MPhil Thesis Defense

Self-Assembly of Two-Dimensional Organic Networks Containing Heavy Metals (Pb, Bi) and Preparation of Spin-Polarized Scanning Tunneling Microscope

Presented by CHEN Cheng

12th Aug. 2014

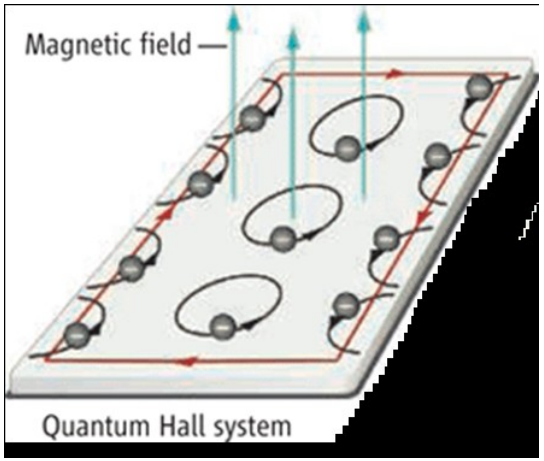
香港科技大學
THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY

Outline

1. Introduction
2. 2D organic networks functionalized by two heavy metals (Pb, Bi)
3. Spin-polarized scanning tunneling microscope (SP-STM)
4. Conclusion

Topological insulator (TI)

- Insulating bulk electronic states & Conducting boundary states



Quantum Hall effect

1st topological state

Extrinsic: Magnetic field

Graphene (QSH, theoretical)

1st topological insulator

Intrinsic: Spin-Orbit Coupling

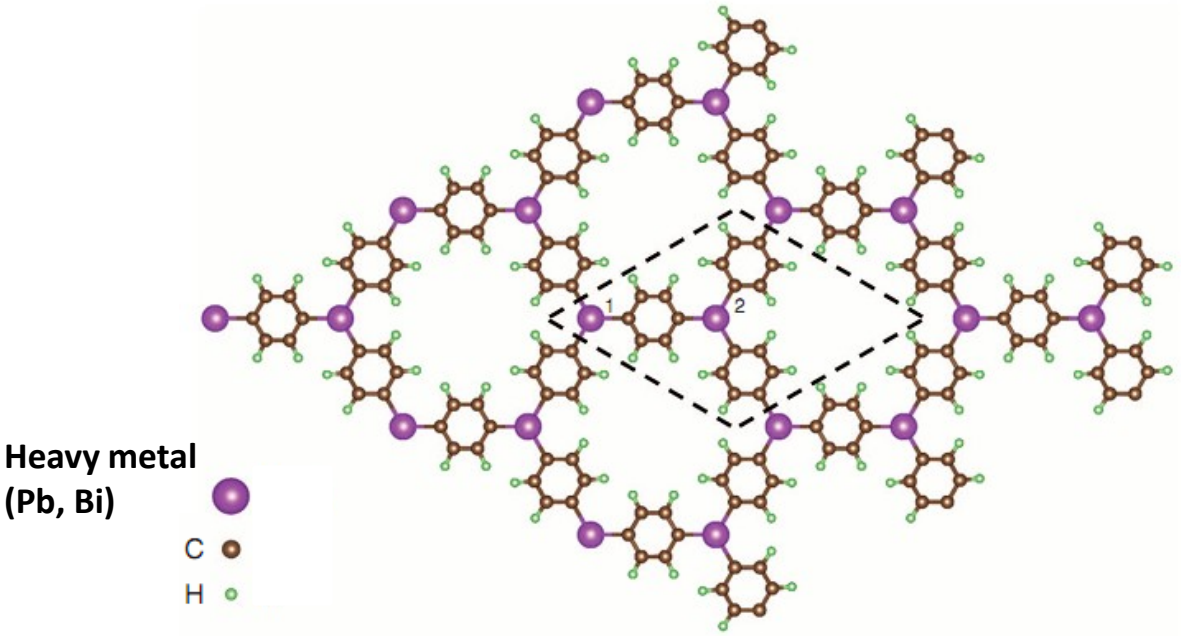
- Topological edge states: robust to disorder on the boundary

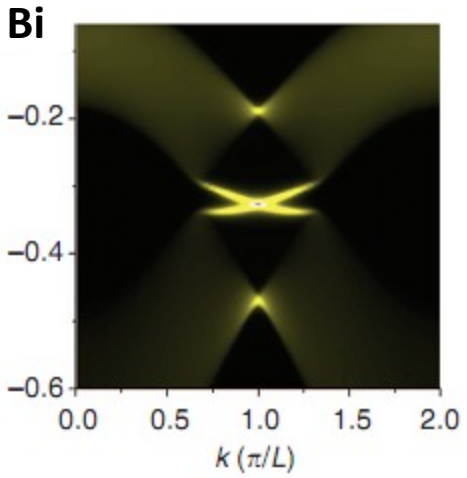
  → Application in spin transfer (Spintronics)

N. Nagaosa, *Science*, 2007, 318, 758.

Organic TI

- Inorgnic TI:
  - 2D: CdTe/HgTe/CdTe quantum well structure (2007)
  - 3D: $Bi_{1-x}Sb_x$ (2008), Bi_2Se_3 (2009), Bi_2Te_3 (250meV gap, RT)(2010)
- Organic TI:





Pb: 8.6 meV Bi: 43 meV

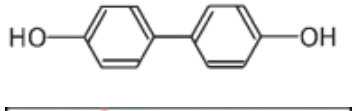
Z. Wang, *et.al.*, *Nat. Comms.*, 2013, 2451.

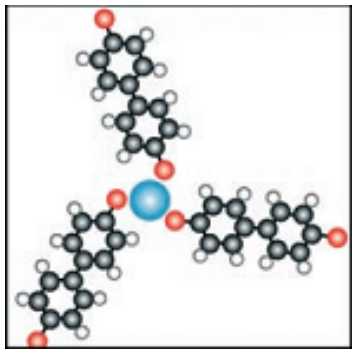
Motivation

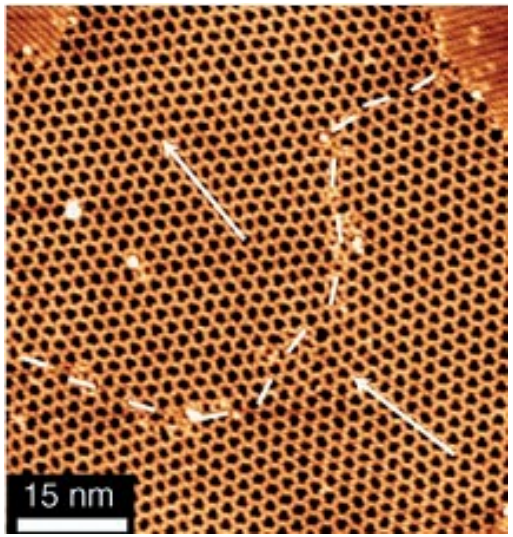
- Self-assembly:
  - Components spontaneously form ordered structures, like DNA
  - Non-covalent intermolecular interaction:

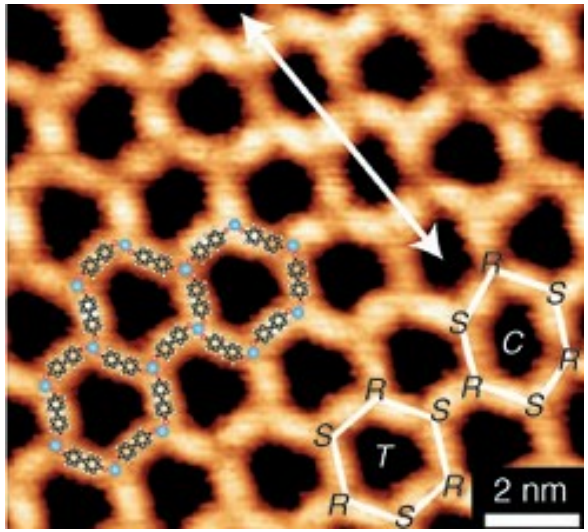
    Coordination bonds for metal-organic network

    No heavy metals, but only transition metals (like Cu, Fe) are involved in self-assembly on surface so far.







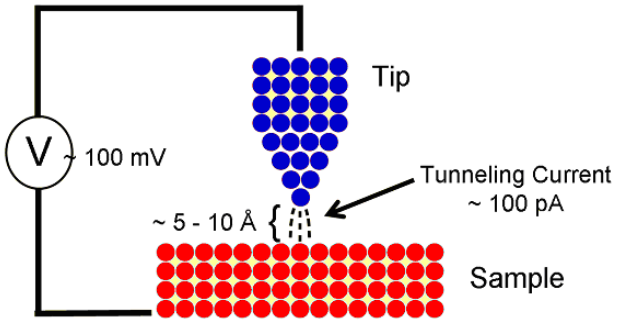


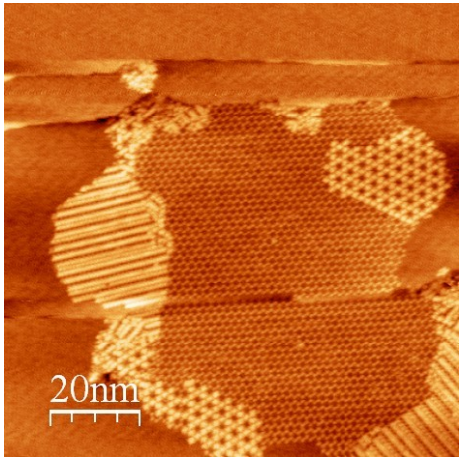
Fe-biphenolate hexagonal network

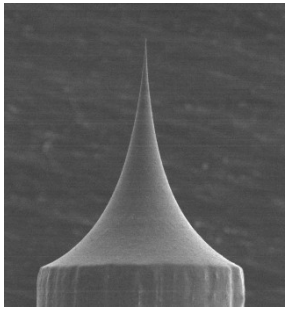
S. Stepanow, *et.al.*, *Angew. Chem.*, 2007, 119, 724 –727.

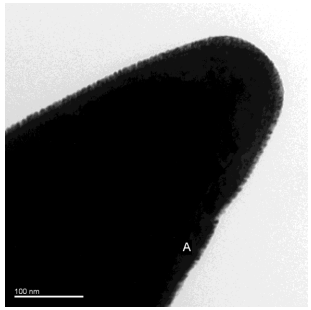
Experimental techniques

- Scanning tunneling microscope (STM)



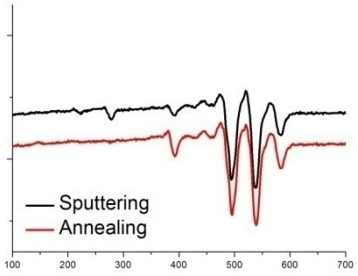


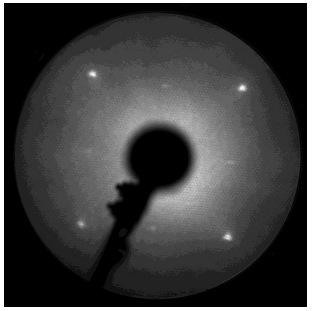




- Scanning electron microscope (SEM)
  Transmission electron microscope (TEM)

- Auger electron spectroscopy (AES)
  Low energy electron diffraction (LEED)

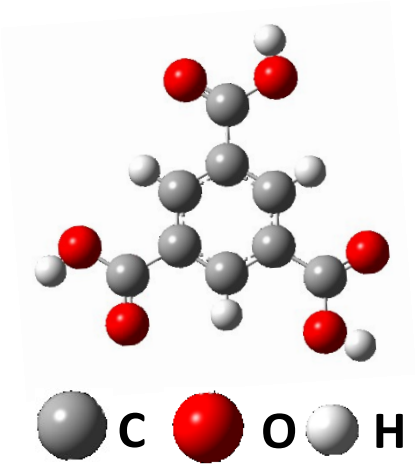




http://www.personal.psu.edu/ewh10/ResearchBackground.htm

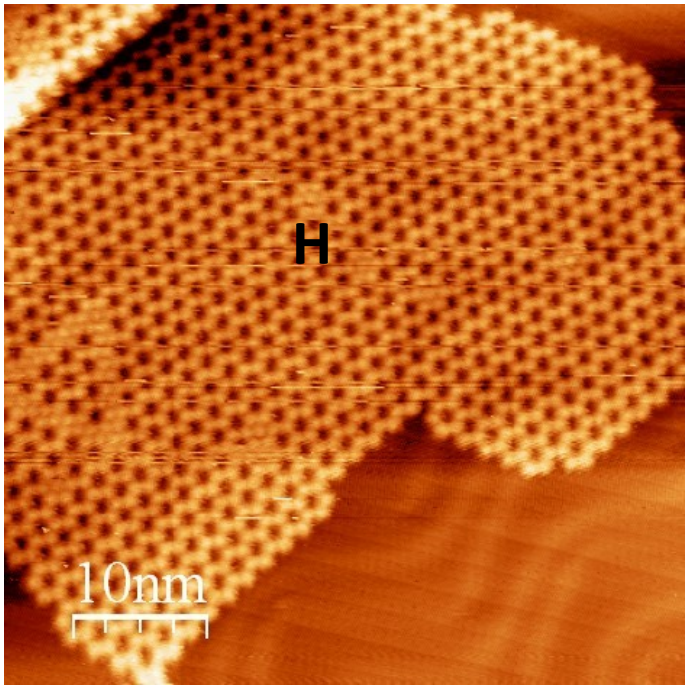
Outline

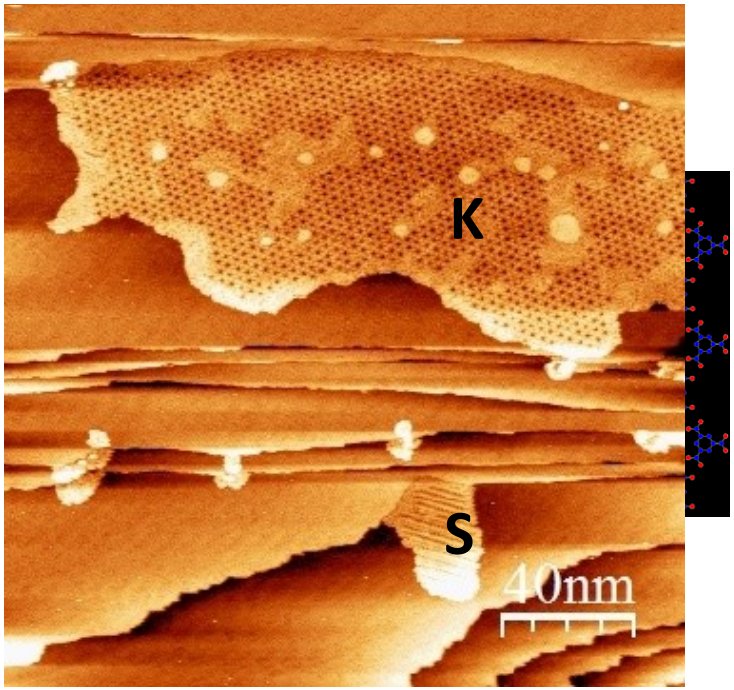
1. Introduction
2. 2D organic networks functionalized by two heavy metals
   a) TMA + Pb: metal-organic network
   b) TMA + Bi: Bi cluster superlattices
3. Spin-polarized scanning tunneling microscope (SP-STM)
4. Conclusion



TMA + Pb: metal-organic network

- Two structures: kagome and stripe structure
  - TMA + Pb / Au(111), annealing at 170°C for 10 mins
  - TMA honeycomb networks disappear after annealing at 170°C for 1 h.

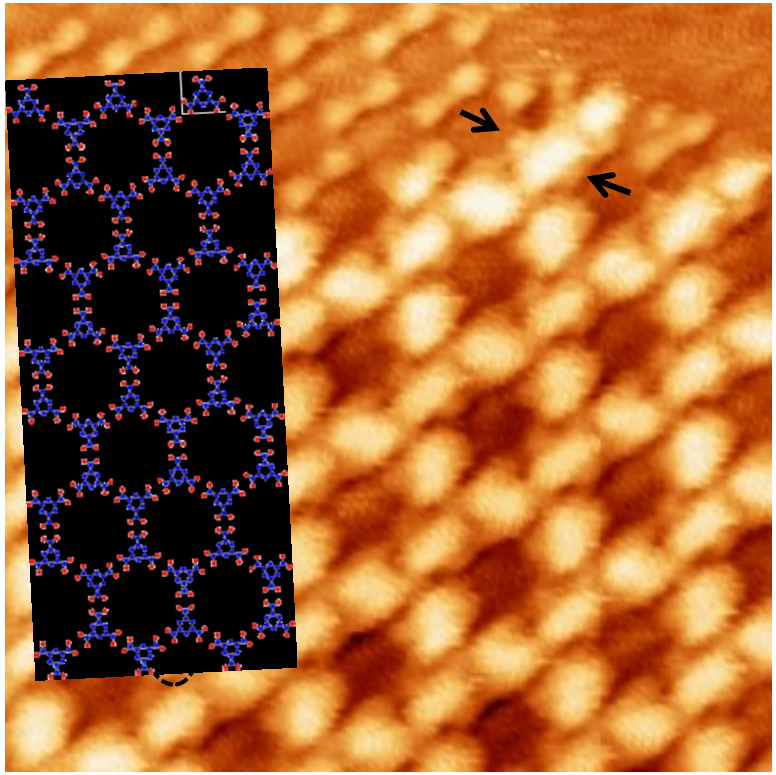


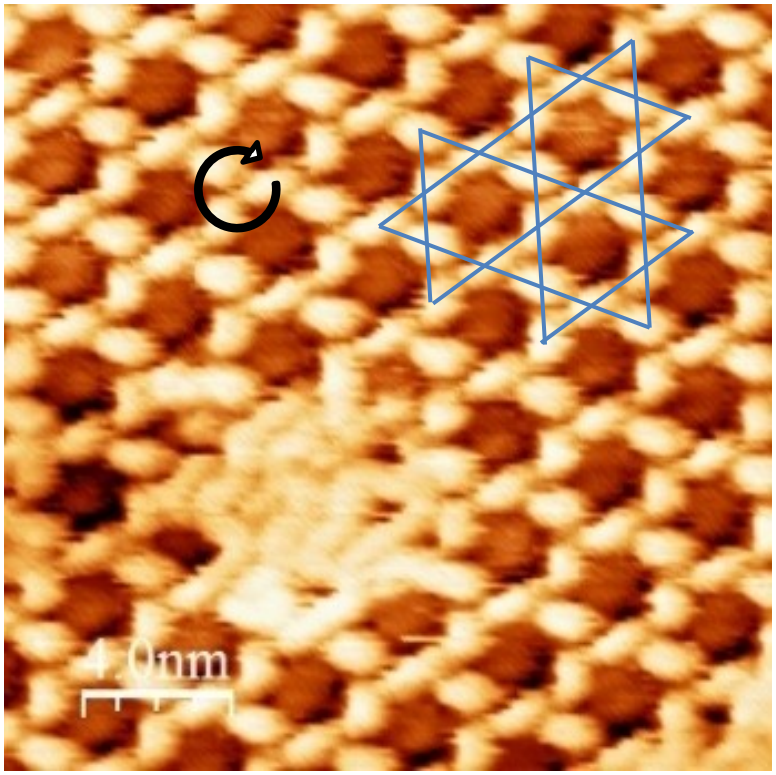


Pure TMA honeycomb network

TMA + Pb: metal-organic network

- Kagome structure
  - Based on TMA honeycomb structure bright protrusion → Pb atoms
  - Chiral

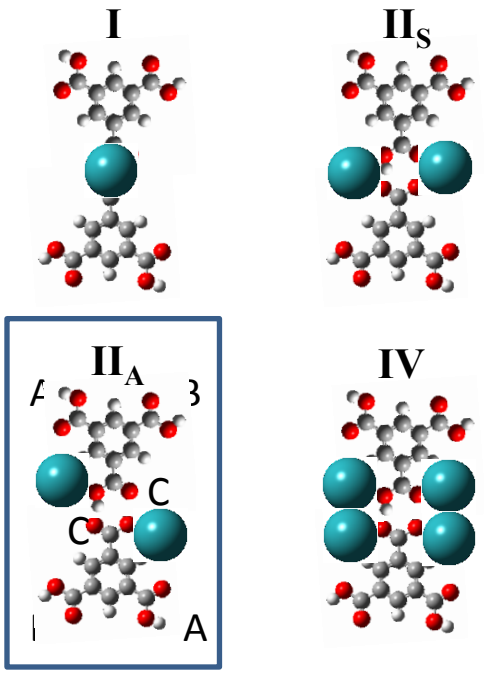


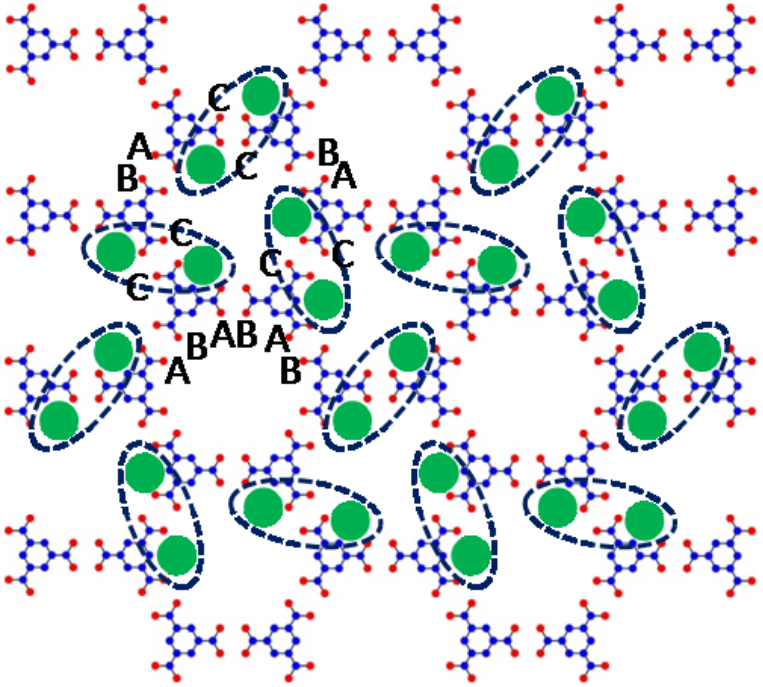


TMA + Pb: metal-organic network

- Kagome structure
  - Bright protrusion → 2 asymmetrically attached Pb atoms
  - C-C, A-B connection:

    Pb atoms share e^- with O and H, modify the dipole of the carboxyl groups
    → strengthen the dimeric hydrogen bonds



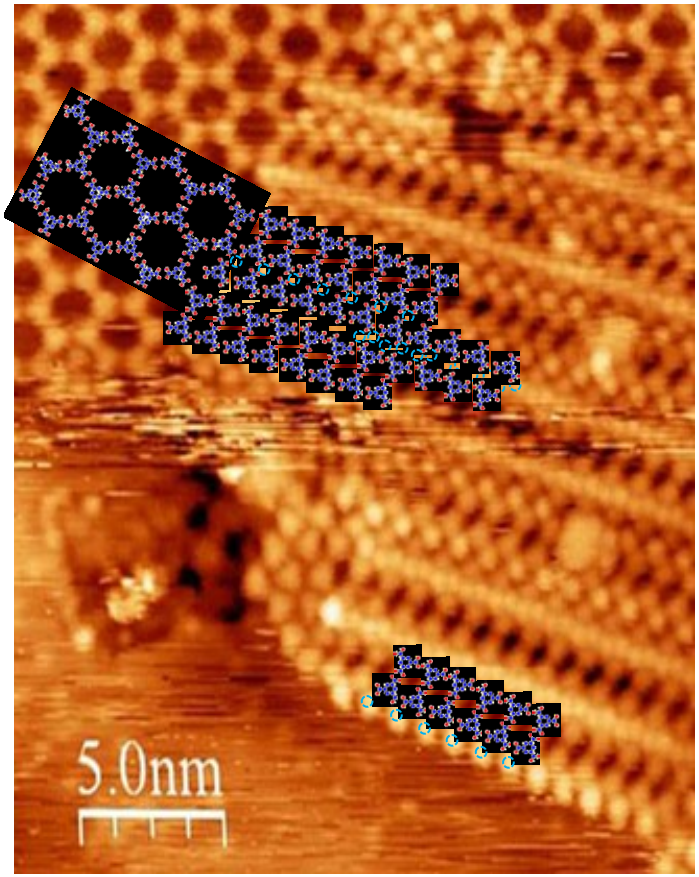


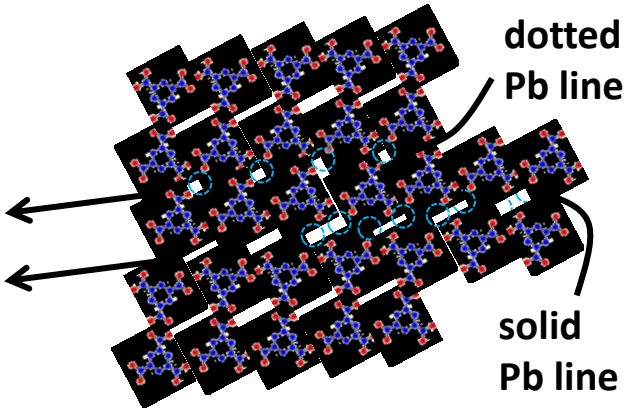
TMA + Pb: metal-organic network

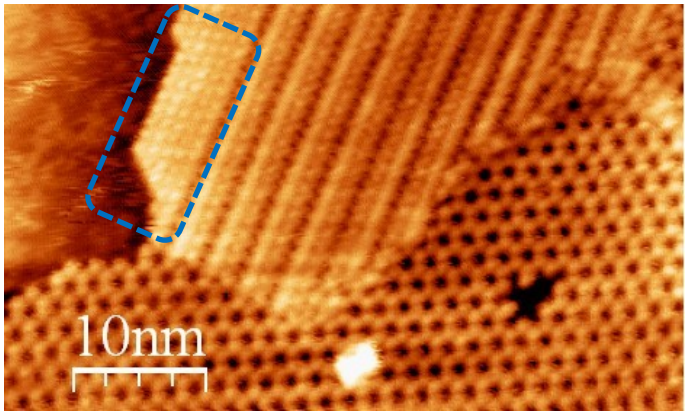
- Stripe structure

Brighter dots → Pb atoms

dotted and “solid” Pb atom line





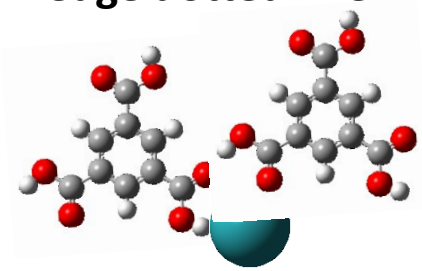


2D dotted-line phase

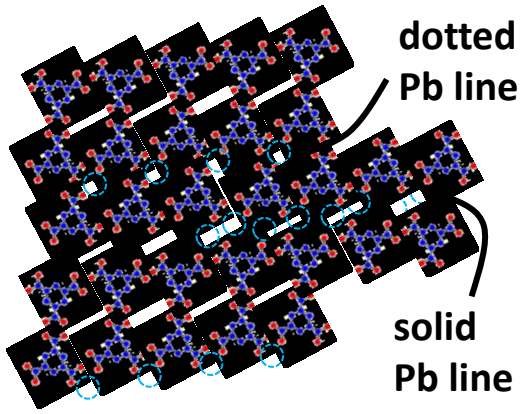
TMA + Pb: metal-organic network

- Stripe structure

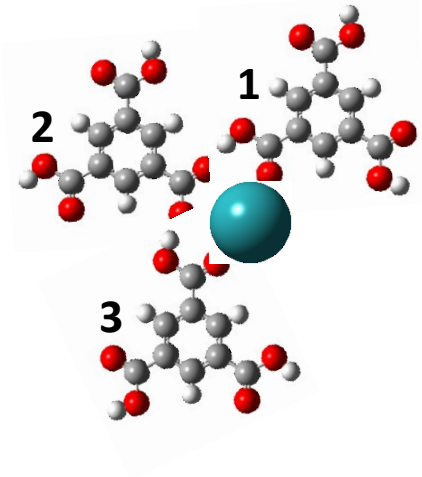
edge dotted line



1 single H-bond
1 Pb-O bond
1 Pb-H bond



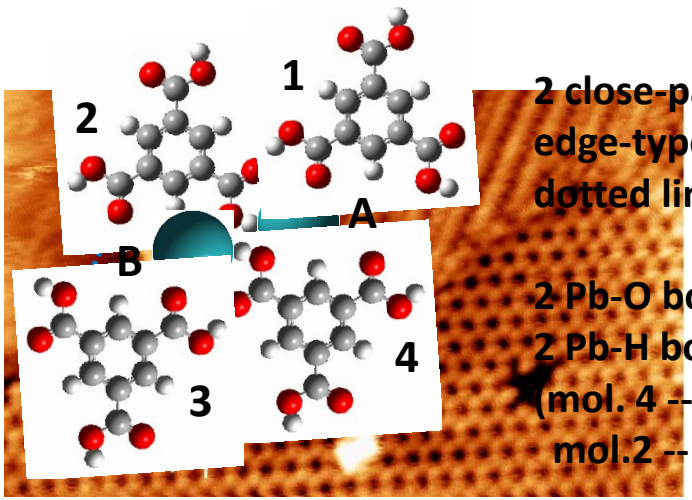
inner dotted line



2 single H-bond
2 Pb-O bond
1 Pb-H bond

Mol. 1 and 3
are symmetric

solid line



2 close-packed
edge-type
dotted line

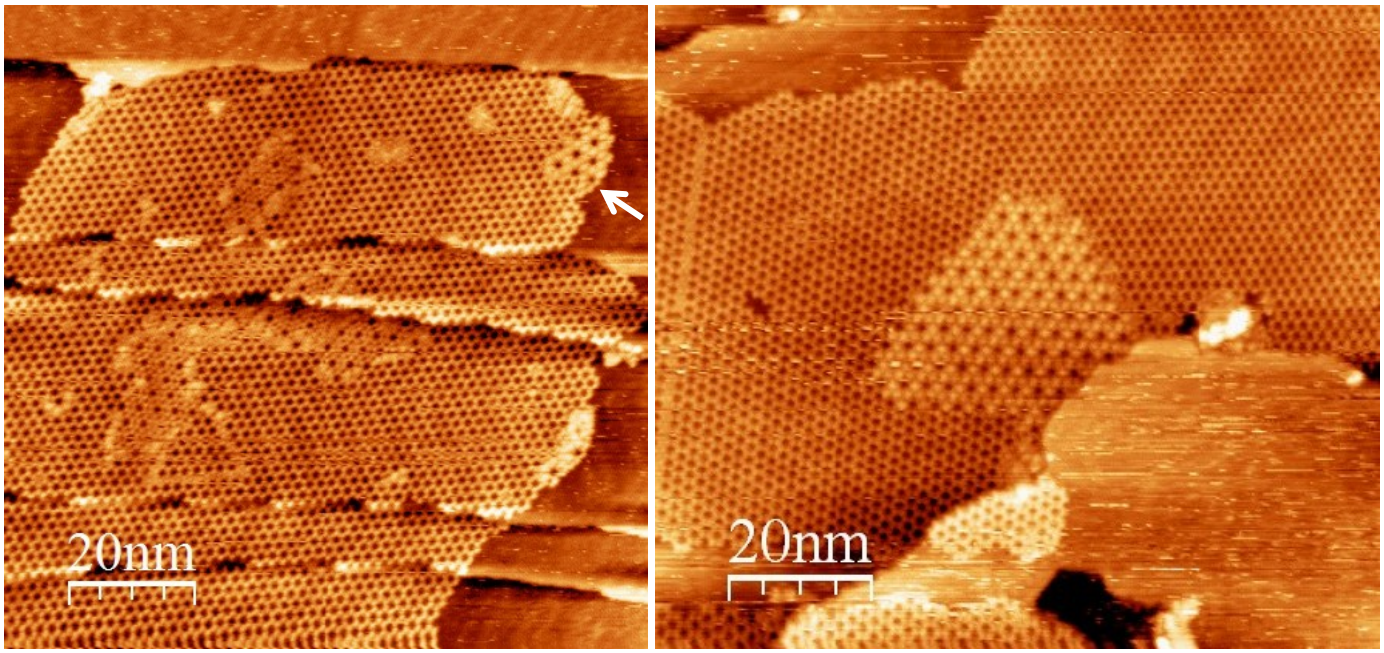
2D
dotted-line
phase

2 Pb-O bond
2 Pb-H bond
(mol. 4 -- Pb atom A
mol.2 -- Pb atom B)

TMA + Pb: metal-organic network

- Growth mechanism: larger kagome structure
  - **Annealing temperature:**

    120 ˚C → 170 ˚C, larger size kagome structure → 220 ˚C, desorbs all the molecules
  - Balance between the assembly rate and the desorption rate



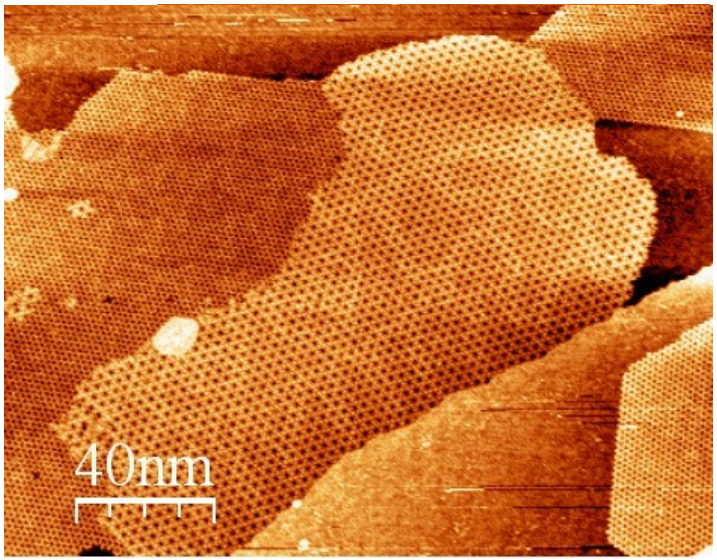
TMA + Pb: metal-organic network

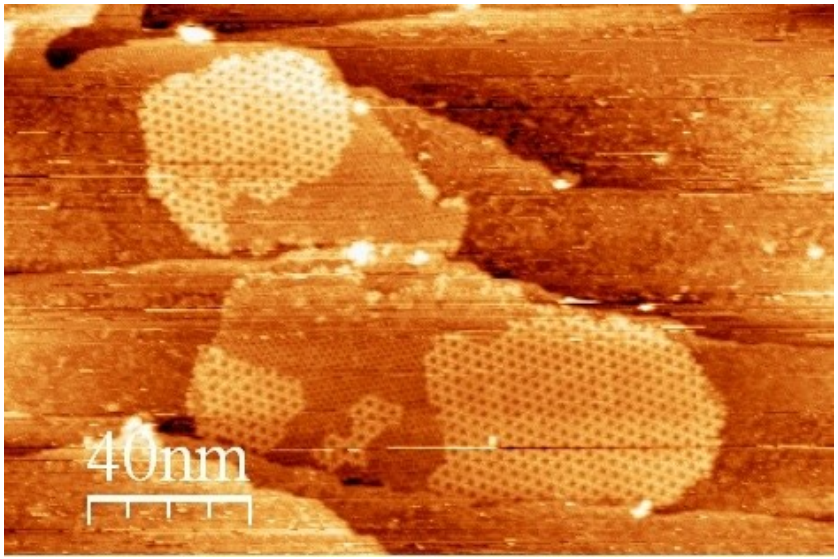
- Growth mechanism: larger kagome structure
  - **Dosage:**

    Pb atoms: 0.02 ML → 0.06 ML, larger size kagome structure → 0.1 ML, irregular clusters of complex of TMA mol. and Pb atoms

    TMA mol.: 0.3 ML → 0.5 ML, huge size kagome structure

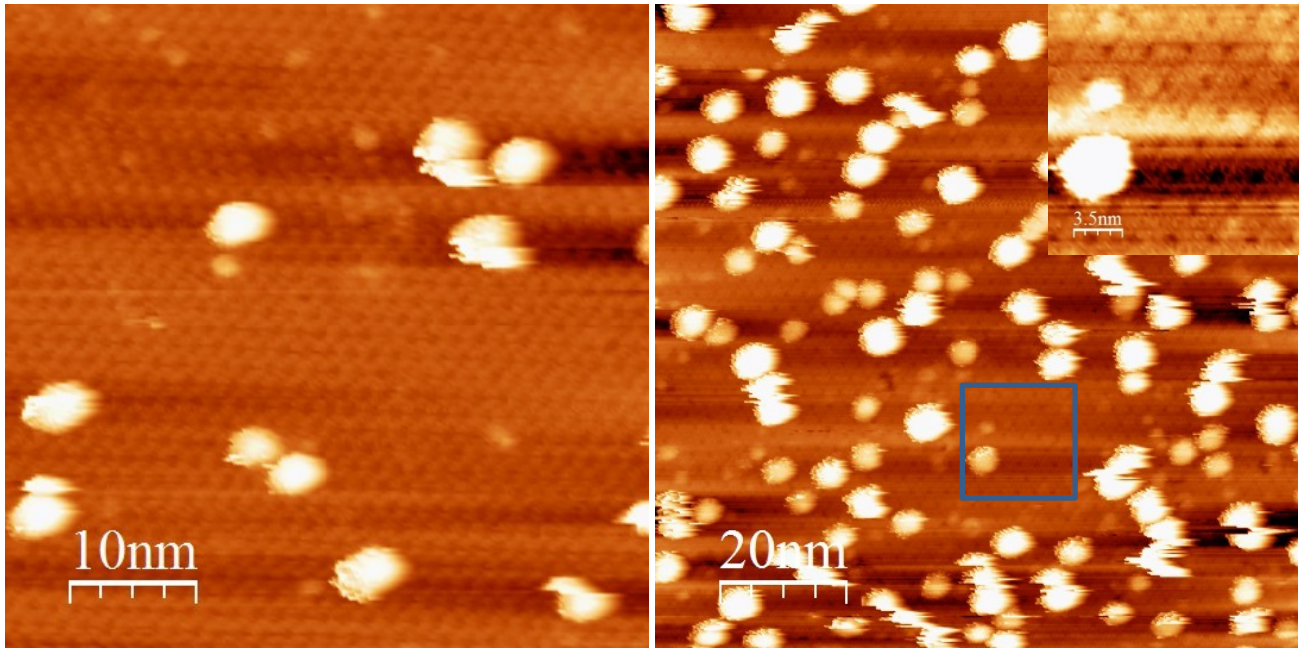
  → **TMA honeycomb networks support the growth of kagome structures**





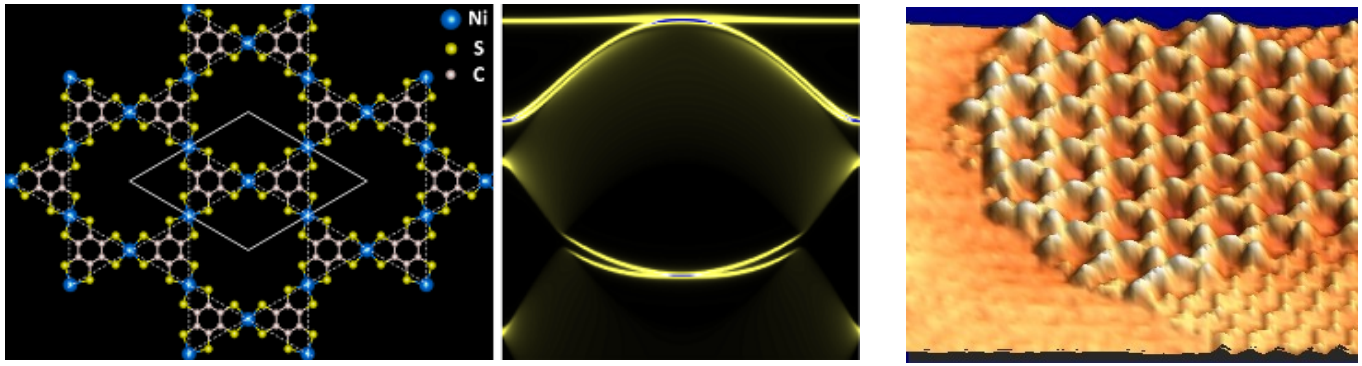
TMA + Pb: metal-organic network

- TMA + Pb on HOPG surface:
  - Pb cluster ~ 1.2 nm high: weak interaction between Pb atom and HOPG
  - **The strong interaction between Au(111) surface and Pb atoms plays a very important role in the formation and stabilization of the kagome and stripe structure.**



TMA + Pb: metal-organic network

- Conculsion:
  - Kagome and stripe structures based on Pb atoms and TMA molecules on Au(111) surface
  - Pb atoms form Pb-functionalized hydrogen bond networks, instead of coordination networks
  - **1st** work of 2D metal-organic networks self-assembled by Pb on surface
  - Topological edge states might exist on the edge of the kagome structure



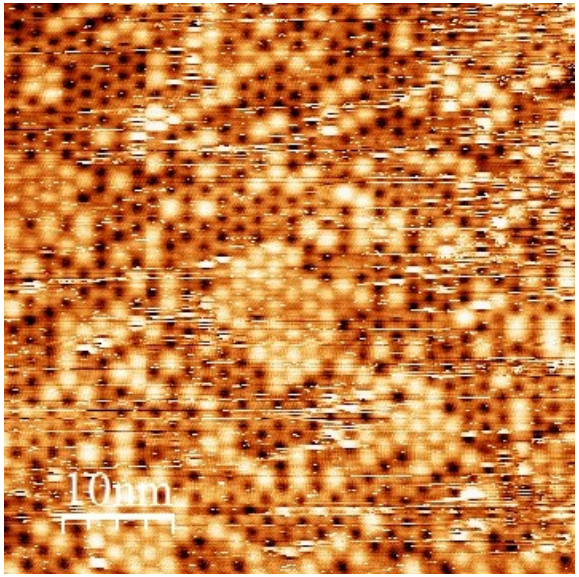
Z. Wang, *et.al.*, *Nano Lett.*, 2013, 13, 2842-2845.

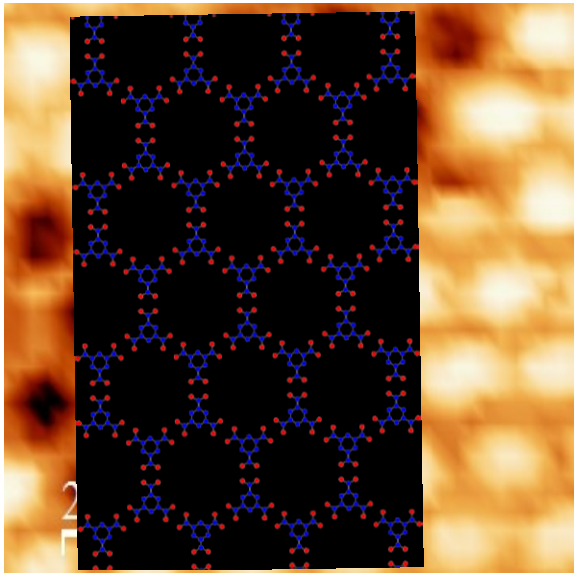
Outline

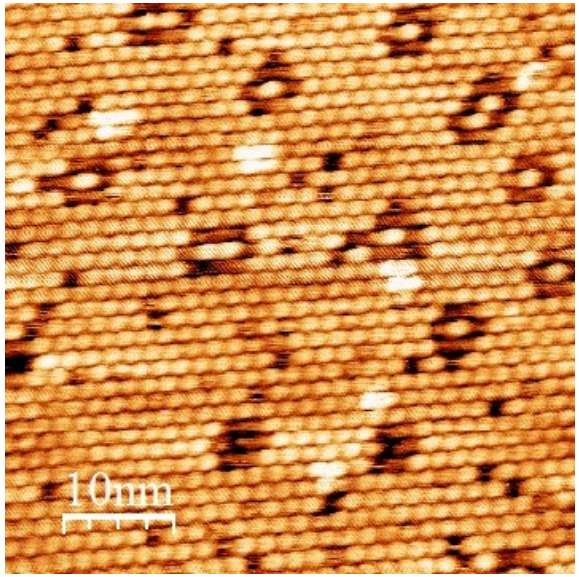
1. Introduction
2. 2D organic networks functionalized by two heavy metals
   a) TMA + Pb: metal-organic network
   b) TMA + Bi: Bi cluster superlattices
3. Spin-polarized scanning tunneling microscope (SP-STM)
4. Conclusion

TMA + Bi: Bi cluster superlattices

- Bi clusters sit in the pores of the honeycomb network following the same periodicity as TMA honeycomb network.
- Intact honeycomb network, as template
- Perfect Bi triangular lattice (2 mins Bi)







TMA + Bi: Bi cluster superlattices

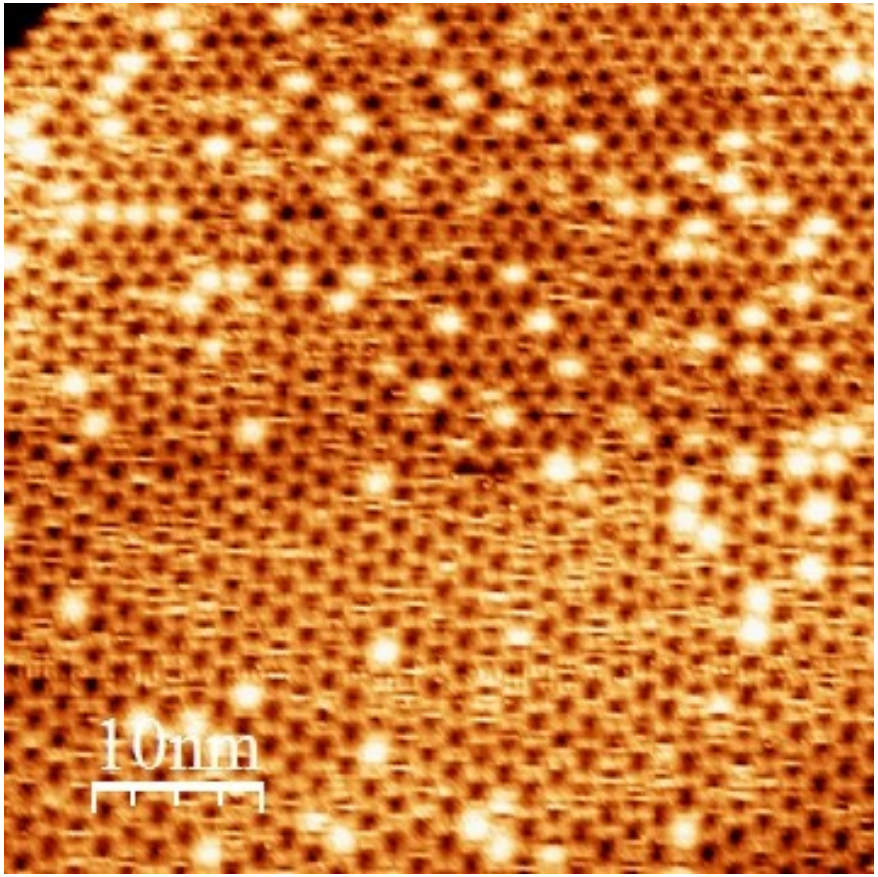
- Bi atoms are desorbed from the surface after annealing at 120 ˚C

→ No strong chemical bond between Bi atoms and TMA mol.

- Assembly process:

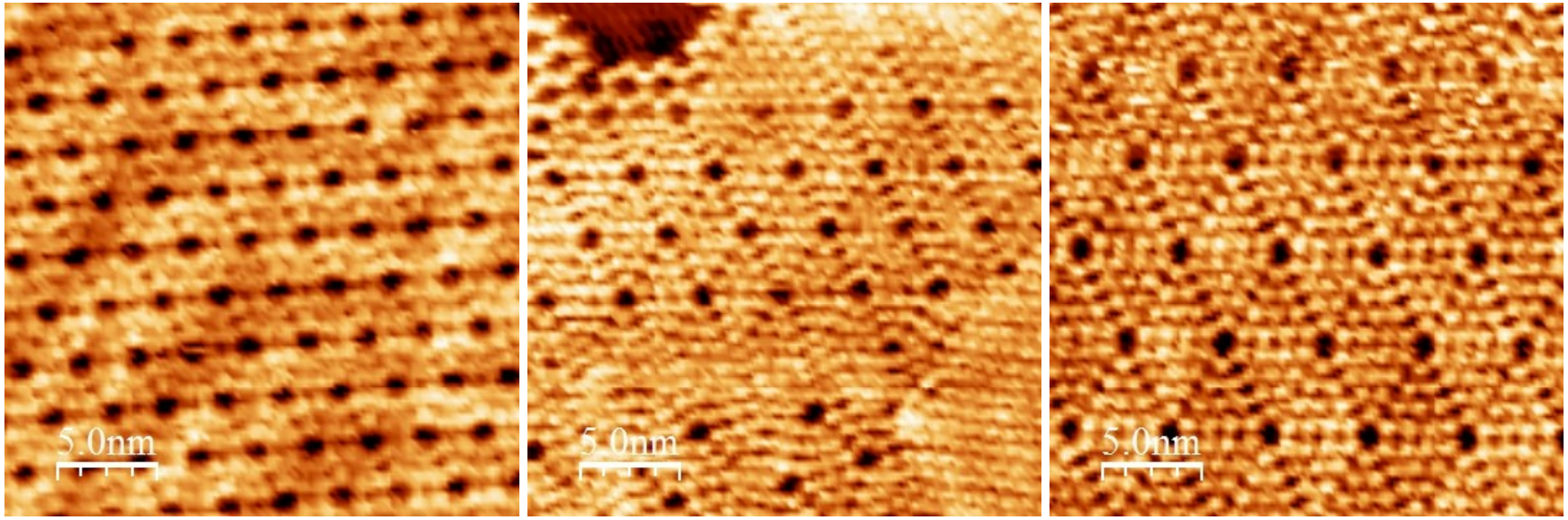
  Bi atoms move freely on TMA honeycomb network,

  Bi atoms are localized in the potential well of the pores of TMA honeycomb network



TMA + Bi: Bi cluster superlattices

- On high density TMA networks
  - Varying Molecules coverage → Different high density TMA phases
  - Different structures are found in one sample even after annealing at 160 ˚C for 10mins



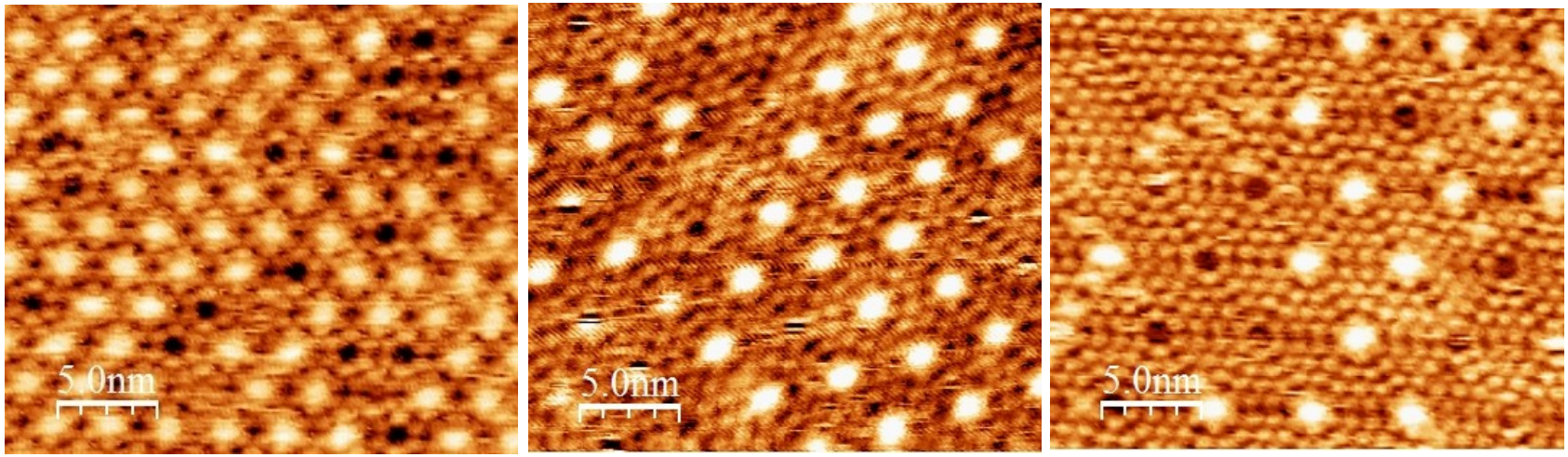
H_{TMA-2}: 1.65nm

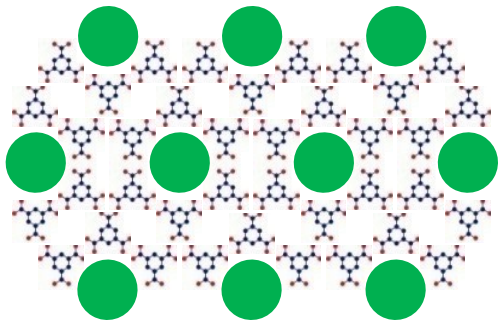
H_{TMA-3}: 2.55nm

H_{TMA-4}: 3.55nm

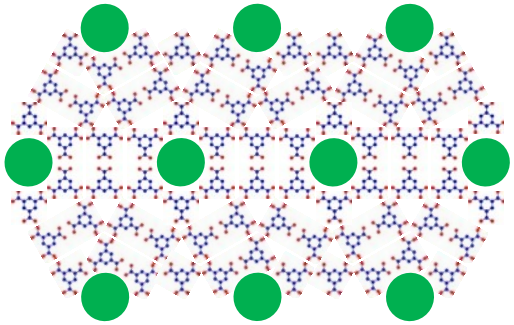
TMA + Bi: Bi cluster superlattices

- On high density TMA networks

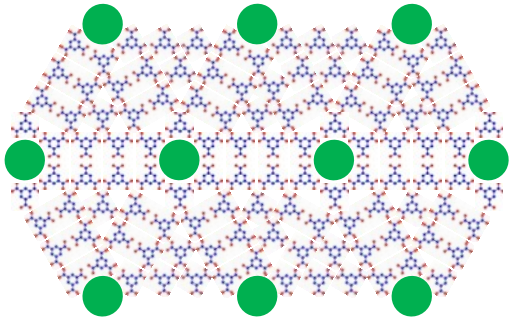




$Bi\text{-}H_{TMA\text{-}2}$



$Bi\text{-}H_{TMA\text{-}3}$



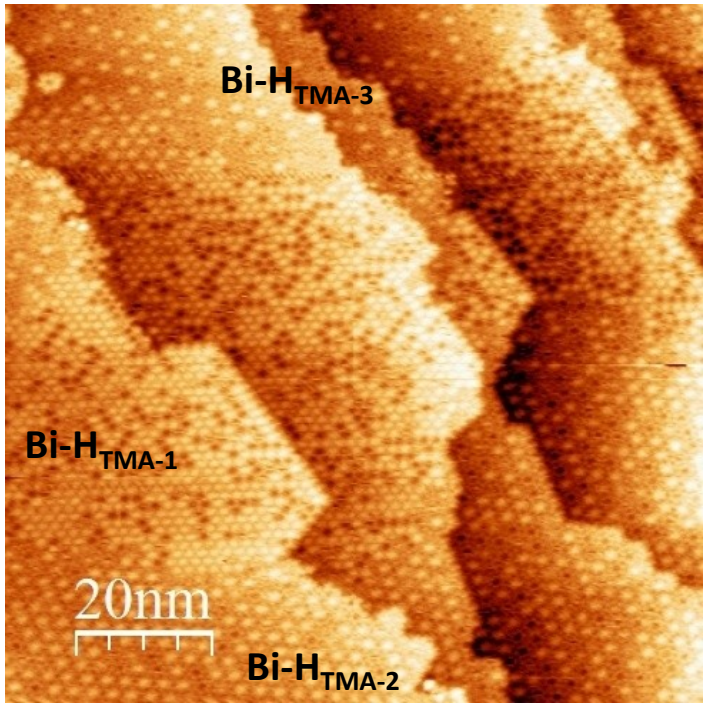
$Bi\text{-}H_{TMA\text{-}4}$

TMA + Bi: Bi cluster superlattices

- On high density TMA networks
  - Lattice constant of Bi cluster superlattices follows the lattice of the TMA porous structures.
  - Local variation of Bi clusters density

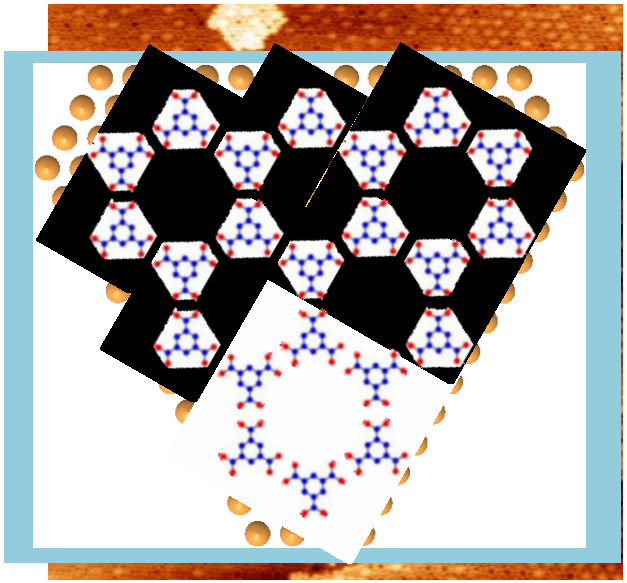
  → **Bi atoms can move from one TMA phase to another TMA phase**

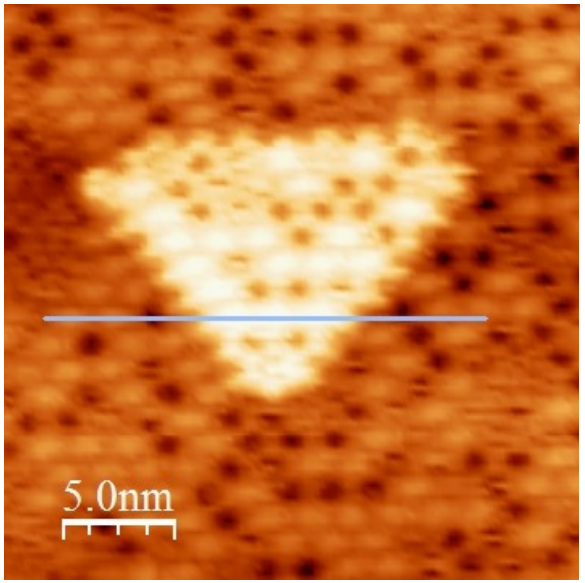
Structure	Lattice constant (nm)	Bi cluster density (1/100nm^2)
Bi-H_{TMA-1}	1.65	42.4
Bi-H_{TMA-2}	2.55	17.8
Bi-H_{TMA-3}	3.55	9.16
Bi-H_{TMA-4}	4.38	6.02
Bi-H_{TMA-5}	5.30	4.11

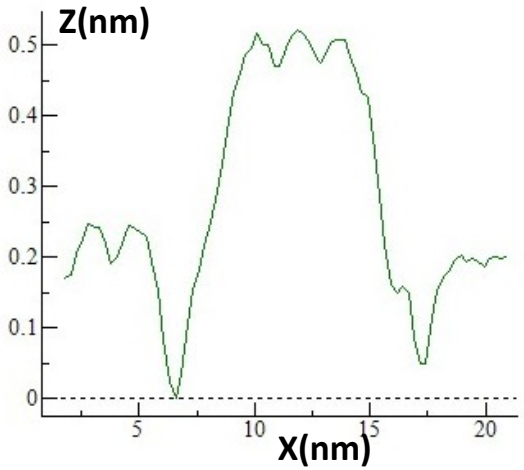


TMA + Bi: Bi cluster superlattices

- Bi islands
  - Increasing Bi dosage → triangular Bi islands (monoatomic high) → in (111) packing
  - On top of the Bi islands, TMA molecules form the same type of network as the neighboring network
  - Bi atoms could occupy the pores of the TMA network on the island





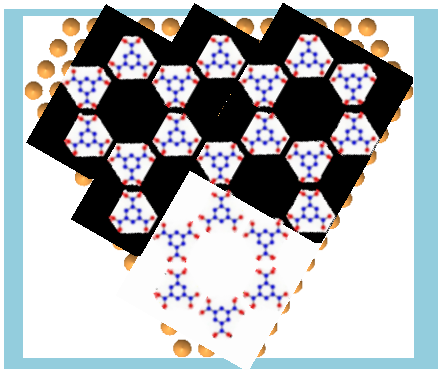


TMA + Bi: Bi cluster superlattices

- Bi islands

Growth mechanism:

- When the pores of TMA network are almost fully occupied, excess Bi atoms start aggregating in 2D islands.
- Since Au(111) surface is energetically favored adsorption site for Bi atoms, and the interaction between TMA molecules and Bi atoms is weak
- Bi atoms penetrate TMA network through the pores and aggregate into island on the Au(111) surface.



TMA + Bi: Bi cluster superlattices

- Determine no. of Bi atoms in a pore
  - Successively depositing equal amount of Bi atoms
  - The average area of Bi islands in unit area in each stage

  → the amount of Bi atoms in islands in unit area, $\boldsymbol{D_i(t)}$
  - The average amount of Bi clusters in unit area in each stage $\boldsymbol{D_c(t)}$

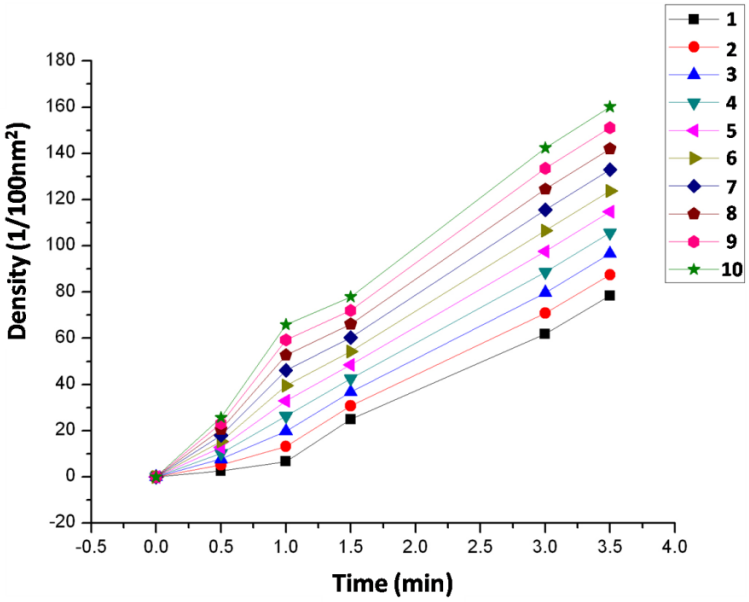
    Assuming the number of Bi atoms in each pore is a constant $\boldsymbol{n}$

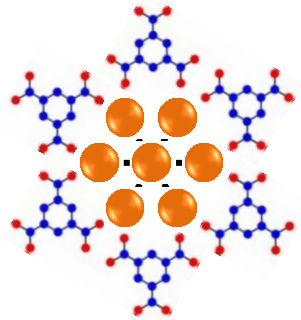
  → the amount of Bi atoms in clusters in unit area, $\boldsymbol{nD_c(t)}$
  - Linear relation between deposition time *t* and total density of Bi atoms in each stage $\boldsymbol{D_i(t) + nD_c(t)}$

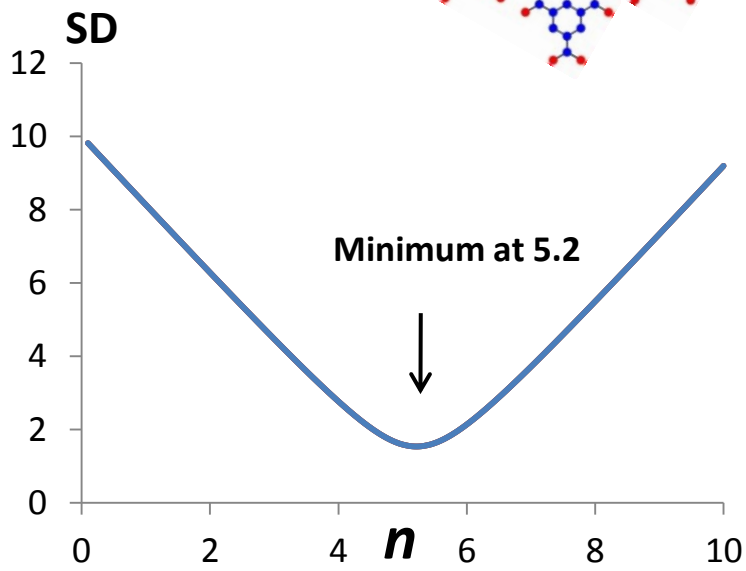
TMA + Bi: Bi cluster superlattices

- Determine no. of Bi atoms in a pore
  - minimum of standard deviation between {t, $D_i(t) + nD_c(t)$} and linear fitting curve $y = k*t$ happens at n = 5.2
  - average 5 Bi atoms in a pore

    (max. 7 in (111) packing)

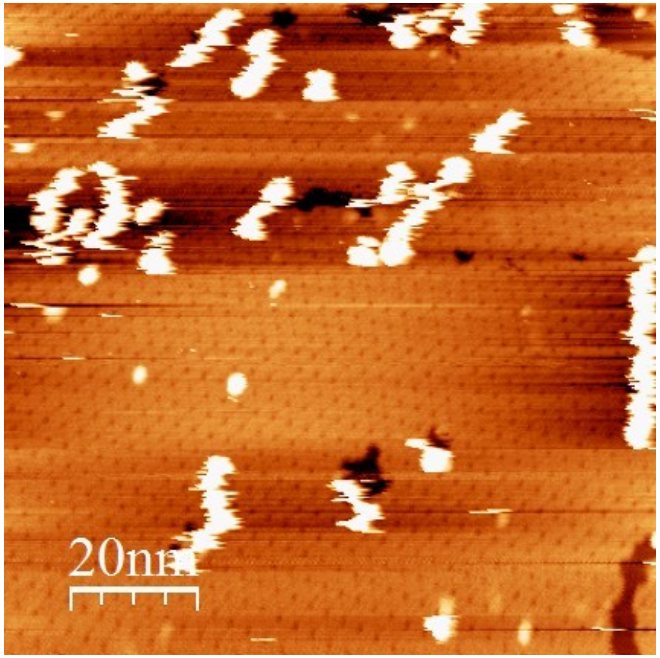






TMA + Bi: Bi cluster superlattices

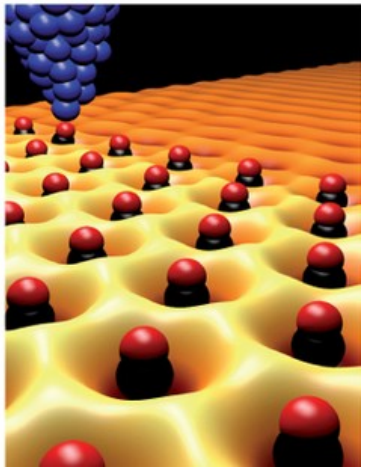
- TMA + Bi on HOPG surface:
  - Irregular Bi clusters --- weak interaction between Bi atoms and HOPG
  - **The attraction between Au(111) surface and Bi atoms induces Bi atoms to reside in the hexagonal pores of TMA structures.**

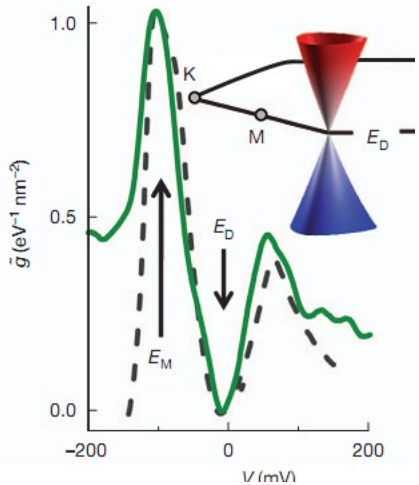


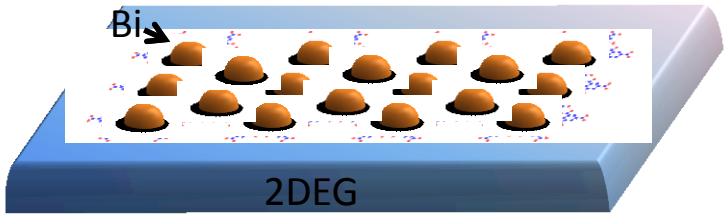
TMA + Bi: Bi cluster superlattices

- Application:
  - Tunable barriers like molecular graphene, generating 2D artificial honeycomb lattice of electrons
  - Simple & fast: self-assembled Bi superlattices in large area
  - Bi cluster superlattices can be grown on Bi islands (strong spin-orbit interaction)

→ **possible candidates for 2D topological insulators**







M. Polini, *et.al.*, *Nature Nano,*, 2013, 8, 625-633; K. Gomes, *et.al.*, *Nature*, 2012, 483, 306.

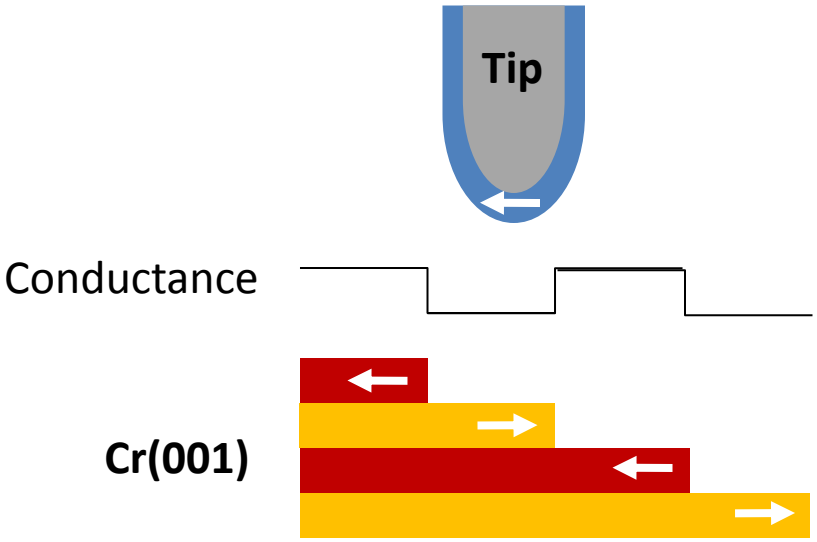
Outline

1. Introduction
2. 2D organic networks functionalized by two heavy metals (Pb, Bi)
3. Spin-polarized scanning tunneling microscope (SP-STM)
4. Conclusion

SP-STM

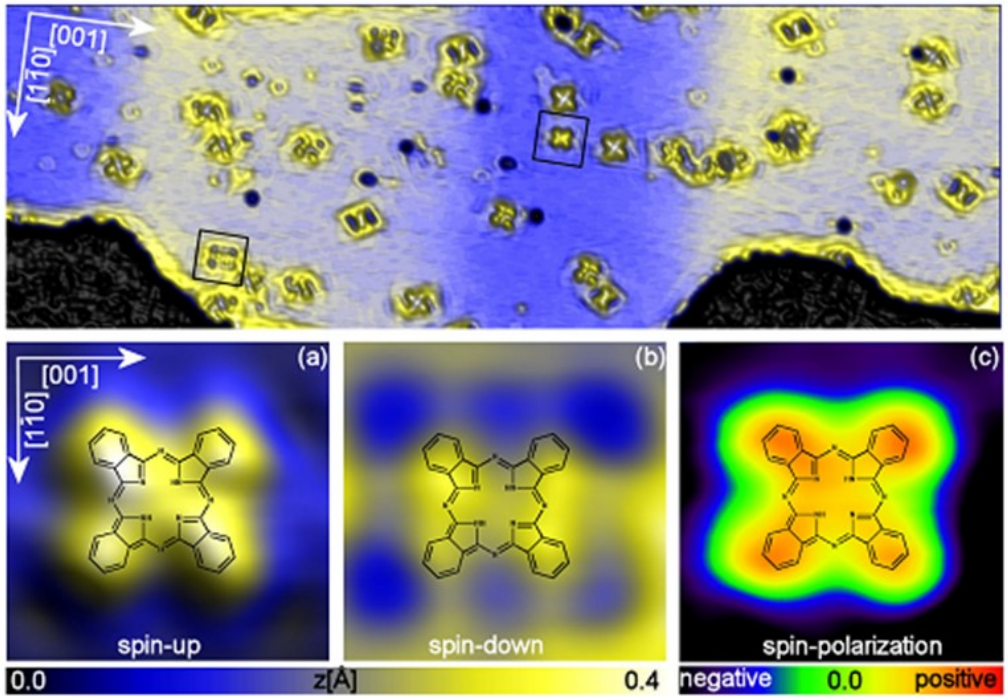
- Principle:
  - Spin-polarized tip
  - Magnetic sample consisting of domains with different spin polarization
  - Same orientation: highest conductance

    opposite orientation: lowest conductance



Application

- Resolve spin states in molecule level
- Application: molecular spintronics, 2D & 3D TI
- ARPES: average over large scale, 3D TI



H_2Pc on different magnetic domain

Deduced spin polarization of H_2Pc molecule

N. Atodiresei, *et.al.*, *Phys. Rev. Lett.*, 2010, 105, 066601.

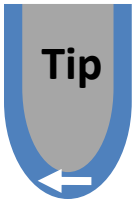
Cr-coated W tip

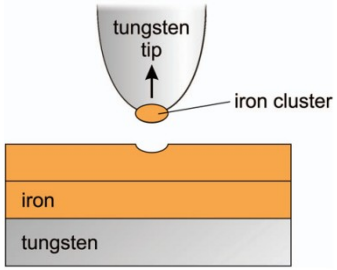
- Spin-polarized tip:
  - Type:

    bulk magnetic materials

    nonmagnetic tips coated thin magnetic film

    nonmagnetic tips with magnetic clusters on the apex of the tips

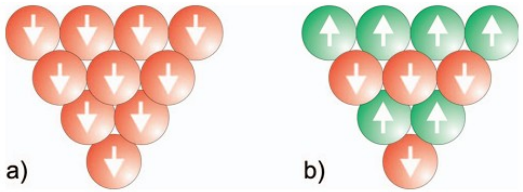




  - Material:

    ferromagnetic (strong magnetic stray field, modify the magnetic structure of the sample)

    antiferromagnetic (negligible stray field)



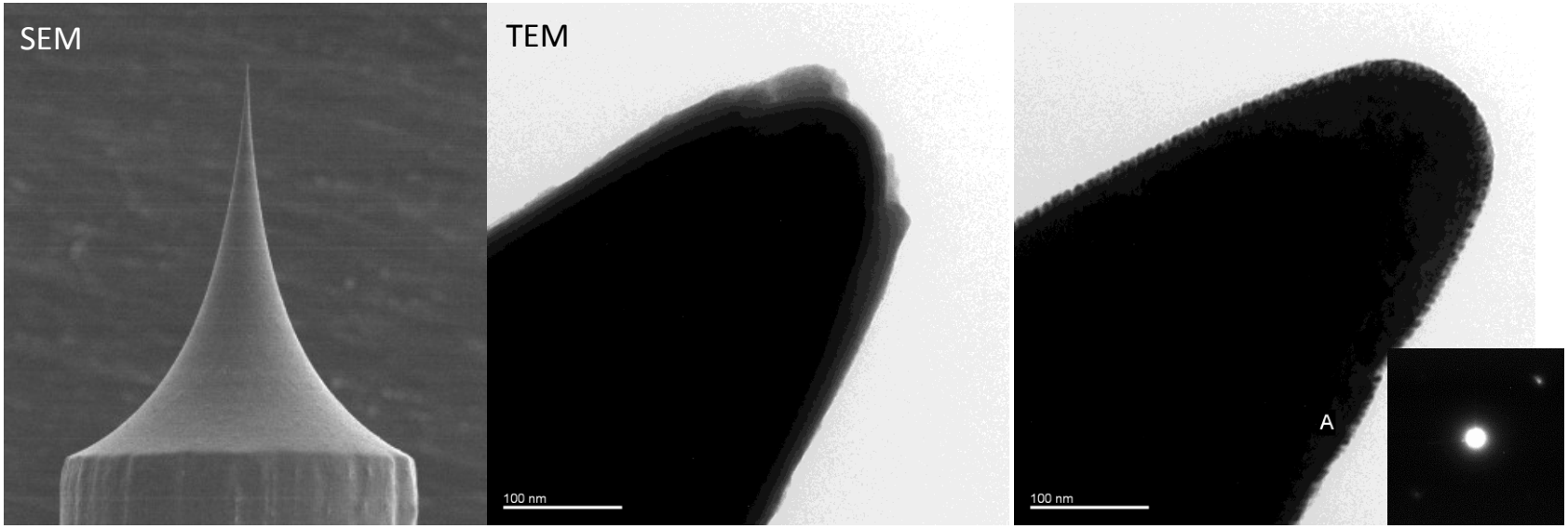
- Chromium-coated tungsten tip
  - antiferromagnetic material
  - 25-45 ML: out-of-plane sensitive 100 ML: in-plane sensitive

R. Wiesendanger, *Rev. Mod. Phys.*, 2009, 81, 1495-1550.

Cr-coated W tip

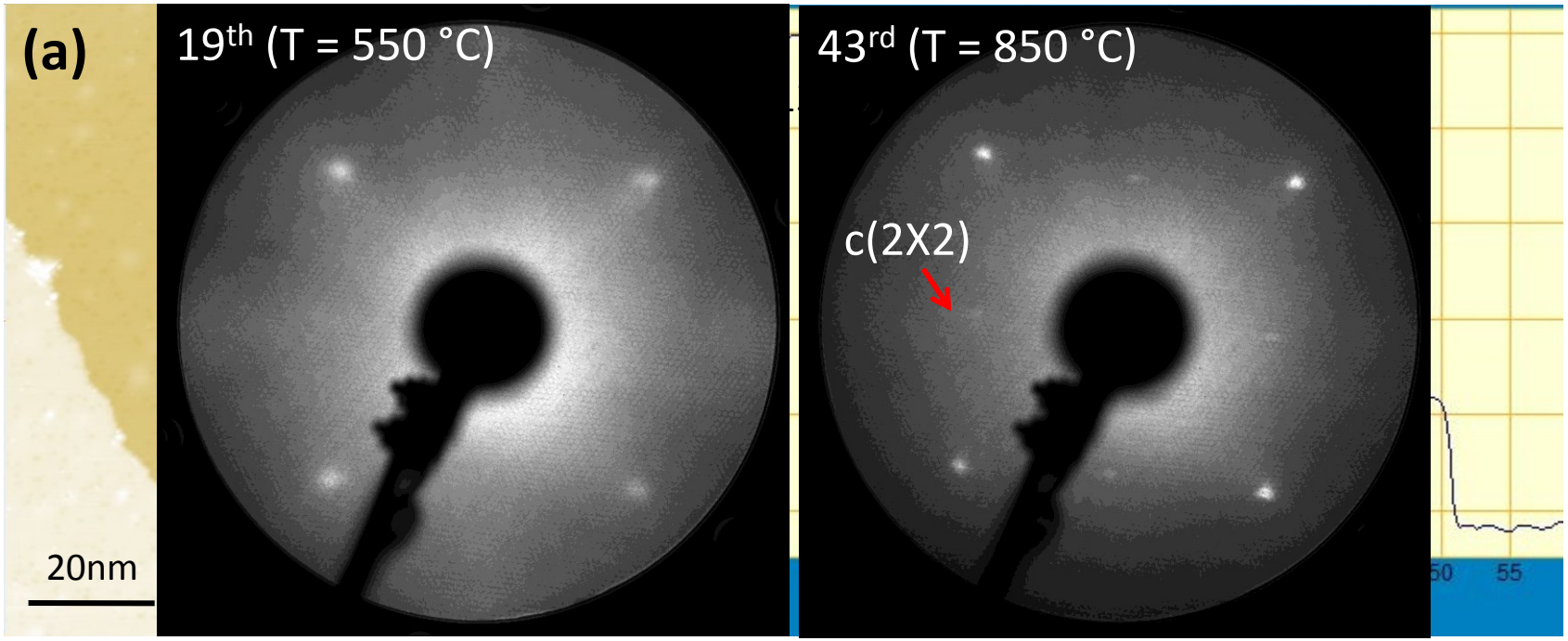
- Procedure:

1. Electrochemical etching
2. Annealing: remove tungsten oxide (WO_2, WO_3)
3. Coating (amorphous Cr) & Post-annealing (crystalline Cr)



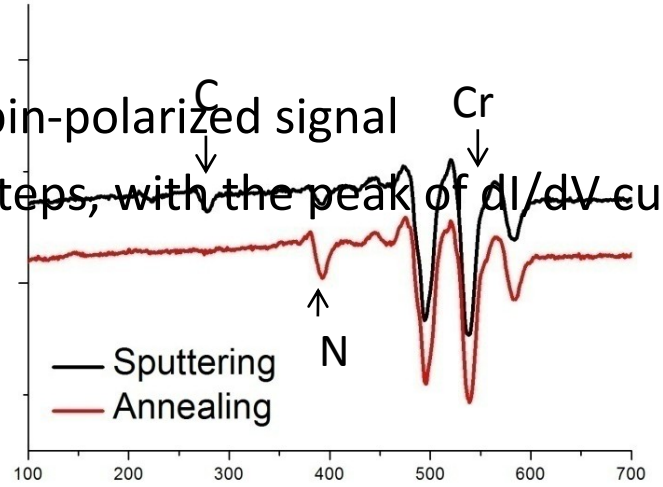
Cr(001)

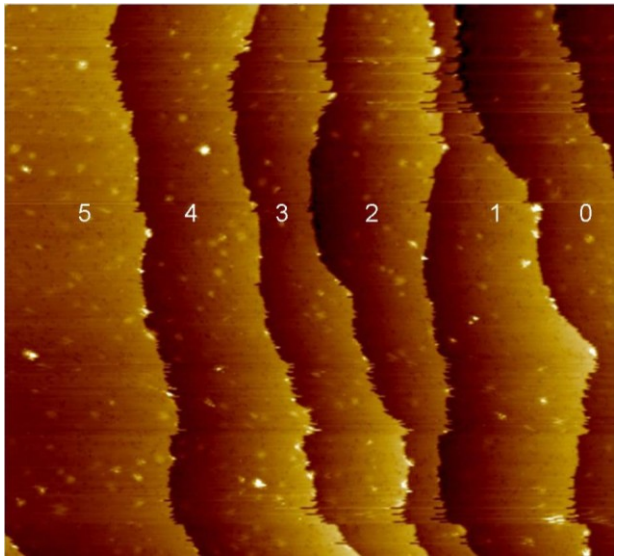
- Magnetic sample: Cr(001)
  - *flat* with monoatomic steps
  - Method: sputtering with Ar-ion and annealing cycle by cycle
  - Monitored by LEED

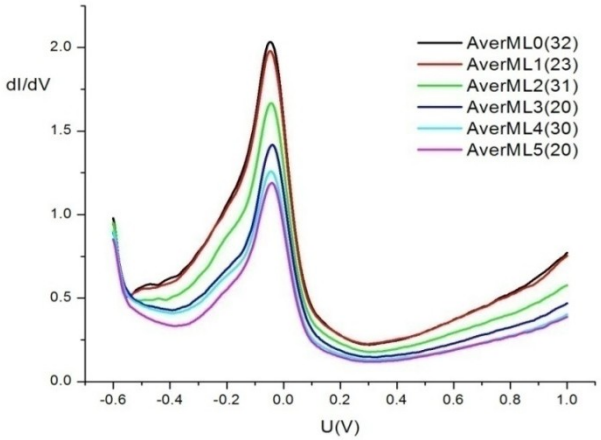


Cr(001)

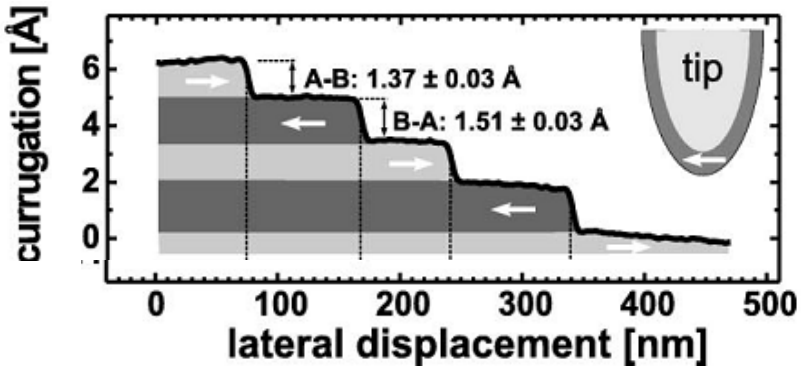
- Magnetic sample: Cr(001)
  - With C and N impurities
  - Similar sample is reported with spin-polarized signal
  - *Flat* substrate with monoatomic steps, with the peak of dI/dV curves locating at -45 meV.
  - Annealing the sample at ~ 750 °C

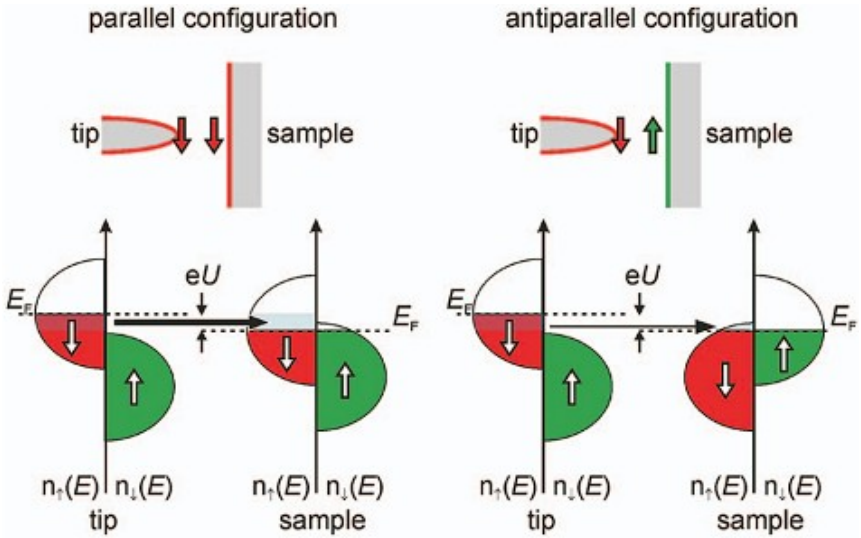






SP-STM Measurement





- Operation modes:
  - **Constant current mode**

    different tip heights on adjacent steps, due to different conductance.

$$P = \frac{exp\left(A\sqrt{\phi}\Delta s\right) - 1}{\quad}$$

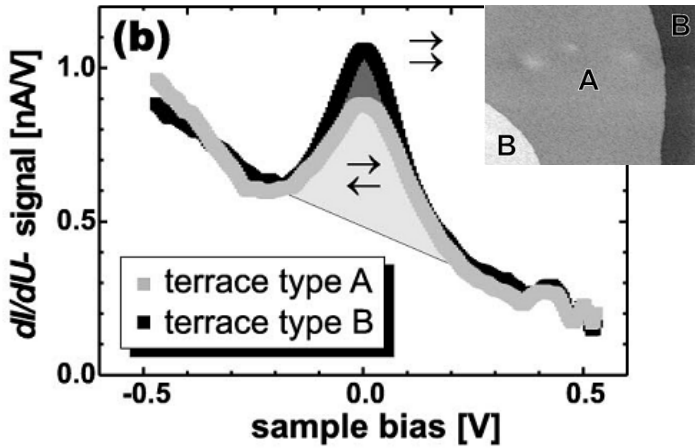
Δs is tip height difference

difference in conductance

~ **total difference** of the local density of state (LDOS) in different spin of the sample **below the bias voltage**.

R. Wiesendanger, *Rev. Mod. Phys.*, 2009, 81, 1495-1550.

SP-STM Measurement



- Operation modes:
  - **dI/dV spectrum measurement**

    dI/dV measurement on different magnetic domain, correlated with the LDOS v.s. bias voltage.

$$P = \frac{dI/dU_{\uparrow\uparrow} - dI/dU_{\uparrow\downarrow}}{dI/dU_{\uparrow\uparrow} + dI/dU_{\uparrow\downarrow}},$$

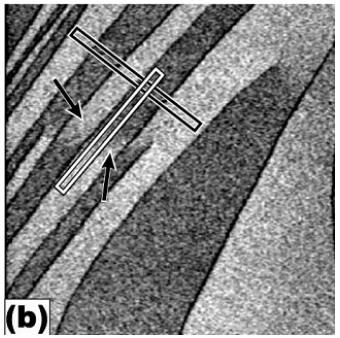
    need a stable spin-polarized tip during measurement

- **dI/dV mapping mode**

  spatial distribution of the dI/dV signal of the same area as STM topograph

  instant imaging of spin-polarized signal

  easy to monitor the change of the SP tip

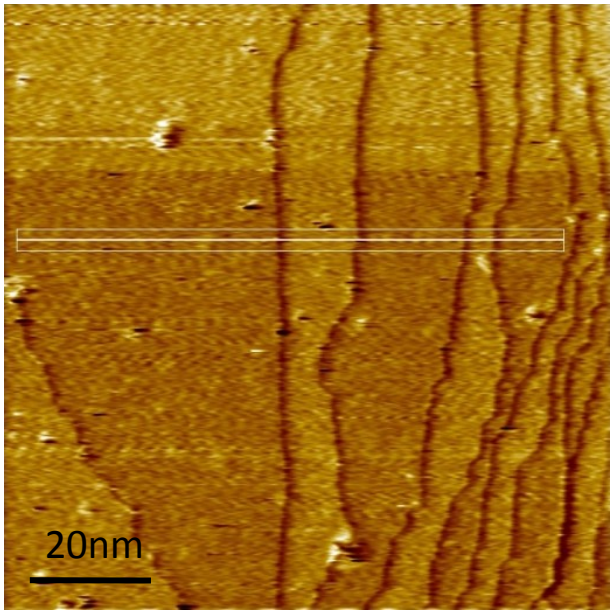


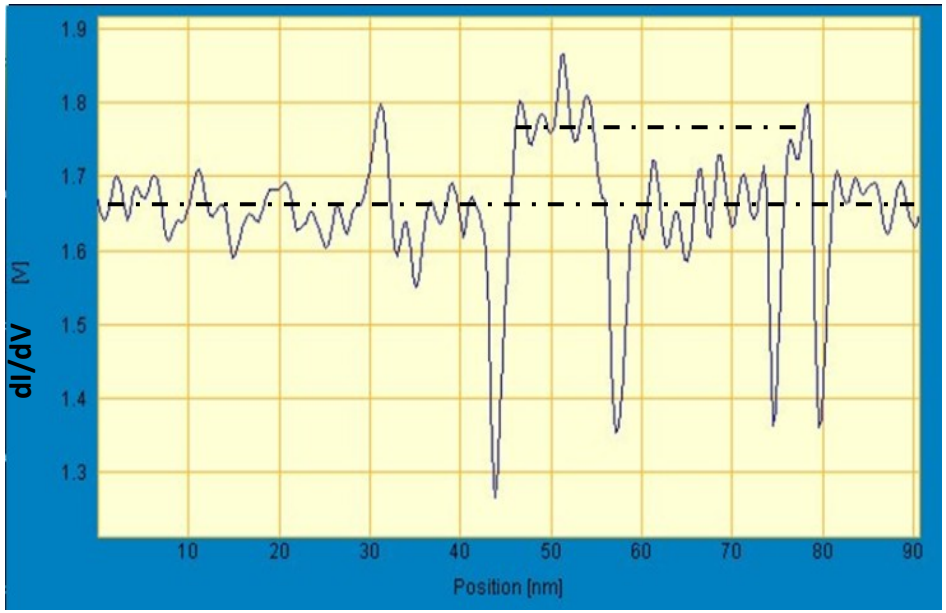
M. Kleiber, *et.al.*, *Phys. Rev. Lett.*, 2000, 85, 4606; R. Wiesendanger, *Rev. Mod. Phys.*, 2009, 81, 1495.

SP-STM Measurement

- Results of SP-STM measurements :
  - Spin-polarized spectroscopic image with spin contrast between adjacent terraces
  - The spin polarization of Cr(001) substrate at – 0.15 V is

$$P = (1.75 - 1.66)/(1.75 + 1.66) = 2.6\ \%$$

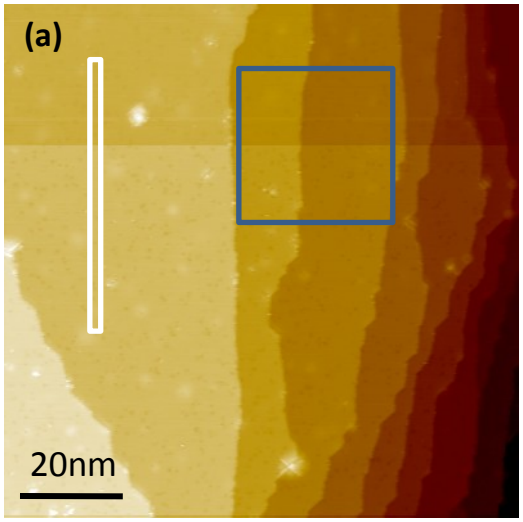


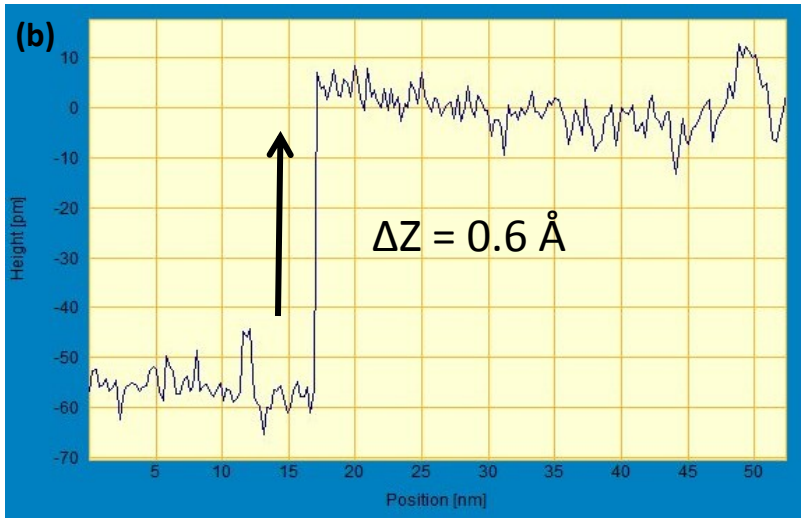


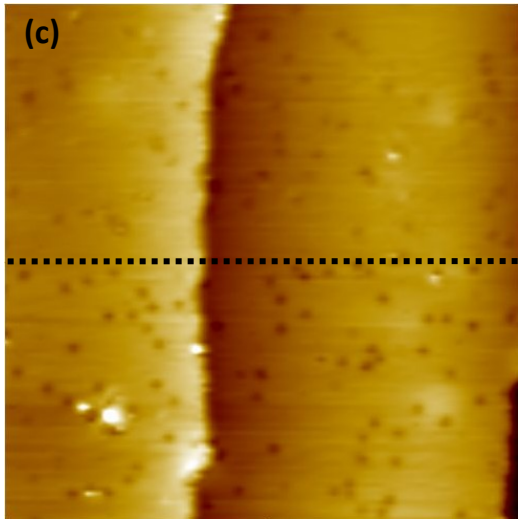
SP-STM Measurement

- Results of SP-STM measurements :
  - No spin-polarized constrast in the upper part of dI/dV spectroscopic image → the tip is unpolarized.
  - An increase of tip height 0.6 Å & contrast in STM image is improved

→ one atom was picked up by the tip

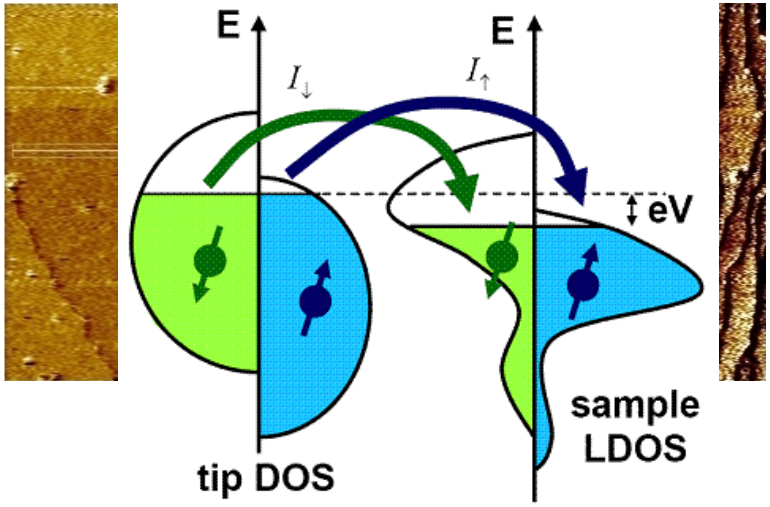






SP-STM Measurement

- Results of SP-STM measurements :
  - For a blunt tip, the spin-polarized tunneling currents generated from different spin sublattices of Cr (antiferromagnetic material) cancel each other.
  - The additional Cr atom sharpens the tip, and improves the spin-polarized signal.



- Reversed contrast at bias voltage -0.20 V

  P = -2.4%

- Positive SP:

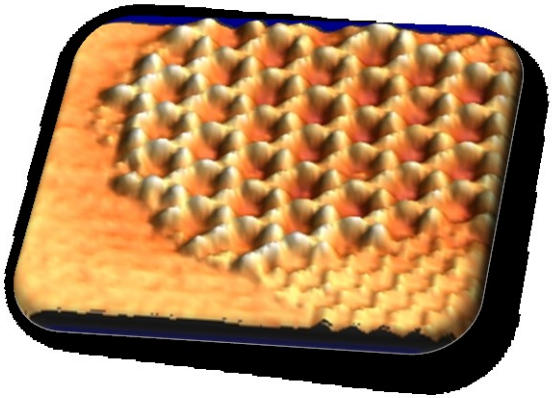
  LDOS of spin-up > LDOS of spin-down

  Negative SP:

  LDOS of spin-up < LDOS of spin-down

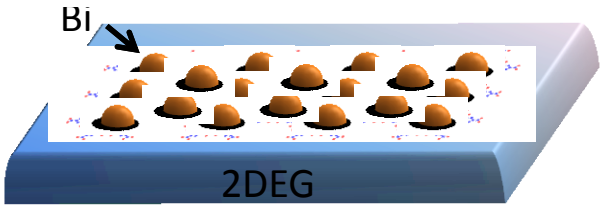
http://hoffman.physics.harvard.edu/research/SPSTMintro.php

Conclusion



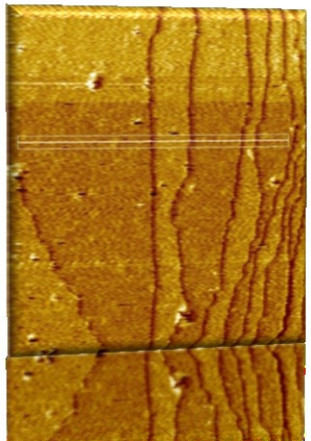
1st work of 2D metal-organic networks self-assembled by Pb on surface

Kagome (*possible 2D TI*) and stripe structures



- 2D tunable Bi cluster superlattices

  Potential candidate for 2D topological insulators



- SP-STM with spin contrast

Acknowledgement

- Supervisor:

  Prof. Nian Lin

- Thesis committee members:

  Prof. Yilong Han

  Prof. Shihe Yang

- Colleagues:

  Weihua Wang
  Lei Dong
  Shiyong Wang
  Tao Lin
  Guoqing Lv
  Guowen Kuang

  Dr. Yuran Niu
  Mr. Patrick Y.P. Luk
  Mr. Ulf Lampe

THANK YOU!