Heavy-metal based coordination structures self-assembled on metal surfaces

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Outline

1. Introduction

- Self-assembly
- Metal-organic coordination frameworks (MOFs)

2. On surface Pb-coordinated MOFs

- 1D and 2D-MOFs with Pb-pyridyl coordination
- 2D-MOFs with Pb-carbonitrile coordination

3. On surface Eu-coordinated MOFs

- 2D-MOFs with Eu-carbonitrile coordination
- 1D and 2D-MOFs with carbonitrile-Eu-terpyridyl coordination

4. Conclusion

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Introduction: top down vs bottom-up

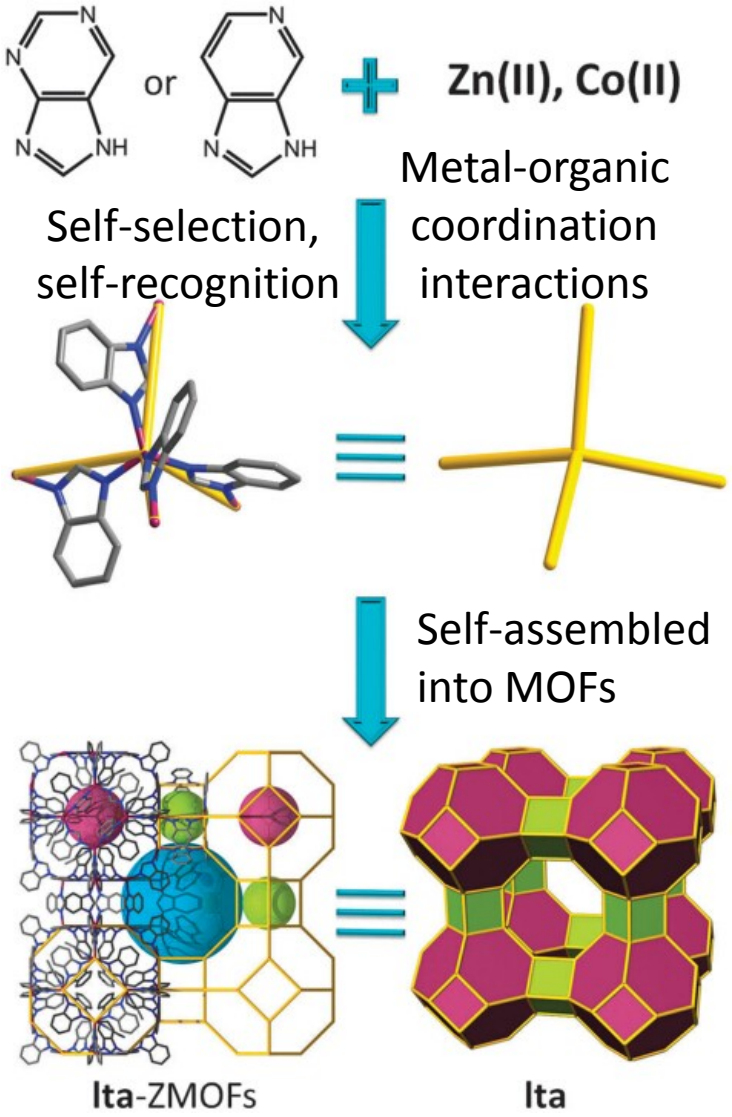
	Top- down methods	Bottom-up methods
advantage	• mature technology, • easier to control the crystal size (~100nm), • independents of molecules, ……	• molecular level control, • high efficiency , • low cost, ……
disadvantage	➢ size limitation, ➢ operation difficulty, ➢ high cost,	➢ prone to producing defects, ➢ molecules limitation, ➢ ……
examples	▪ photo lithography, ▪ electron beam lithography, ▪ etching, ……	▪ self-assembly, ▪ chemical synthesis, ▪ position assembly, ……

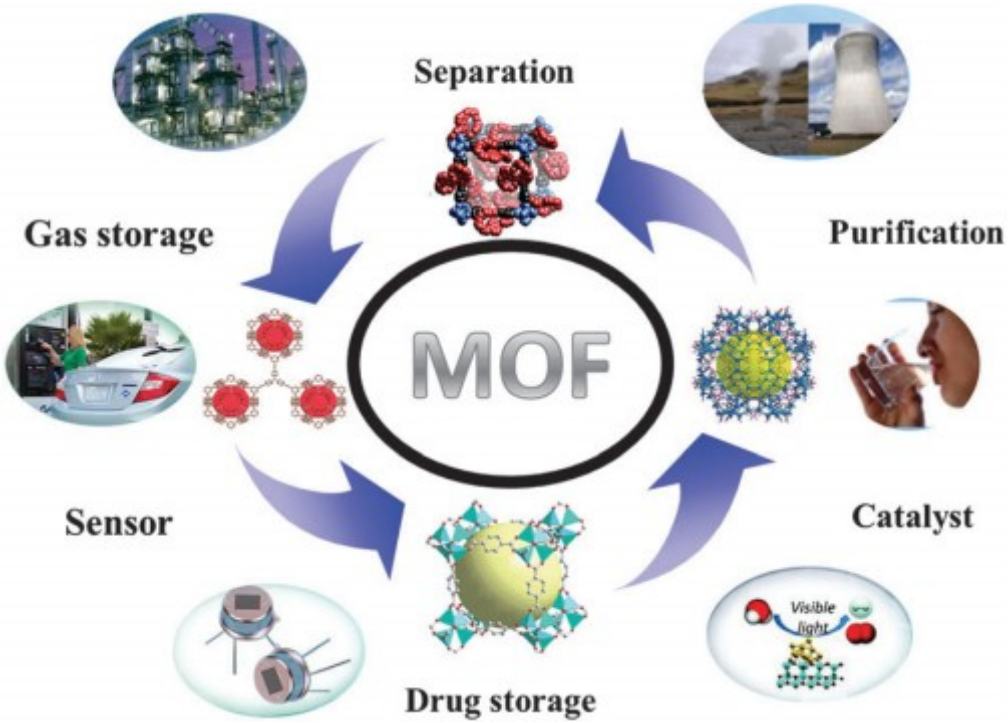
Atomic-level modification of structure;
Non-covalent interactions, reversible;
Defect free and self-healing;
Complex structures and materials

J. V. Barth, Nat. **2005**, 437, 671.
Gates, B. D., Chem. Rev. **2005,** 105, 1171.
http://www.slideshare.net/sasujani/nanotechnology-basic-introduction-to-the-nanotechnology

Introduction: Self-assembly and MOFs

Self-assembly in 3D





high thermal and chemical stability;
unprecedented internal surface areas;
high void volumes and low densities ;
novel electric and magnetic properties

Mohamed E. et al., Chem. Soc. Rev., **2015**,44, 228

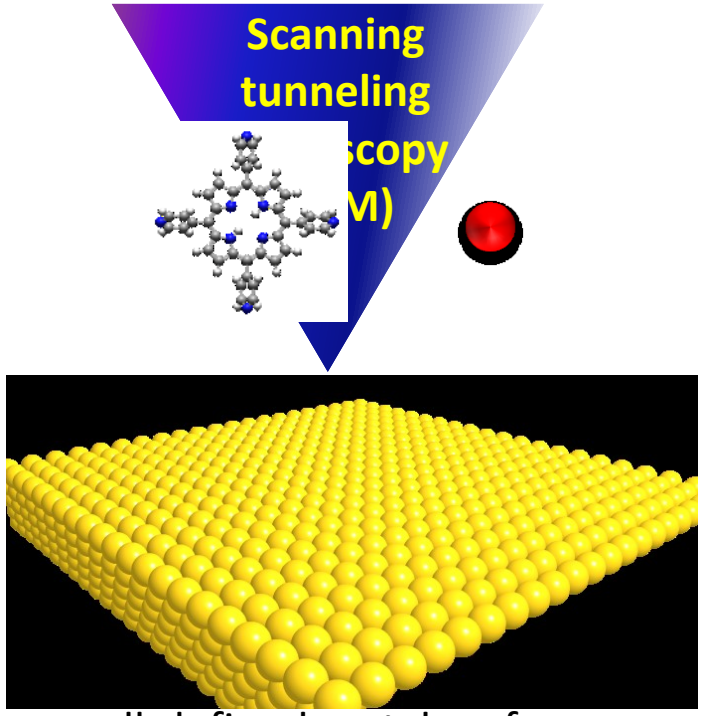
Chaemchuen S. et al., Chem. Soc. Rev., **2013**, 42, 9304

Introduction: Self-assembly in 2D

3D to low-dimensional systems

→ single molecule level

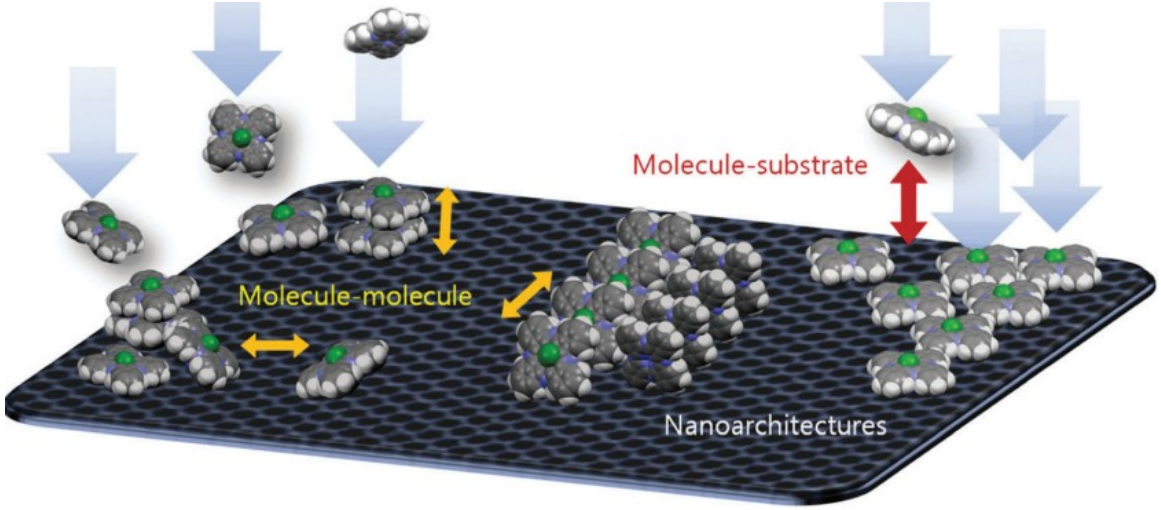
Surface sensitive techniques



well-defined metal surfaces
(e.g. the Au(111) surface)

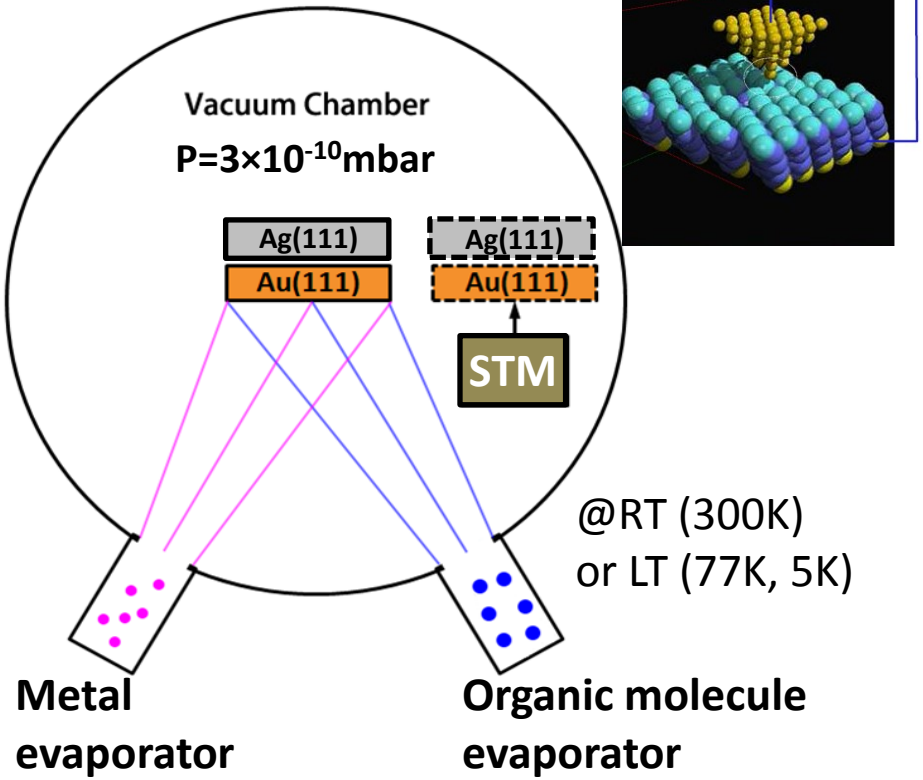
Molecule-molecule/metal interactions

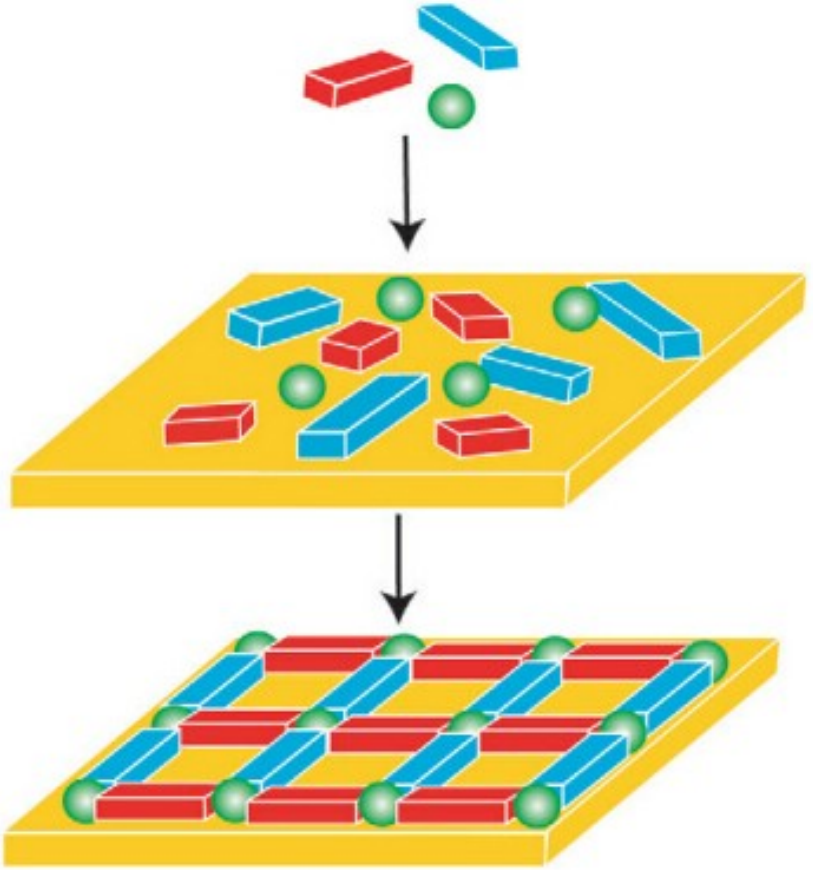
Molecule-substrate interactions



Sosa-Vargas L. et al., Mater. Horiz., **2017**, 4, 570

Introduction: Experimental setup





Stepanow S. et al., J. Phys.: Condens. Matter, **2008**, 20, 184002

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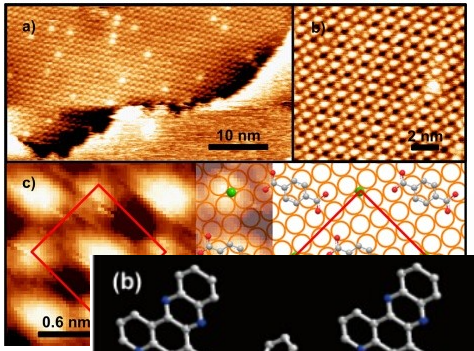
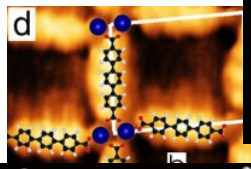
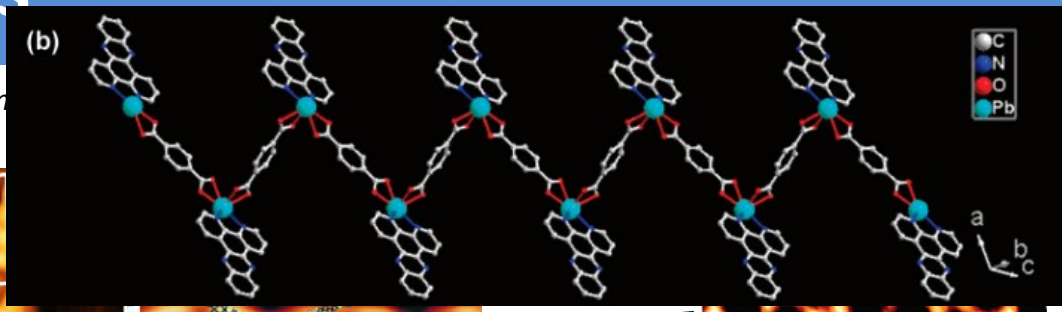
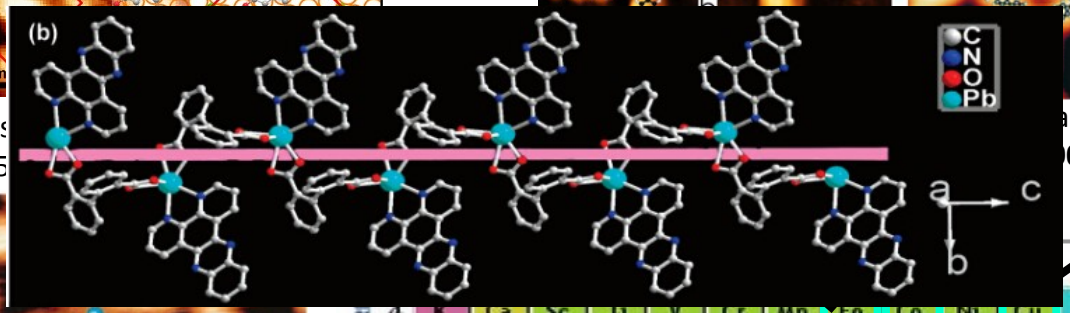
2D coordination systems



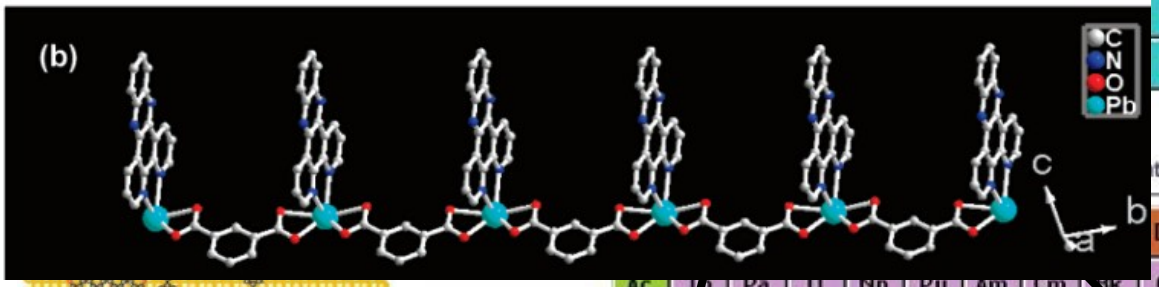
Stepanow, S. *J. Phys.: Conden*
2008, *20*, 184002

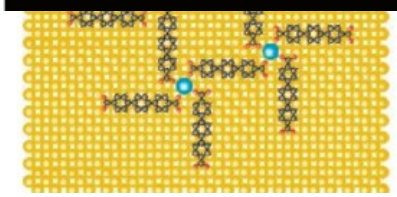






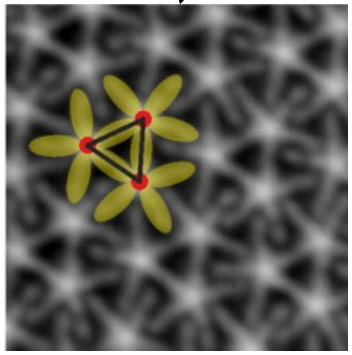
Skoms
14165

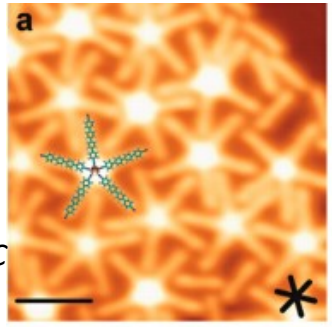




Stepanow, S. *ACS Nano* **2010**, *4*, 1813

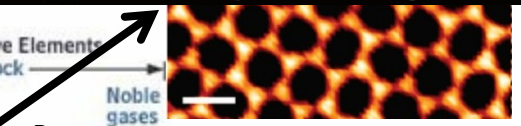
Ecija, D. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 6678.

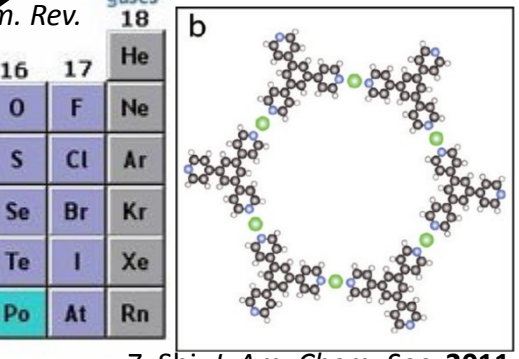




Yang J., Inorg. Chem., **2007**, 46, 6542–6555.

Urgel, J. I. *J. Phys. Chem. C* **2014**, *118*, 12908.





Z. Shi, *J. Am. Chem. Soc.* **2011**, 133, 6150

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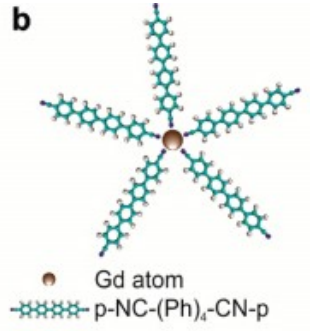
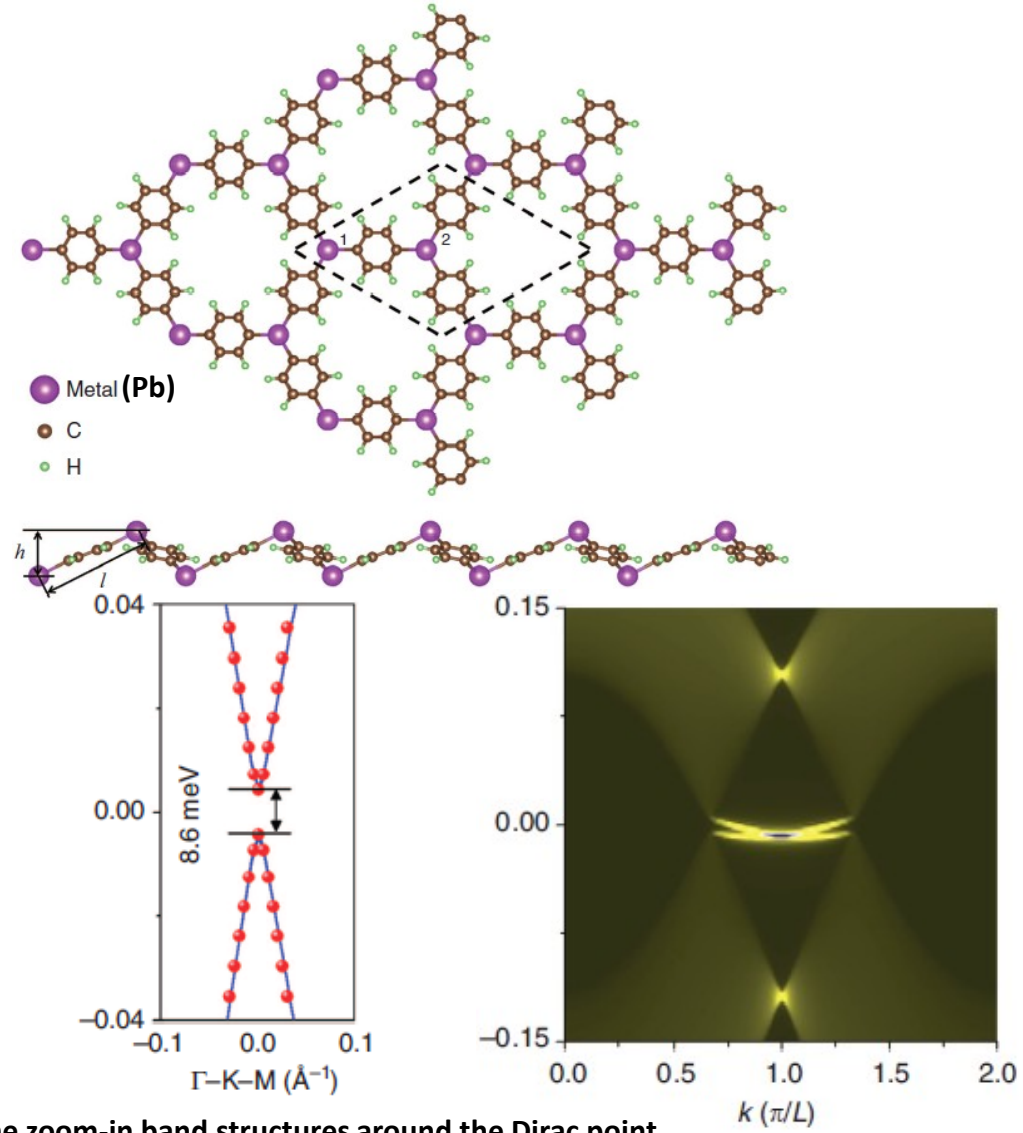


Theoretical prediction



nontrivial topological gapless edge states that connect the band edge states between K and K' and form a one-dimensional (1D) Dirac cone at the boundary of the Brillouin zone (BZ)

Left: The zoom-in band structures around the Dirac point

Right: Energy and momentum-dependent LDOS of the zigzag edge of the semi-infinite triphenyl-lead (TL) lattice, L is the unit cell length along the edge.

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

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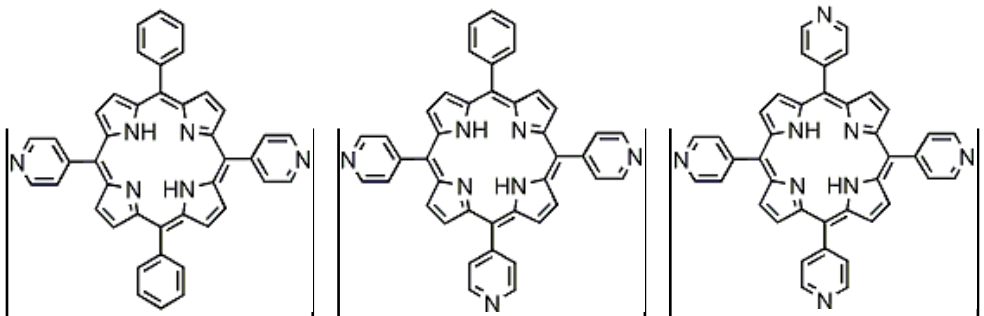
Molecules and metal

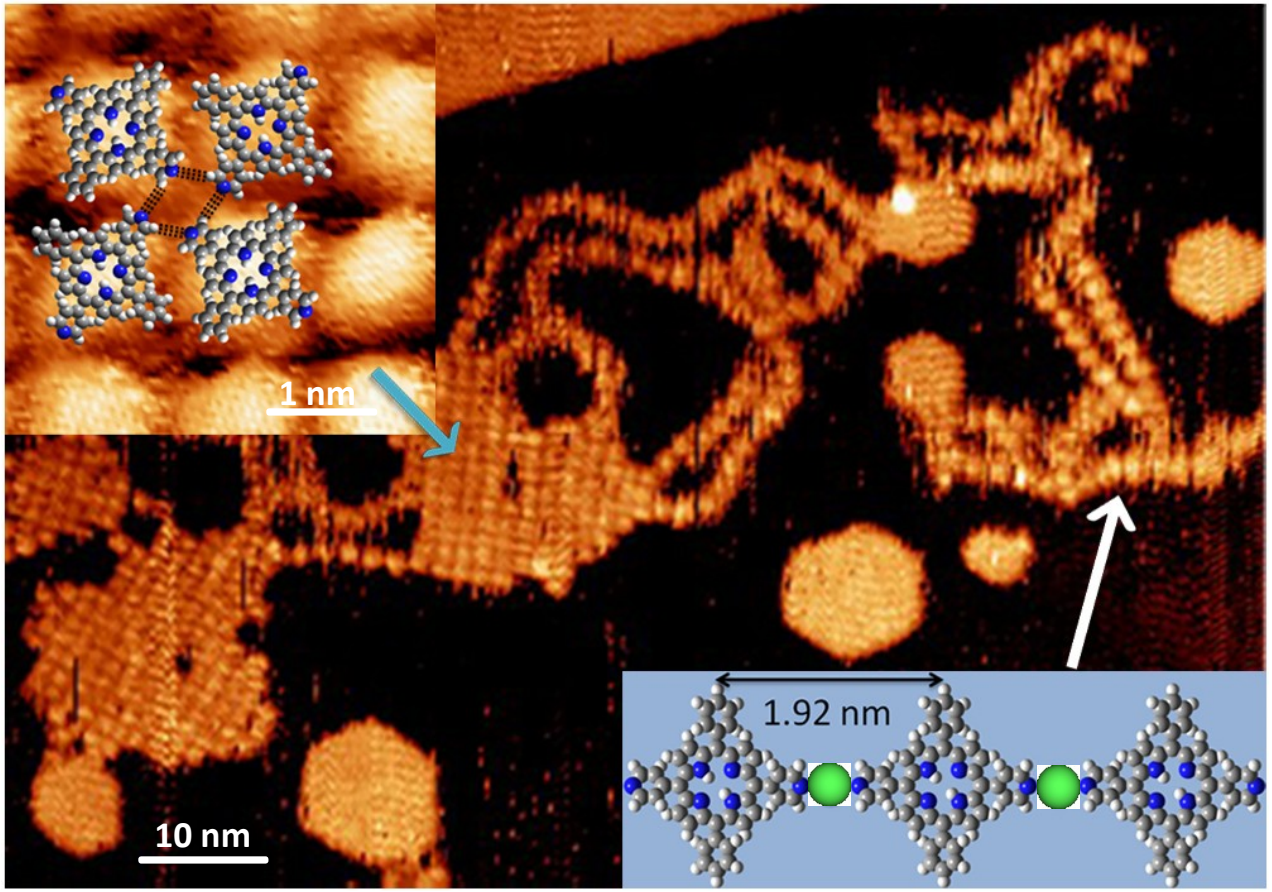


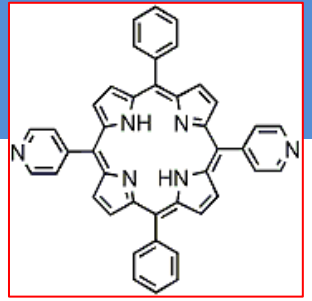
Pb

Radius
1.47 Å

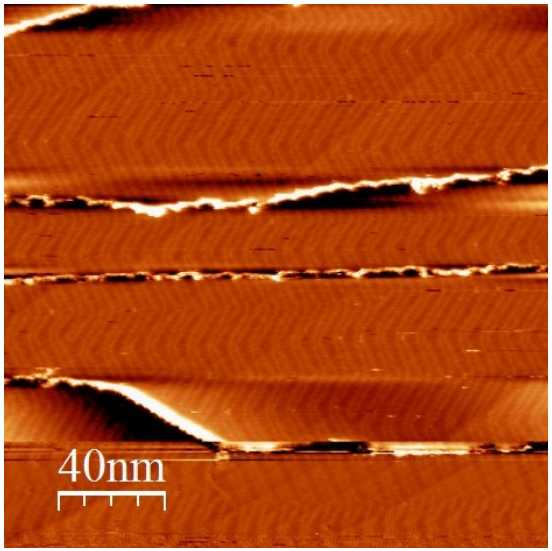
on Au(111)
@RT (300K)

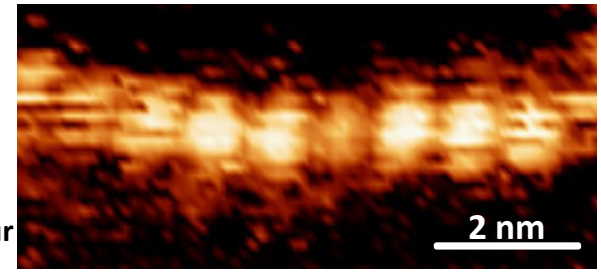
Results: 1D chains





Pure molecule





Zoom-in of **SR** chain

moving features indicates a weak interactions

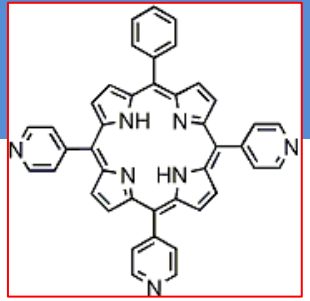
Figure 1. An overview STM topograph showing molecule 1 and Pb form sing-row (SR) chains. Inset: magnified view of a closely-packed island with the tentative model overlaid, the four black dashed lines inside the model indicate the hydrogen bonds(left); tentative model of the SR chain(right). Note that the hexagonal islands are Pb islands, and blue and white arrows indicate the closely-packed islands of molecules and chains, respectively. Color code: C, gray; N, blue; H, white; Pb, green.

Distance between two neighboring linkers : 1.92nm

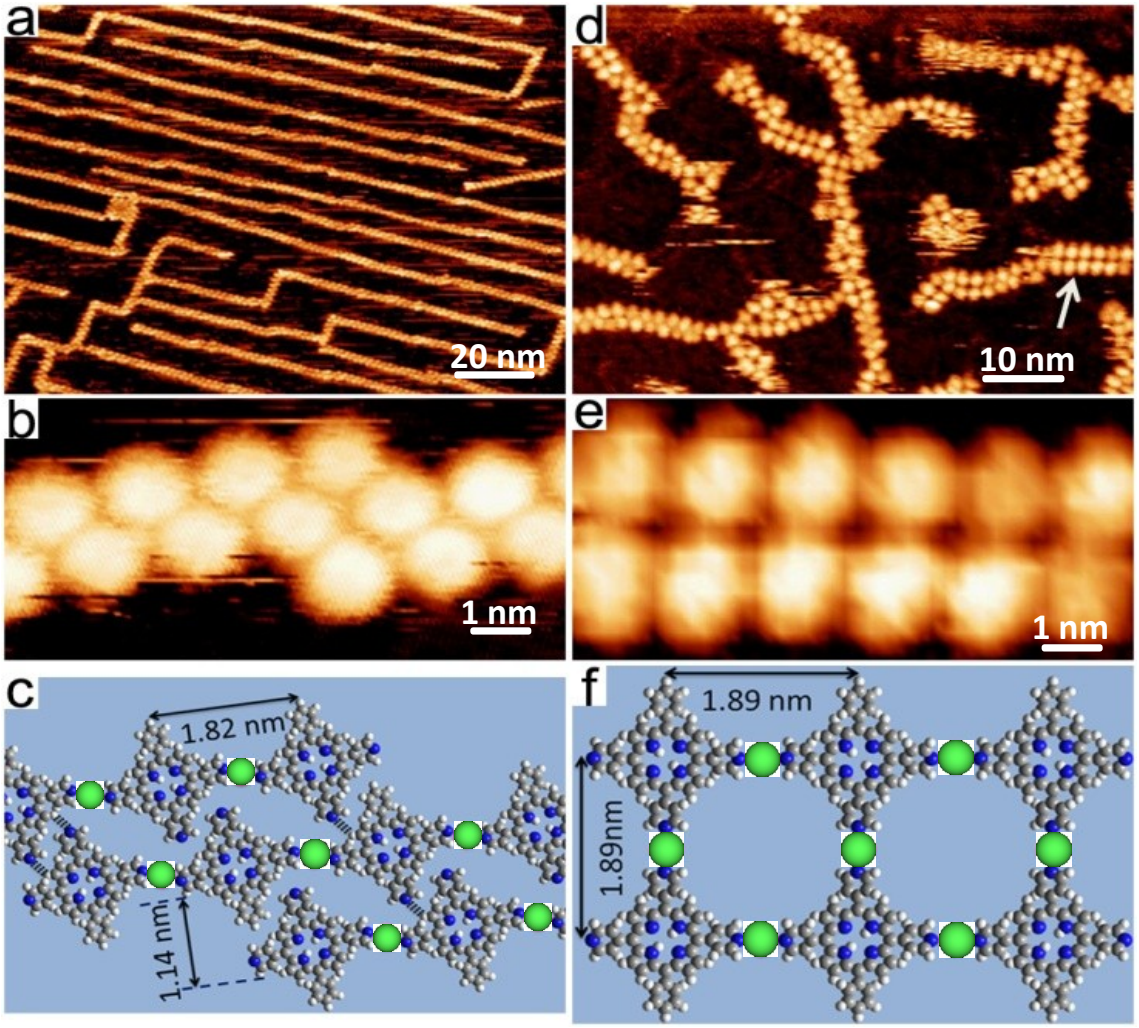
N-Pb: 2.0 Å;

J. Mater. Chem. C, 3, 3252 (2015).

Results: Ladders



400K



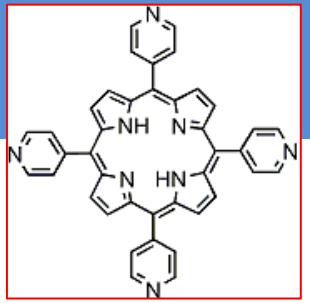
450K

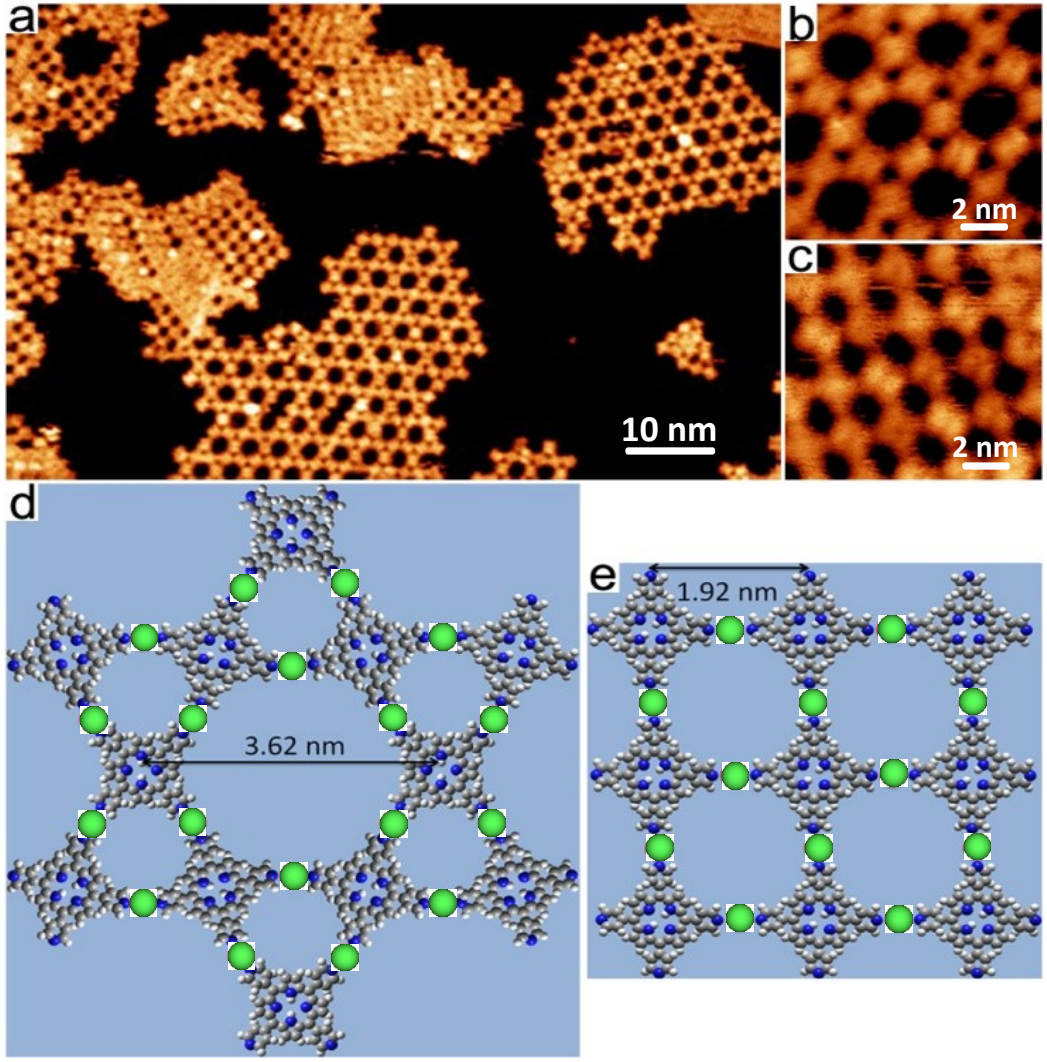
N-Pb: 2.0 Å;

Figure 2. (a) and (d) STM topograph showing the DR chains and the ladder structures formed out of 2 and Pb, respectively. White arrow indicates the ladder structures. (b) and (e) High-resolution images of a DR chain and a ladder structure. (c) and (f) Tentative model of the DR chains and the ladder structure, respectively. The two black dashed lines indicate the position of hydrogen bonds.

J. Mater. Chem. C, 3, 3252 (2015).

Results: 2D MOFs





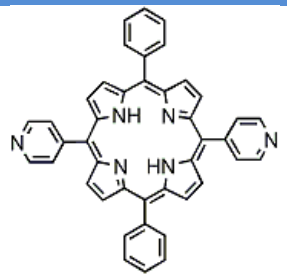
The 2D MOFs are not homogeneous, with limited area,
Can we achieve large area 2D MOFs?

Annealing

Figure 3. (a) STM topograph showing 3 and Pb form close-packed islands, Kagome and rhombus networks. (b) and (c) High-resolution images of the Kagome and rhombus networks. (d) and (e) Tentative models of the Kagome and rhombus networks.

J. Mater. Chem. C, 3, 3252 (2015).

Thermal stability



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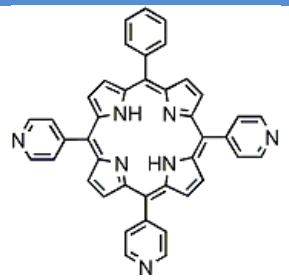

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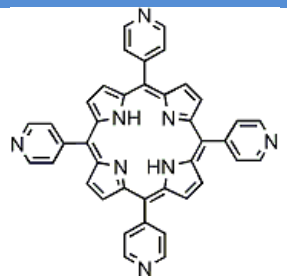

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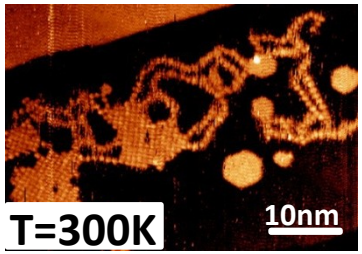
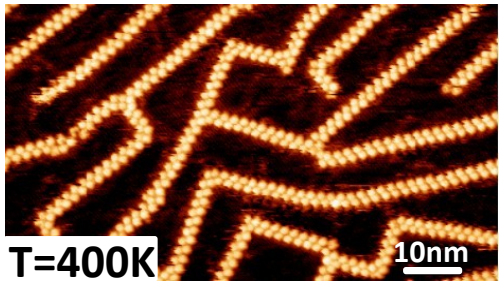
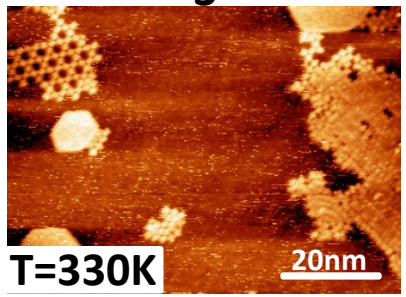
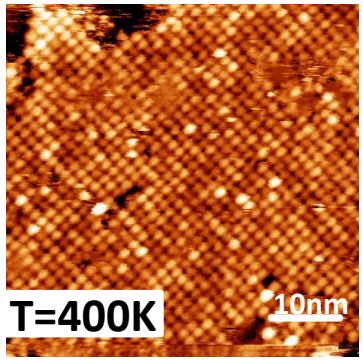
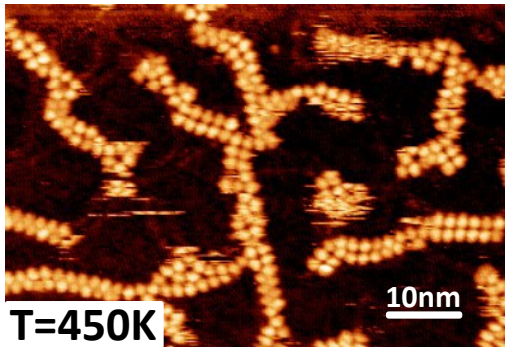
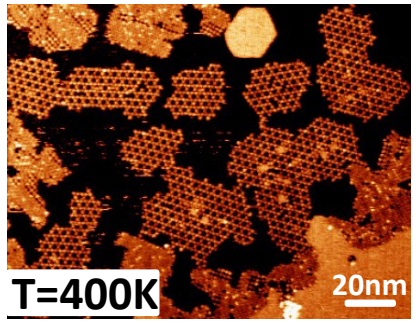


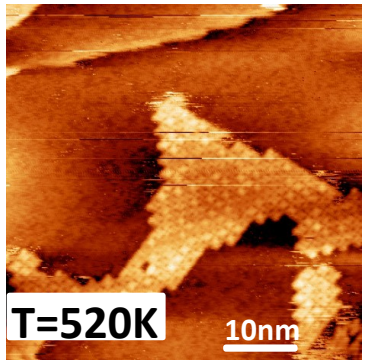


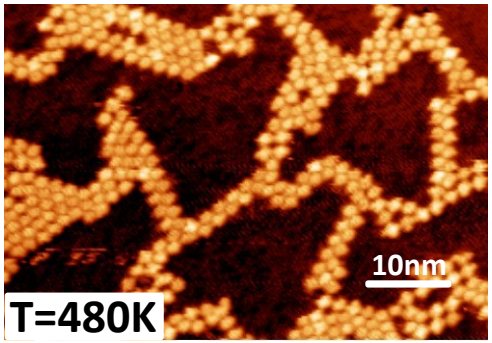


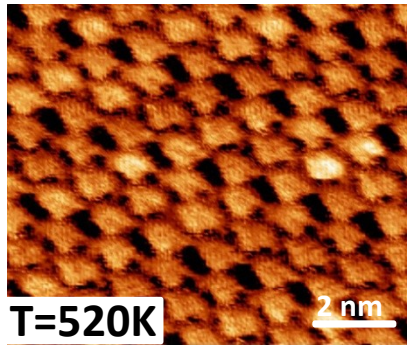






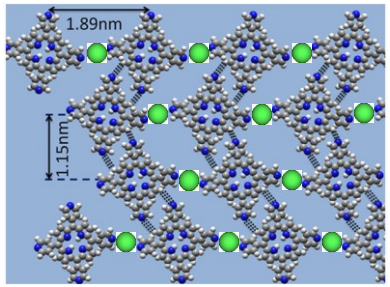




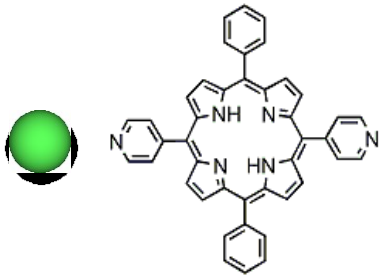


Annealing can not achieve high quality networks!

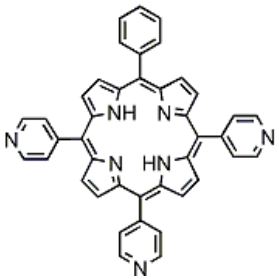
1. Weak coordination interaction, comparable with H bond
2. Pb atoms intermix in Au(111);



Conclusion



1



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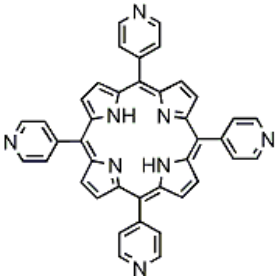

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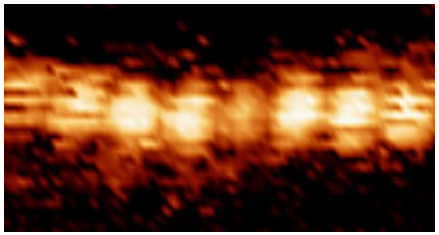
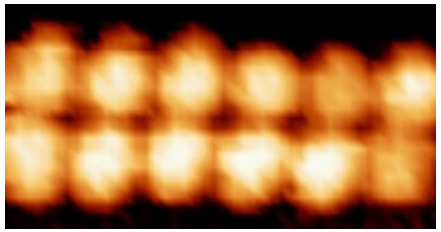
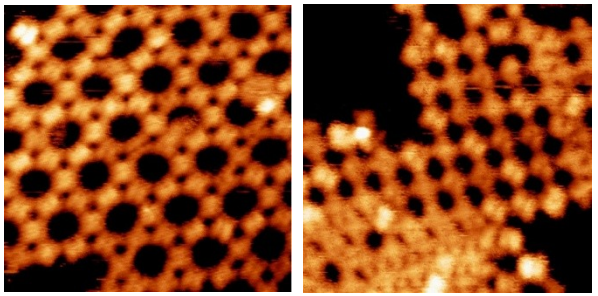
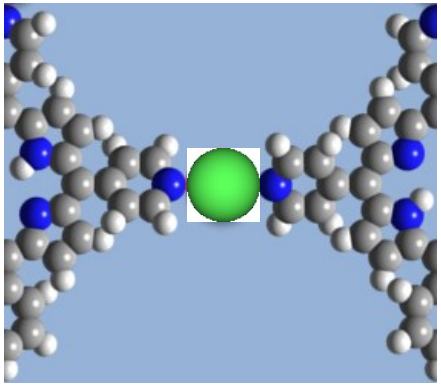


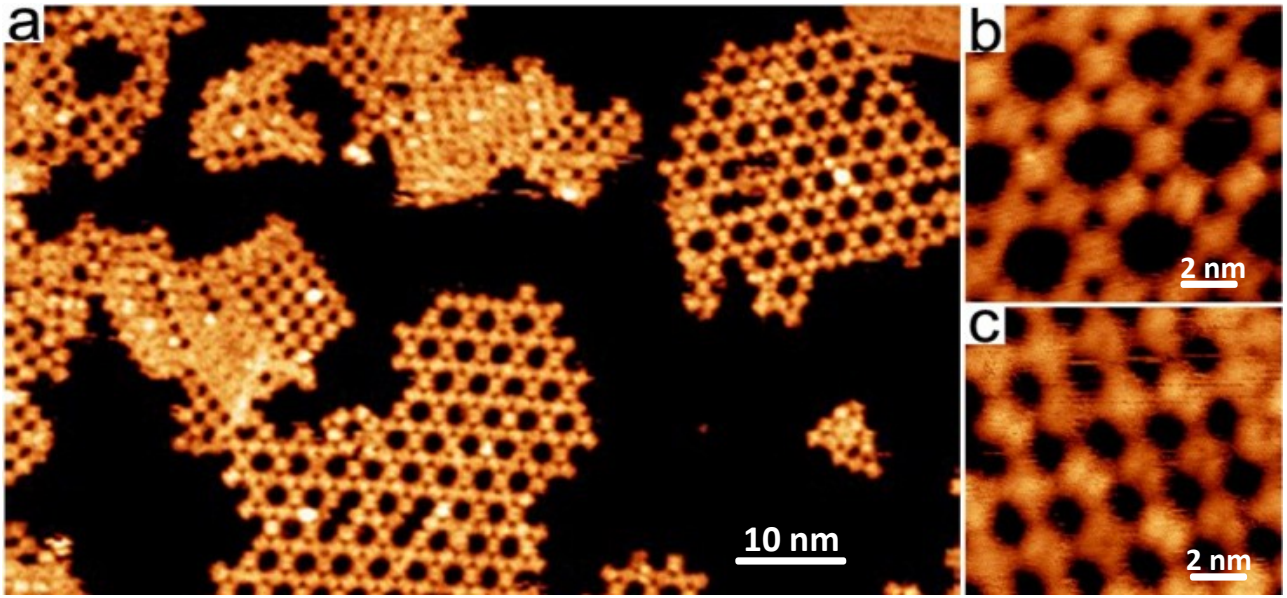






- Weak coordination bond.

Homogeneous MOFs with Pb

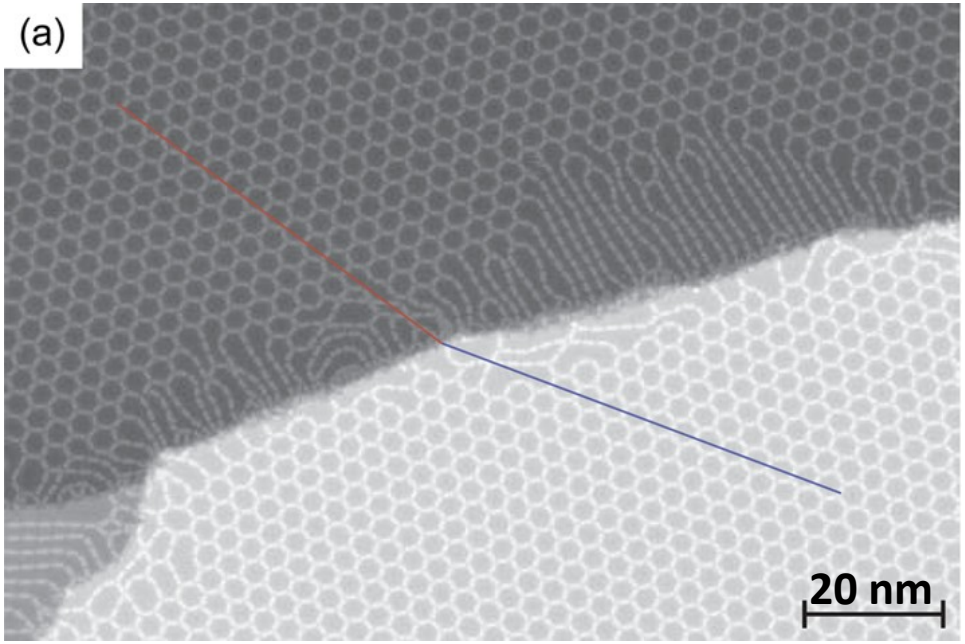


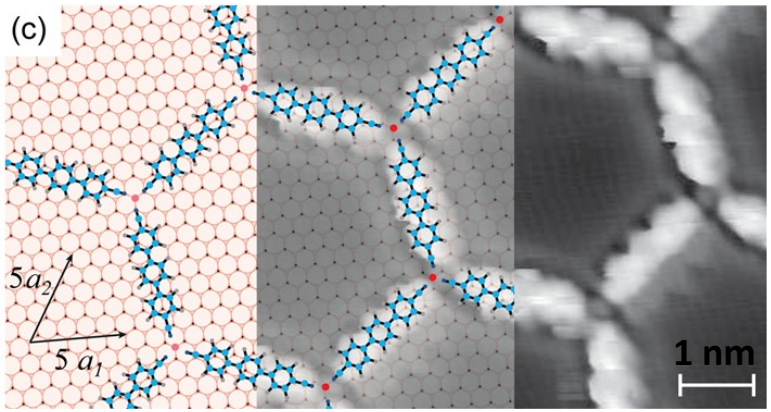
The 2D-MOFs involving Pb is not homogeneous,
and the domain area is not as large as the conventional 2D-MOFs based on transition metals.

How to design and fabricate defect free and large area 2D-MOFs with Pb?

2D-MOFs with CN- ligands

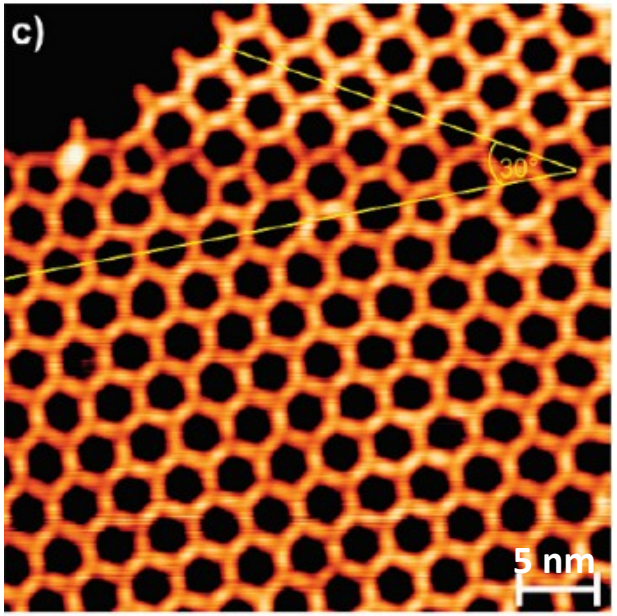
CN-Cu

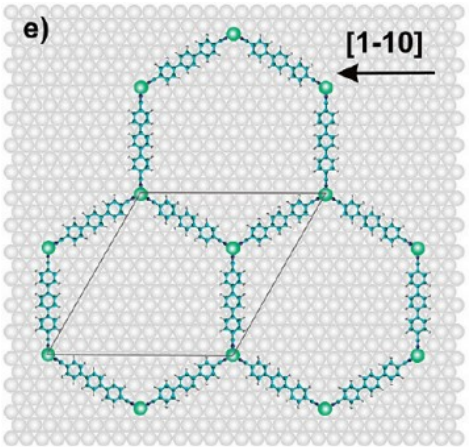




Pacchioni G. E. et al., *J. Phys. Chem. C,* **2015**, 119, 25442.

CN-Co





Schlickum U., et al., *J. Phys. Chem. C,* **2010**, 114, 15602.

Outline

1. Introduction

2. On surface Pb-coordinated metal-organic frameworks (MOFs)

- 1D and 2D-MOFs with Pb-pyridyl coordination
- 2D-MOFs with Pb-carbonitrile coordination

3. On surface Eu-coordinated MOFs

- 2D-MOFs with Eu-carbonitrile coordination
- 1D and 2D-MOFs with carbonitrile-Eu-terpyridyl coordination

4. Conclusion

Theoretical prediction

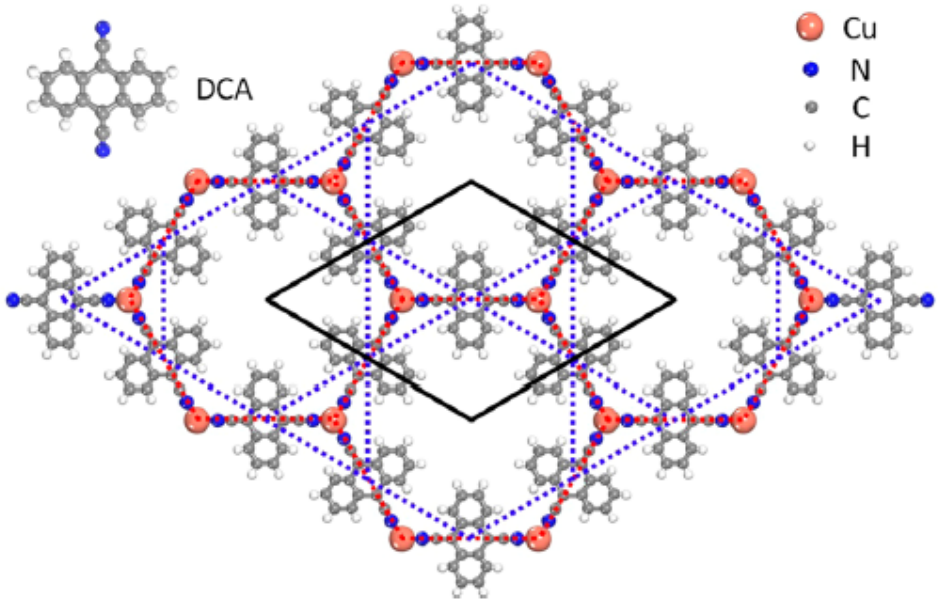


Figure 1. Schematic atomic structure of Cu–DCA film. The top left inset shows the DCA molecule. The red dashed, blue dashed, and black lines outline the honeycomb lattice by the Cu atoms, the Kagome lattice by the DCA molecules, and the unit cell, respectively.

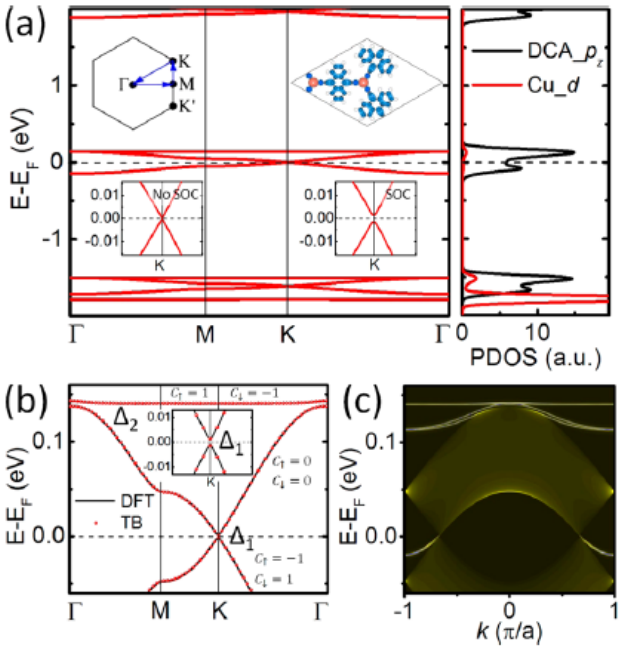


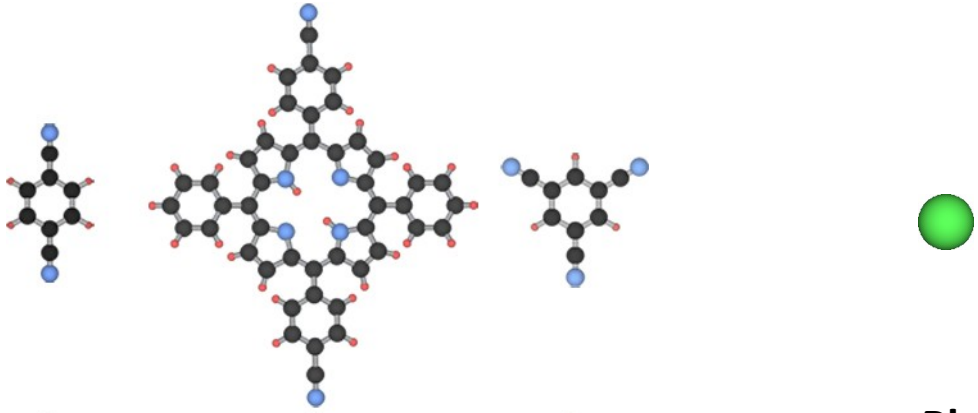
Figure 2. Electronic structures of Cu–DCA film. (a) Band structures and PDOS, where the top right inset indicates the charge distribution around the Fermi level, and the bottom two insets show the zoom-in bands without and with SOC, respectively. (b) The comparison between first-principles and single-orbital TB band structures around two SOC gaps (Δ_1 and Δ_2). (c) The semi-infinite Dirac edge states within the SOC gaps.

	Cu-DAC	Au-DAC
a (Å)	20.36	21.06
E_g (meV)	2.9	10.9

Pb is heavier than Au, so the band gap of the similar lattice involved Pb will be larger.

Zhang L. Z., Gao h.-J., Liu F. et.al, *Nano Lett.* **2016**, 16, 2072

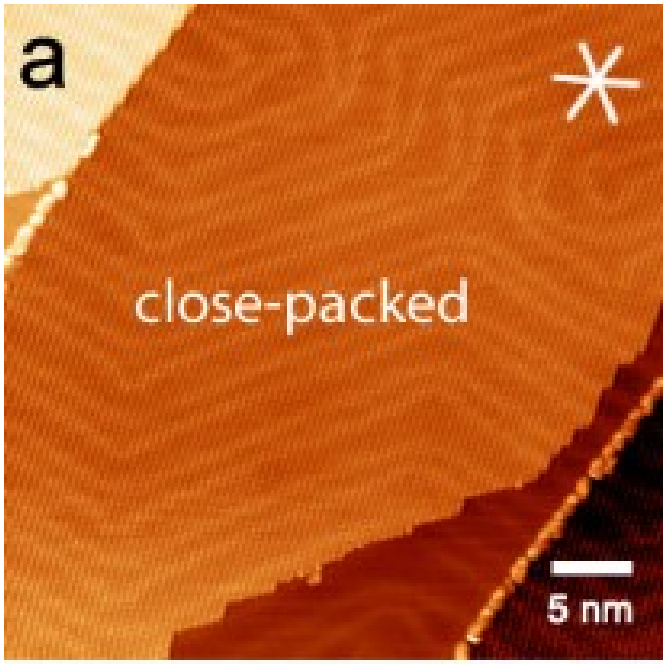
Molecules and metal

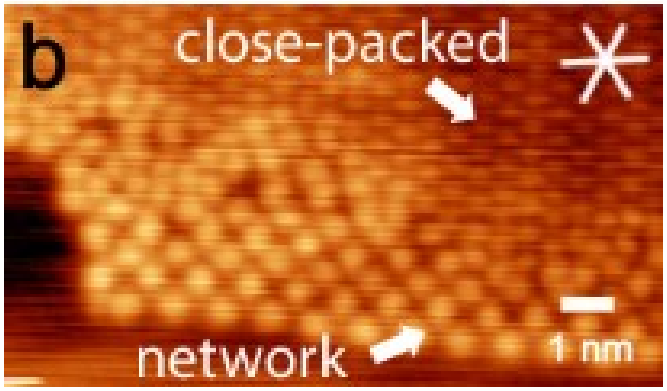


Color codes: C: black; H: red; N: blue; Pb: green.

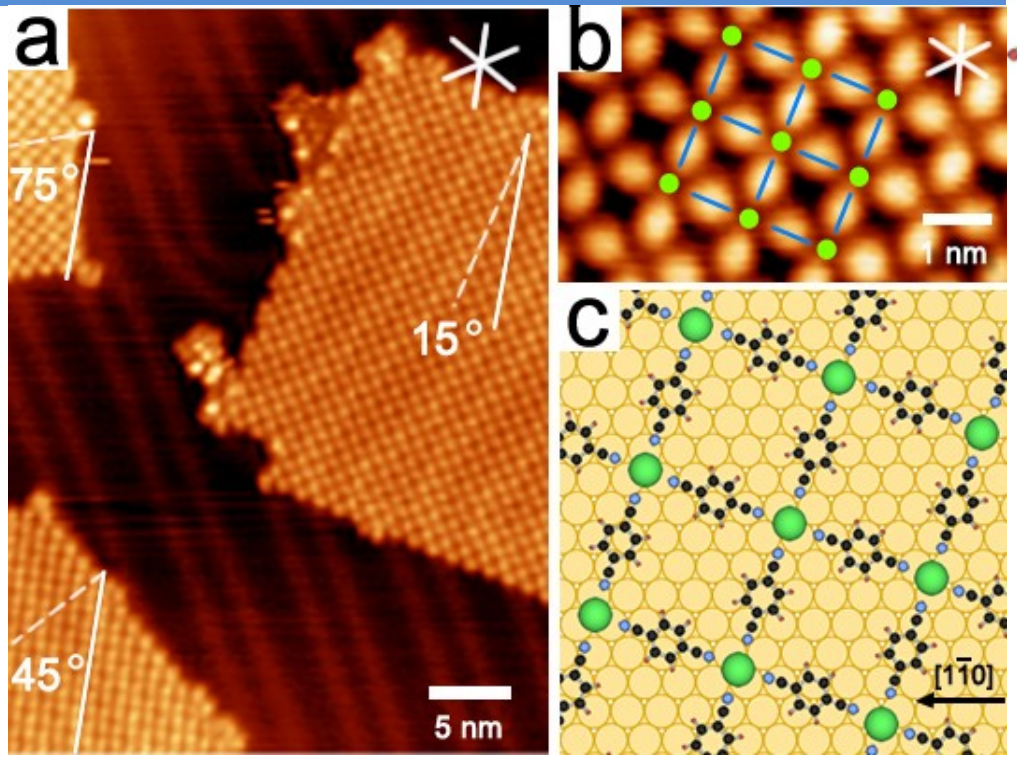
on Au(111)
@RT (300K) or LN_2(77K)

Results: square lattice @77K





Close packed molecular islands, linked by N…H hydrogen bonds

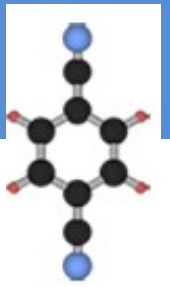


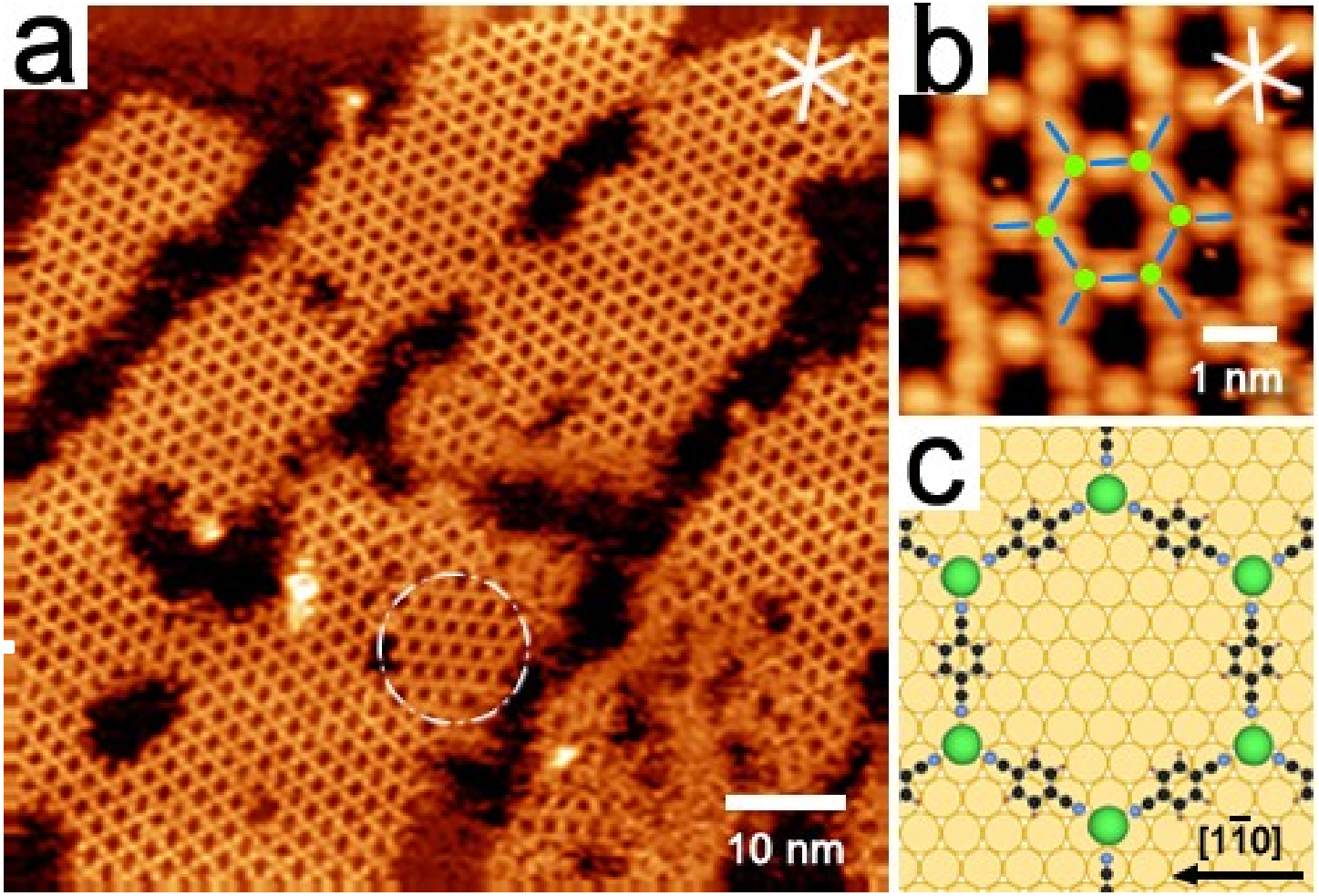
2D-MOFs, 4-fold Pb-CN coordination motif,
Square lattice constant: 1.30nm, **Pb-N: ~2.5Å**

After annealing the sample to 100 °C, the square network vanished.

Bond cleavage and molecular linkers desorbed from the substrate.

Results: Honeycomb networks

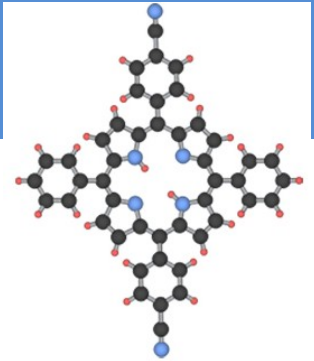


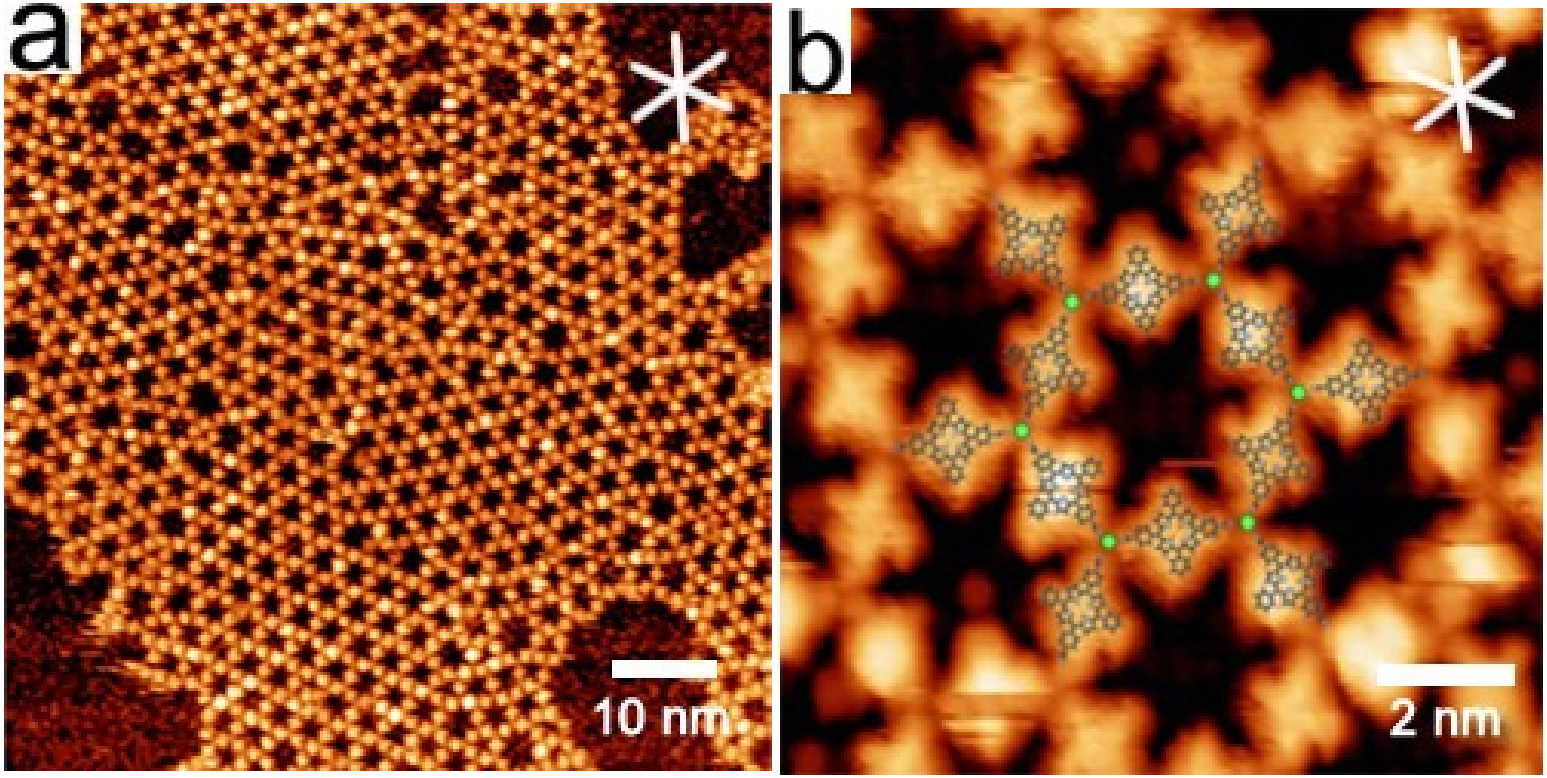


After annealing the sample to 100 ˚C, the networks vanished.

Linker 4 first, then dosed Pb
2D-MOFs, 3-fold Pb-CN coordination motif,
honeycomb lattice: 1.30nm, Pb-N: ~2.0Å,
White circle: 30° rotation against the majority
orientation

Results: Hexagonal networks, @300K



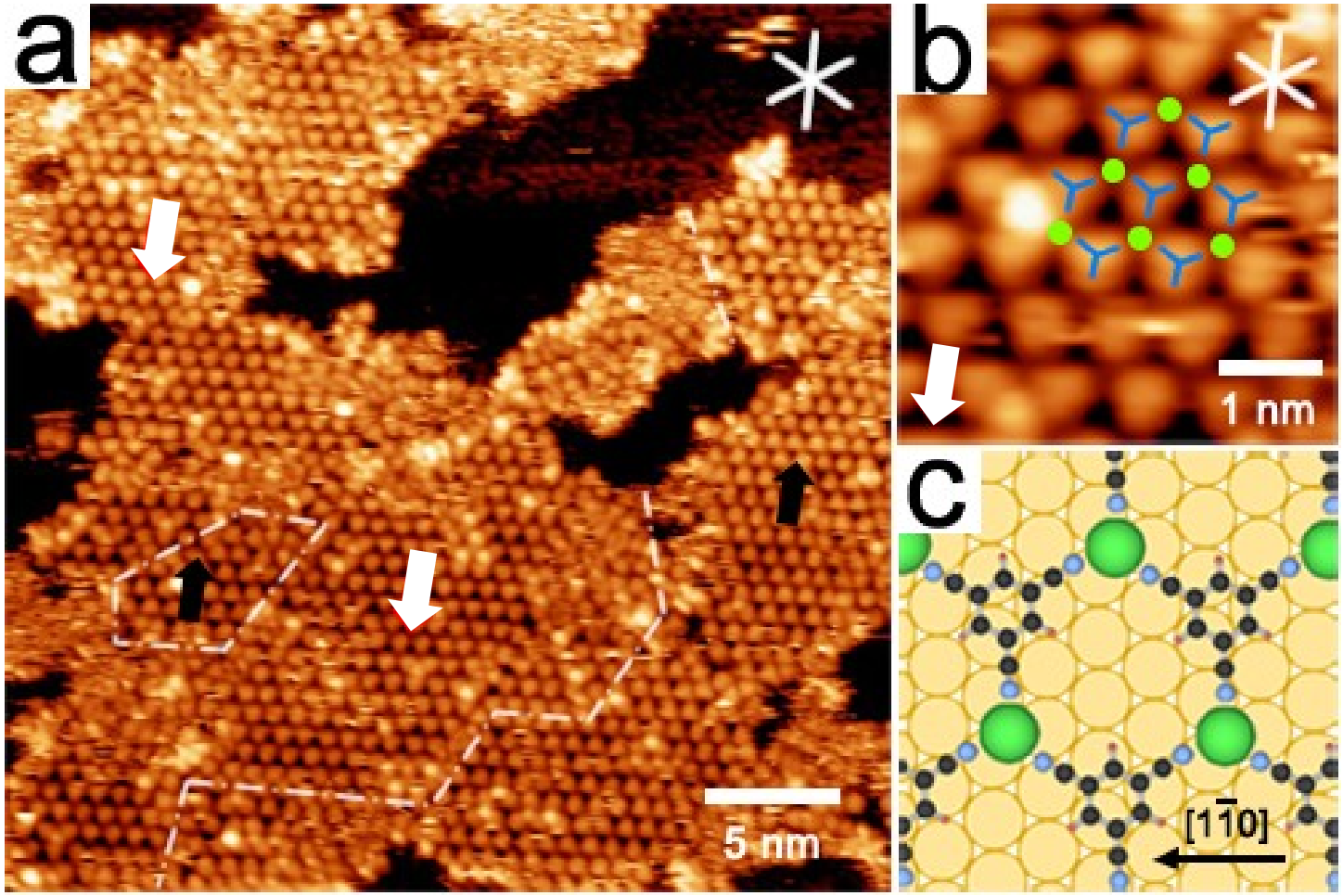


Many domains with different Orientations.

Annealing treatment could not improve the quality of networks

2D-MOFs, 3-fold Pb-CN coordination motif, hexagonal lattice: 3.92nm Pb-N: ~2.0Å

Results: Molecule 6, @300K

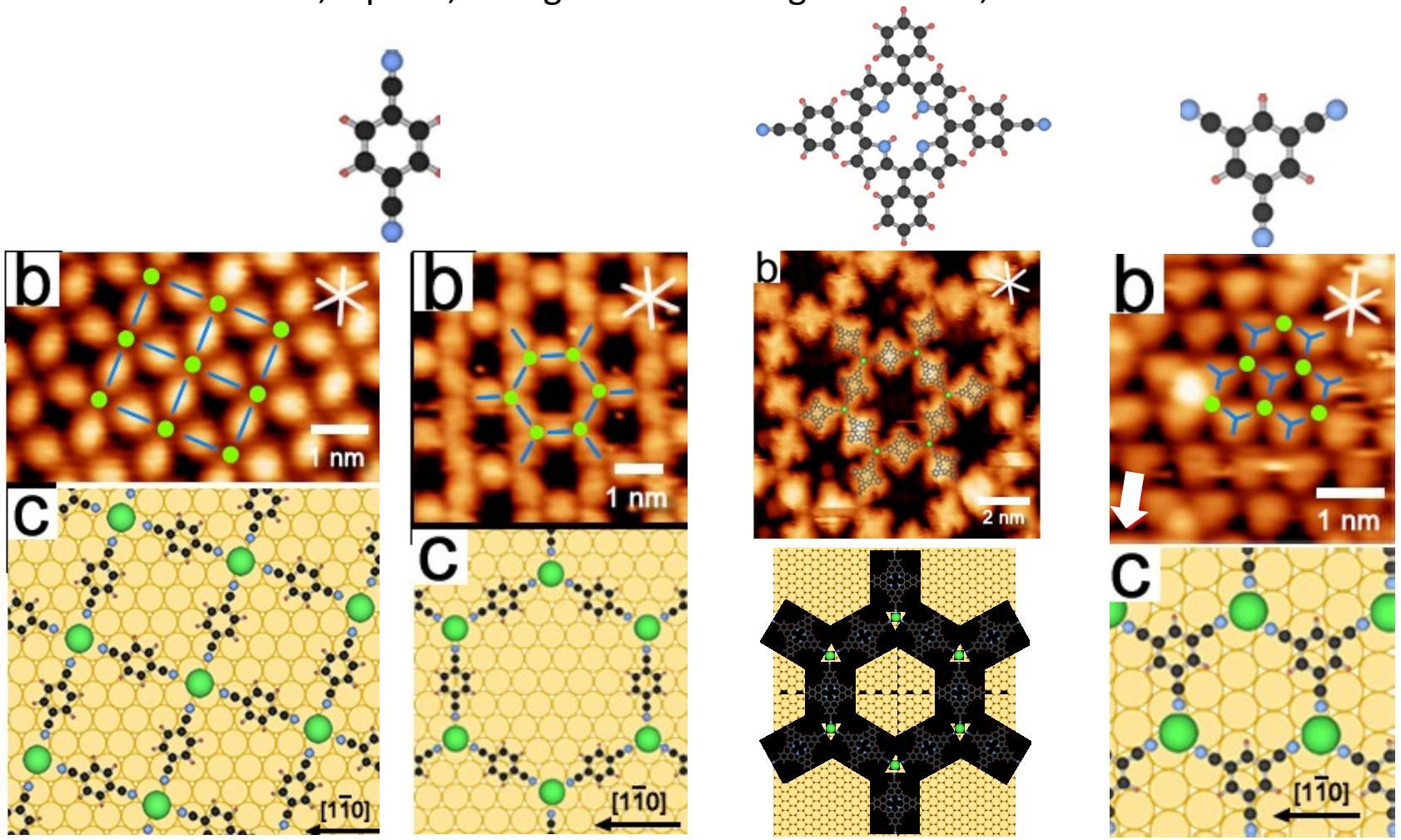


2D-MOFs, 3-fold Pb-CN coordination motif, triangular lattice: 1.05nm, Pb-N: ~2.0Å, white and black arrows indicate two mirror-reflected orientations.

After annealing the sample to 100 ˚C, the networks vanished.

Conclusion

- Pb atoms can coordinate with CN ligand;
- Flexible coordination, 3-fold, 4-fold;
- Linkers difference, square, hexagonal and triangular lattice;



@ 77K @300 K @300 K @300 K

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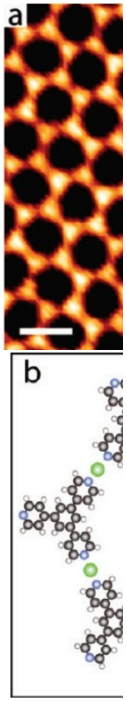
Versatile morphologies



Z. Shi, *J. Am.* 133, 6150

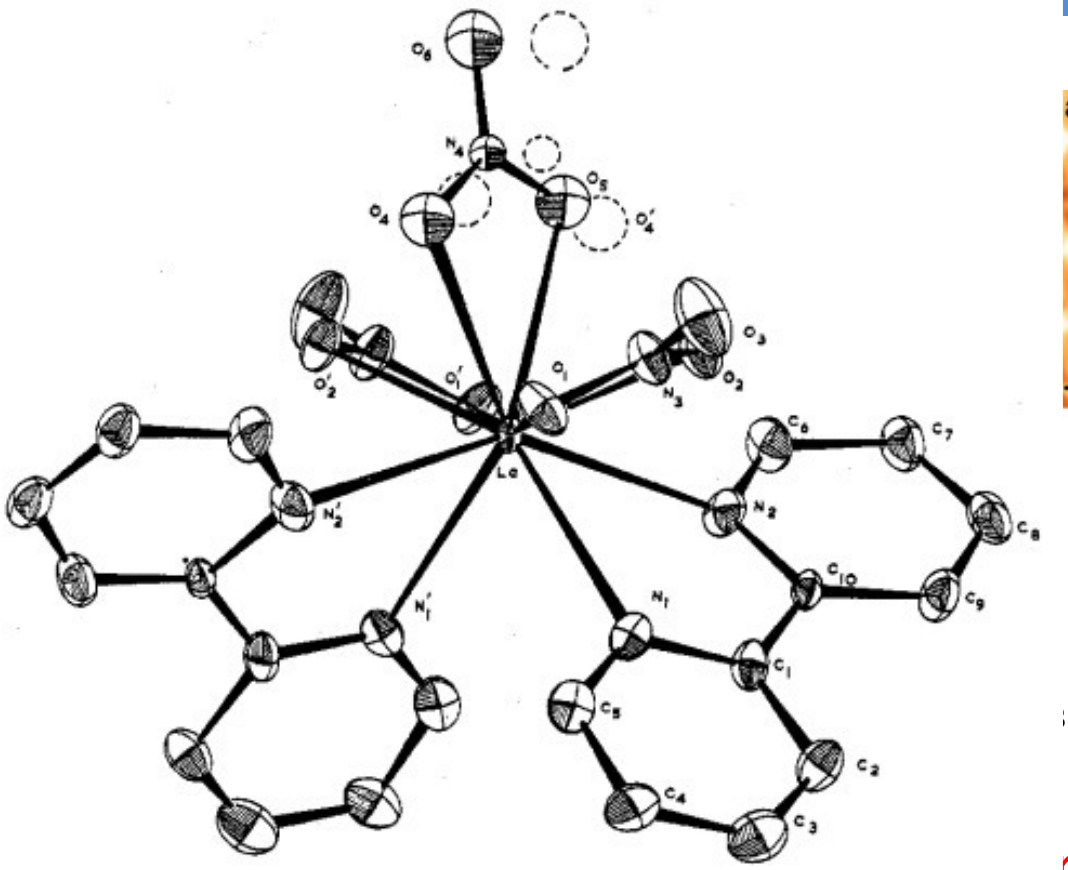
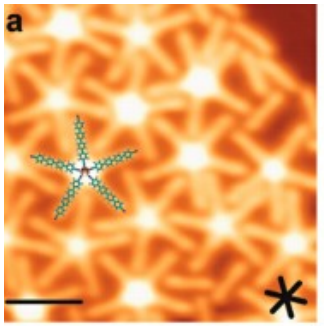
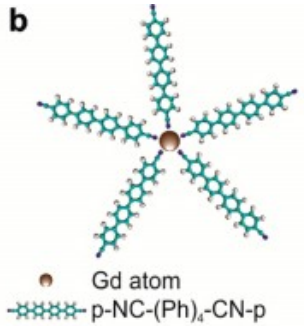


Figure 2.—The $La(NO_3)_3(C_{10}H_8N_2)_2$ molecule projected onto (001) and illustrating the orientations and relative magnitudes of the thermal ellipsoids. The position of one of the "half" nitrate ions is indicated by broken lines.





Urgel, J. I. *J. Phys. Chem. C* **2014**, *118*, 12908.

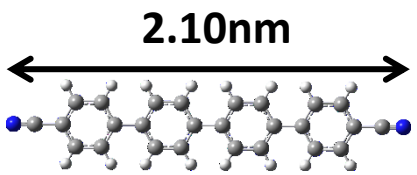
r even higher?

Due to the shielding of the 4f orbitals by filled subshells of higher principal quantum numbers, ligand-field effects are much weaker

Versatile morphology and exhibit potential appilcations in many fields, such as optics, magnetism and catalyst.

Al-Kharaghouli, A. R., Wood, J. S. Inorg. Chem. **1972**, 11, 2293.

Molecules and metal



7

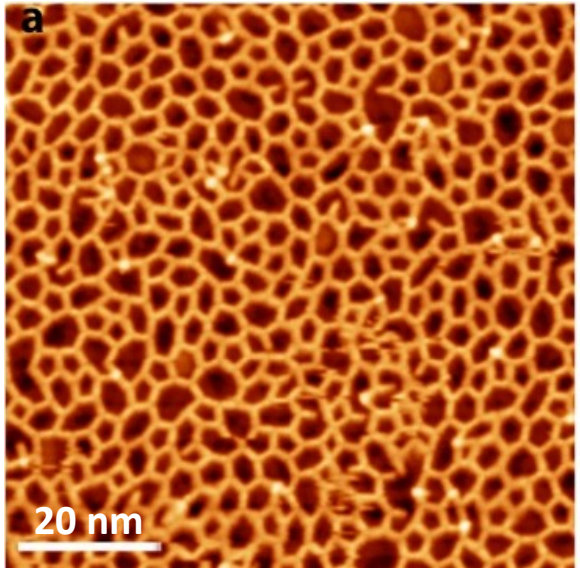
Radius=1.85Å

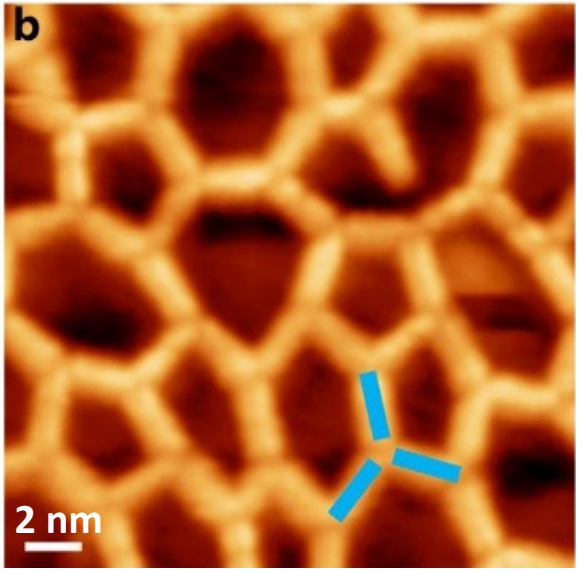
Eu

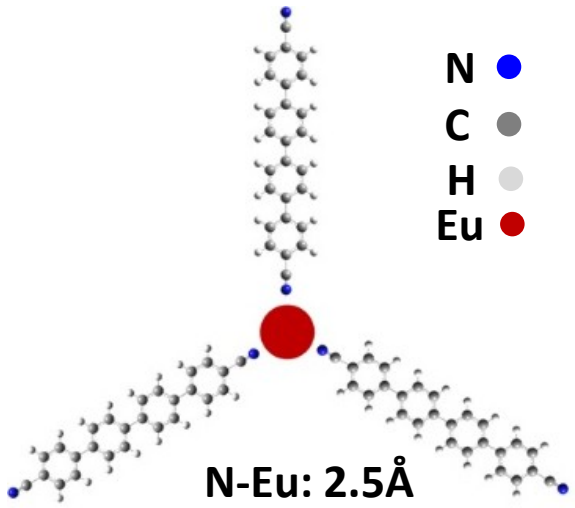
N
C
H
Eu

on Au(111) and Ag(111) surfaces
@RT (300K)

Results: [Eu]:[7]=2:3 irregular pores

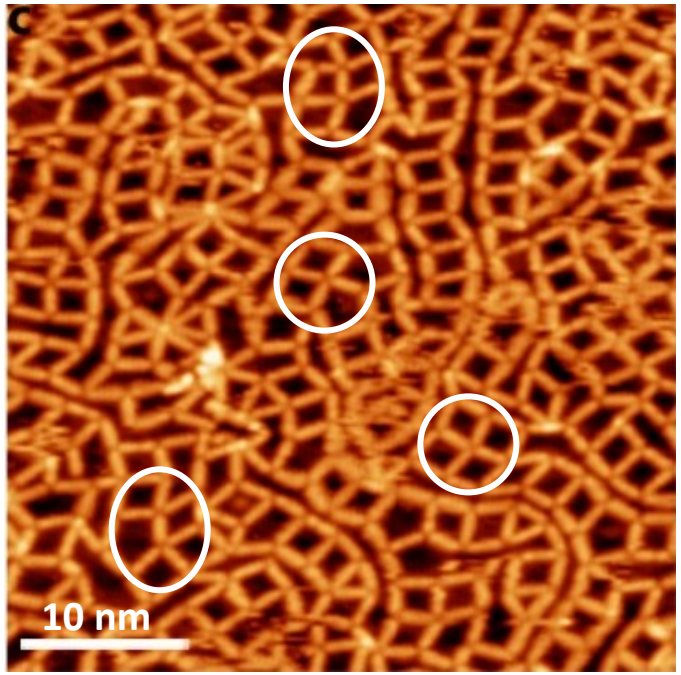






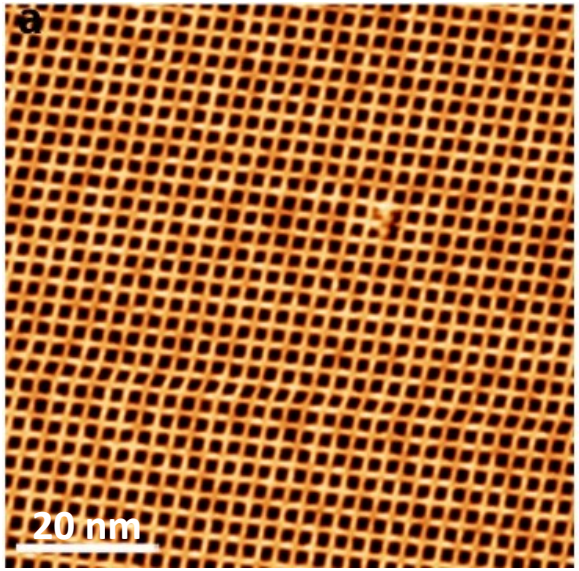
3-fold Eu-CN coordination motif,
Flexible intersect angle, not 120°

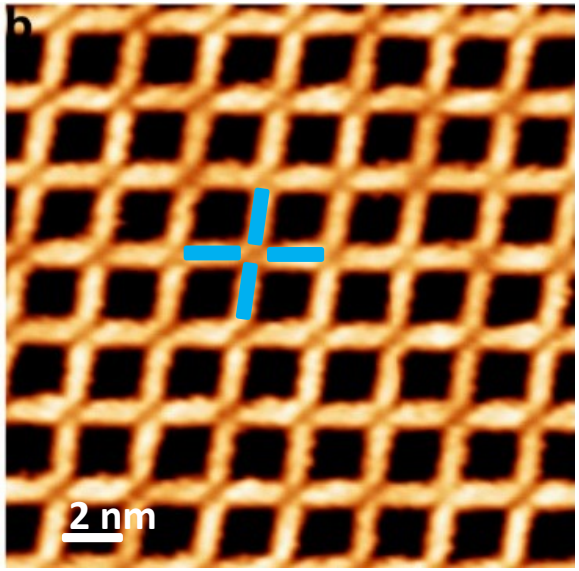
Slightly increased the amounts of 7,
4-fold motif were observed.

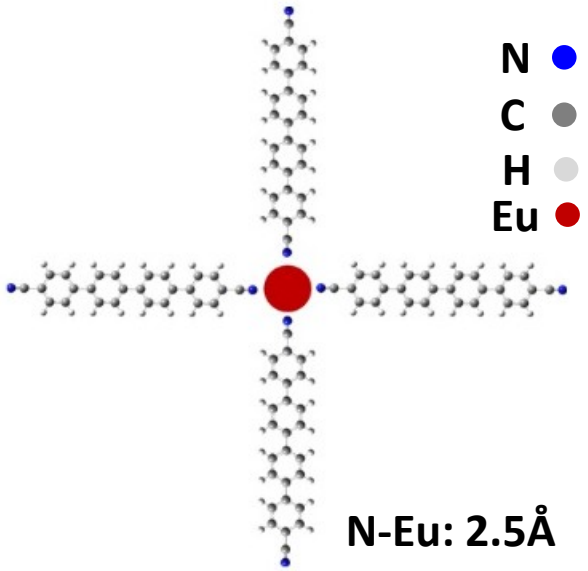


Nat. Chem., 8, 657 (2016)

Results: [Eu]:[7]=2:4 square lattice

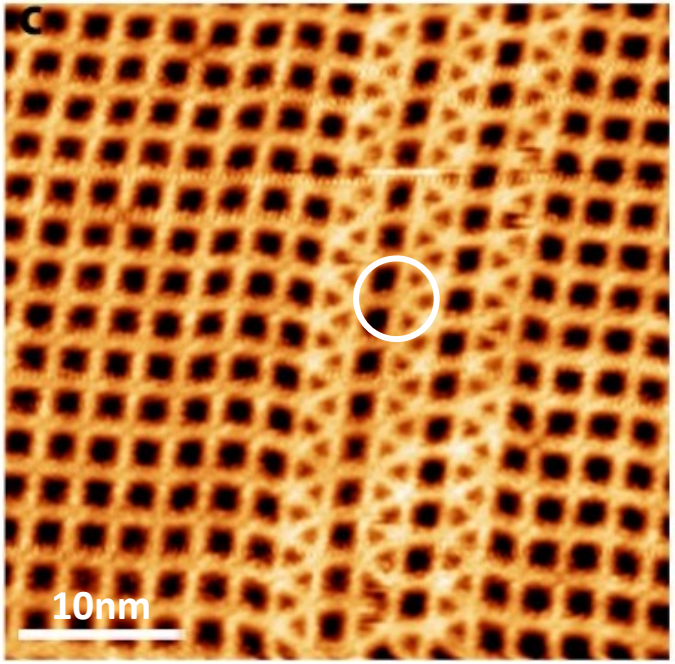






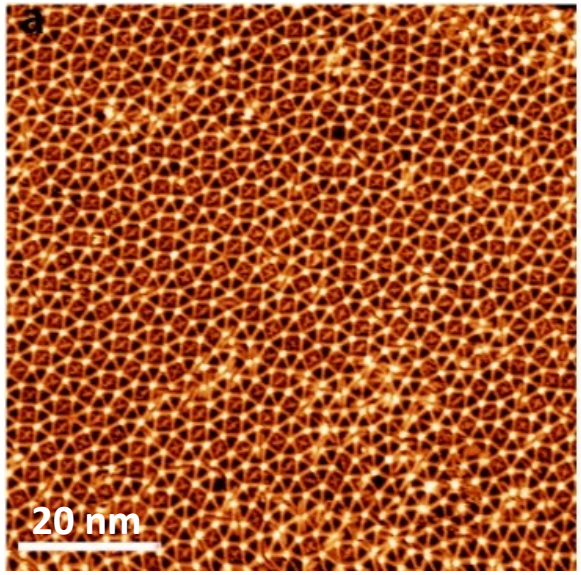
4-fold Eu-CN coordination motif,
Square MOFs, extended to large areas
Herringbone could be observed

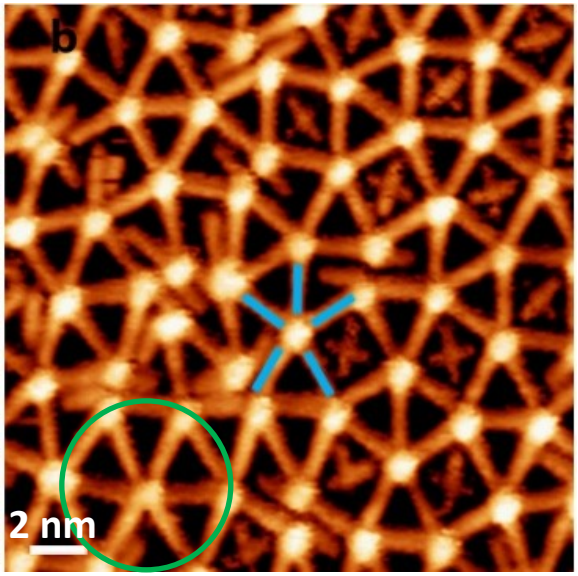
Slightly increased the amounts of 7, 5-fold motif were inserted between square lattice.

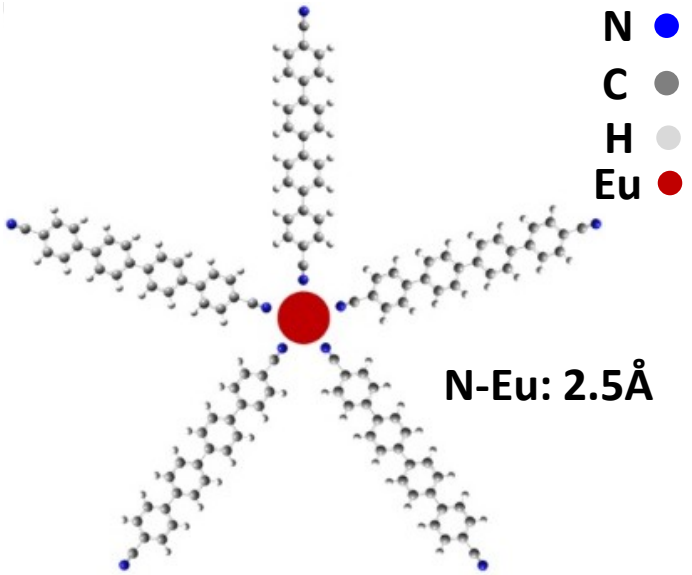


Nat. Chem., 8, 657 (2016)

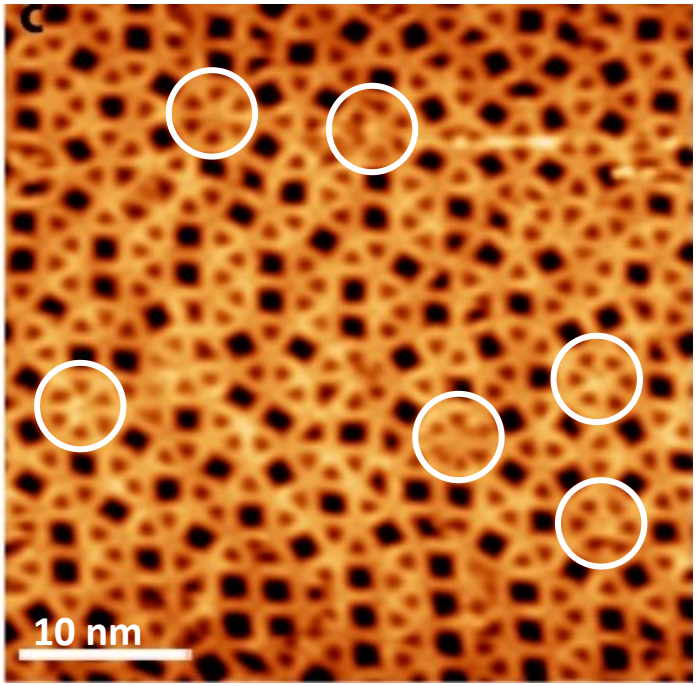
Results: [Eu]:[7]=2:5 five-vertex stars







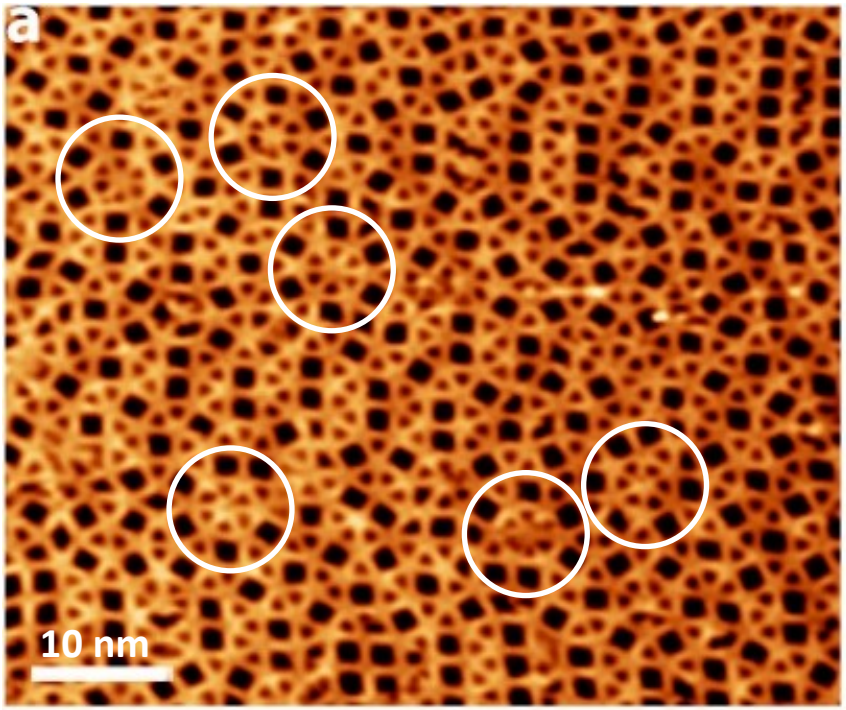
5-fold Eu-CN coordination motif,
Star-like MOFs, extended to large areas,
Cross-like species: initial ligands 7
Green circle: 6-fold motif

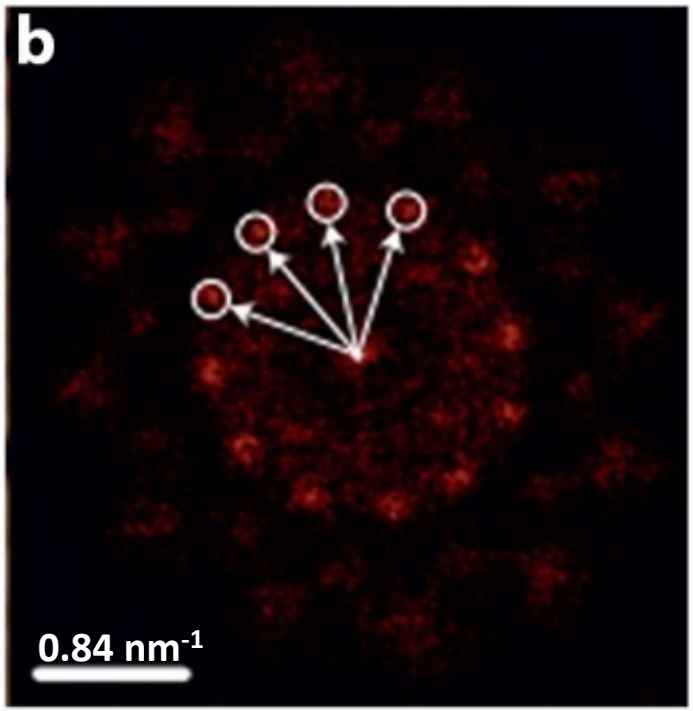


Slightly increased the amounts of 7,more 6-fold coordination motifs.

Nat. Chem., 8, 657 (2016)

Results: [Eu]:[7]=2:5.1 quasicrystal MOFs





comprises a repetition of dodecagonal structural units with an adequate distribution of triangles and squares

The 12-fold Fourier transform indicated a random square–triangle tiling dodecagonal quasicrystals stabilized by metal-organic coordination bond

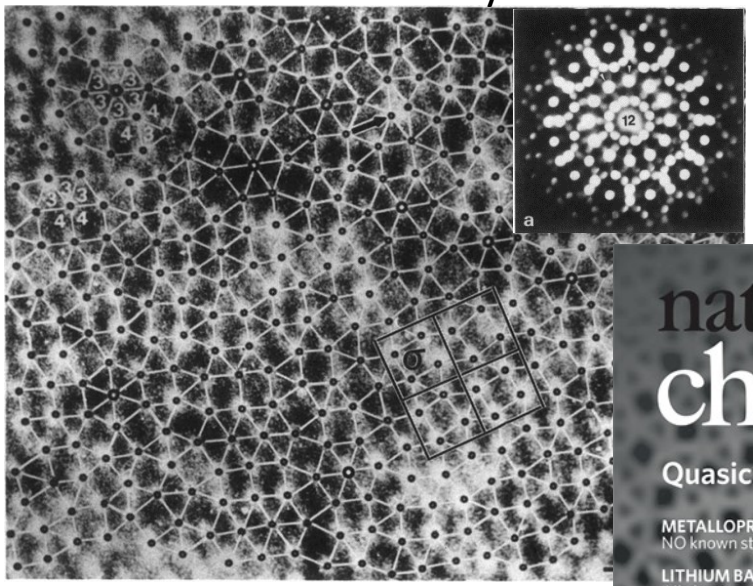
Quasicrystal: a structure that is ordered but not periodic.
The pattern can continuously fill all available space, but it lacks translational symmetry.
The Bragg diffraction pattern of quasicrystals shows sharp peaks with other symmetry orders, compare with crystals (2,3,4,6 fold symmetry)

Nat. Chem., 8, 657 (2016)

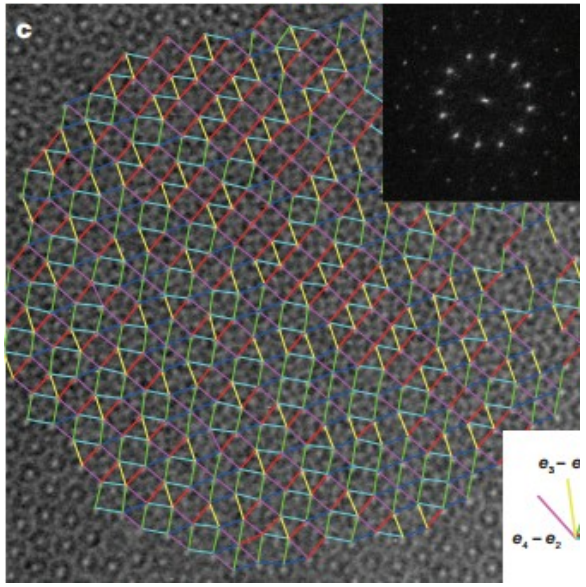
https://en.wikipedia.org/wiki/Quasicrystal

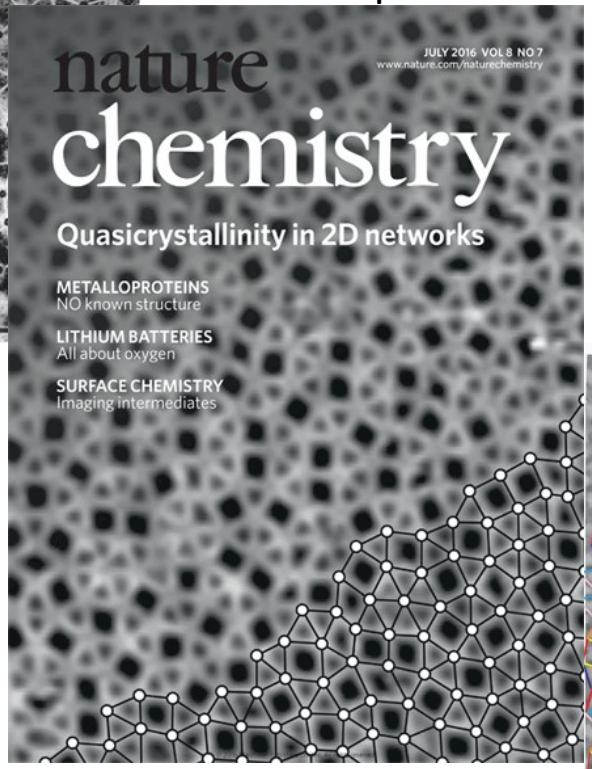
Results: other quasicrystal systems

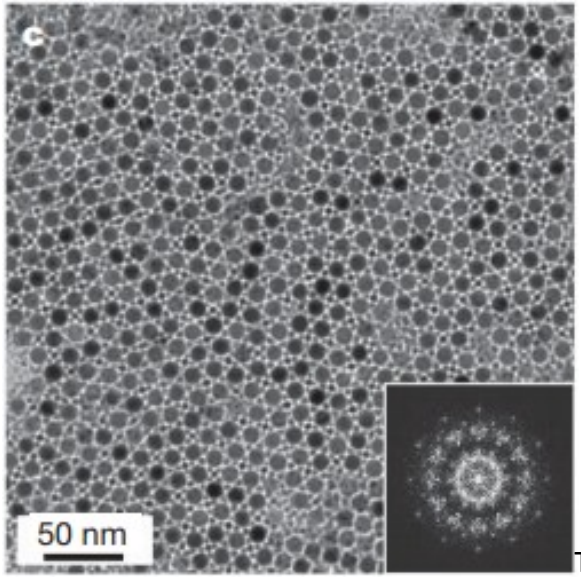
V_3Ni_2 and $V_{15}Ni_{10}Si$ alloy films

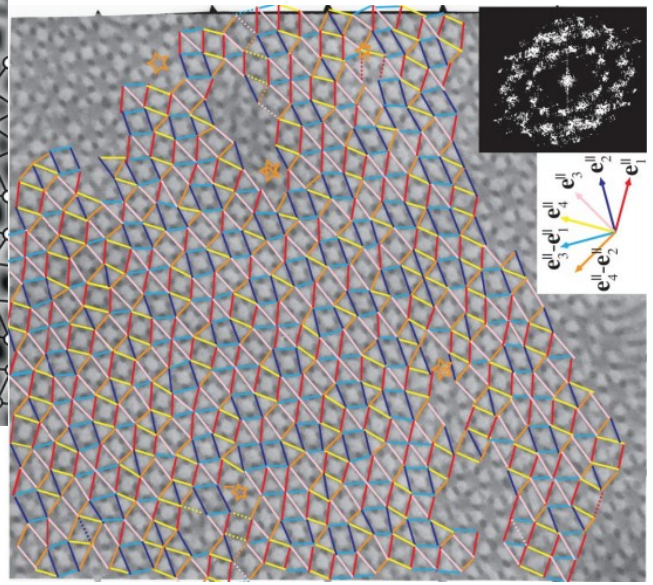


Mesoporous silica







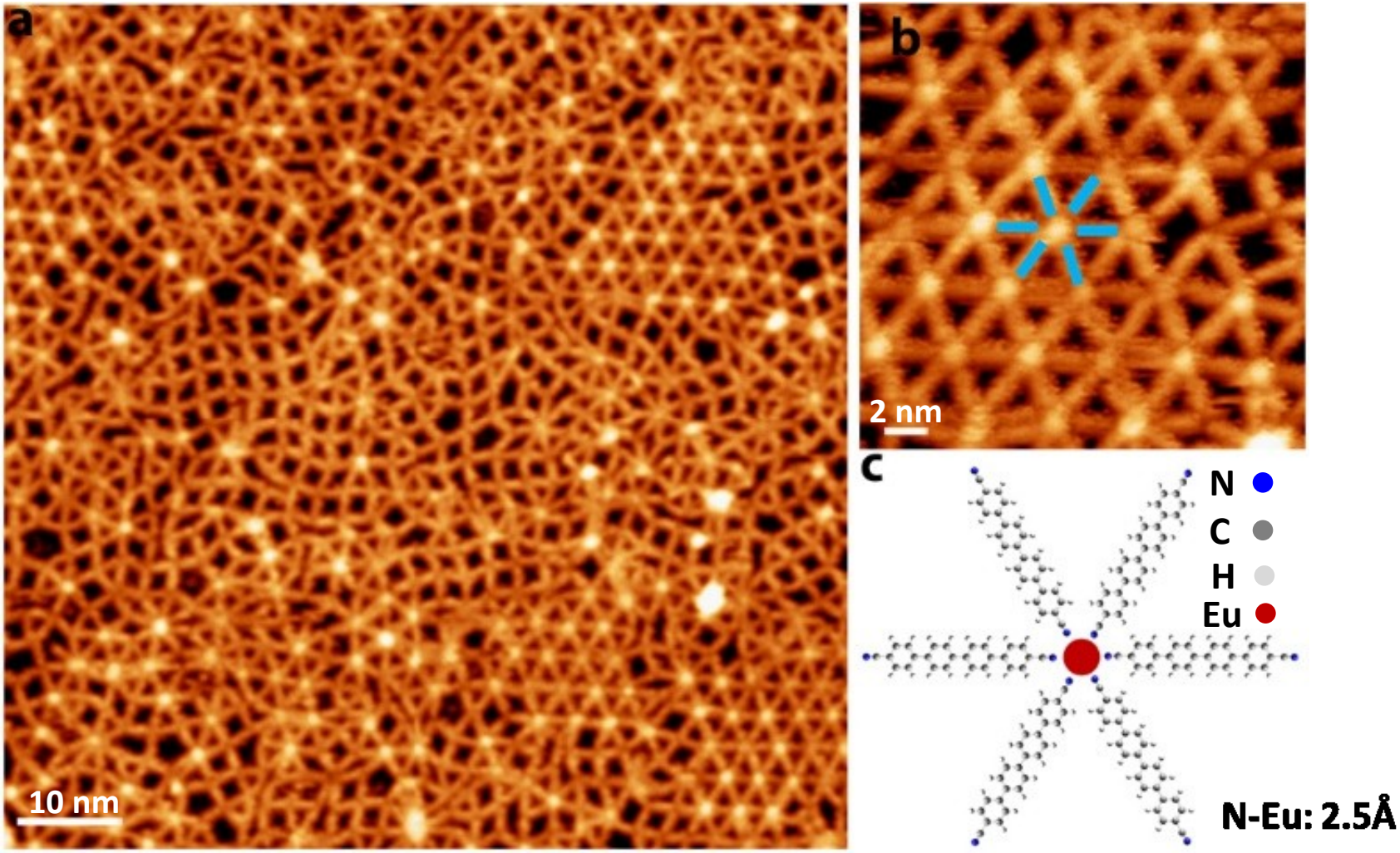


Quasicrystal MOFs on surface!

Talapin, D. V. et al., Nature, **2009**, 461, 964.

Chen, H. et al., Phys. Rev. Lett., **1989**, 60, 1645. Xiao, C. et al., Nature, **2012**, 487, 349. Hayashida, K., Phys. Rev. Lett., **2007**, 98, 195502.

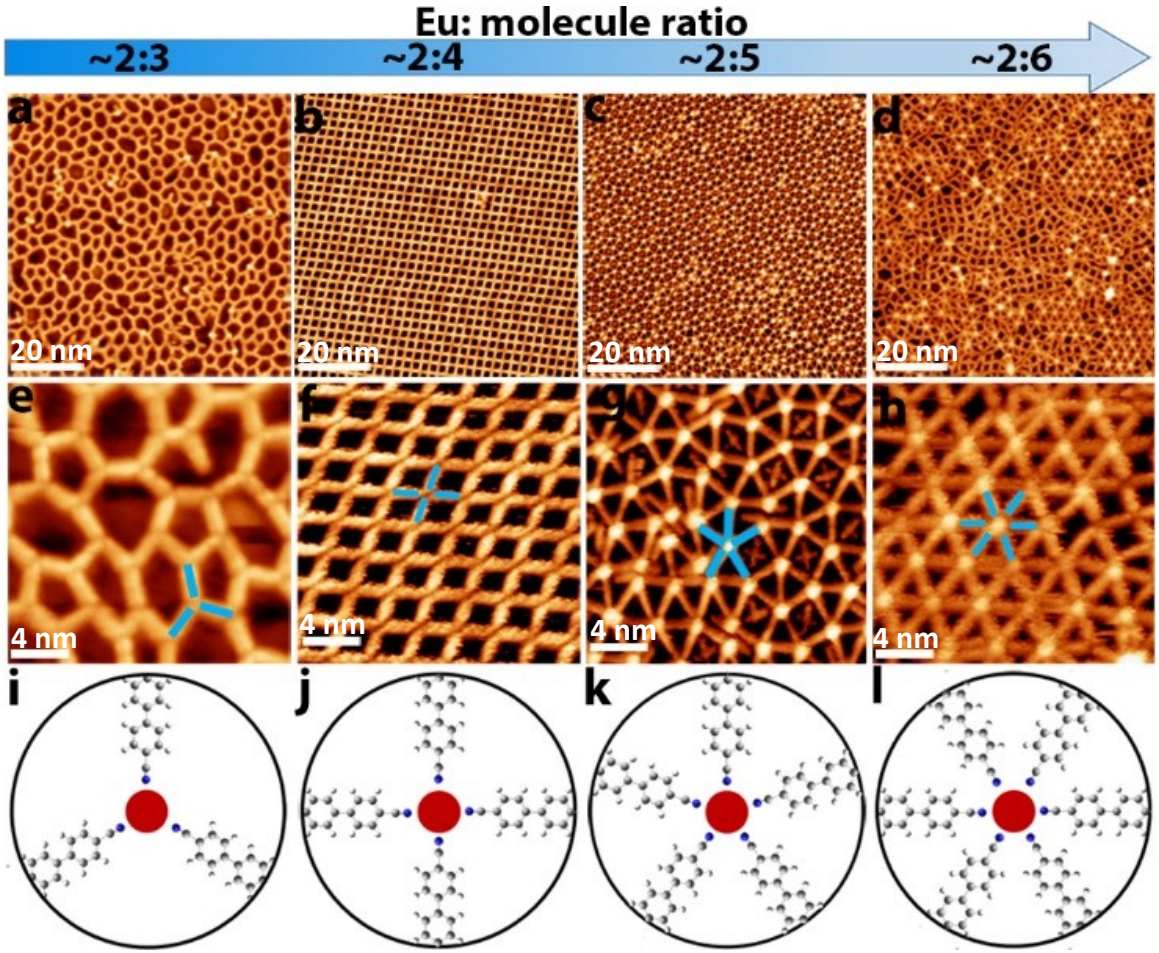
Results: [Eu]:[7]=2:6 hexagonal lattice



distorted squares and hexagonal lattices
Many domain boundaries;
Hexagonal lattice: 6-fold motif

Nat. Chem., 8, 657 (2016)

Conclusion



- At a specific ratio, quasicrystal MOFs, 12-fold Fourier transform
- On Ag(111), only 4-fold and 5-fold Eu-CN coordination motif, no quasicrystal structures.

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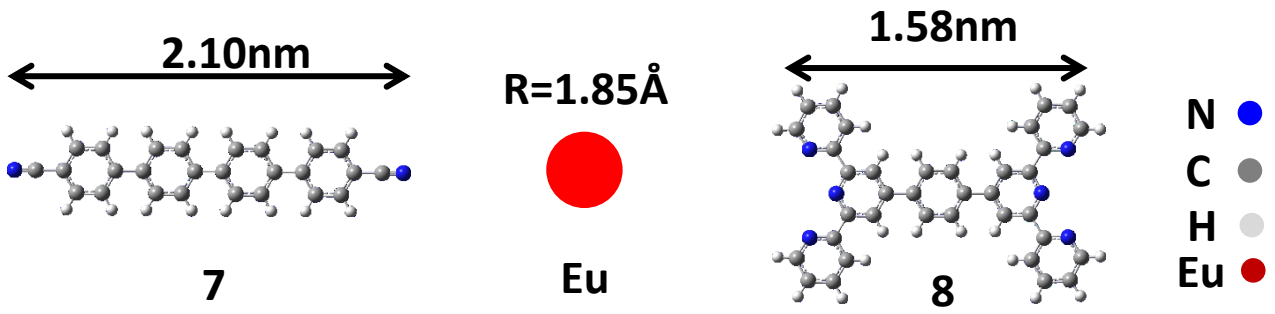
- 2D-MOFs with Pb-carbonitrile coordination

3. On surface Eu-coordinated MOFs

- 2D-MOFs with Eu-carbonitrile coordination
- 1D and 2D-MOFs with carbonitrile-Eu-terpyridyl coordination

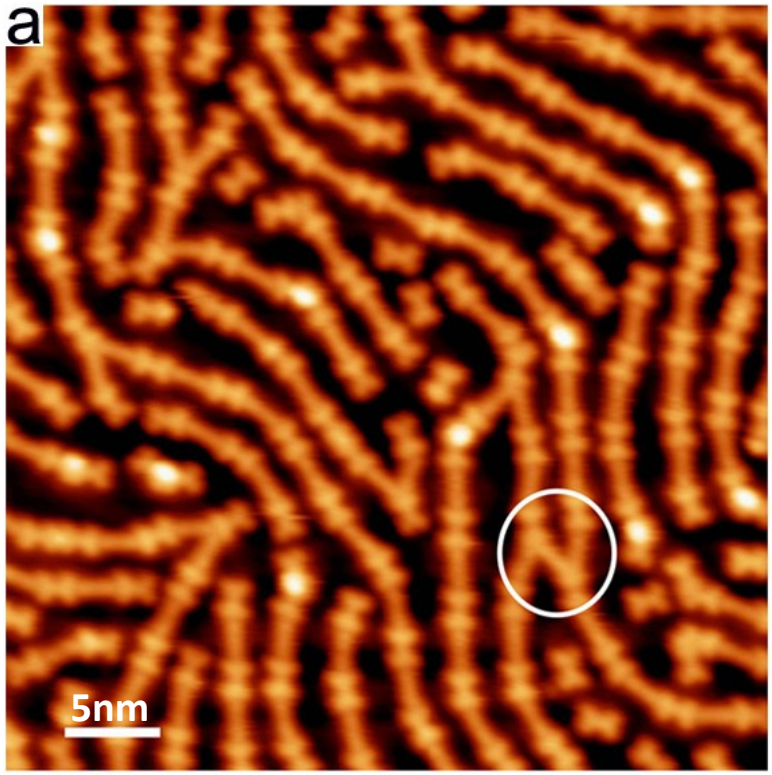
4. Conclusion

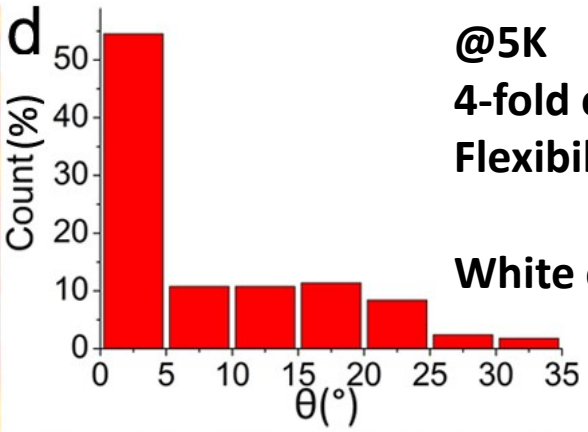
Molecules and metal

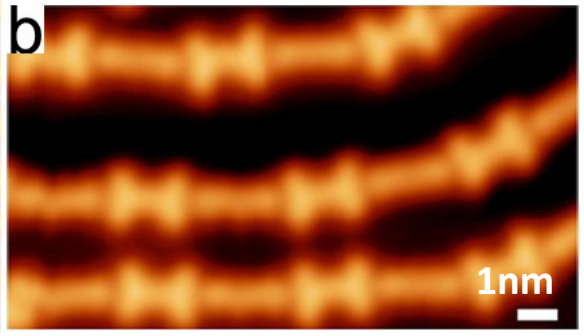


on Au(111)
@LN_2 (77K) or LHe (5K)

Results: [7]/[8]=0.7 Chain

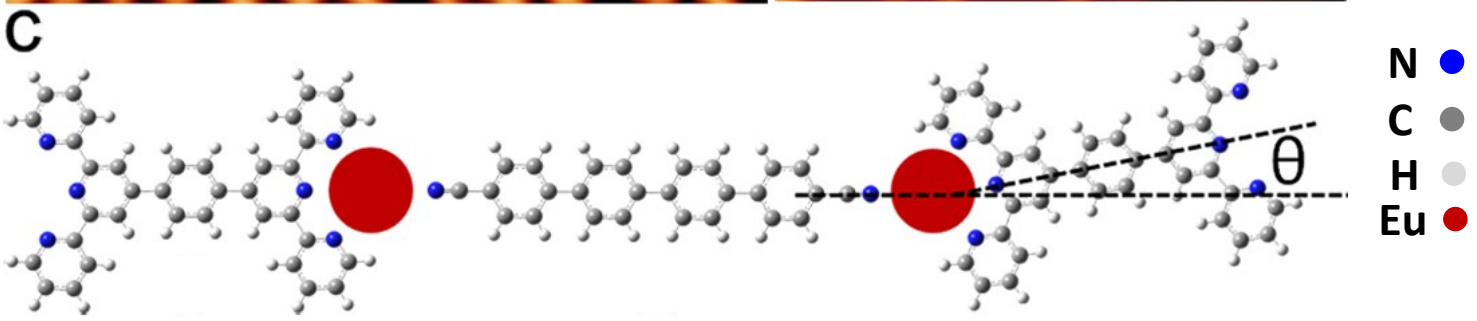






@5K
4-fold coordination motif
Flexibility of the chains

White circle: three-way junctions



N-Eu: 2.5Å

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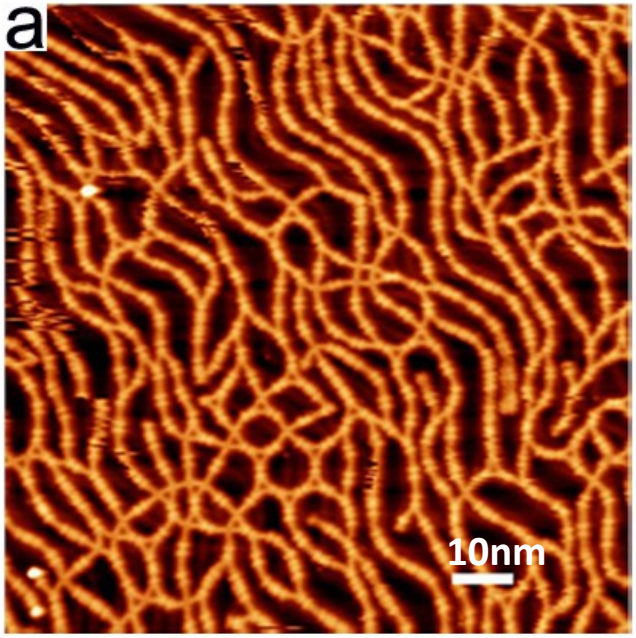
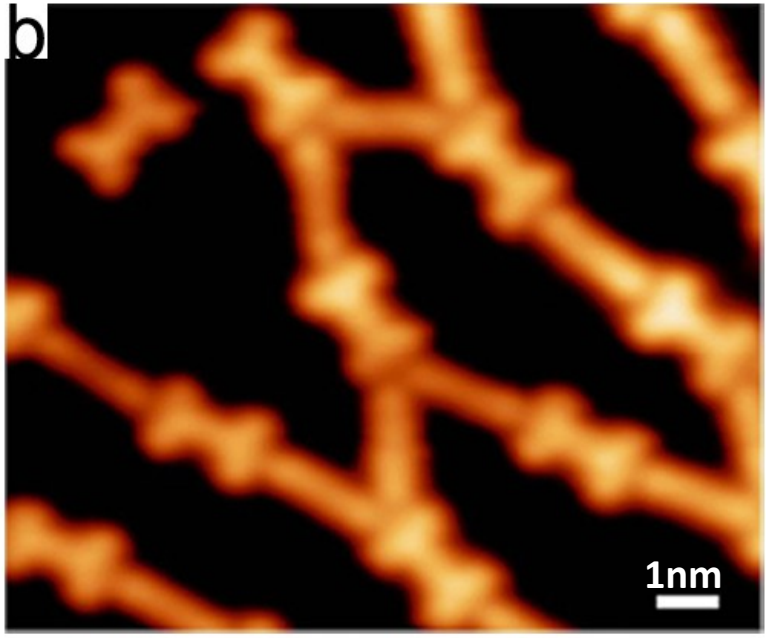
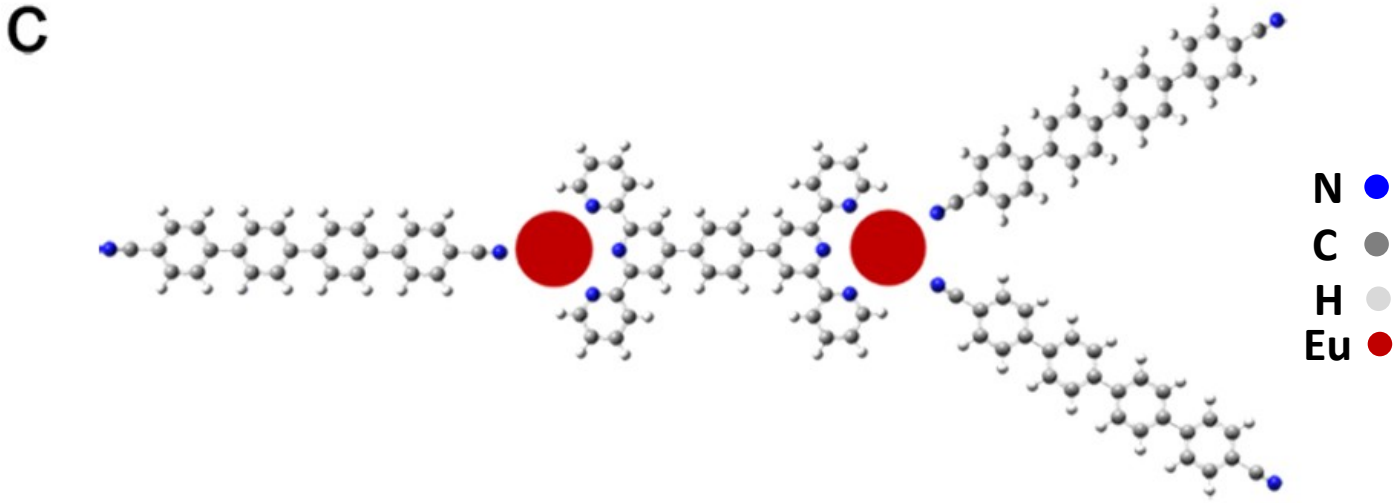
Results: [7]/[8]=0.9 Mixture phase





Chains become less while more junctions

Quasi-hexagonal structure



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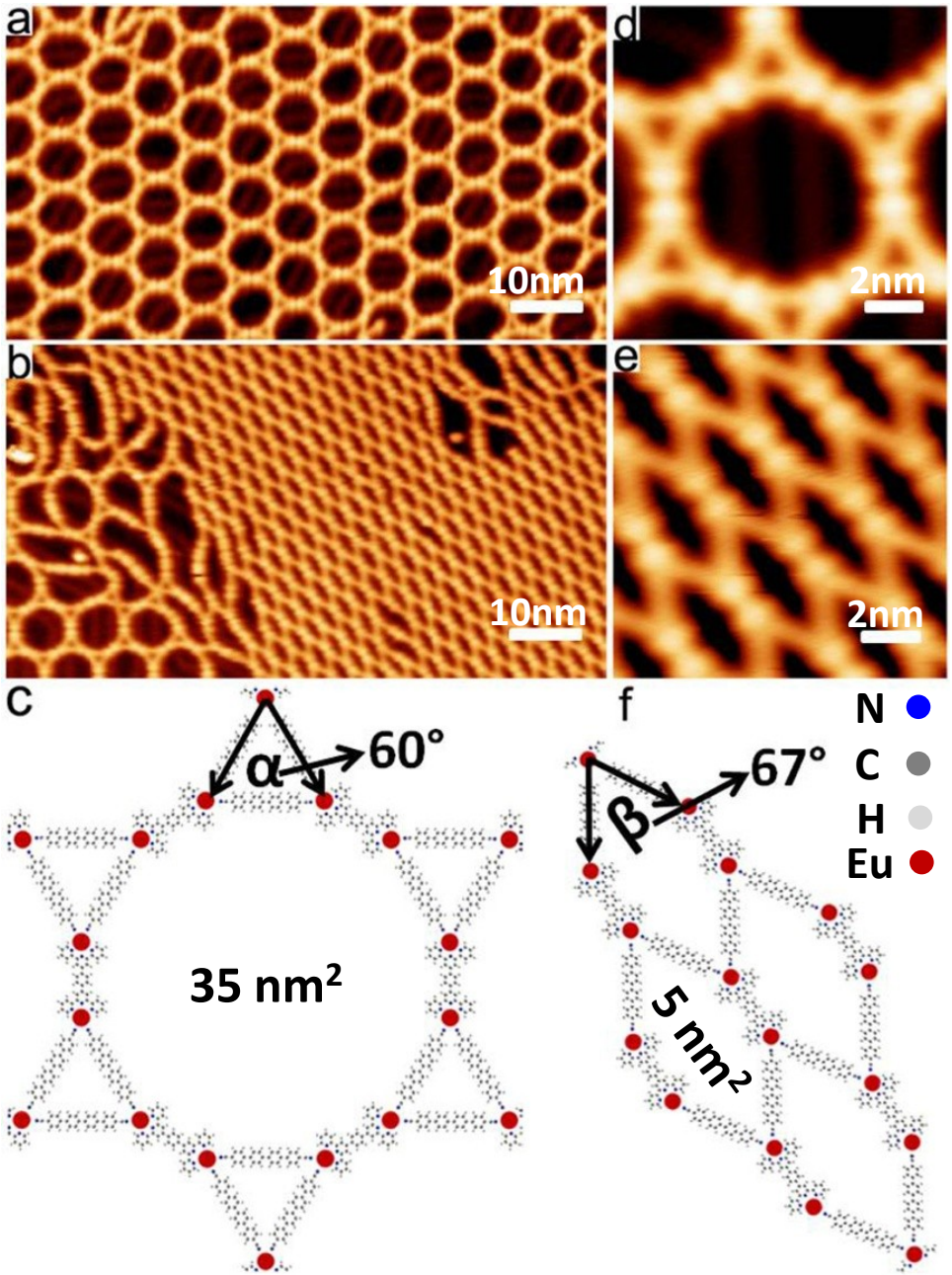
Results: [7]/[8]=1.8 2D networks



No chains

2D networks
Hexagon: dodecagon pores and triangles
surface density:
5 molecules **7** and 10 molecules **8** per 100 nm^2.

Fishing-net: elongated hexagonal pores
surface density:
8.7 linkers **7** and 17.4 linkers **8** per 100 nm^2,
is ~80% higher than the hexagonal phase

Largest 2D pores

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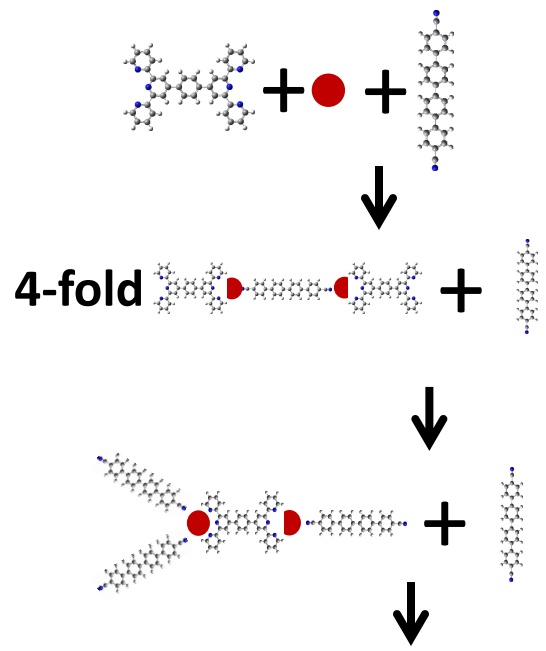
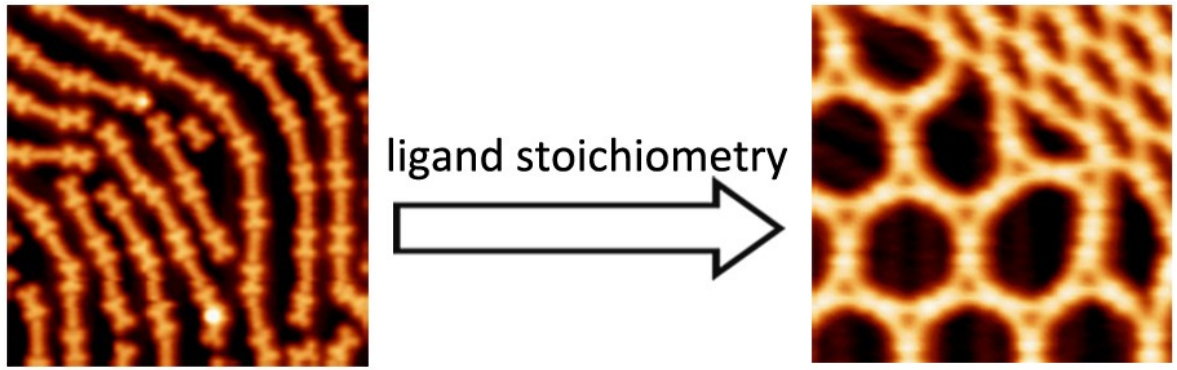
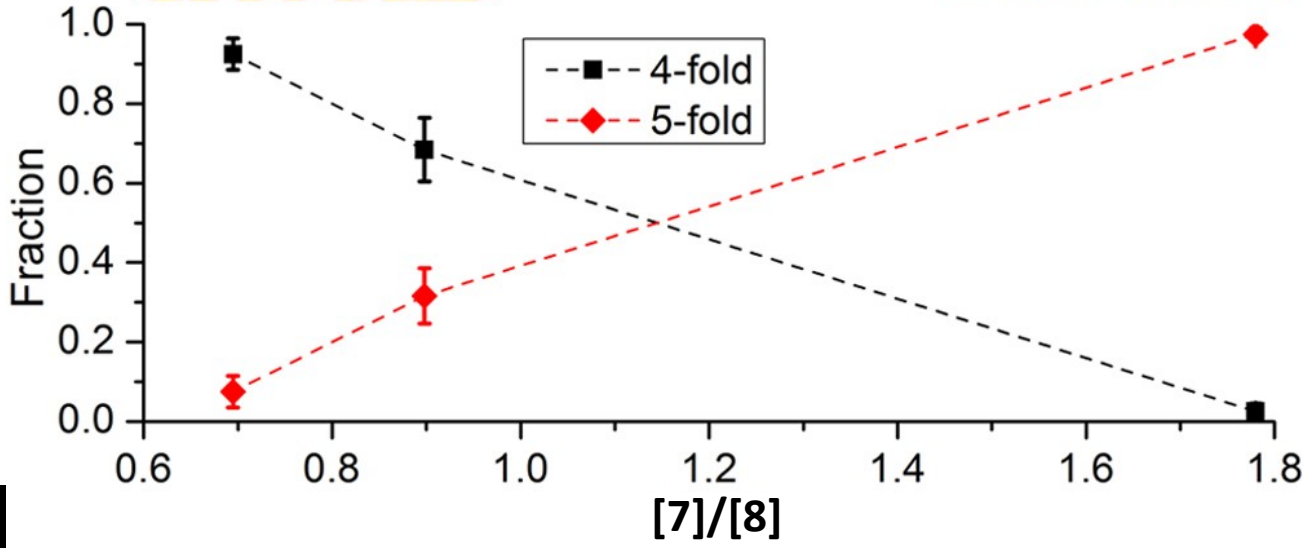
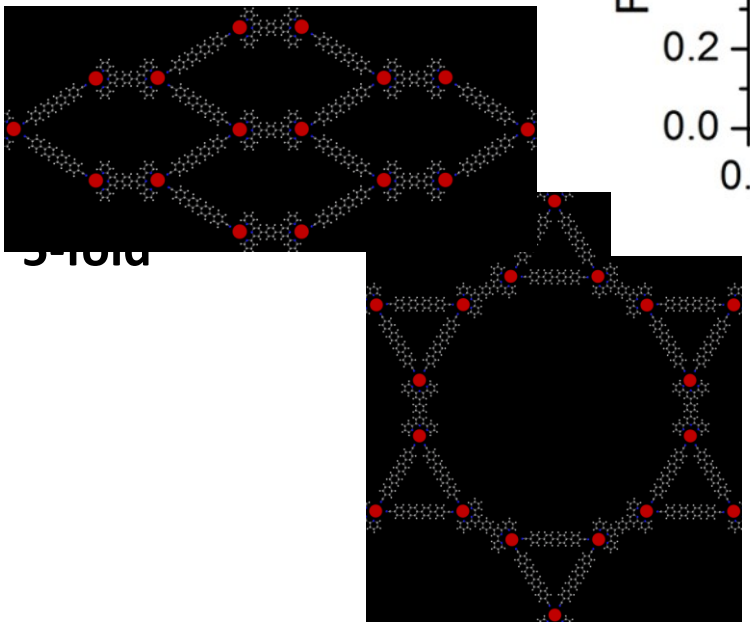
Ligand stoichiometry









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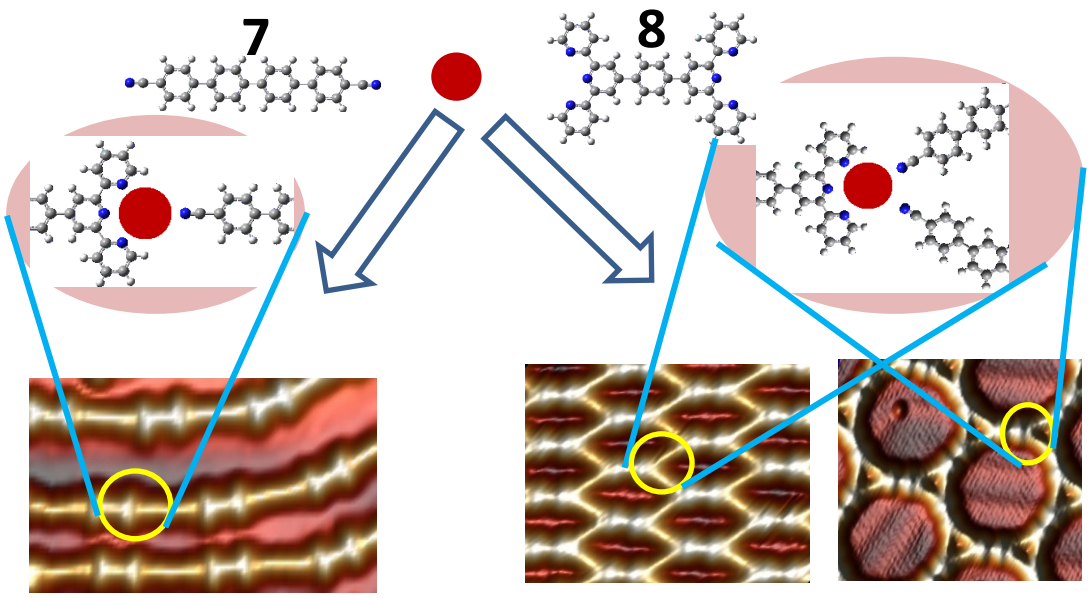
Conclusion

- Eu atoms can be ligated by terpyridyl and carbonitrile ligands;
- 4-fold or 5-fold coordination scheme;
- Chains & 2D networks, high selectivity;
- Versatile and flexible coordination motifs.



Outline

1. Introduction

2. On surface Pb-coordinated metal-organic frameworks (MOFs)

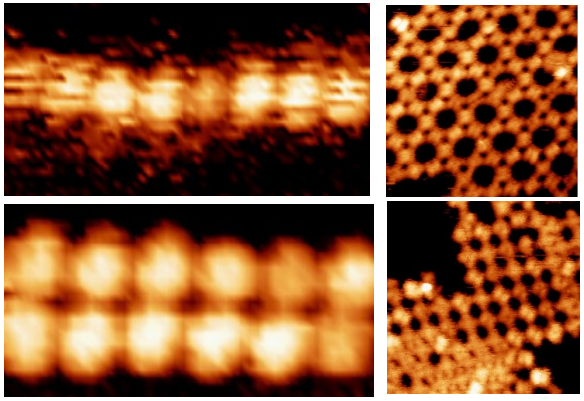
- 1D and 2D-MOFs with Pb-pyridyl coordination
- 2D-MOFs with Pb-carbonitrile coordination

3. On surface Eu-coordinated MOFs

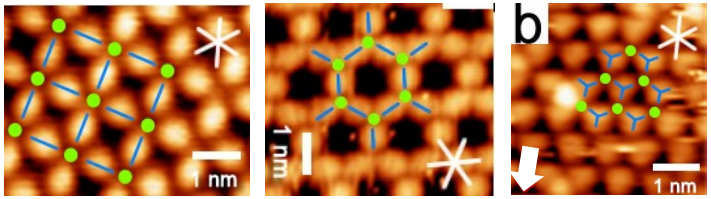
- 2D-MOFs with Eu-carbonitrile coordination
- 1D and 2D-MOFs with carbonitrile-Eu-terpyridyl coordination

4. Conclusion

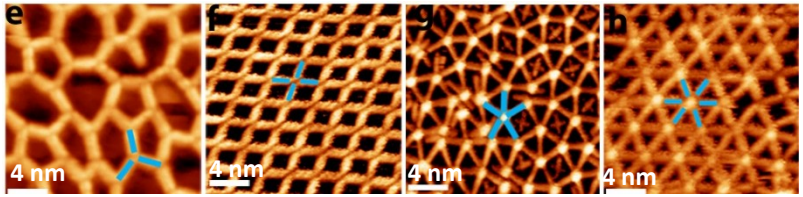
Summary



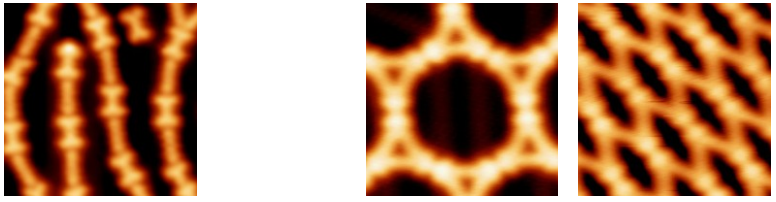
•1 Pb-py, Molecular configuration



•2. Pb-CN, Temperature & building blocks



•3 Eu-CN,[metal]/[ligand], quasicrystal MOFs



•4 CN-Eu-terpy, [ligand 7]/[ligand8], 1D & 2D MOFs

Publication

[7]. **G. Lyu** et al., STM and MD investigations of 2D-MOFs variation on a Au(111) surface, in prepare.

[6]. **G. Lyu** et al., Metal-organic networks comprising of Pb-carbonitrile coordination self-assembled on a Au(111) surface (manuscript)

[5]. R. Zhang, **G. Lyu**, D. Li, P. N. Liu, N. Lin, Template-controlled Sonogashira cross-coupling reactions on a Au(111) surface, **Chem. Commun.**, 53, 1731 (2017).

[4]. J. Urgel, D. Écija, **G. Lyu**, R. Zhang, C. A. Palma, W. Auwärter, N. Lin, J. V. Barth, Quasicrystallinity expressed in two-dimensional coordination networks, **Nat. Chem.**, 8, 657 (2016)

[3]. **G. Lyu**, Q. Zhang, J. Urgel, G. Kuang, W. Auwärter, D. Écija, J. V. Barth, Johannes, N Lin, Tunable surface-confined lanthanide-directed networks by exploiting coordinative flexibility through ligand stoichiometry, **Chem. Commun.**, 52, 1618 (2016)

[2]. R. Zhang, **G. Lyu**, C. Chen, T. Lin, P. N. Liu, N. Lin, Two-dimensional superlattices of Bi nanoclusters formed on a Au(111) surface using porous supramolecular templates, **ACS Nano**, 9, 8547 (2015)

[1]. **G. Lyu**, R. Zhang, X. Zhang, P. N. Liu, N. Lin, On-surface assembly of low-dimensional Pb-coordinated metal-organic structures**, J. Mater. Chem. C**, 3, 3252 (2015).

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THANK YOU!