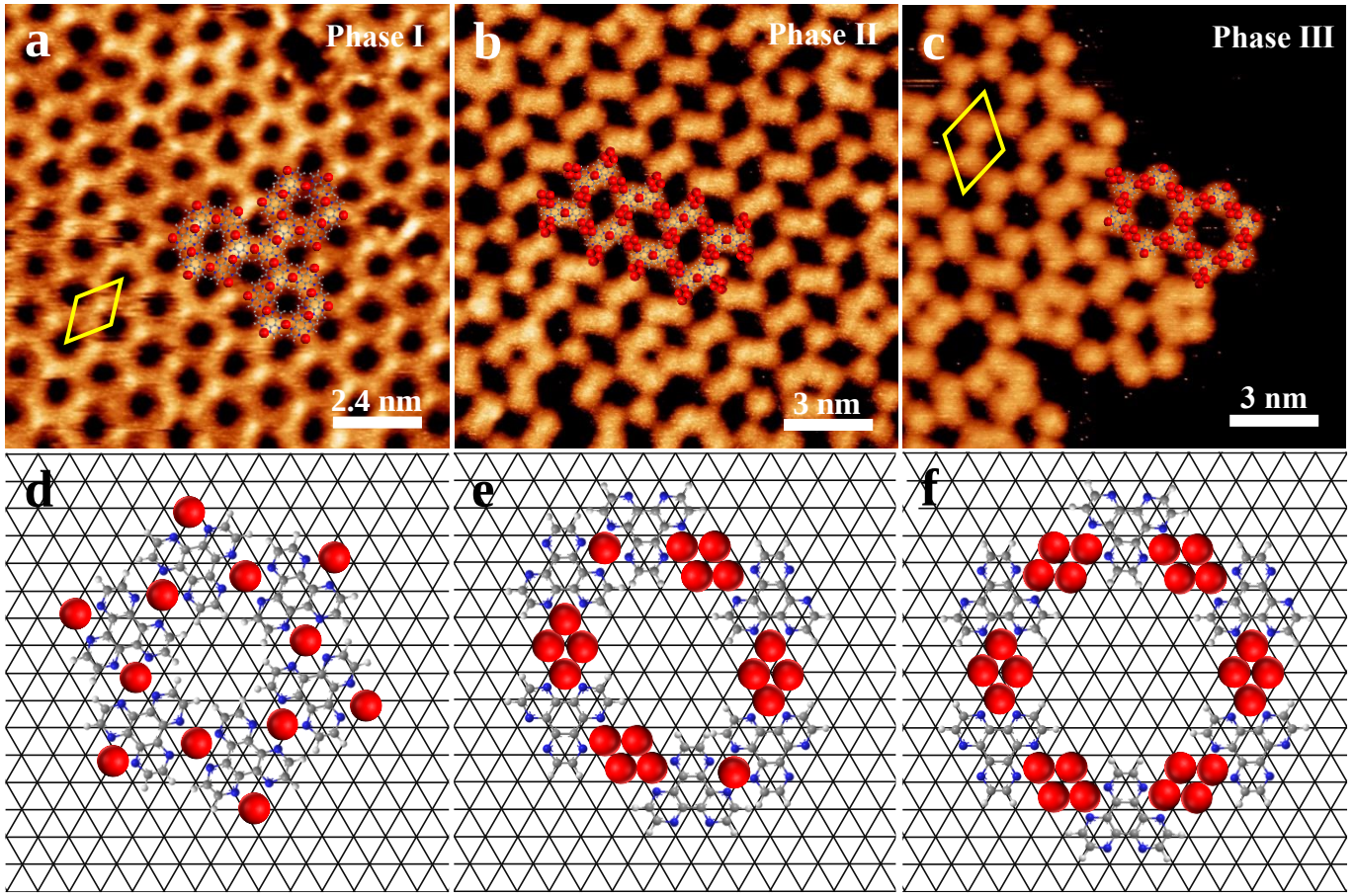


Cu-HAT coordination structures grown on Cu(111) substrate at RT



Cu-HAT coordination structures at RT

- Phase I: dominant; porous hexagonal network; two orientations: 26˚(red and blue);
- Phase II: a transitional phase; lacking long-range periodicity or a fixed orientation;
- Phase III: six bright balls; evenly divides two orientations of Phase I (yellow);



Phase I

- Cu_3HAT_2 framework;
- Lattice constant 14.1 Å;
- Cu-N bond length 2.14 Å;
- Mismatch Cu(111) lattice

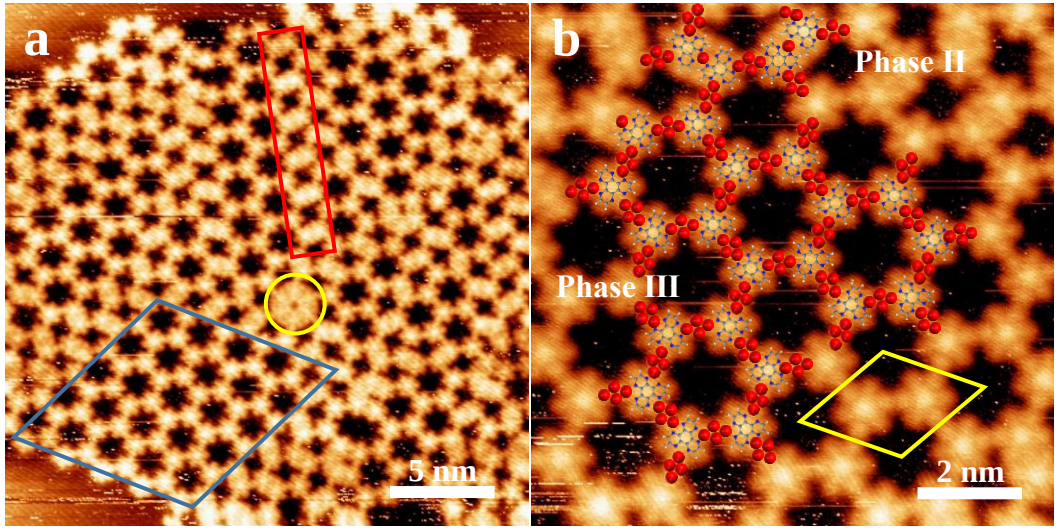
Phase II

- Dimers; rhombus pores;
- CuN_4 coordination; Cu_4N_4 coordination;

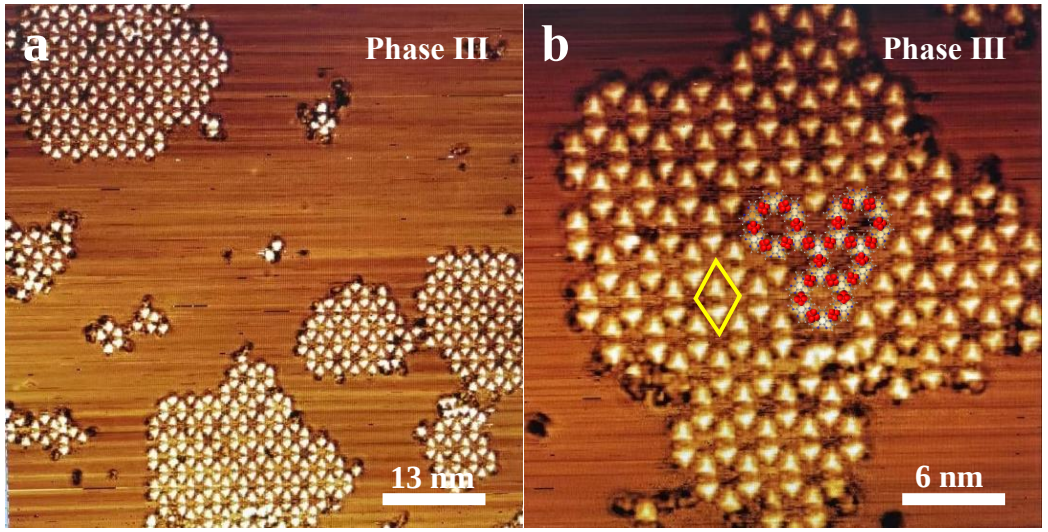
Phase III

- $(Cu4)_3HAT_2$ framework;
- lattice constant 20.48 Å;
- Cu-N bond length 1.89 Å;
- Low-energy sites: Cu “bridge”, HAT “hollow”.

Cu-HAT coordination structures on Cu(111) substrate after annealing treatment at 423 K



Mixed-phase Cu-HAT coordination structures



Pure $(Cu_4)_3HAT_2$ (Phase III) framework[1]

Three types of structures

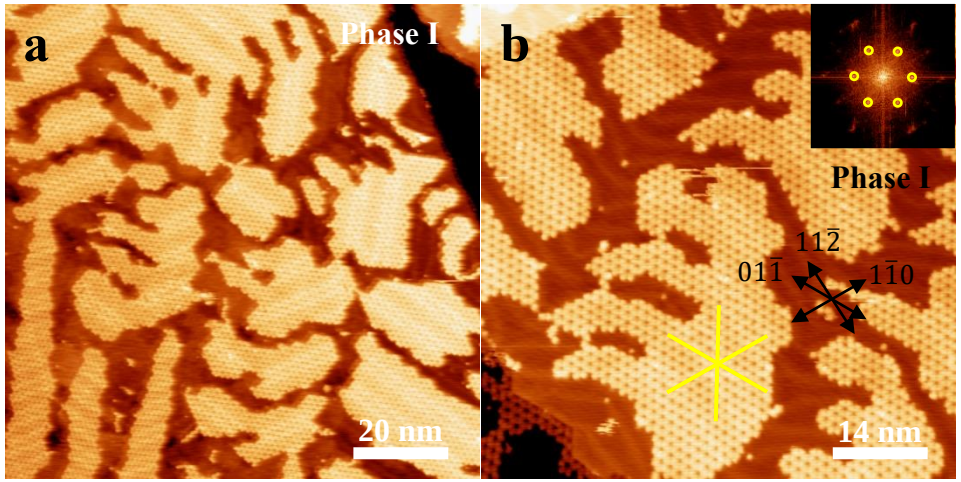
- Yellow frame: a hexagon consisting of six HAT linked via CuN_4 coordination;
- Red frame: Phase II; a ladder-like structure formed by six CuN_4-coordinated HAT dimers;
- Blue frame: regular framework of Phase III; Cu_4N_4 coordination;
- Template effect of the Cu(111) substrate.

Pure $(Cu_4)_3HAT_2$ (Phase III) framework

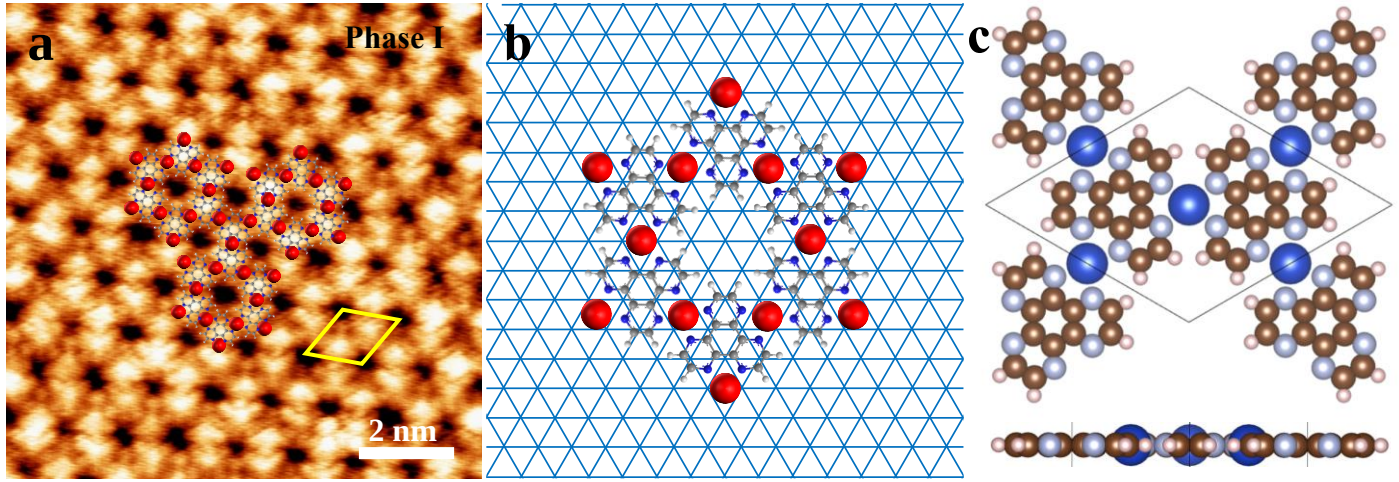
- RT;
- HAT deposition with low flux and low coverage;
- Lattice constant 21.0 ±0.3 Å;
- Energetically favored Cu_4N_4 coordination.

[1]Data from Prof. Z. L. Shi's group (SUDA)

Cu_3HAT_2 framework self-assembled on Au(111) substrate



Annealed Cu_3HAT_2 framework on Au(111)



Proposed Cu_3HAT_2 framework model and DFT-simualted structure

Cu-HAT coordination on Au(111) after 373K annealing treatment

- Clear herringbone: weak interaction;
- One phase: Cu_3HAT_2 framework (phase I);
- Lattice constant 14.0 ± 0.1 Å;
- Yellow orientation: along $[1\bar{1}0]$;

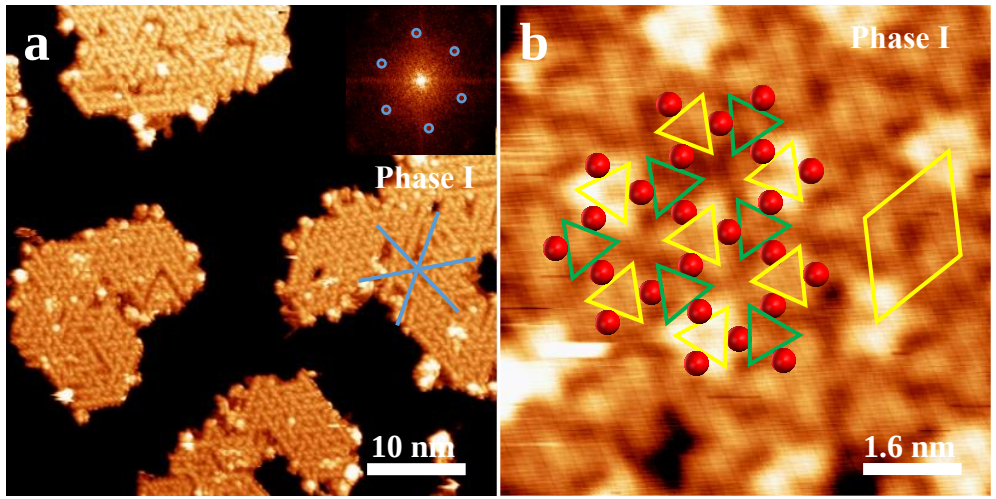
Proposed structures on Au(111)

- Lattice constant 14.4Å ($5a_0$, a_0=2.88Å);
- Cu-N bond length is 2.178 Å;
- Cu adatoms at “bridge” sites;
- HAT molecules’ centers at “hollow” sites.

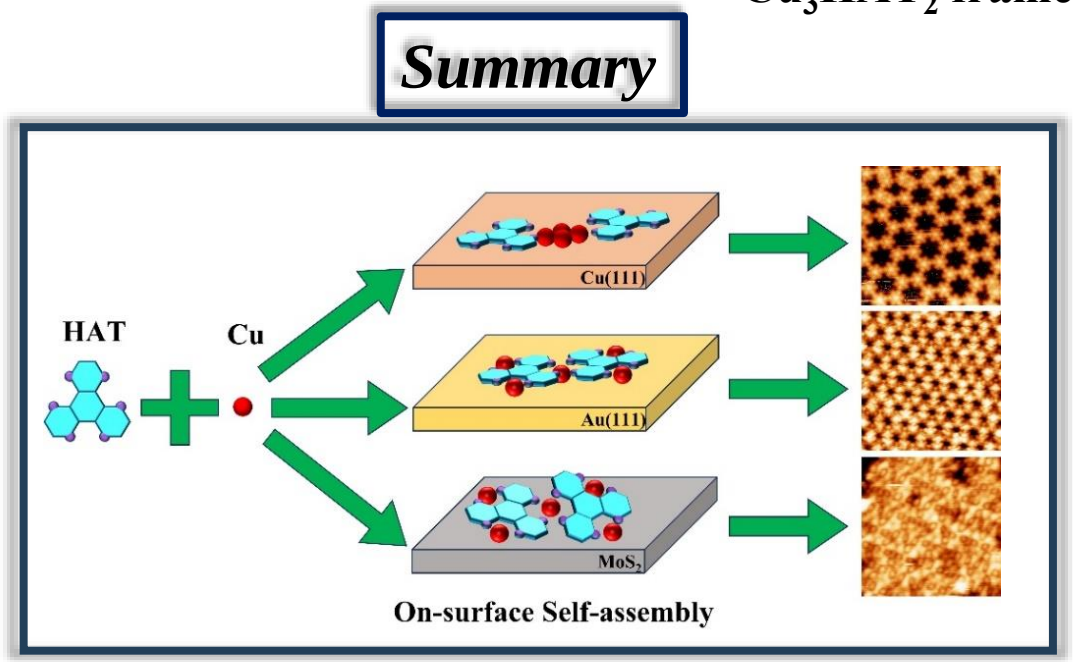
Cu_3HAT_2 framework self-assembled on bulk MoS_2 substrate

Cu-HAT coordination on MoS_2 surface

- free-standing;
- Cross-linked zigzag chains; buckled;
- Cu_3HAT_2;
- Lattice constant 14.4±0.2 Å;
- One orientation (blue).



Cu_3HAT_2 framework on MoS_2 surface



OUTLINE

Part 1 Introduction

Part 2 Synthesis of Single-Layer Two-Dimensional Metal-Organic Frameworks **$M_3(HAT)_2$** (M= **Ni**, **Fe**, **Co**, HAT=1,4,5,8,9,12-Hexaazatriphenylene) Using an **On-Surface Reaction**

Part 3 **Templated Growth** of Two-Dimensional Conjugated Metal-Organic Frameworks **Cu-HAT** on **Cu(111), Au(111)** and **MoS_2** Substrates

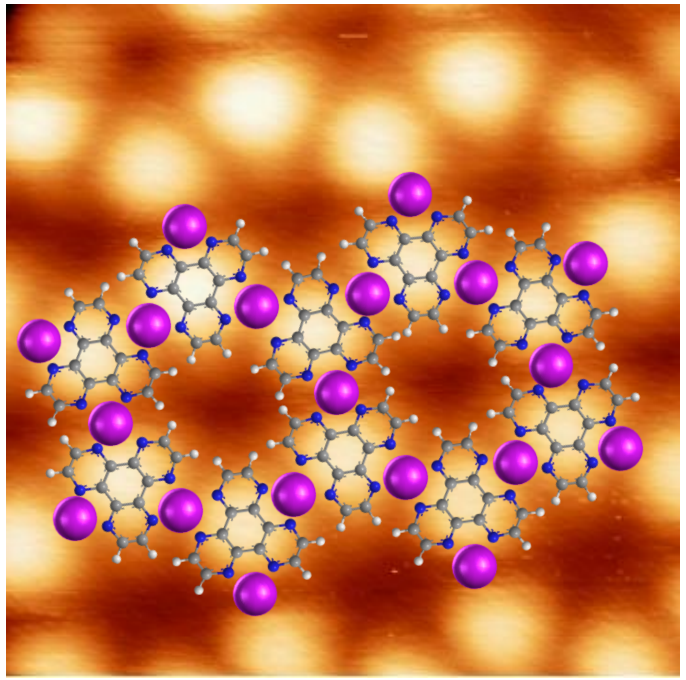
Part 4 Self-Assembly of Two-Dimensional Conjugated Metal-Organic Frameworks **$M_3(HAT)_2$** (M=Ni, Co) on a **MoS_2** Surface

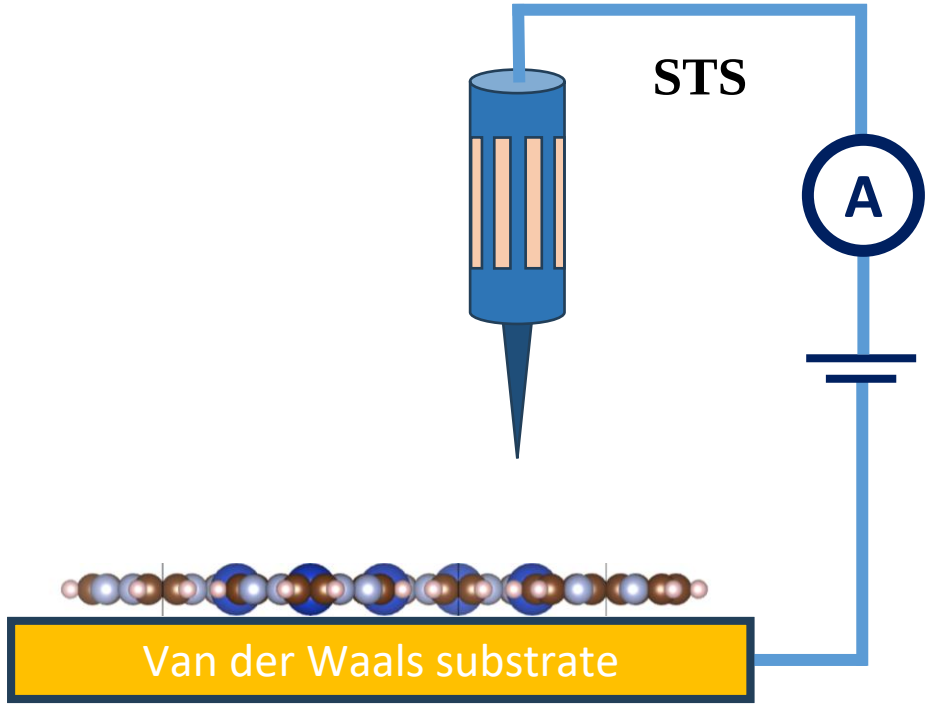
Part 5 Summary and Perspectives

PART 04

Self-Assembly of Two-Dimensional Conjugated Metal-Organic Frameworks $M_3(HAT)_2$ (M=Ni, Co) on a MoS_2 Surface

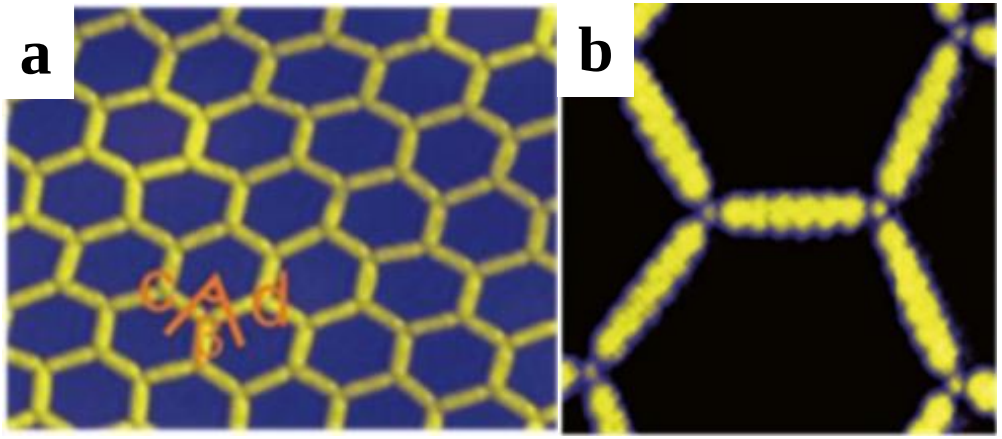
- Review: **2D MOFs** self-assembled on **van der Waals** surfaces
- **HAT** molecules self-assembled on **MoS_2** surface
- **$Ni_3(HAT)_2$** framework self-assembled on **MoS_2** surface
- **$Co_3(HAT)_2$** framework self-assembled on **MoS_2** surface





2D MOFs self-assembled on van der Waals surfaces

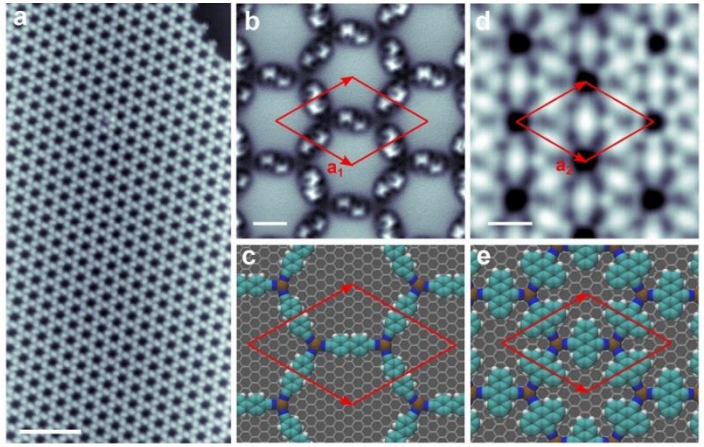
1



J. Li, et al. *J. Phys. Chem. C*, **2019**, 123, 12730.

$(NC\text{-}Ph_6\text{-}CN)_3Cu_2$/G/Ir(111)

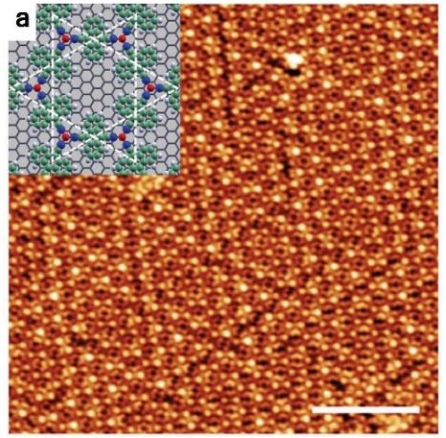
2



A. Kumar, et al. *Nano Lett.*, **2018**, 18, 5596.

$DCBP_3Co_2$ (DCA_3Co_2)/G/Ir(111)

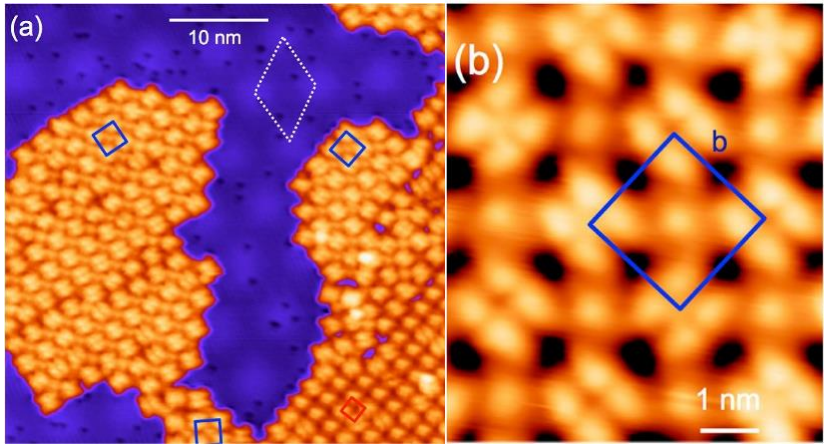
3



L. Yan, et al. *Adv. Funct. Mater.*, **2021**, 31, 2100519.

DCA_3Cu_2/G/Ir(111)

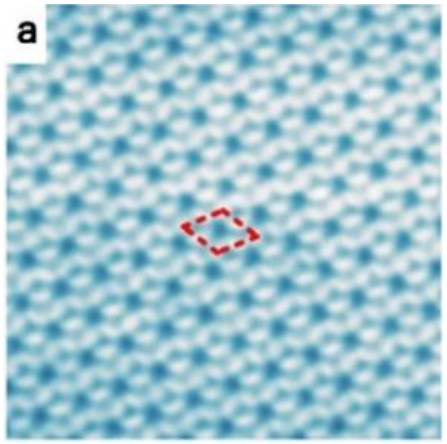
4



W. Auwärter, et al. *J. Am. Chem. Soc.*, **2015**, 137, 2420−2423.

Co-TPCN/BN/Cu(111)

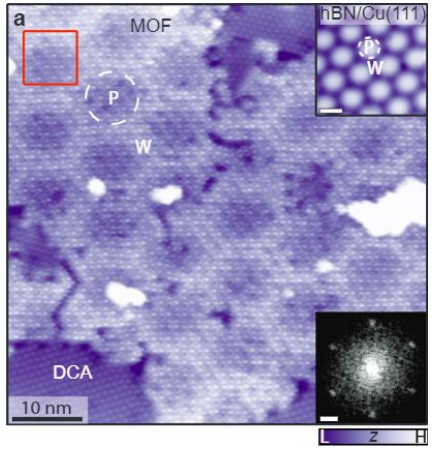
5



L. Yan, et al. *ACS Nano*, **2021**, 15, 11, 1781.

Cu-DCA/$NbSe_2$

6



B. Lowe, et al. arXiv:2305.14983.

Cu-DCA/BN/Cu(111)

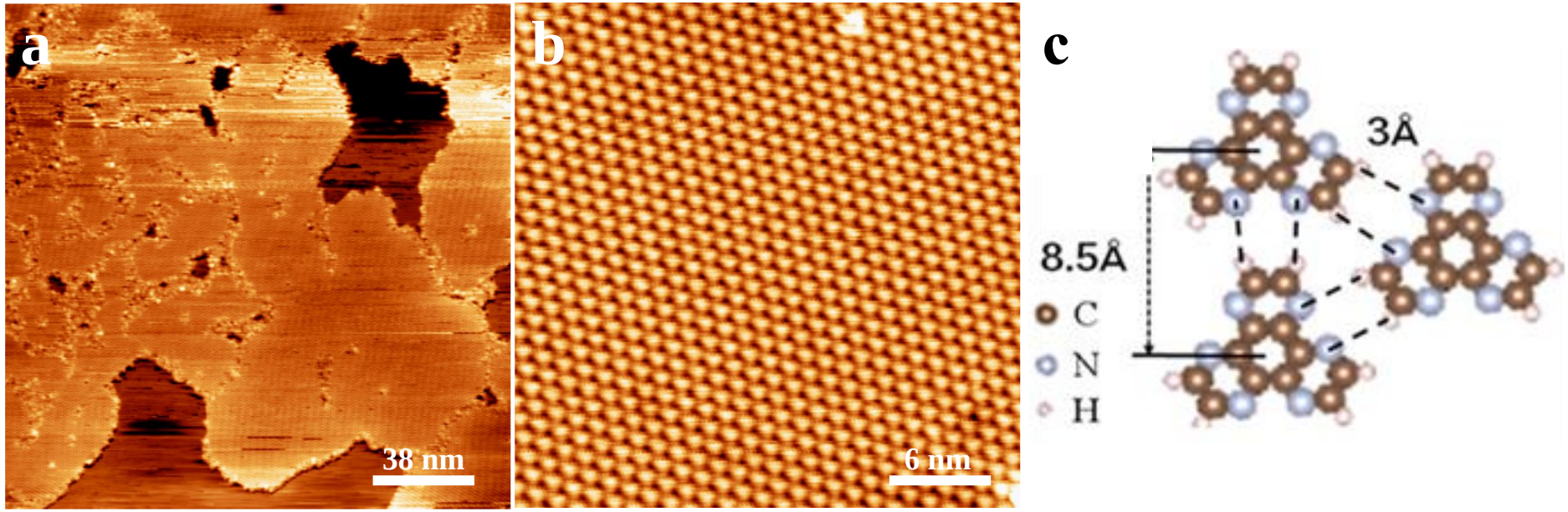
Cyano group

- C≡N;
- Strong coordination bond;
- No dehydrogenation reaction;
- Low conjugation.

HAT

MoS_2

HAT molecules self-assembled on MoS_2 surface

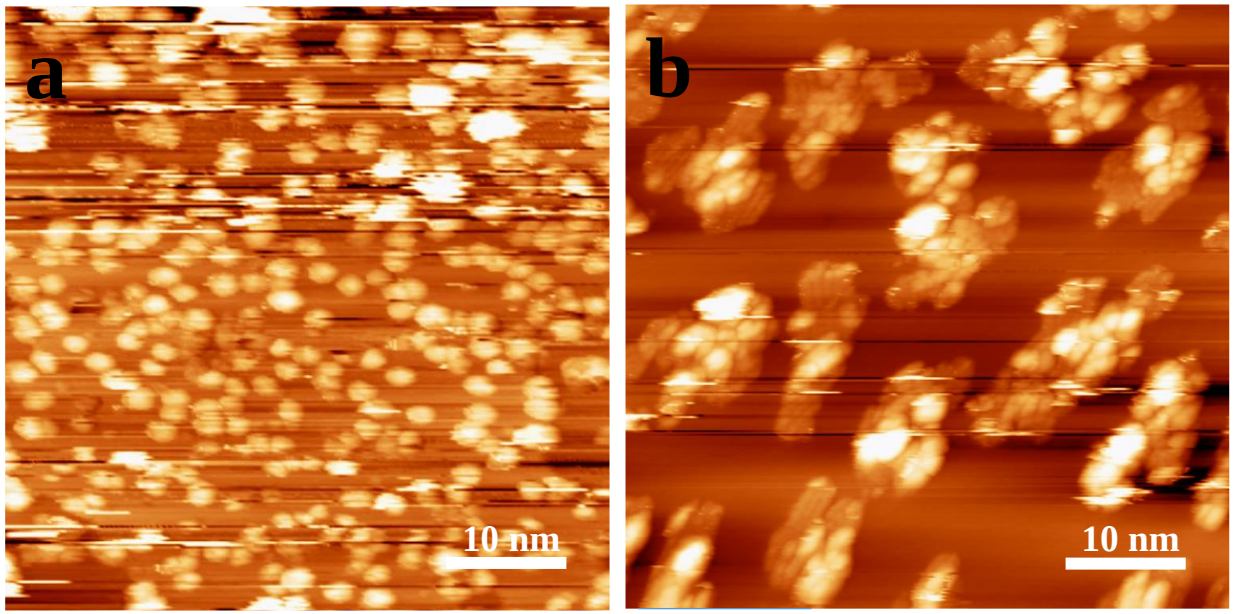


Close-packed HAT molecular islands on MoS_2 surface

HAT molecular self-assembly on MoS_2 surface

- Close-packed molecular islands;
- Weak interaction;
- Triangular lattice;
- Lattice constant 8.7 Å(8.5 Å);
- An ideal flat substrate for supramolecular self-assembly.

Fe and HAT deposition on MoS_2 surface

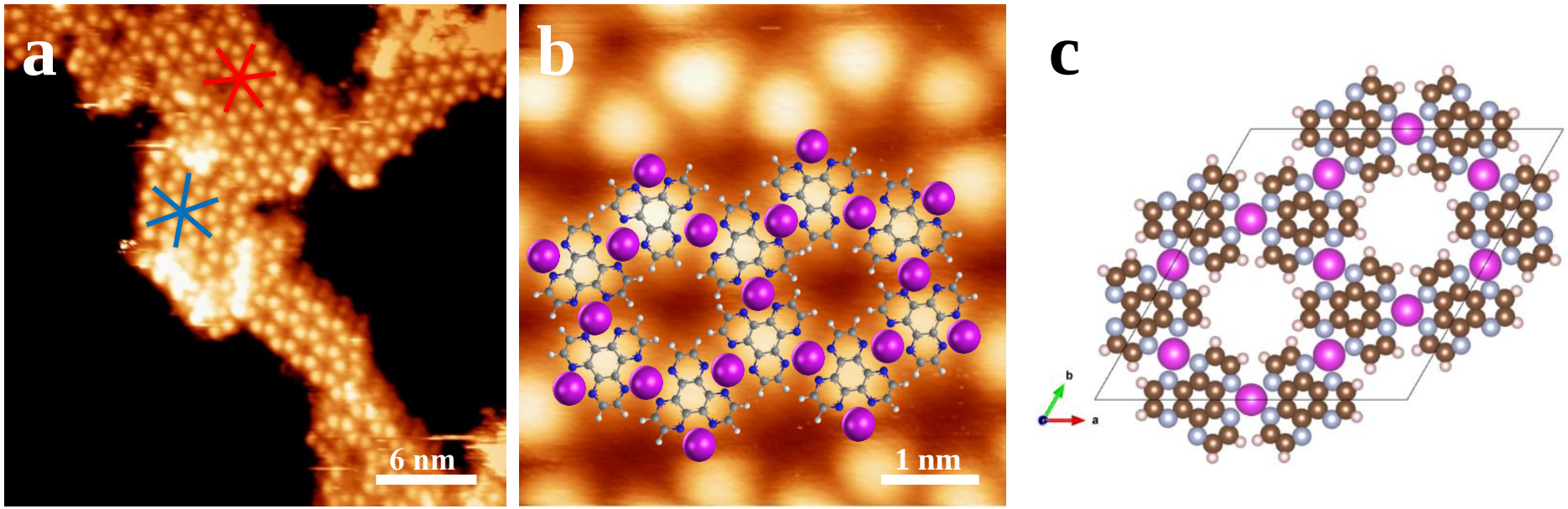


Fe cluster and HAT molecular islands on MoS_2 surface

Fe+HAT on MoS_2 surface

- RT: Fe clusters; HAT close-packed islands.
- After annealing treatment:
  Fe clusters, surrounded by HAT molecules.

$Ni_3(HAT)_2$ framework self-assembled on MoS_2 surface

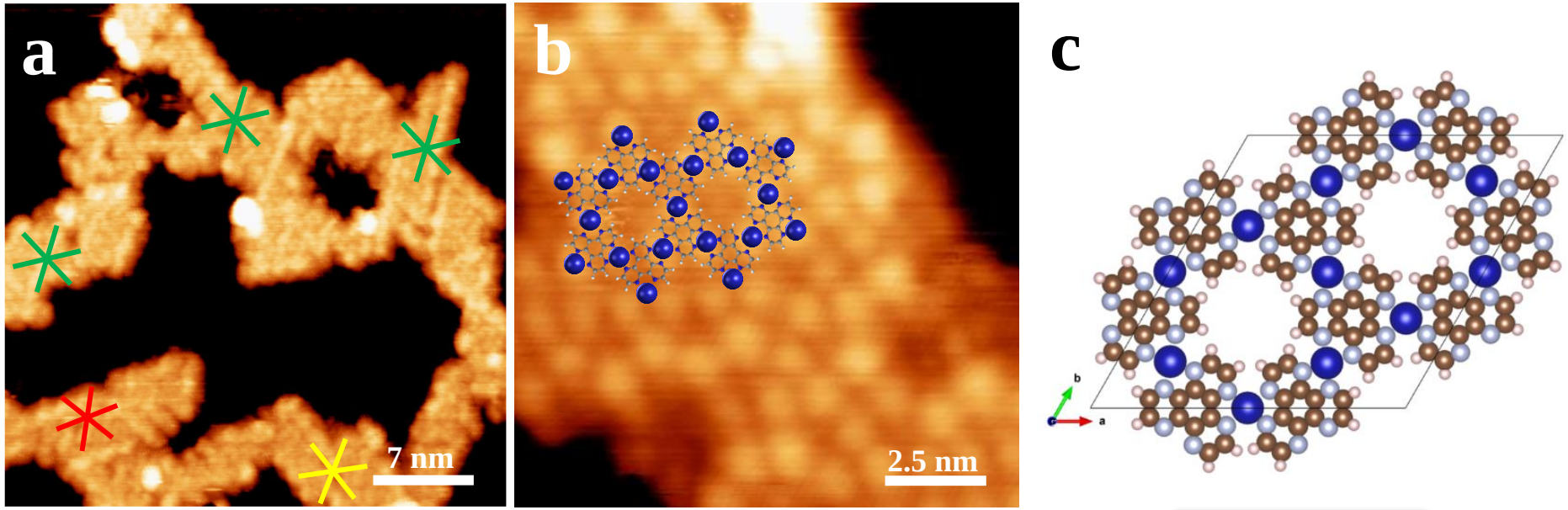


Ni-HAT framework on MoS_2 surface

Ni-HAT 2D c-MOF on MoS_2

- Irregular, long and narrow;
- Random orientations: tilted 5˚- 15˚;
- Six-petal-flower: six HAT molecules;
- $Ni_3(HAT)_2$: Honeycomb lattice (HAT), Kagome lattice (Ni);
- Lattice constant 13.9±0.2 Å;
- Periodic features.

$Co_3(HAT)_2$ framework self-assembled on MoS_2 surface

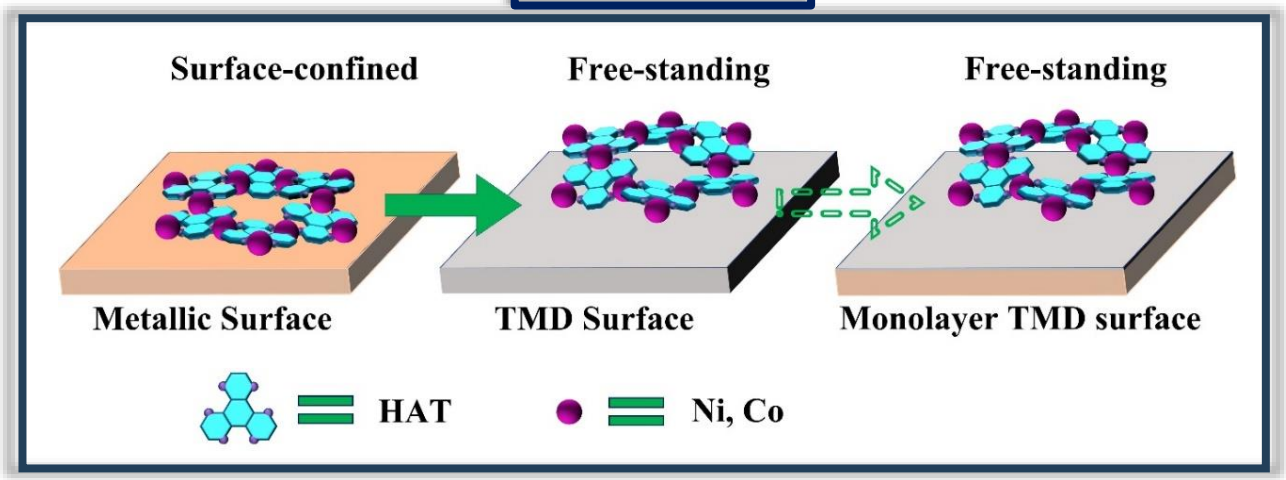


Co-HAT framework on MoS_2 surface

Co-HAT 2D c-MOF on MoS_2

- Irregular, long and narrow;
- Random orientations: tilted 8˚- 12˚;
- $Co_3(HAT)_2$: Honeycomb lattice (HAT), Kagome lattice (Co);
- Lattice constant 13.8±0.2 Å;
- Non-periodic and bulked.

Summary



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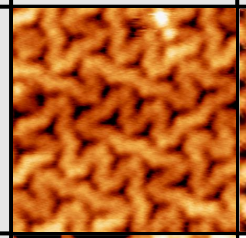
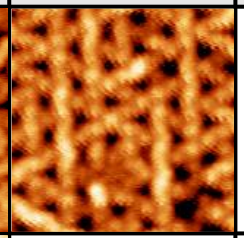
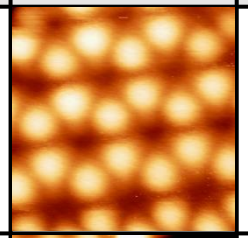
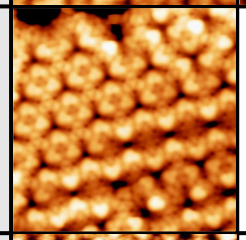
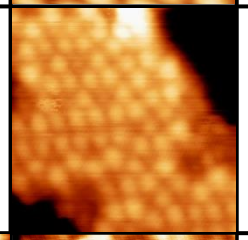
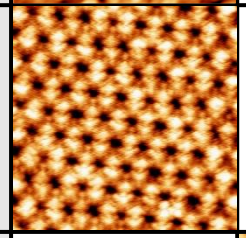
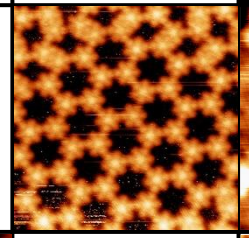
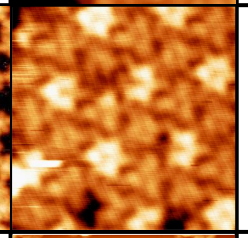
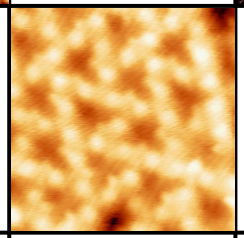
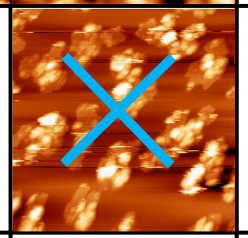
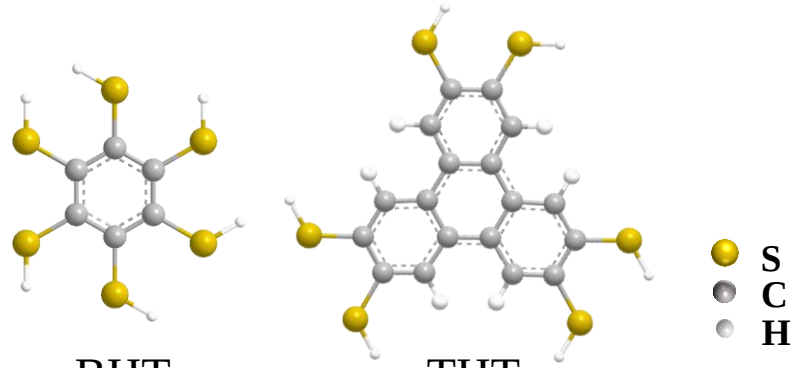
Summary and perspectives

	Au(111)	Ag(111)	Cu(111)	Bulk MoS_2	monolayer MoS_2 (TMDs)
Ni					
Co					
Cu					
Fe					
Mn Pb …..					

- Synthesis method: on-surface coordination self-assembly
- Organic ligand: HAT, → BHT, THT...



BHT THT

- Metal centers: Ni, Fe, Co, Cu, → Mn, Pb...
- Substrates: Au(111), Ag(111), Cu(111), bulk MoS_2, → monolayer MoS_2 (TMDs)...
- Characterization method: STM, DFT, → STS, ARPES...

Acknowledgements

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Synthesis and Characterization of Two-Dimensional Conjugated Metal-Organic Frameworks Self-Assembled on Metallic and Transition-Metal Dichalcogenides Surfaces

THANKS

LYU Chengkun

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