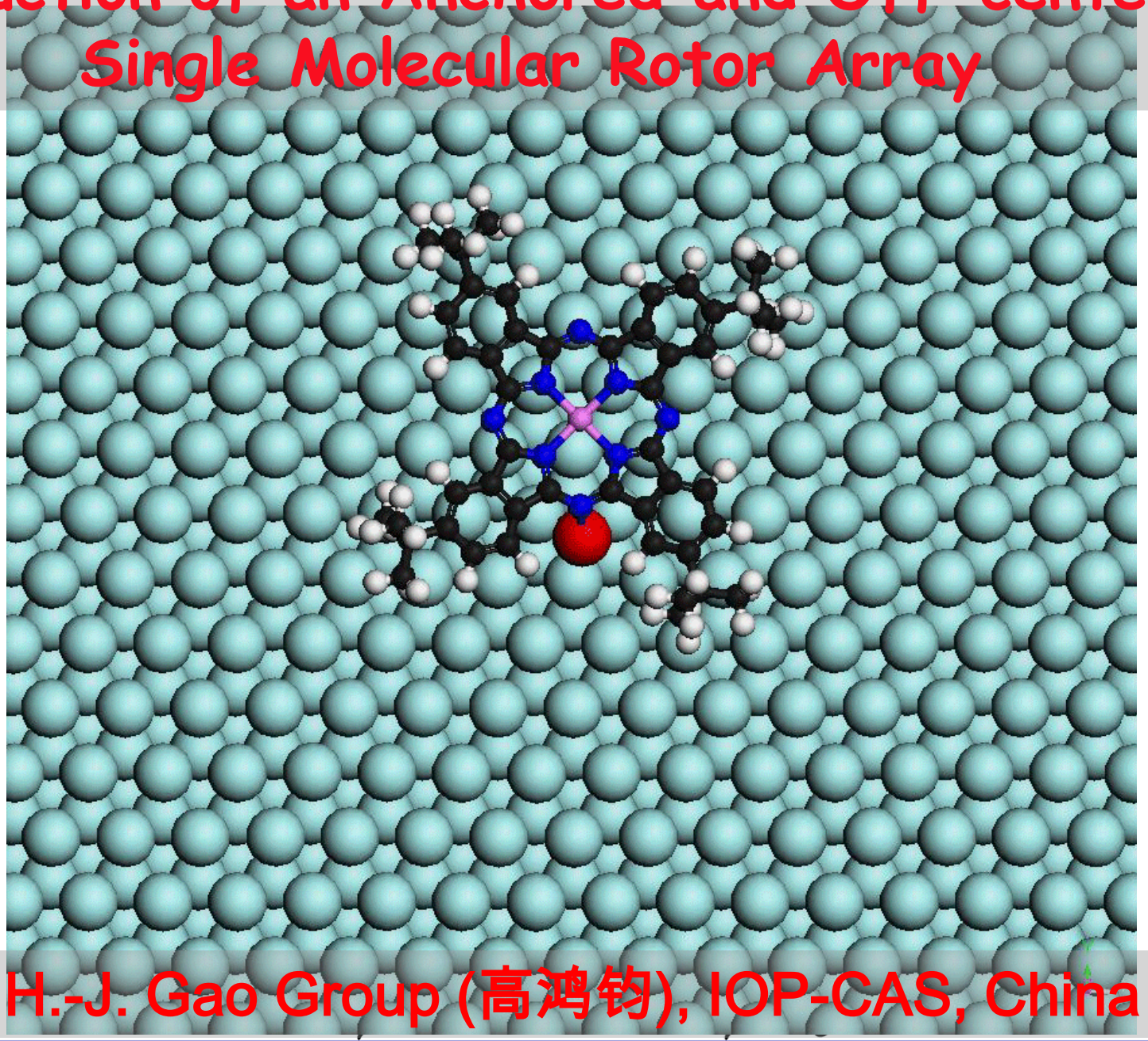
Construction of an Anchored and Off-centered Single Molecular Rotor Array

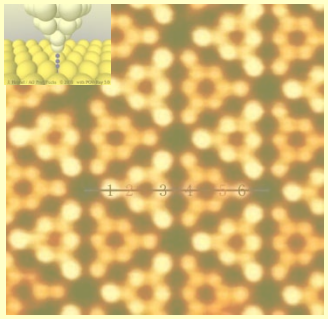


H.-J. Gao Group (高鸿钧), IOP-CAS, China

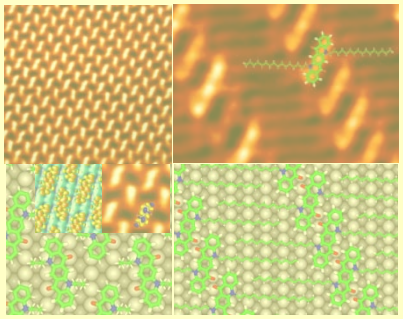
Construction of Anchored Molecular Rotor Array and Site-specific Kondo Effects of Single Molecules at Metal Surfaces

Hongjun Gao

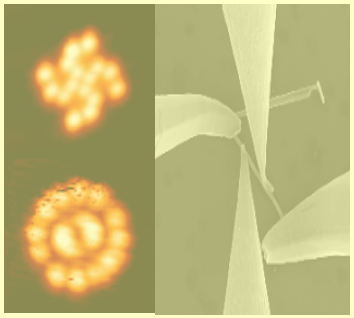
Institute of Physics
Chinese Academy of Sciences, Beijing, China
(http://nano.iphy.ac.cn)



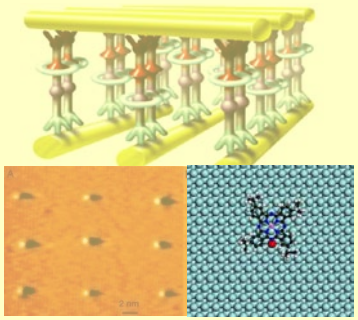
"Seeing"



"Understanding"



"Controlling"

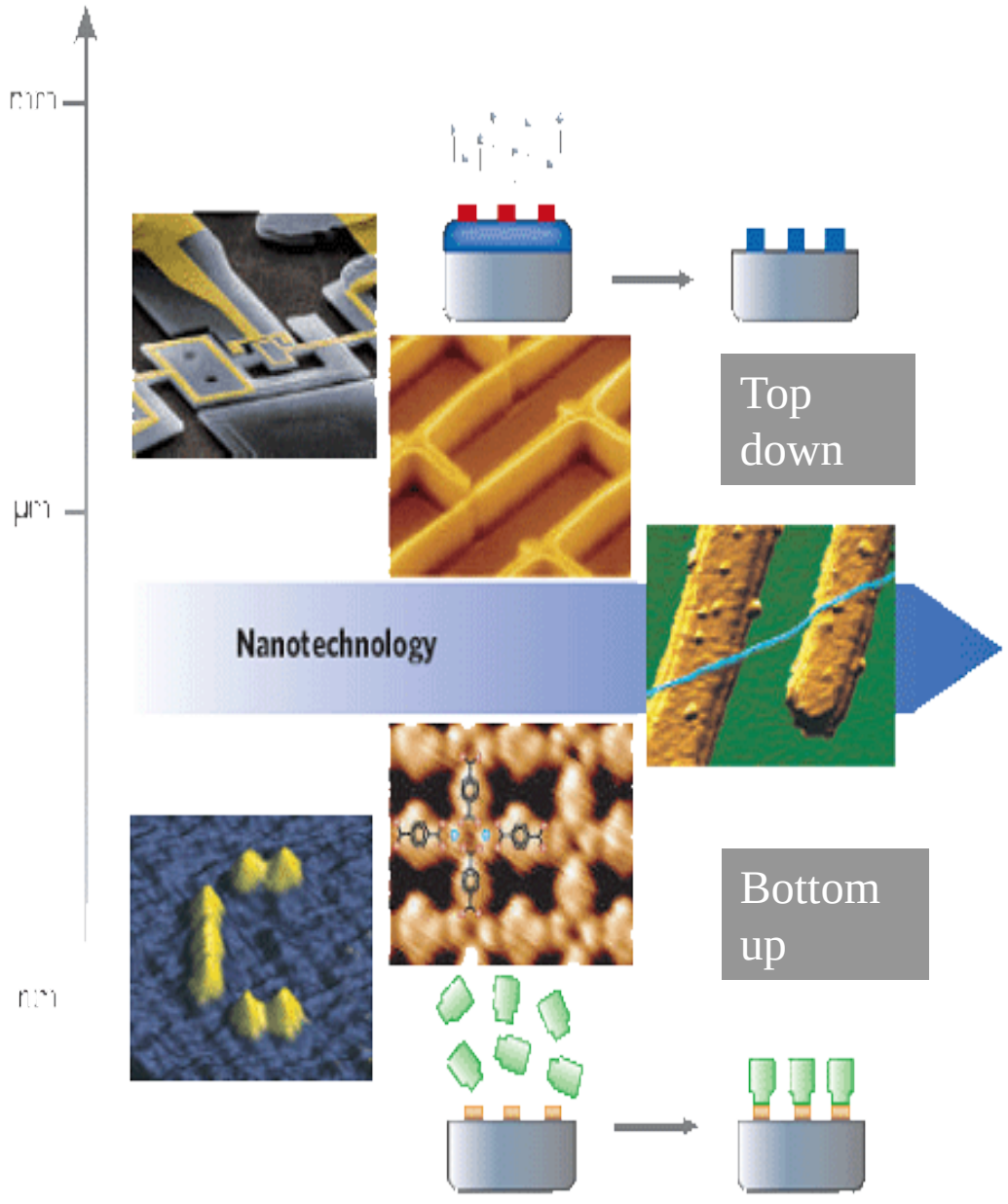


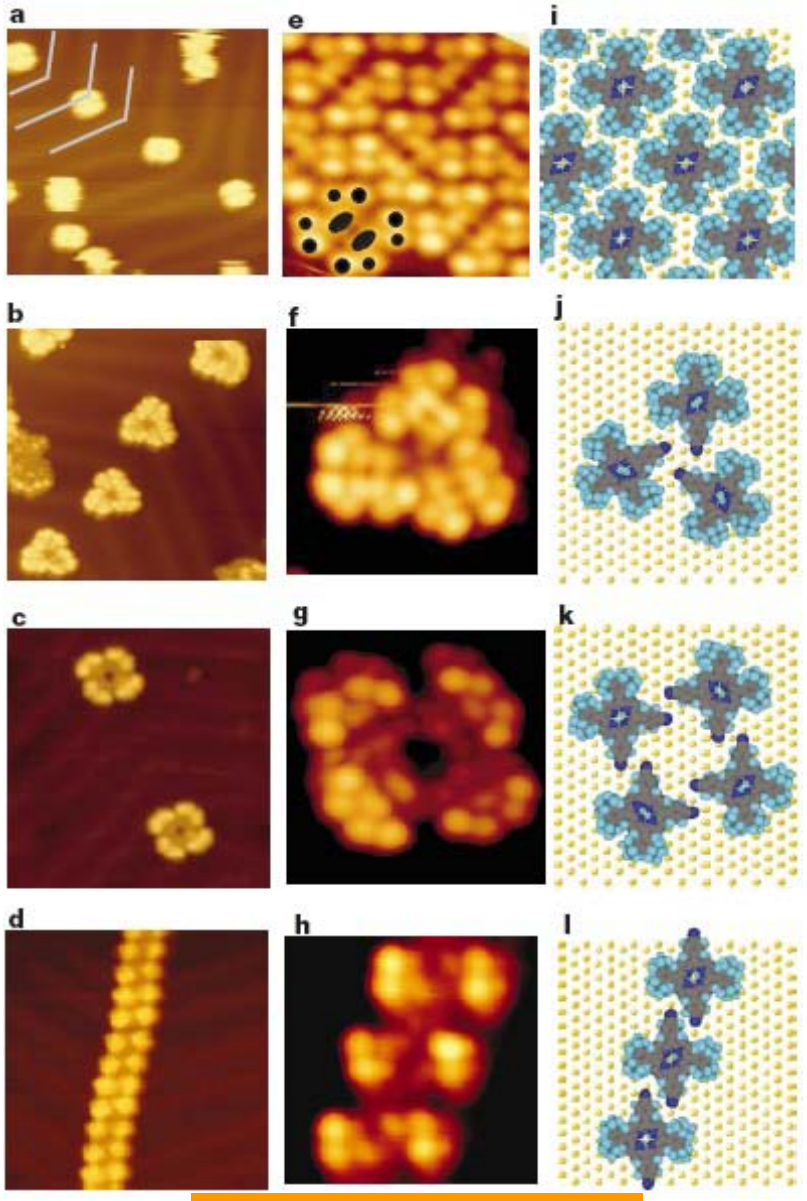
"Functionalizing"

OUTLINE

- Introduction
- *"Anchored" Single Molecular Rotor Array on Metal Surfaces*
- Site-specific Kondo Effects in PcFe Molecules
- Epitaxial Grwoth of Graphene on Metal Surfaces
- Conclusions

Formation of Functional Nanostructures





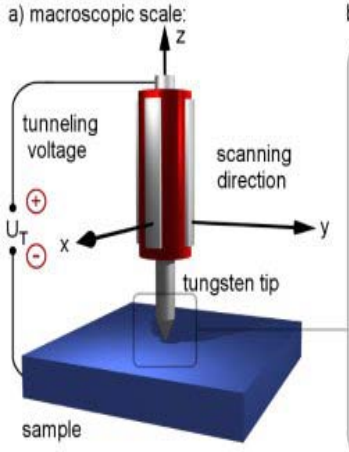
Nature, 413, 619(2001)

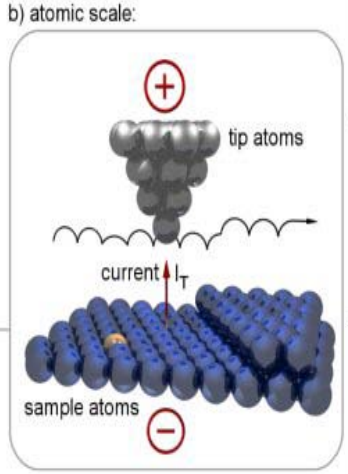
Scanning Tunneling Microscopy and Spectroscopy

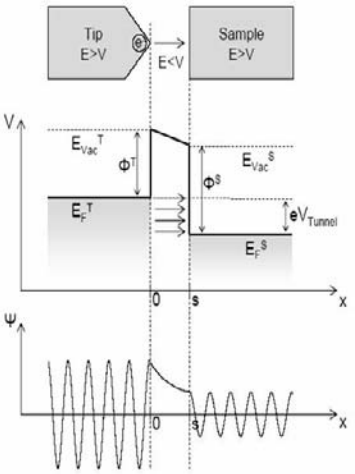
Imaging

Spectroscopy

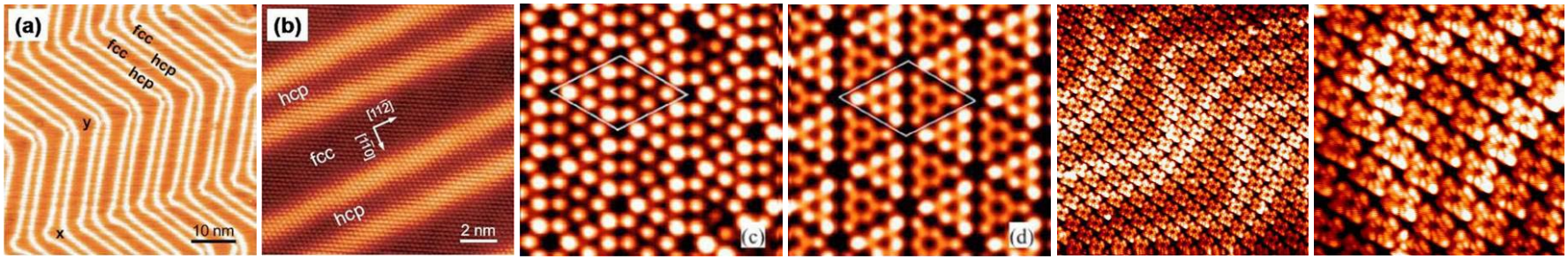
Manipulation







$$I = 2e\frac{2\pi}{\hbar}\int_{-\infty}^{\infty}\left[f(E_F - eV + \varepsilon) - f(E_F + \varepsilon)\right]\times \rho_S(E_F - eV + \varepsilon)\rho_T(E_F + \varepsilon)\left|M\right|^2 d\varepsilon$$



Main Facility

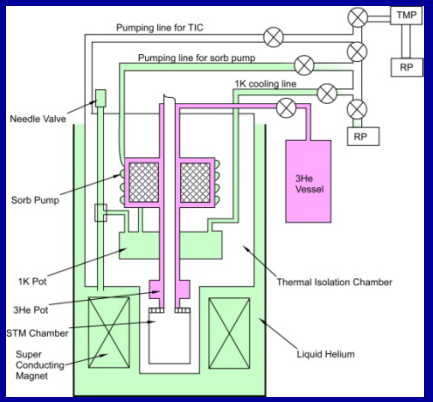
400 mK-11T UHV-STM with BME

RT-STM Head

USM 1300S-^{3}He
STM System

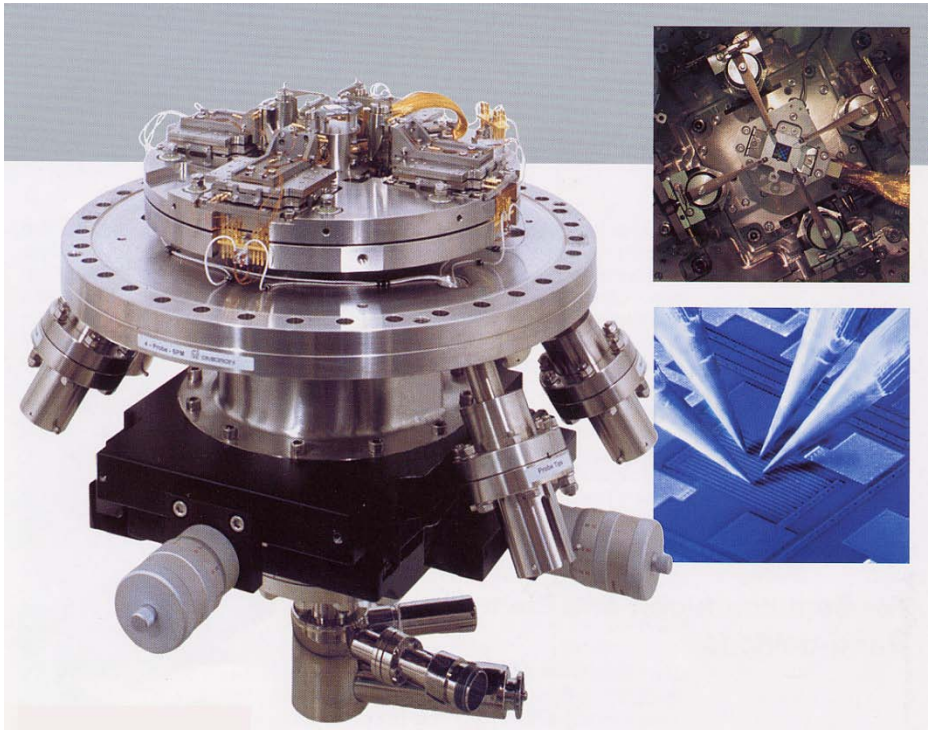
LT-STM Head

Cleaving and
Cooling Stage



^{3}He Circulatory
Refrigeration

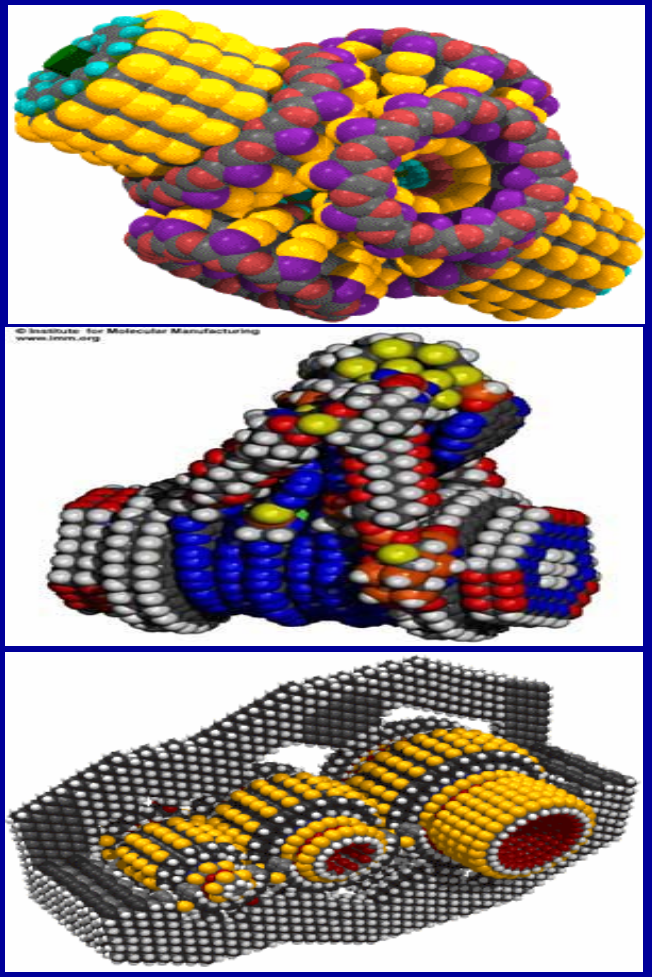
4PSTM-MBE System

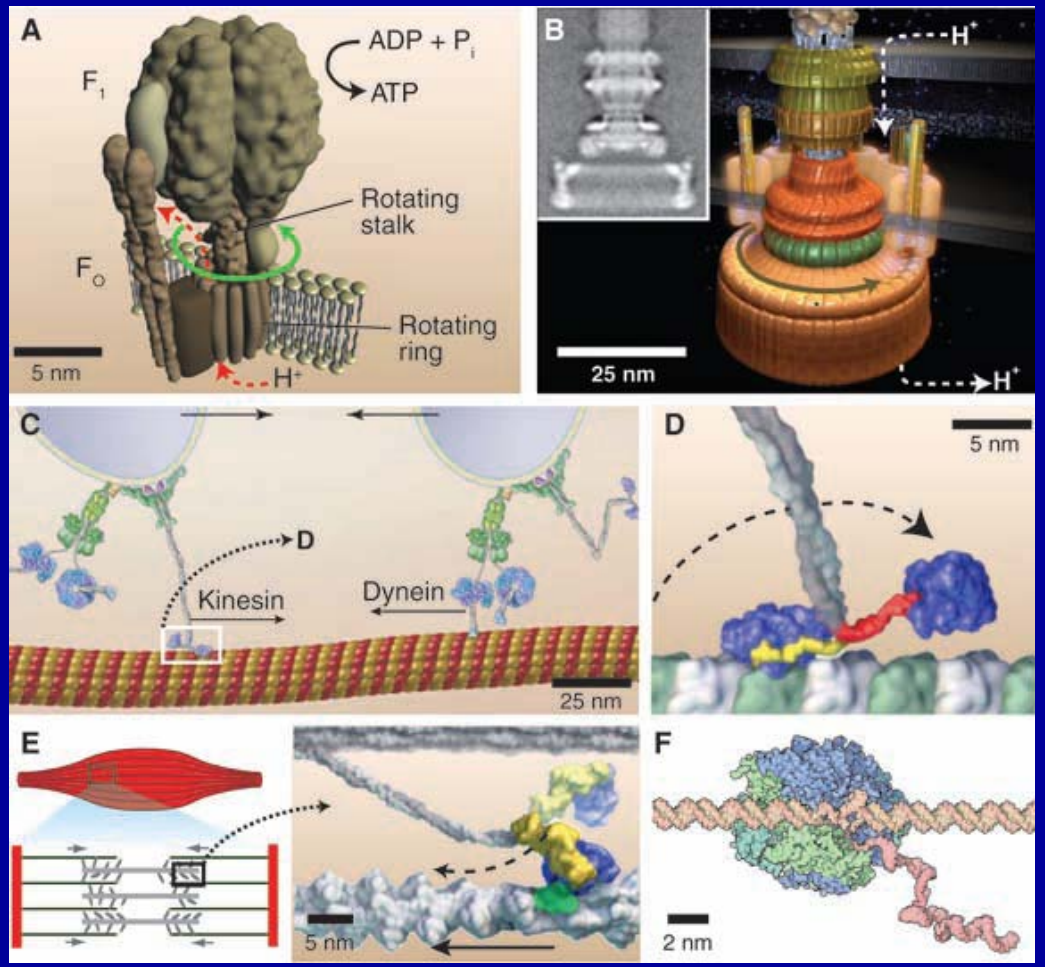


- **Four independent STMs**
- **Atomic resolution (with IDE air spring)**
- **Temperature: from 30K to 500K (with CryoVac)**

Adsorption Behavior of Metal–Pc Molecules on Au(111) surface: Anchored and Off-Centered Single Molecular Motor Array On Metal Surface

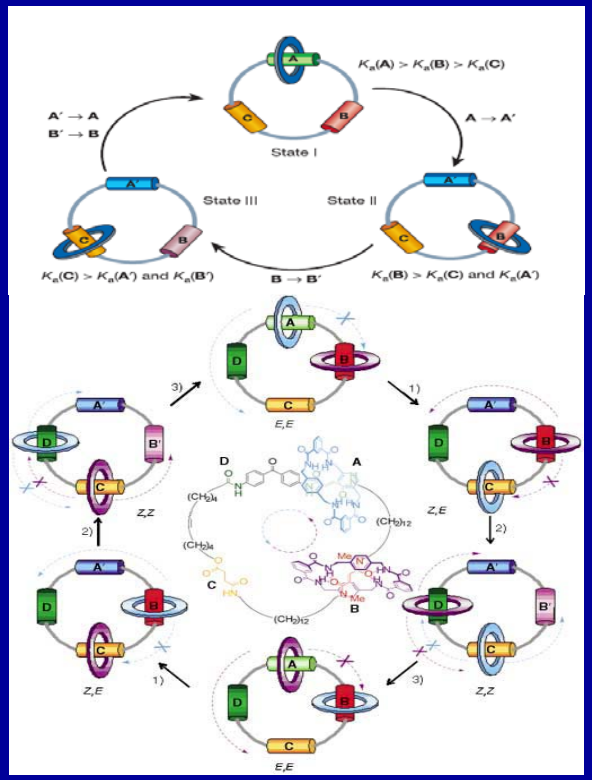
Molecular Motor



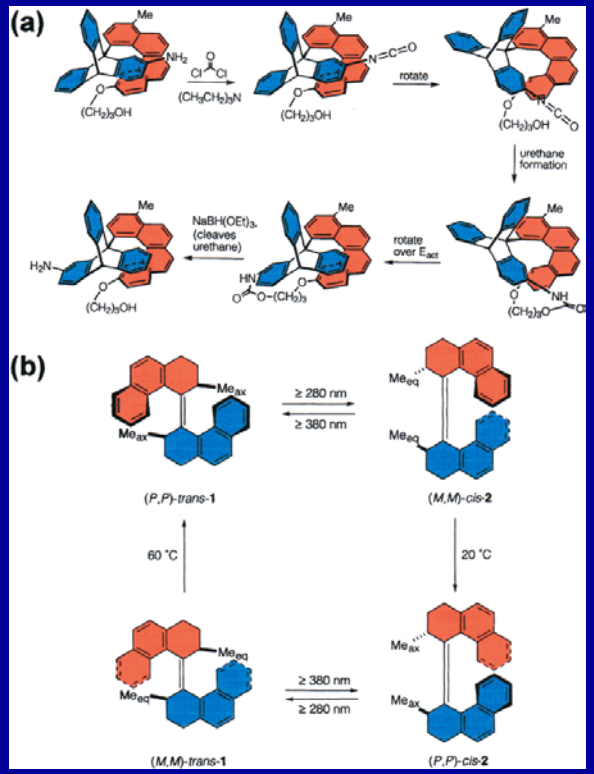


Artificial Molecular Rotor

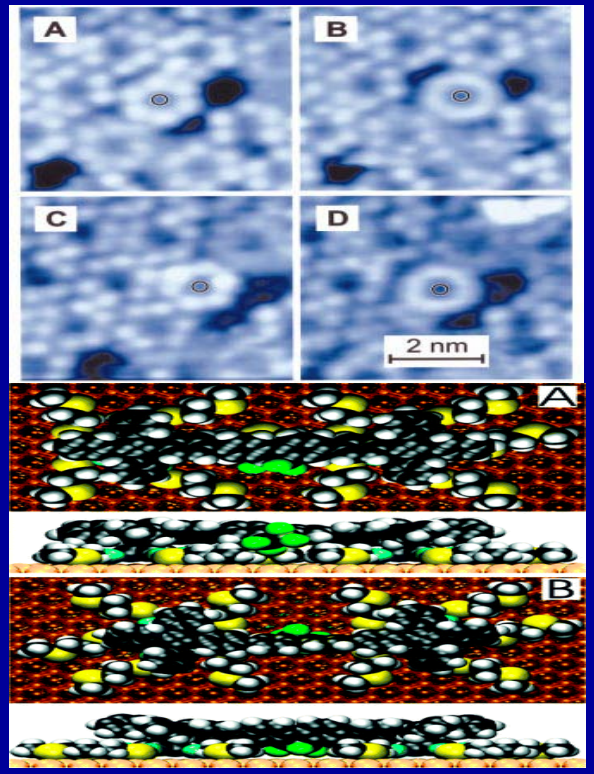
Rotaxane Based



Chirality Based

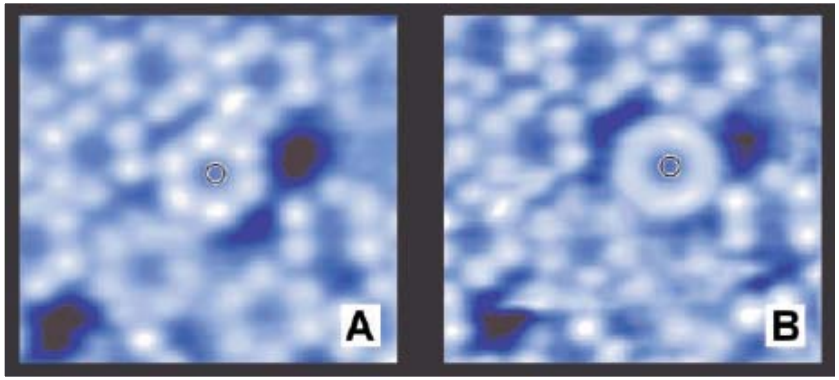


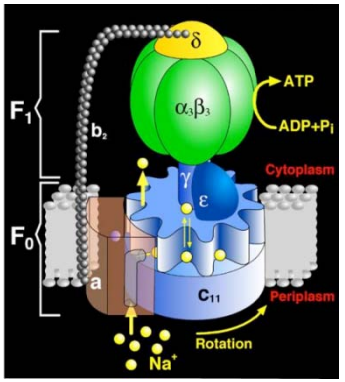
Flat Molecule Based



J. V. Hernandez *et al.*, *Science* **306**, 1532 (2004);
Feringa *et al.*, *Nature* **424**, 174 (2003); T. R. Kelly *et al. Nanotechnology* **14**, 566 (2003);
J. K. Gimzewski *et al.*, *Science* **281**, 531 (1998); D.Horinek *et al.*, *PNAS* **102**, 14175 (2005)

Single-molecule Rotor Operating within a Supramolecular Bearing at Room Temperature





- Molecules that can participate in weak and directional non-covalent bonds may be programmed to form desired supramolecular structures

- Control by surface mobility of molecules, their lateral interactions and their coupling to the surface atomic lattice.

4-trans-2-(pyrid-4-yl-vinyl) benzoic acid on Ag(1,1,1)

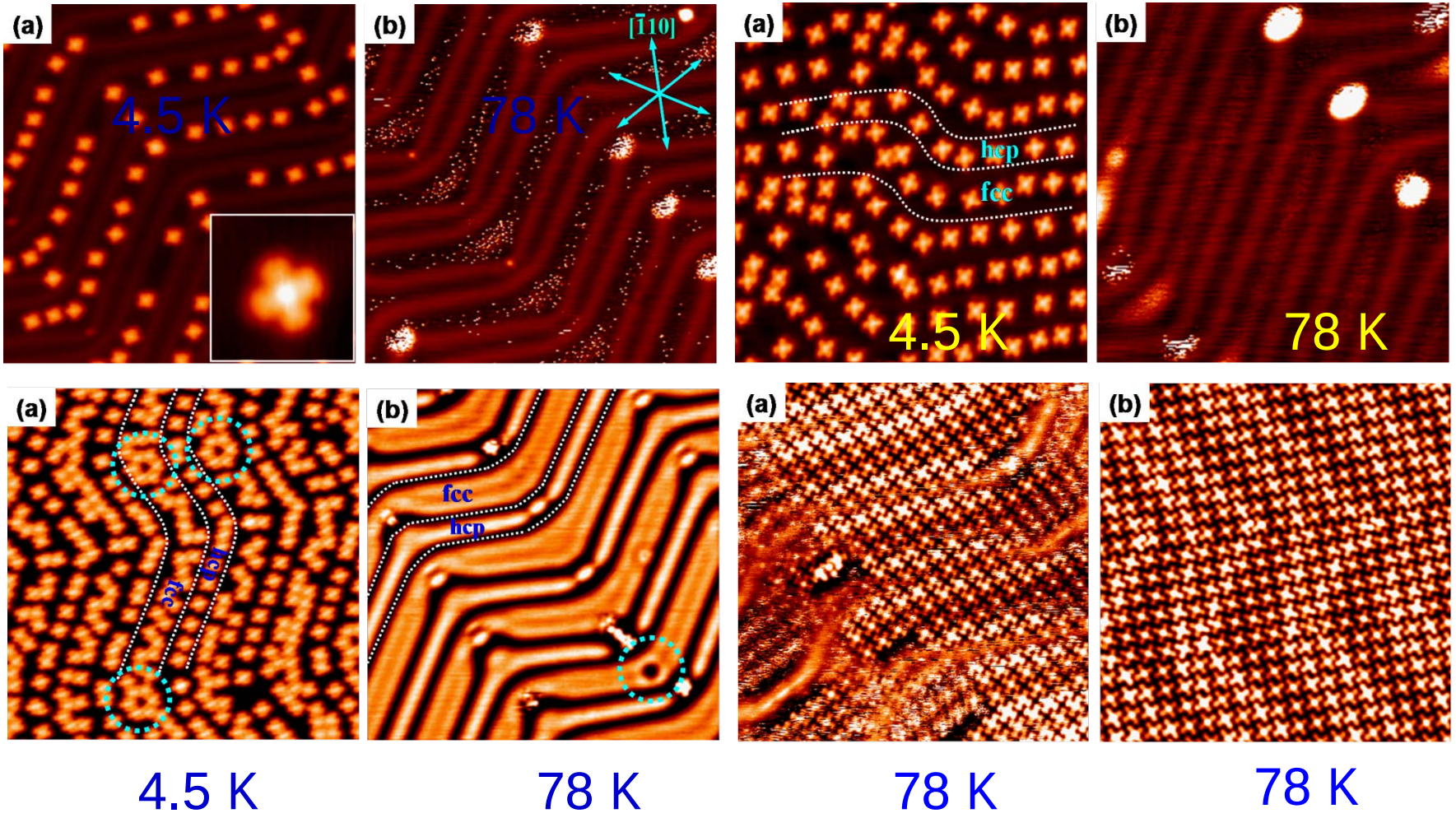
Left deposition at T = 125 K. right deposition at T=300K

Scan at 77K

Barth, J. V. Transport of adsorbates at metal surfaces: From thermal migration to hot precursors. *Surf. Sci. Rep.* 40, 75–150(2000).

Gimzewski, J. K. & Joachim, C. Nanoscale science of single molecules using local probes. *Science* 283, 1683–1688(1999).

Self-assembly and Diffusion Behavior Property of Pc Molecules on Metal Surface



Challenges for Molecular Rotors

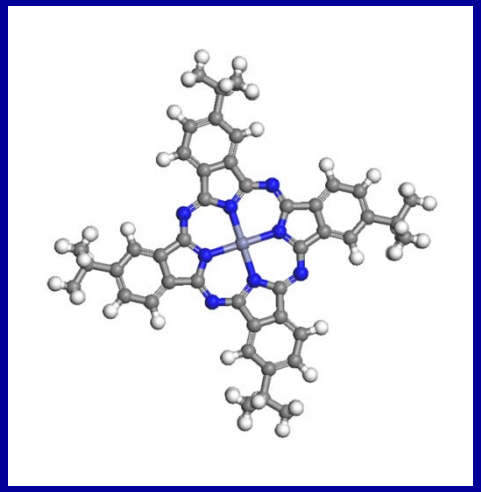
- An axis for molecular rotation
- Manipulation of the rotation axis position
- Controllable rotation direction and frequency
- Integration of single molecular rotors

into smart complex molecular machines

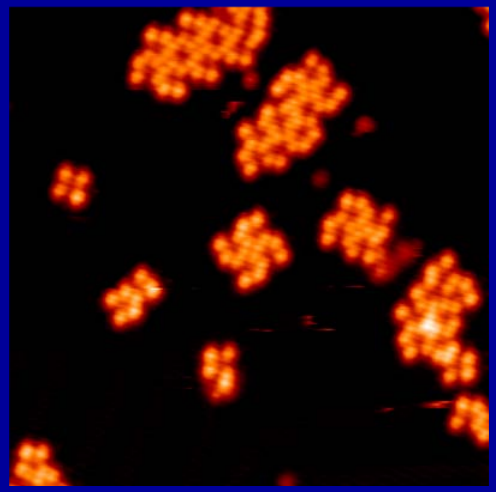
Questions:

- Can we anchor a single molecule on metal surface
- Can we manipulate the physical properties using the site specific adsorption ?
- How ???

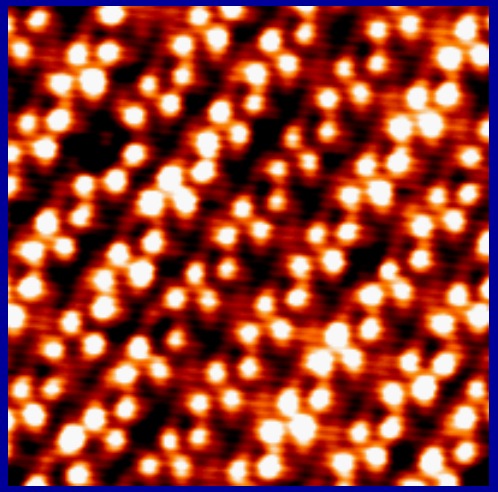
$(t\text{-Bu})_4$-ZnPc / Au(111) @ LHe



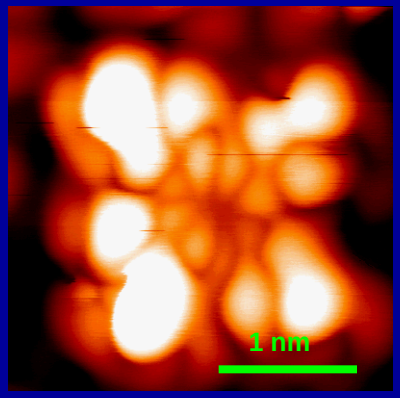
(t-Bu)$_4$-ZnPc Molecule

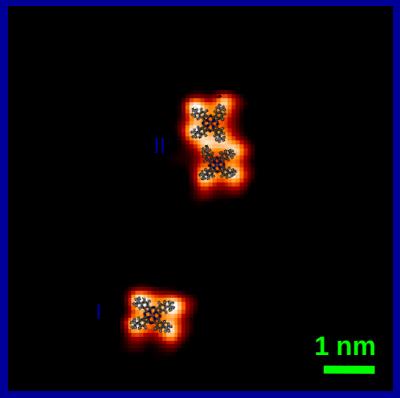


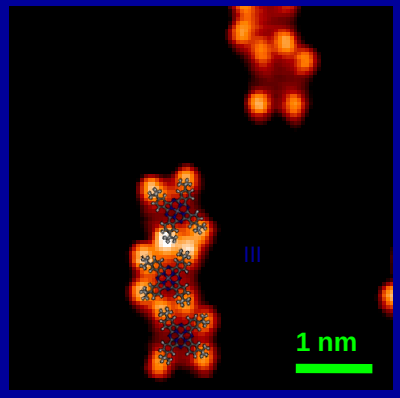
LHe, 30nm x 30nm, -1.9V, 0.1nA

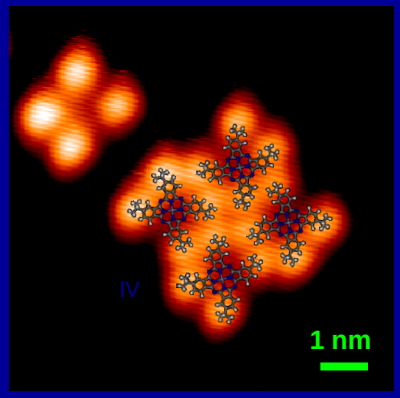


LHe, 10nm x 10nm, -1.2V, 1.0nA

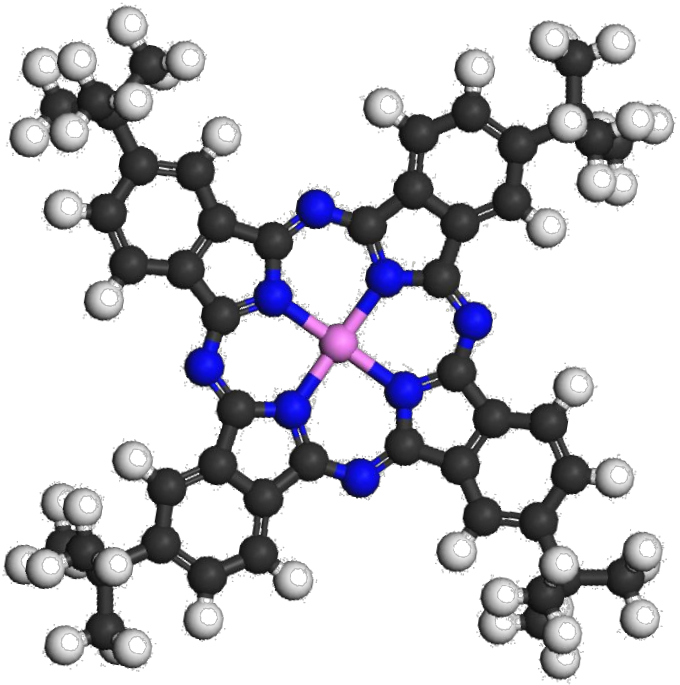


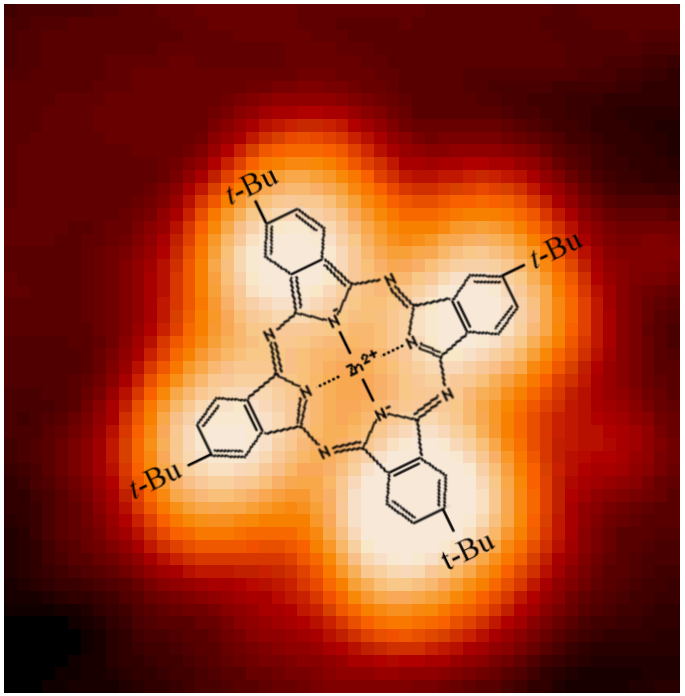






$(tBu)_4ZnPc$ Molecular Structure



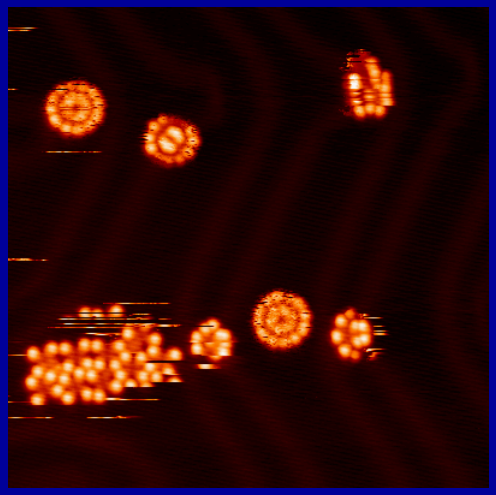


- Full name: tetra-*tert*-butyl zinc phthalocyanine

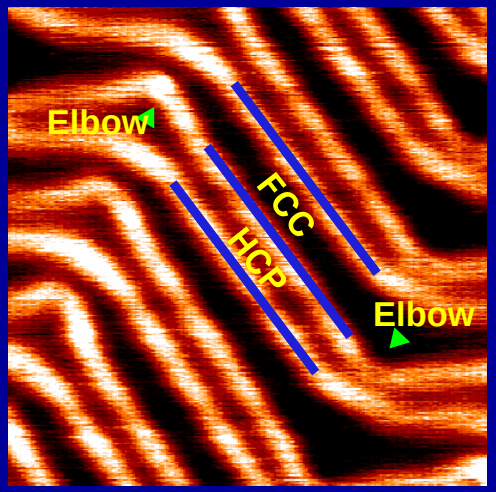
  ($C_{48}H_{48}N_8Zn$)

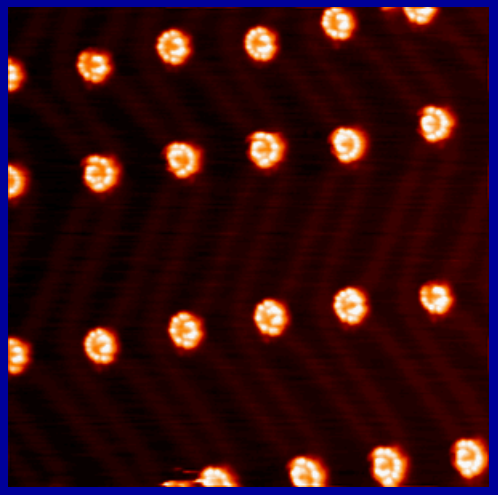
- STM image of single stationary molecule: four bright lobes

(*t*-Bu)$_4$-ZnPc / Au(111) @ LN$_2$

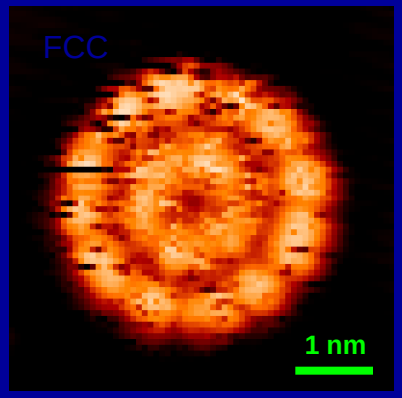


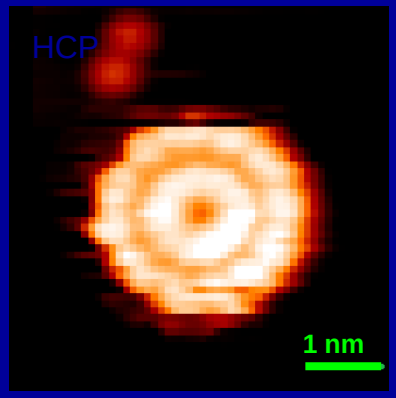
LN2, 30nm x 30nm, -1.8V, 0.05nA

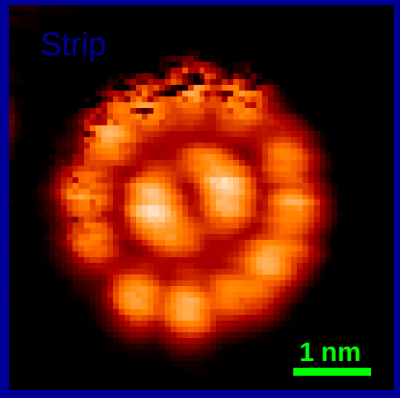


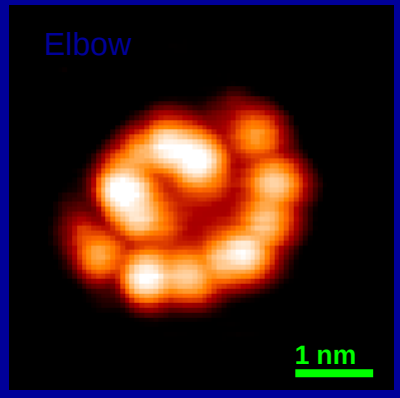


LN2, 40nm x 40nm, -1.3V, 0.07nA

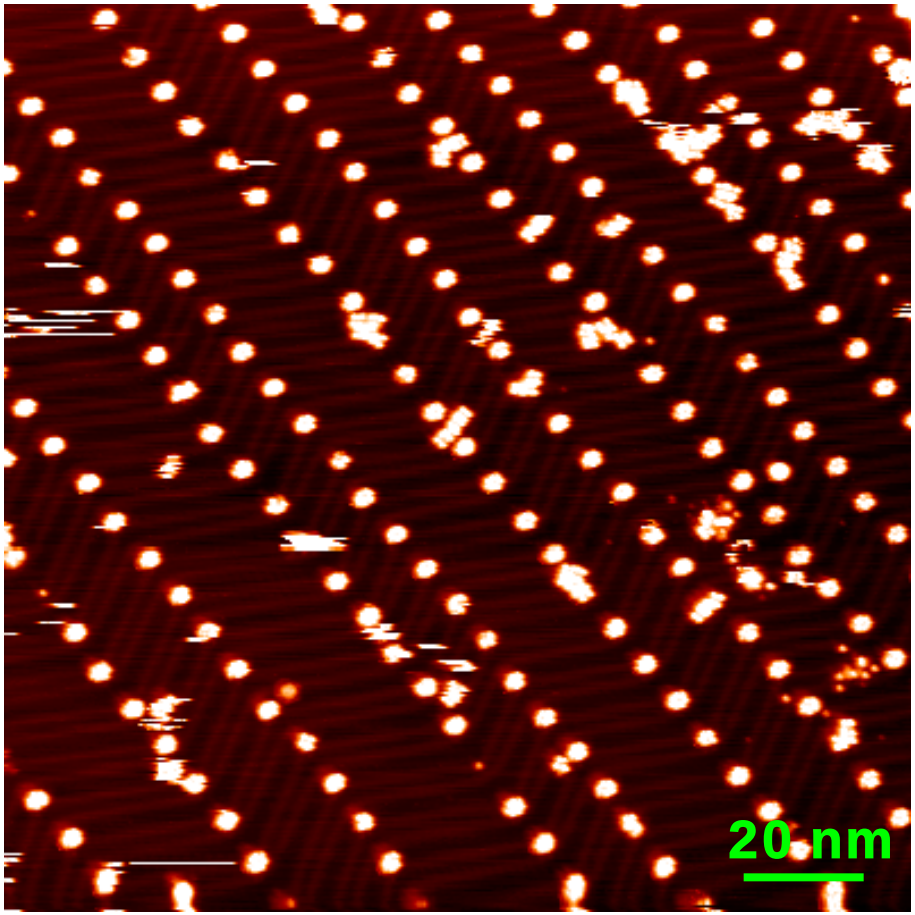


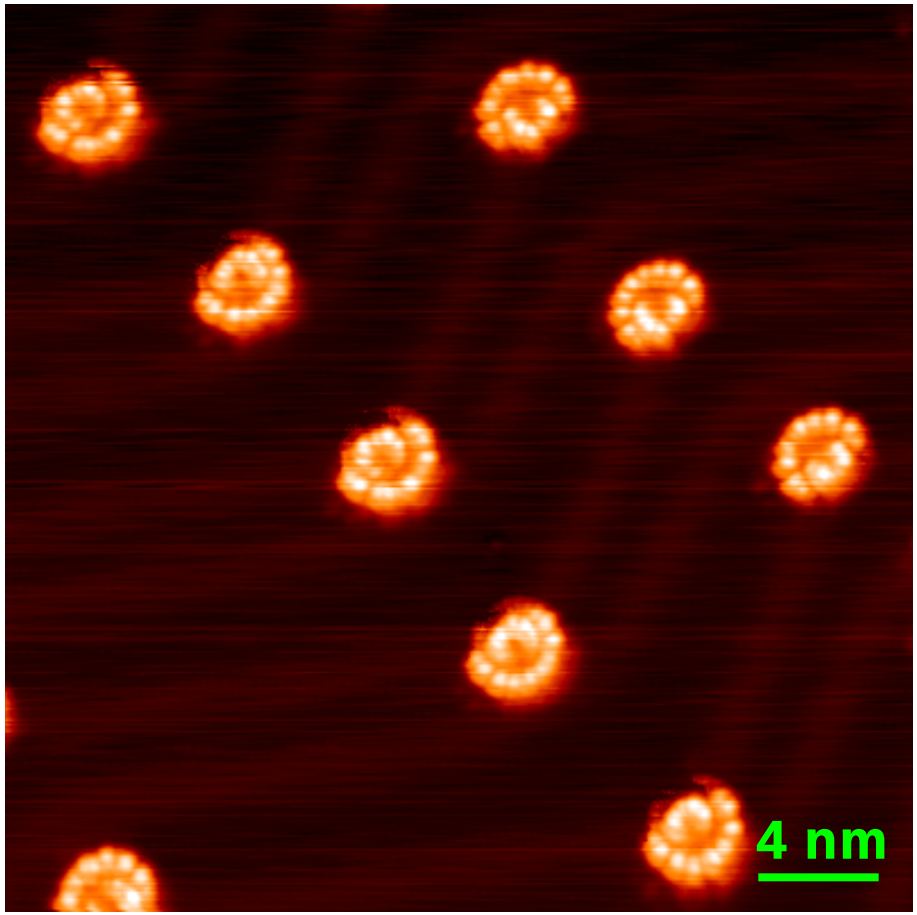






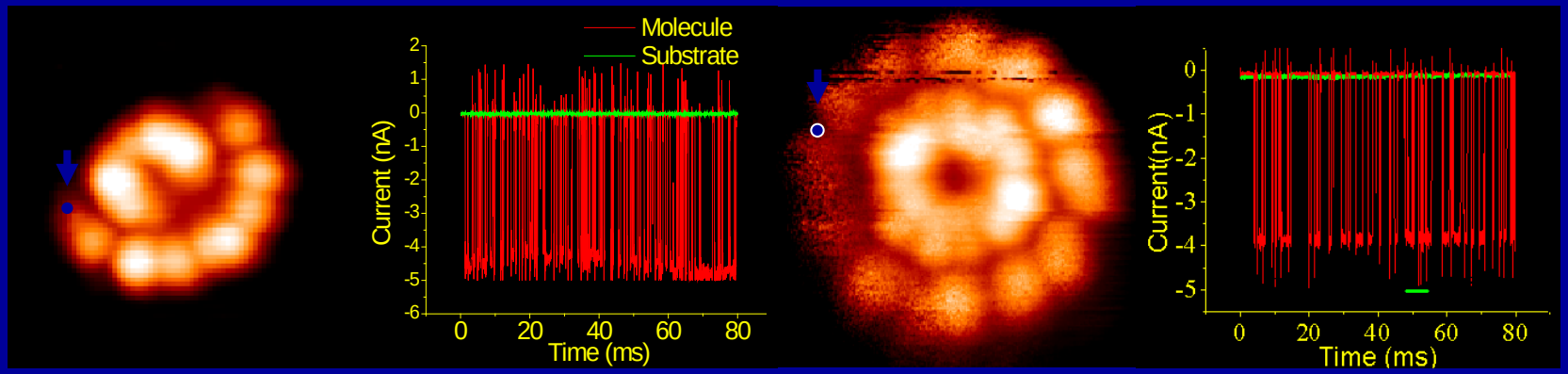
Array of Single Molecular Rotors





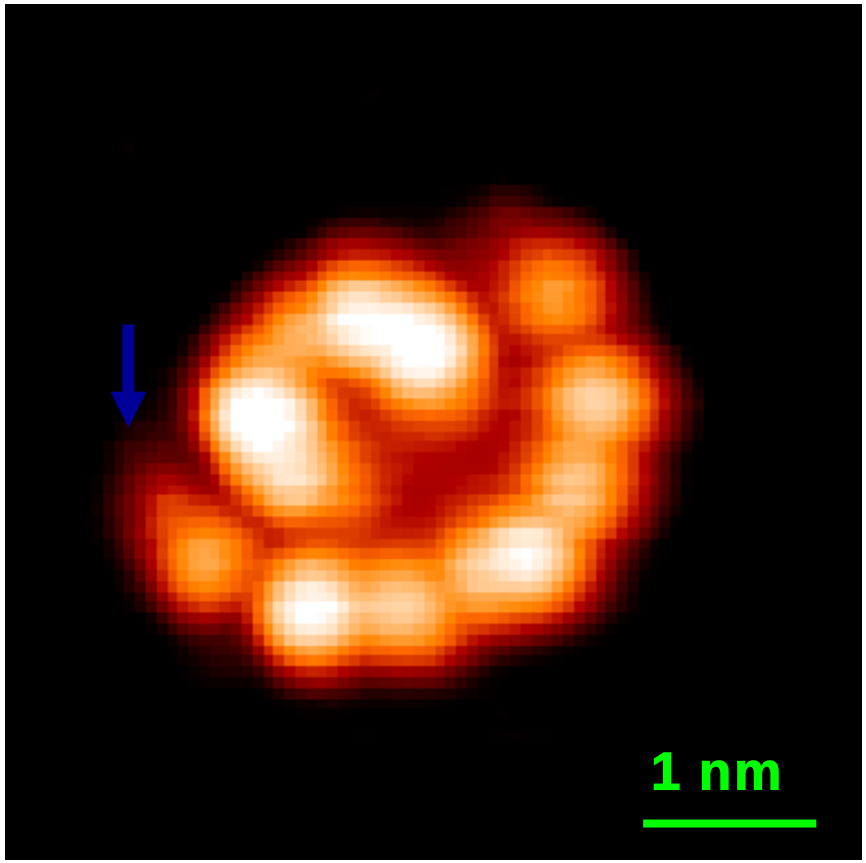
Rotor, Impurity or Aggregation?

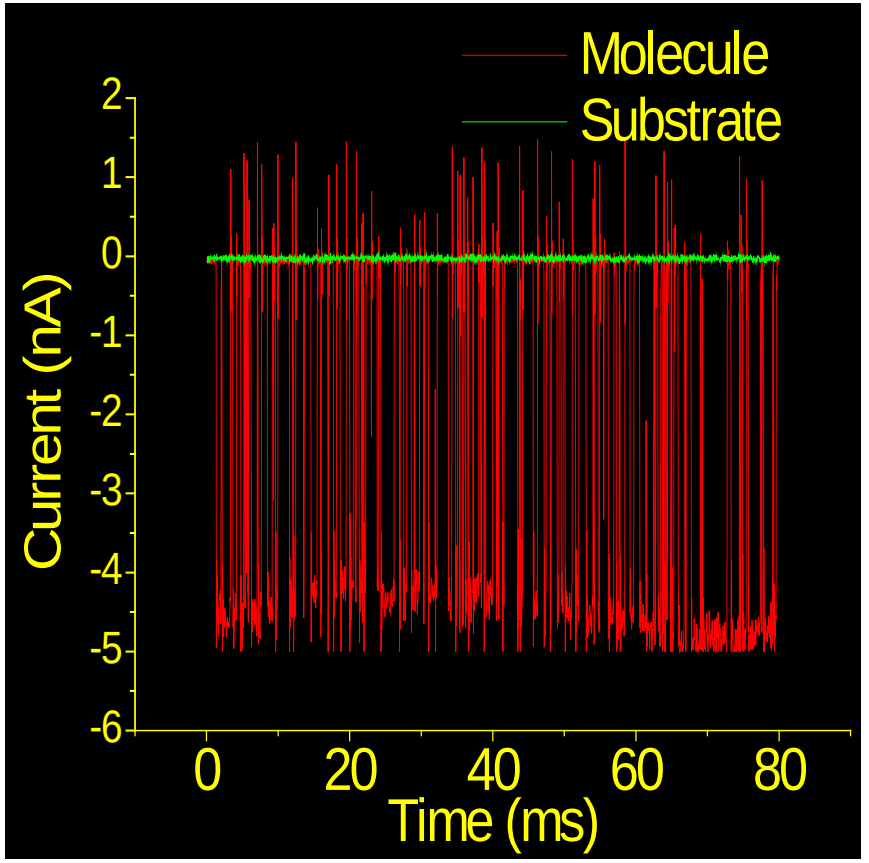
- Impurities should have higher evaporating temperature due to complex structure.
  - Not like impurity
- Patterns are only seen under LN_2, but not under LHe.
  - Not like impurities, nor molecular aggregation.



- I-t spectroscopy shows that they are moving all the time!

Tunneling Current Oscillation

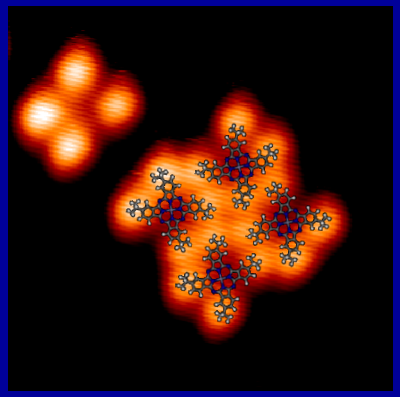


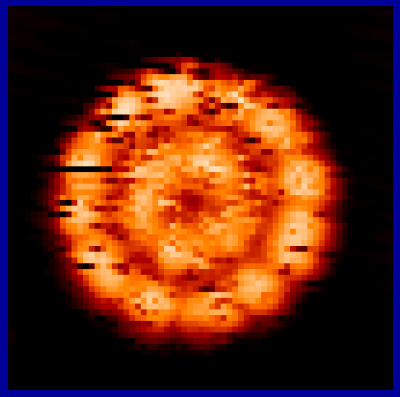


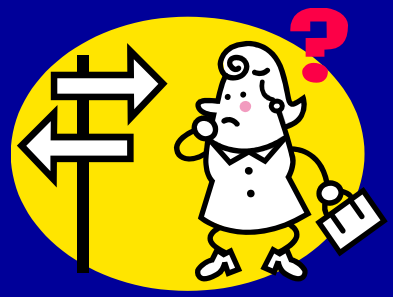
- Single Site *I-t* Measurement (-1.8 V)
- Current Oscillation between 0 and 5 nA
- Molecular Motion

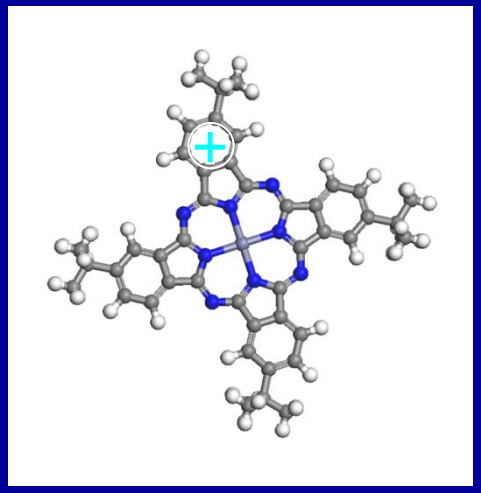
More Decisive Evidence

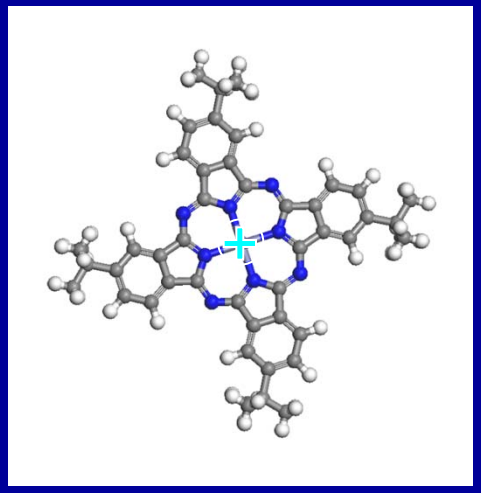
Conjectures

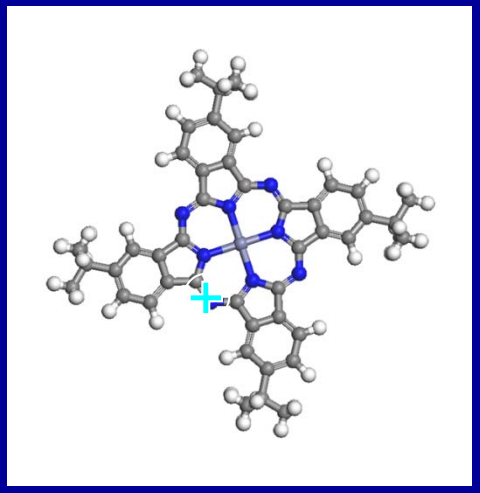




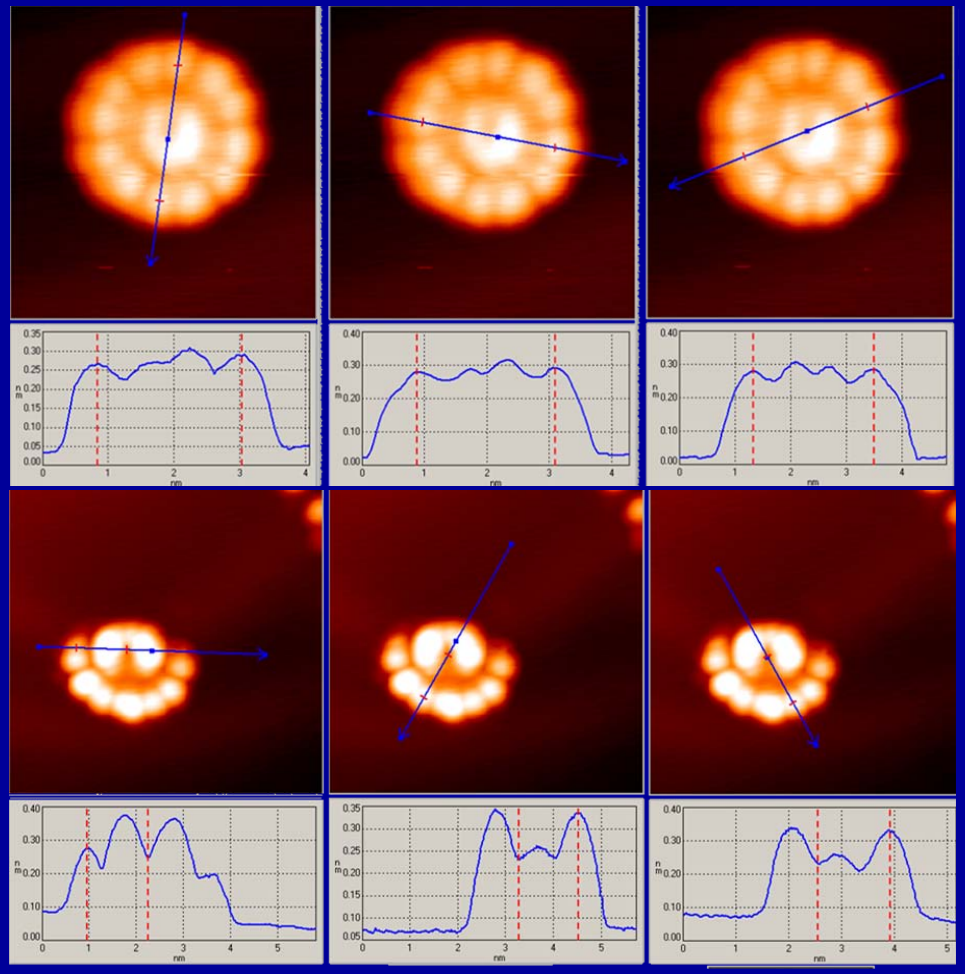




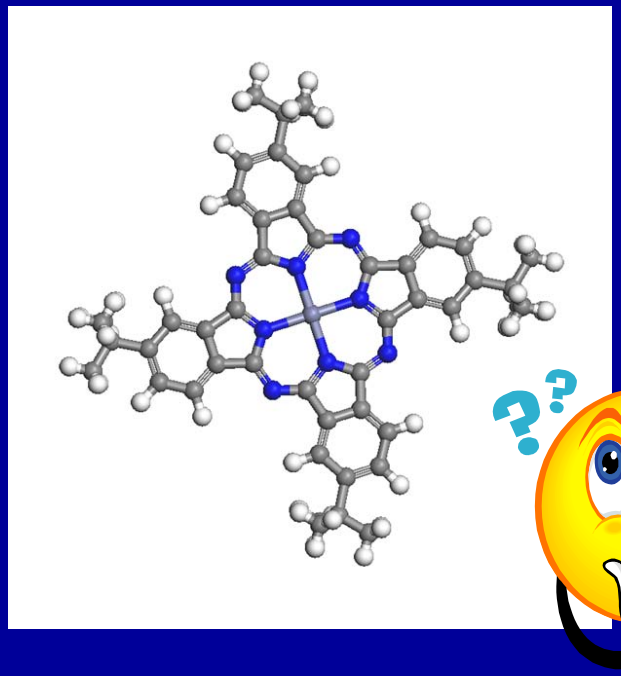




Rotating Center

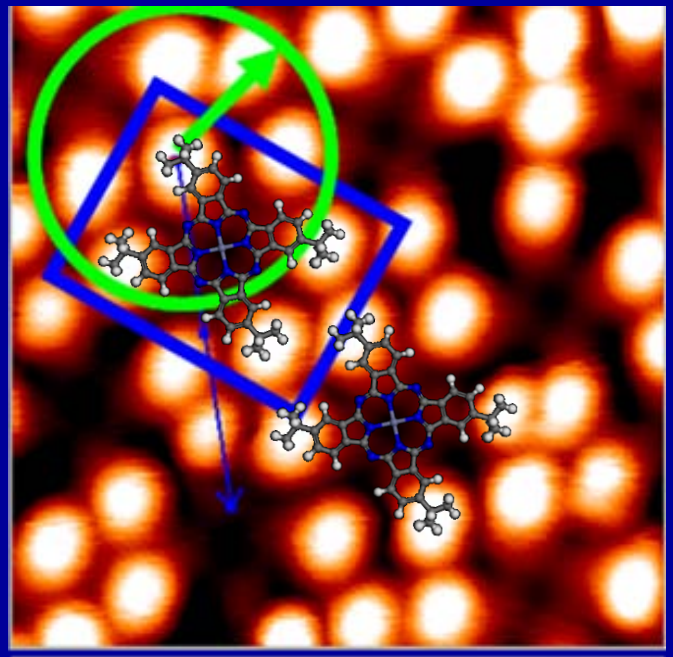


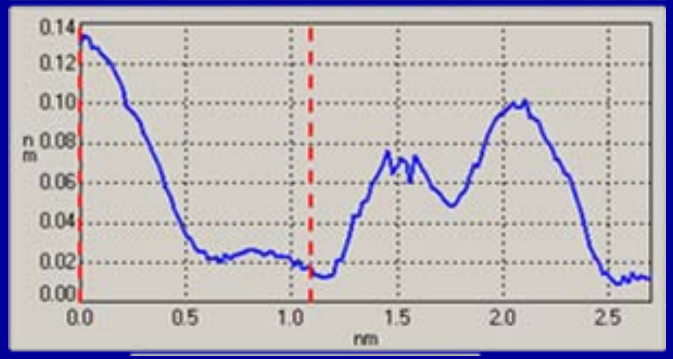
Average R=D/2 ~ 1.1nm

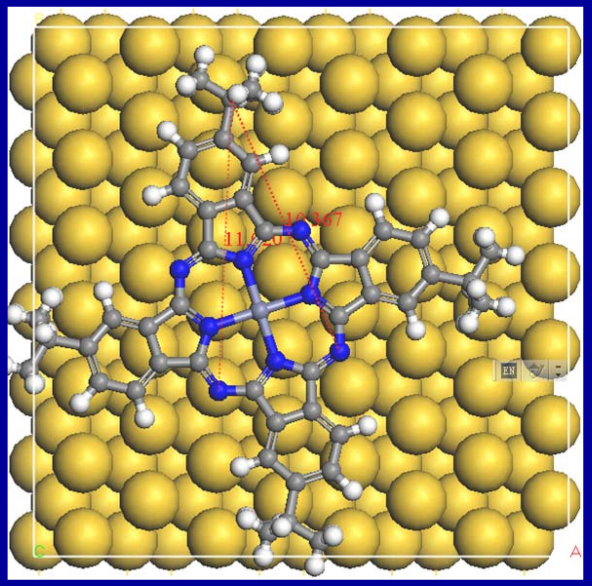


Average R ~ 1.2nm

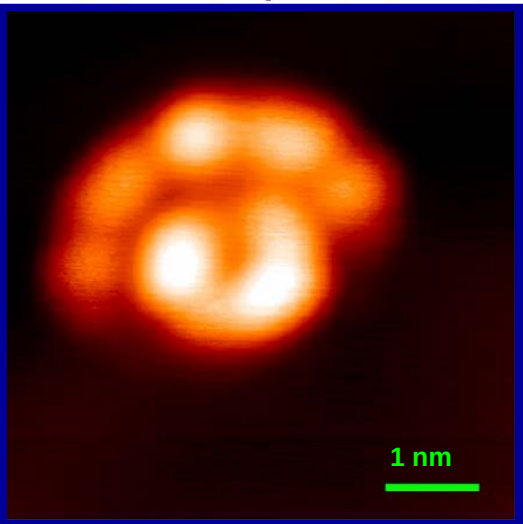
Rotating Center

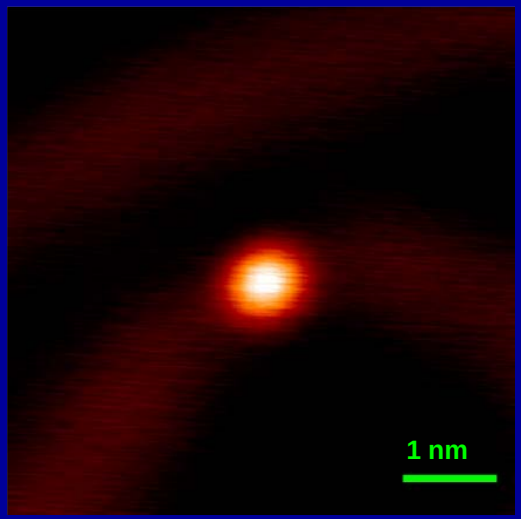




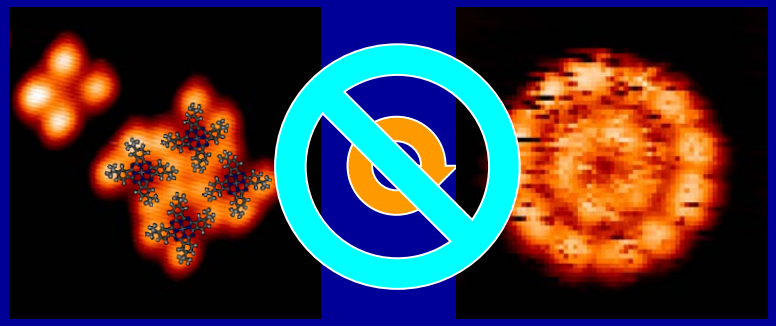


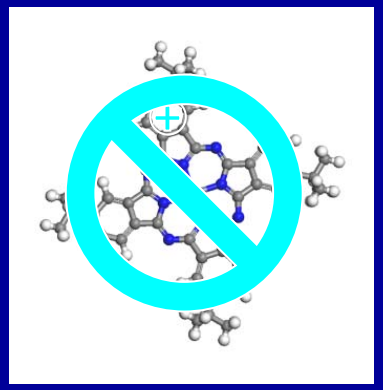
There are 4 N atoms!

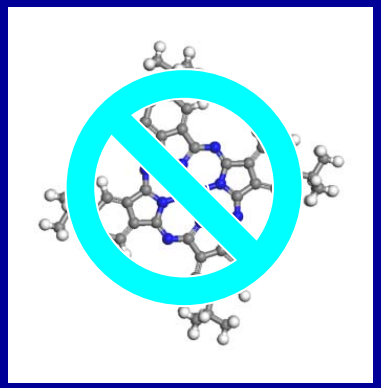


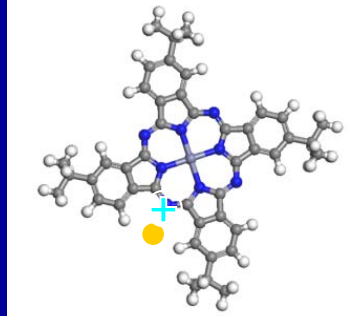


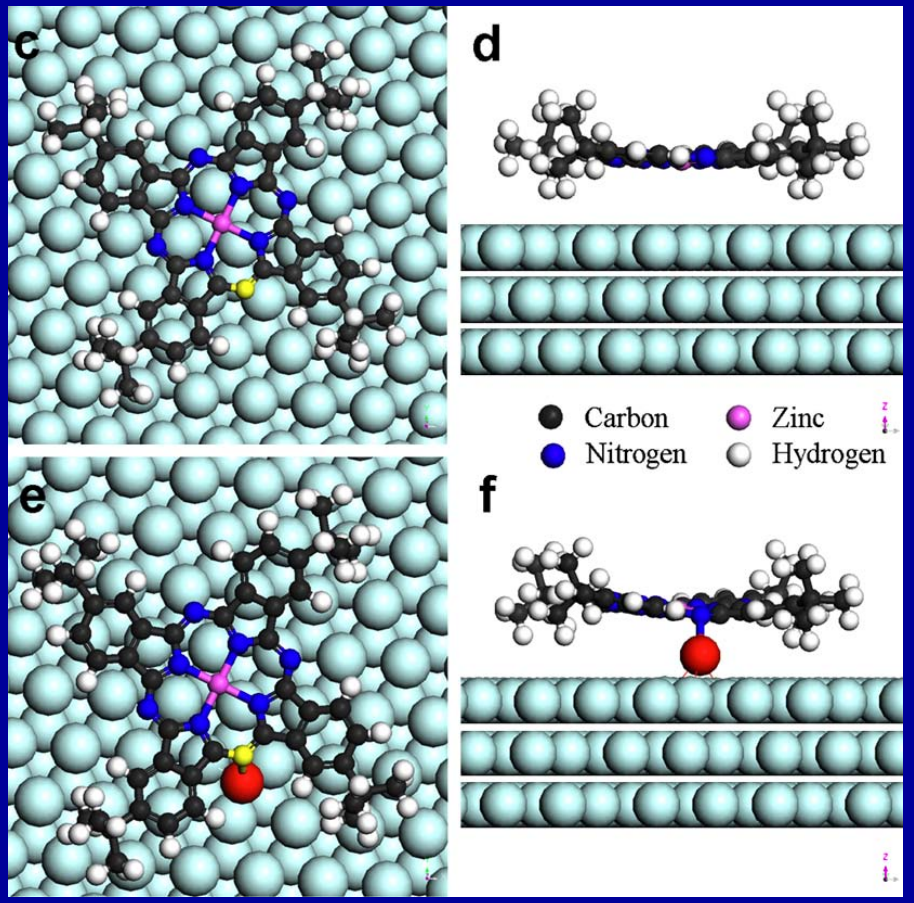
Formation Mechanism





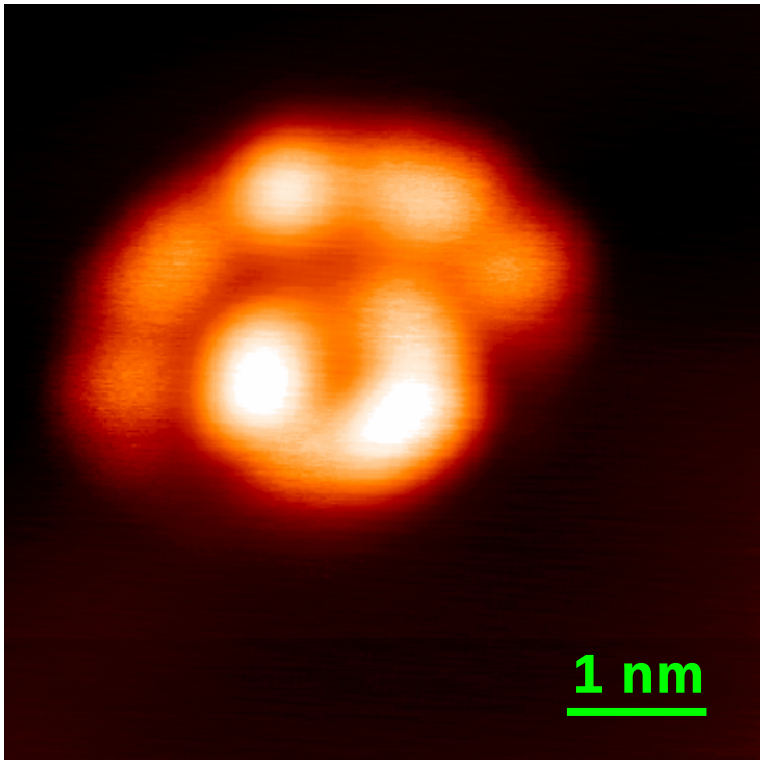


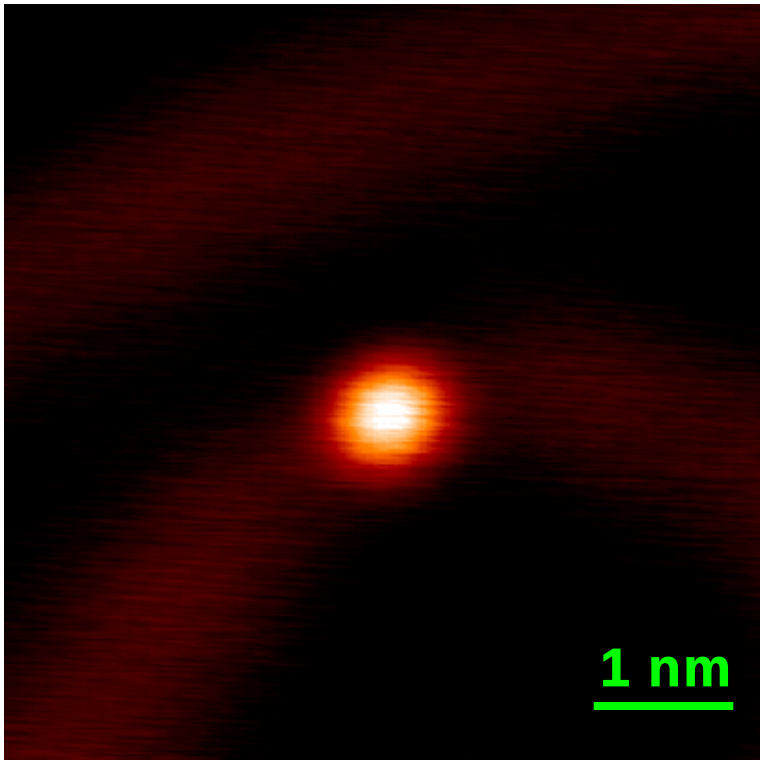




The Underlying Au Adatom

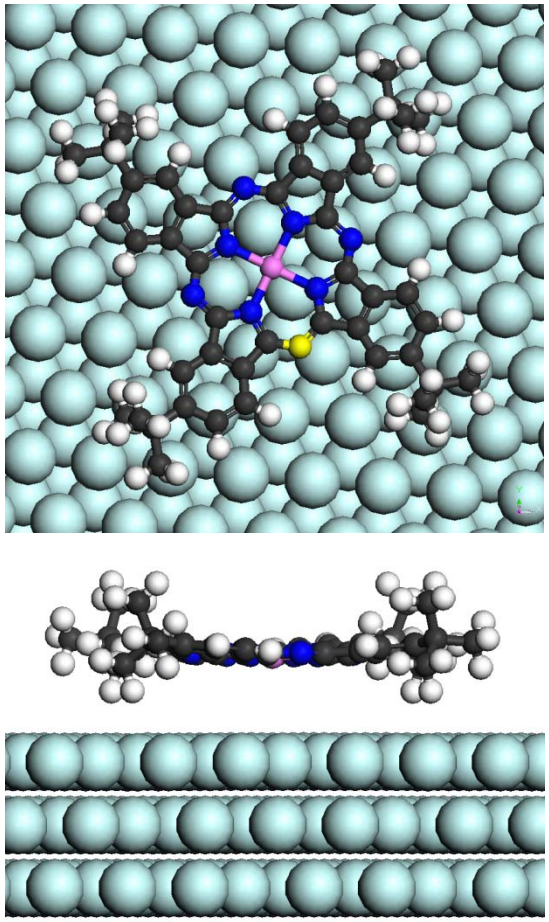
- Bright Spots Left After Removing Molecules
- Center Position of Molecular Rotor
- Gold Adatoms



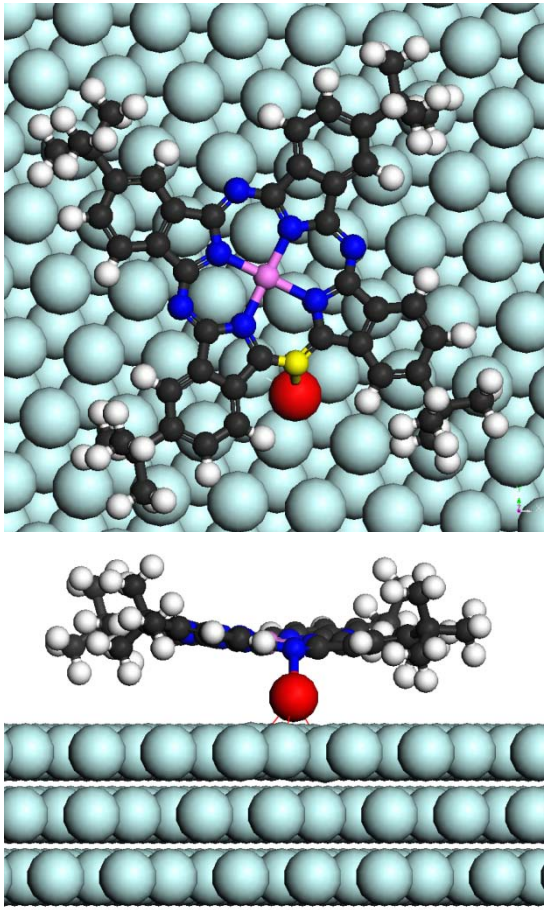


Role of Gold Adatom in Adsorption

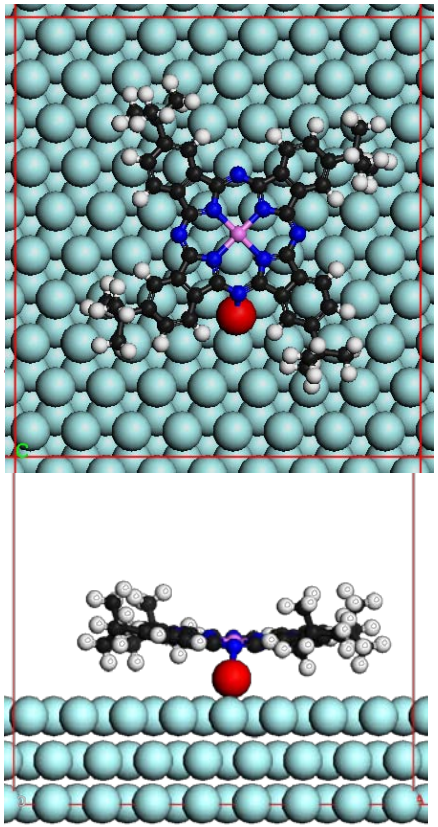
E_{ad} = 219 meV



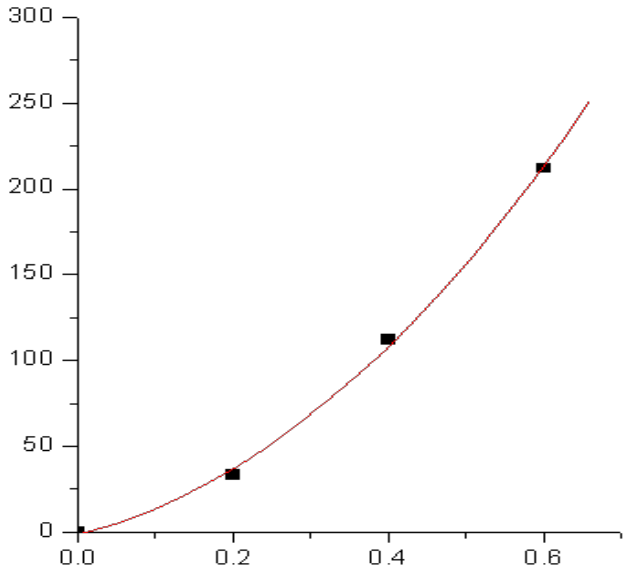
E_{ad} = 804 meV



Lateral Translation Energy of the Molecule: Adsorption and Rotation around Au Adatom



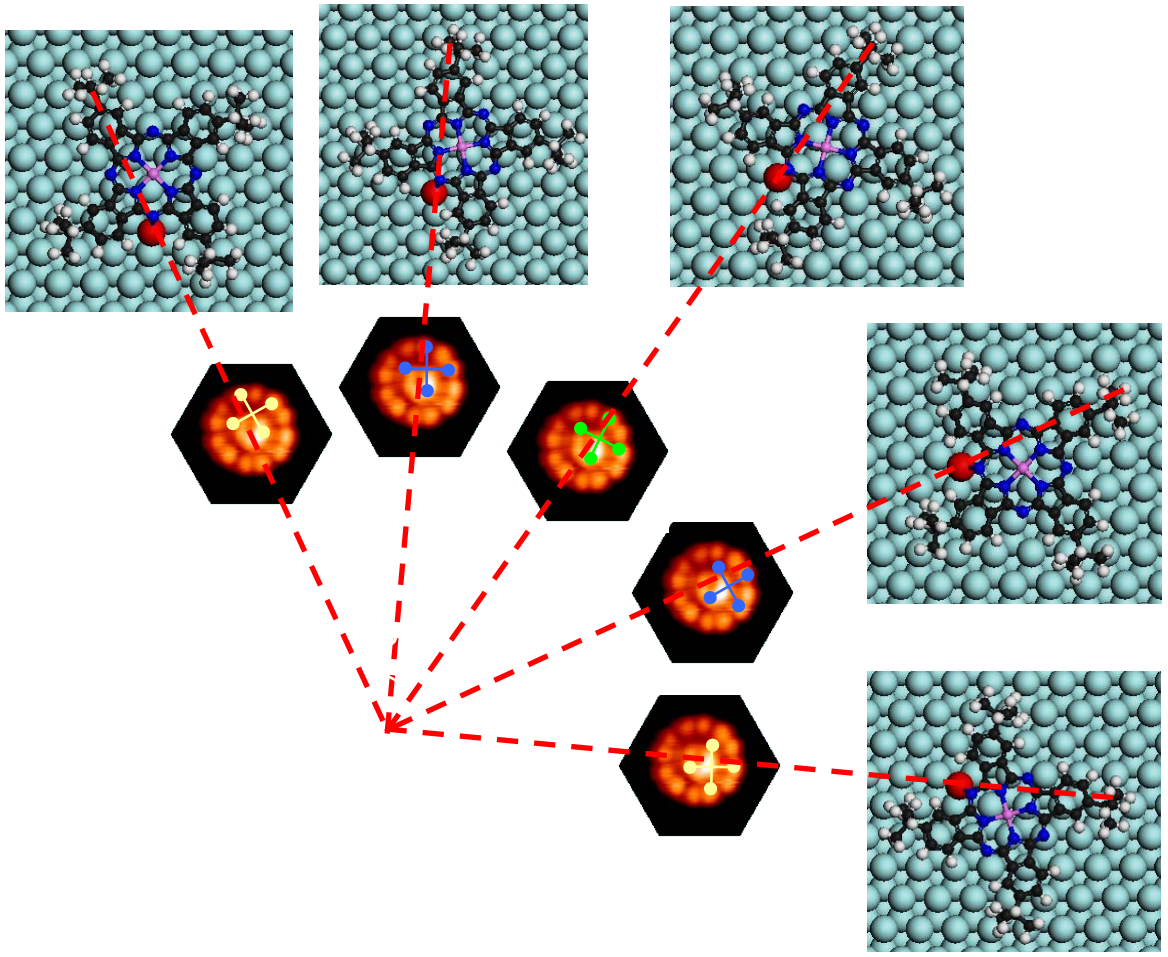
Lateral Translation

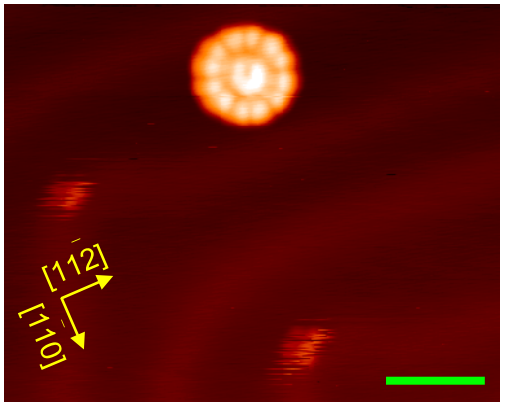


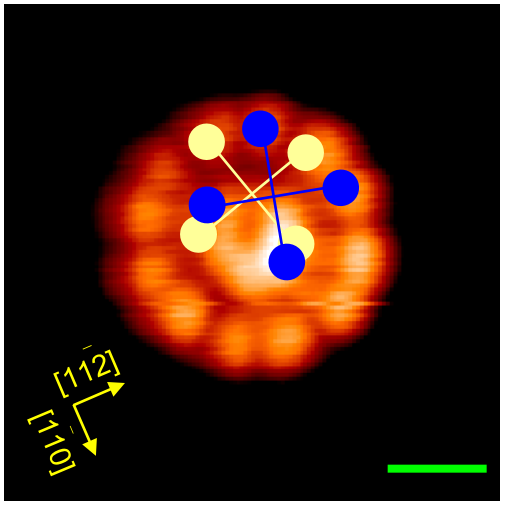
The diffusion barrier along different directions is still high (30°)

L. Gao/ H.-J. Gao et al. Phys. Rev. Lett. 101, 197209(2008)

Ab Initio Calculations of Meta-stable Configurations and Comparison with Experimental Observations

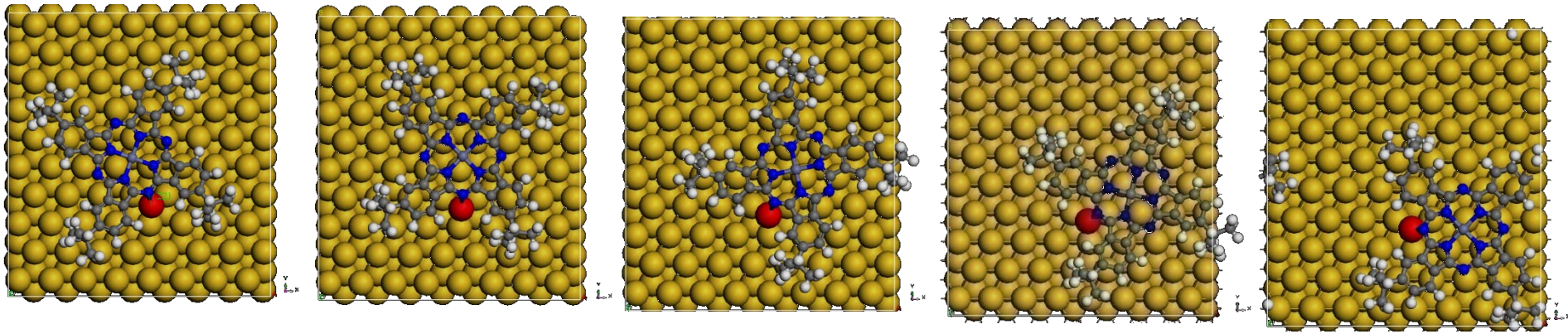






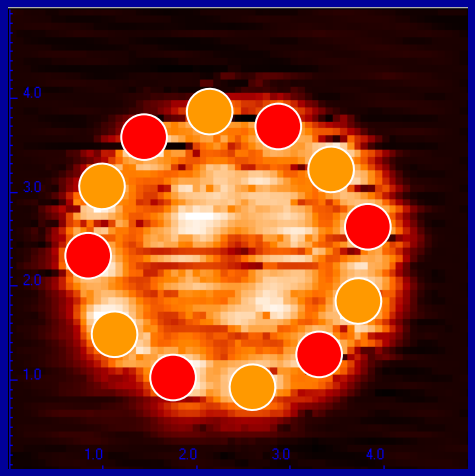
- 12 stable adsorption sites with 30° distance
- Switching between them with high frequency

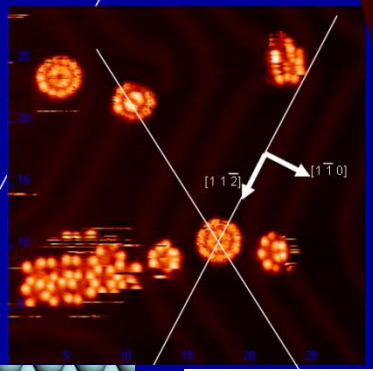
Energy Barriers between Molecular Configurations of Rotation around Au Adatom

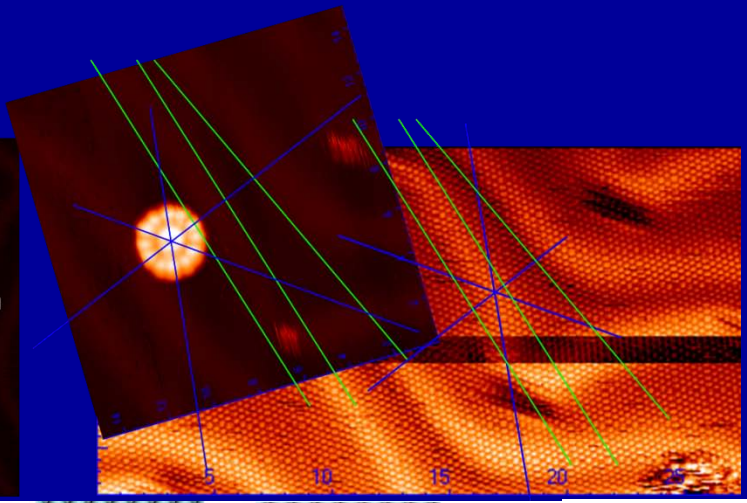


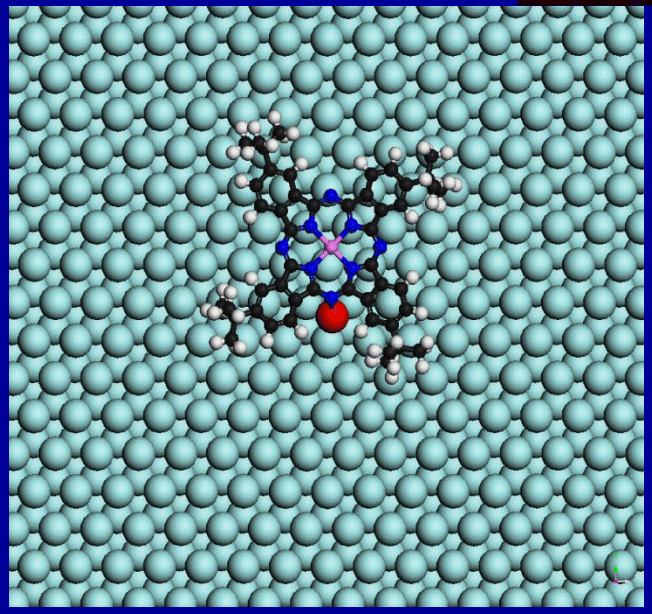
-16meV 9 meV -22 meV 18 meV

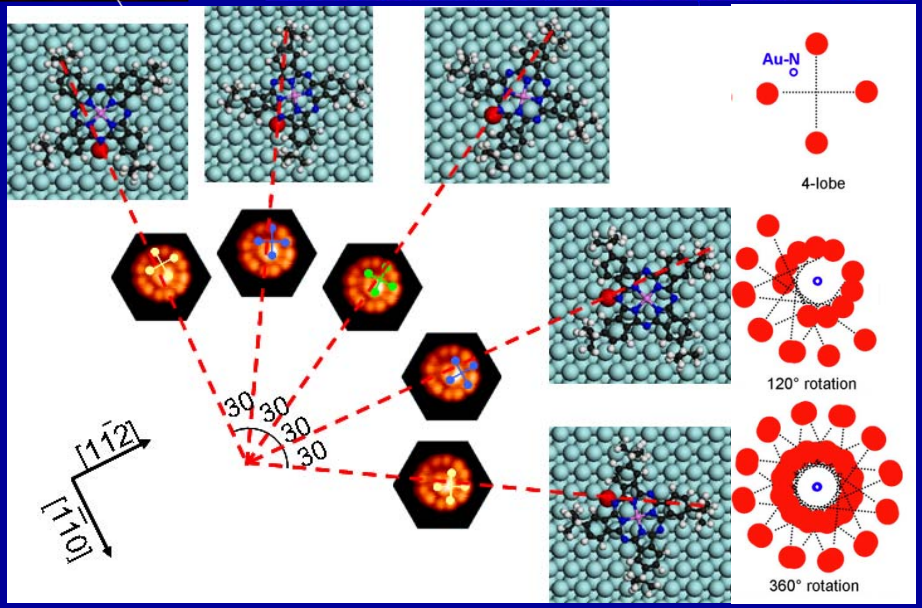
Rotating of a Single Molecule Anchored at an Adatom on Au(111)



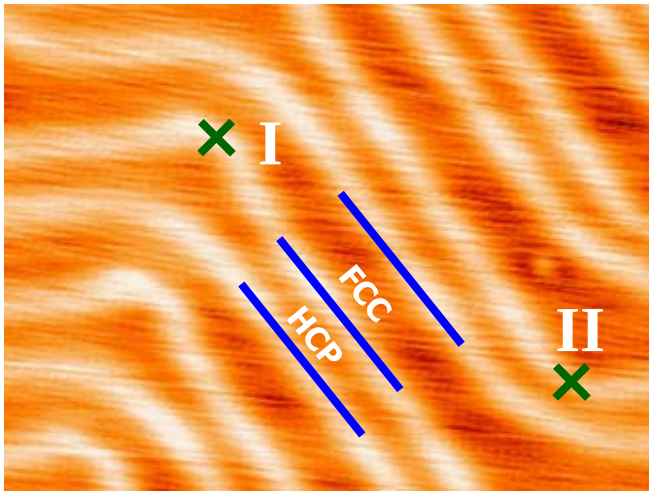


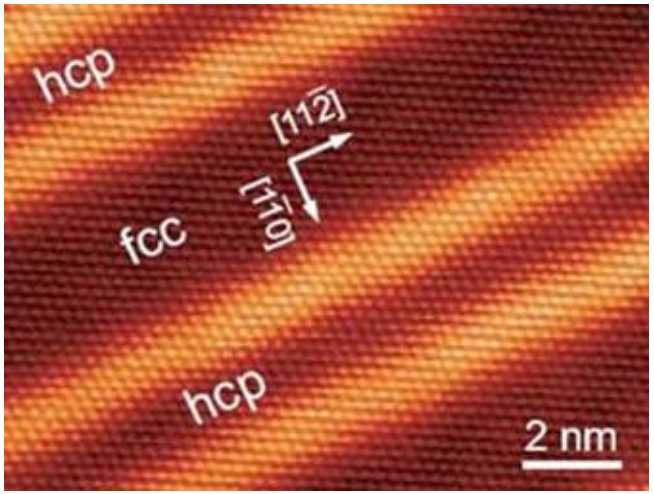


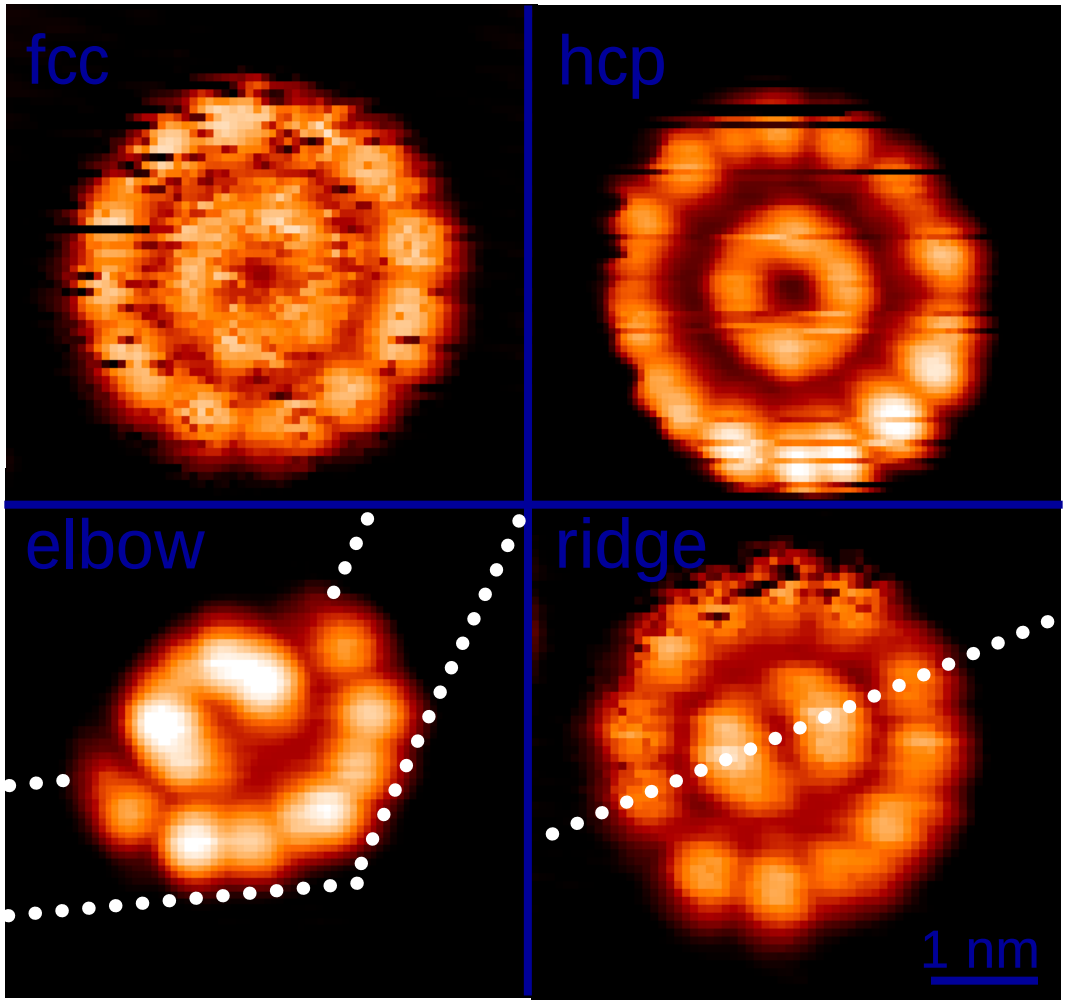




Rotors at Different Locations



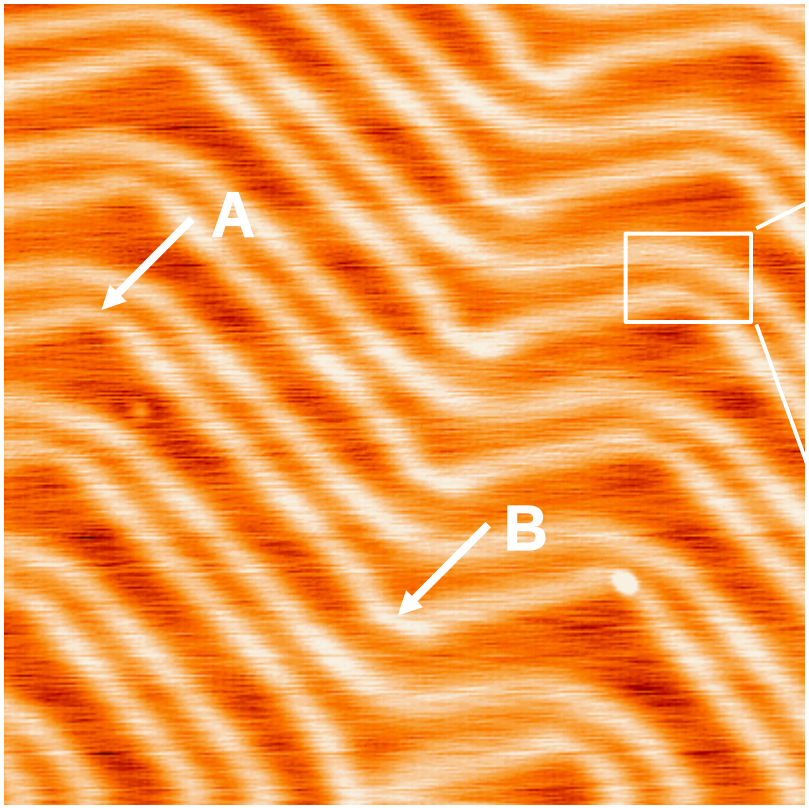


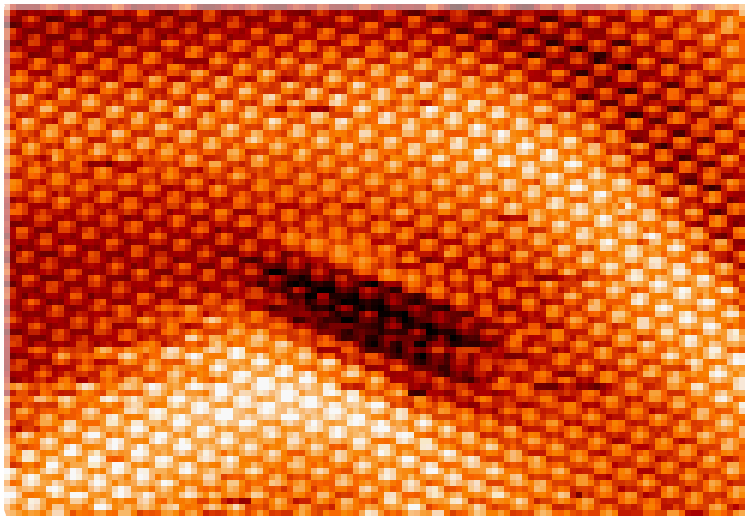


Question: What is the physical origin of these flower-shaped and folding-fan features ?

Origin of Au Adatoms

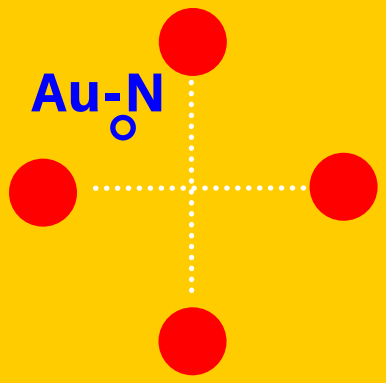
- **The herringbone reconstruction provides reactive Au adatoms**
- **The dislocations at the elbow sites are the likely sources.**



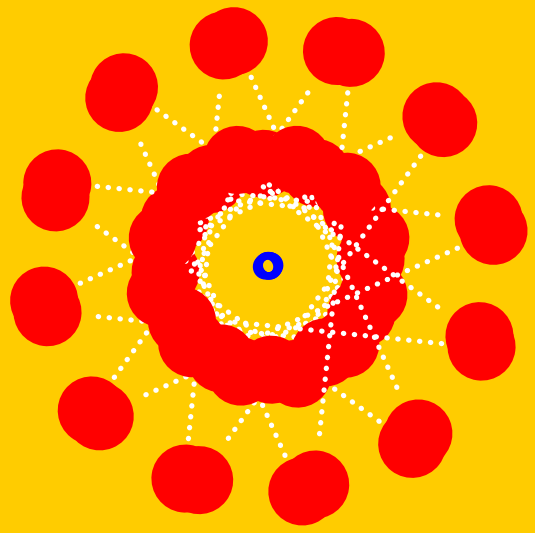


Molecular Rotation in FCC Region

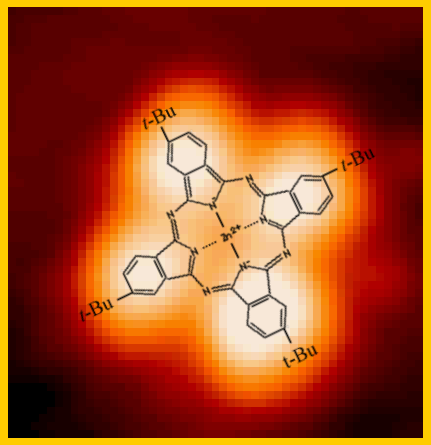
- **In most of the cases, 12 sites, step 30°**

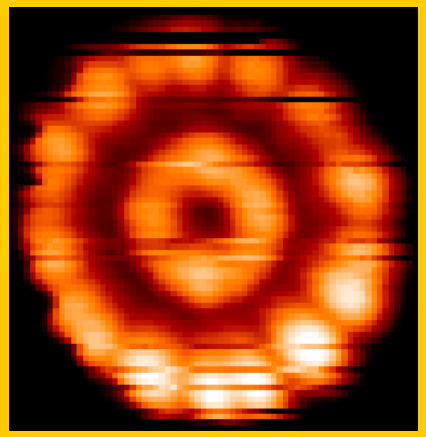


4-lobe



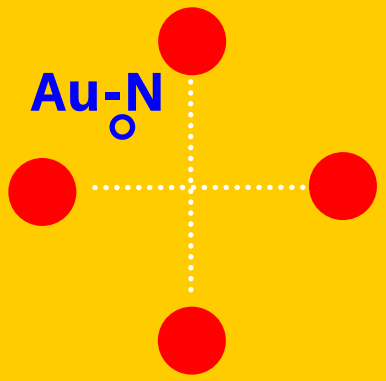
360° rotation

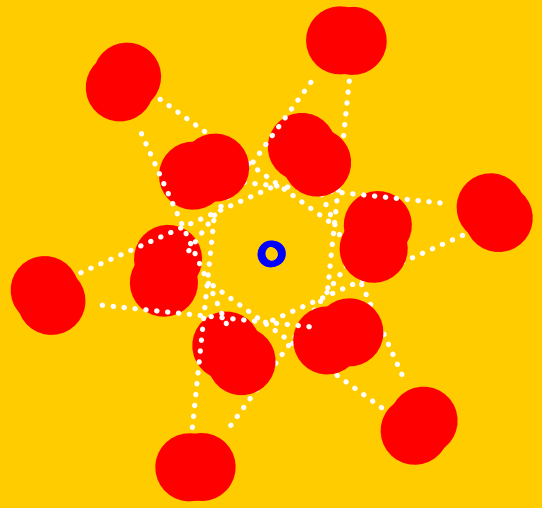


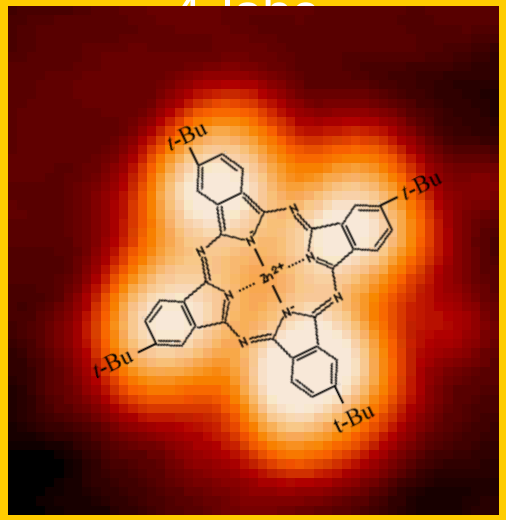


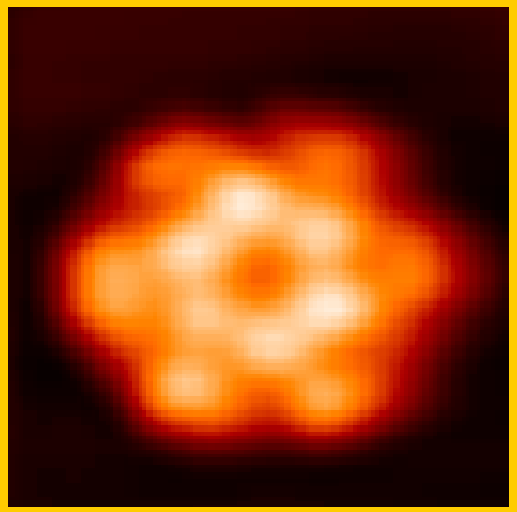
Molecular Rotation in FCC Region

- **In few cases, 6 sites, step 60°**



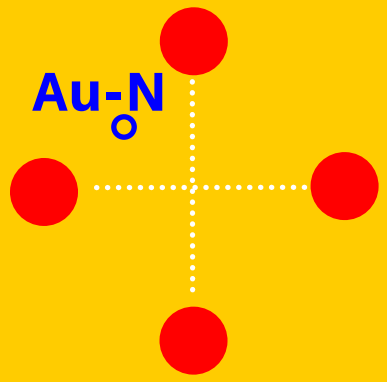




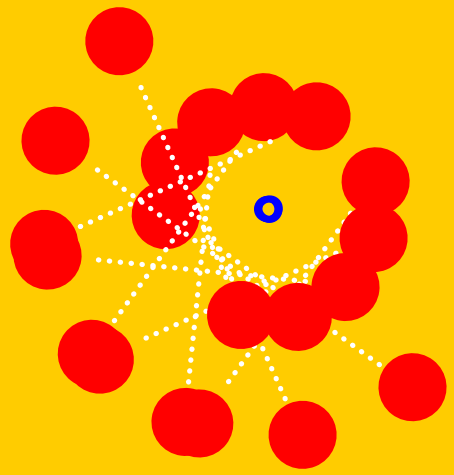


Molecular Rotation at the Elbow Sites

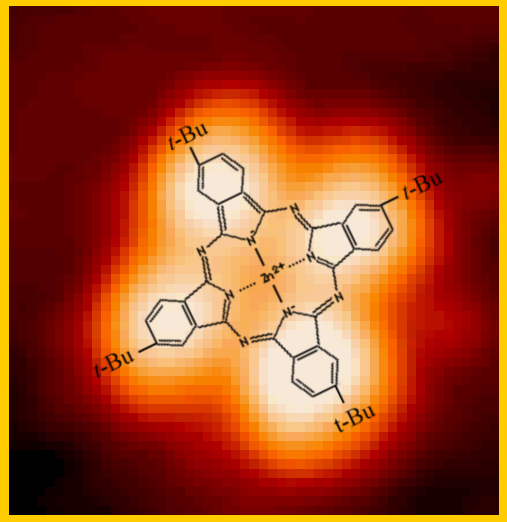
- **In most of the cases, 5 sites, step 30°**

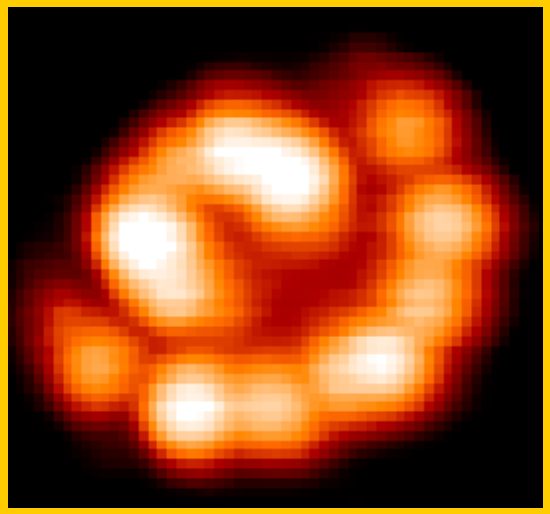


4-lobe



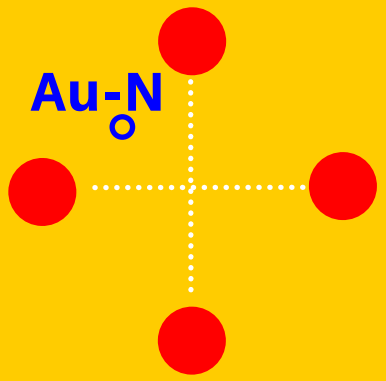
120° rotation



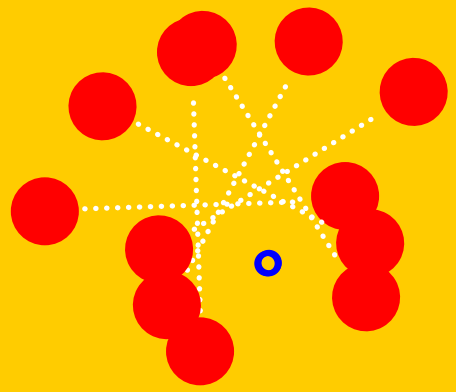


Molecular Rotation at the Elbow Sites

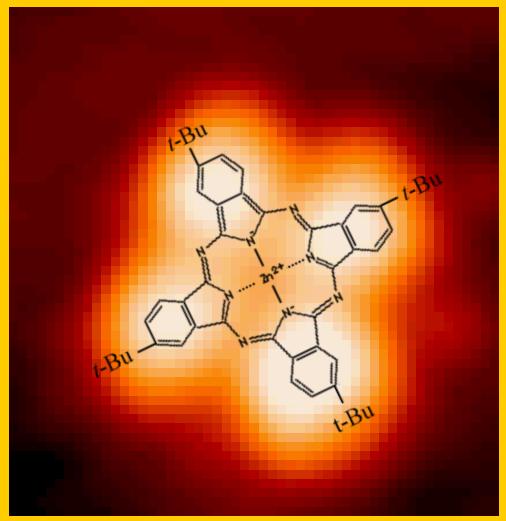
- **In few cases, 3 sites, step 30°**

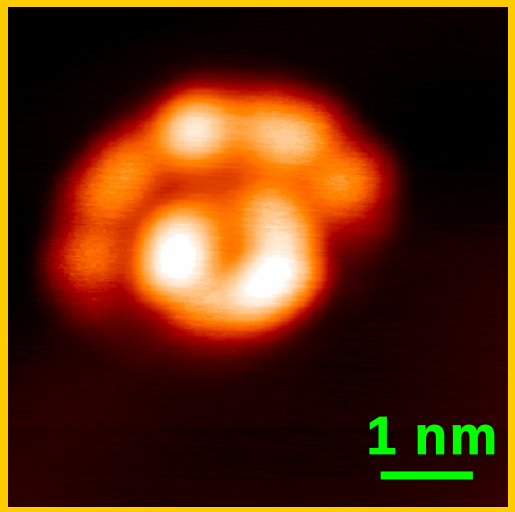


4-lobe



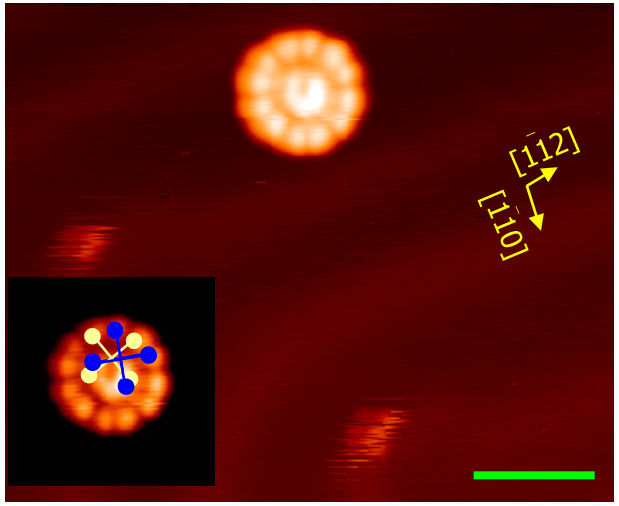
60° rotation

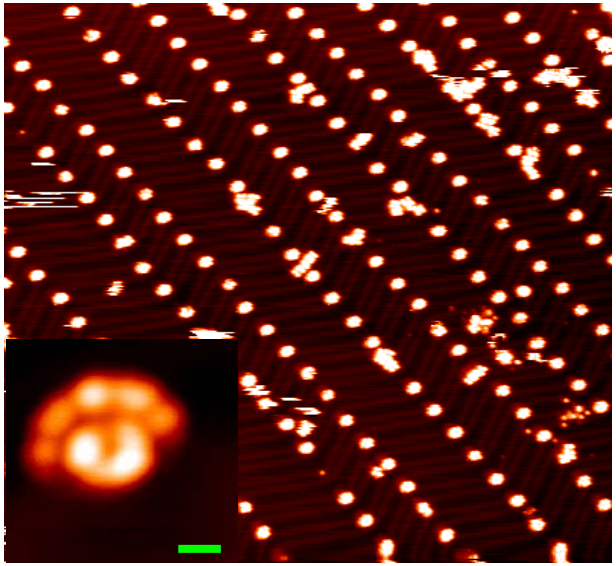


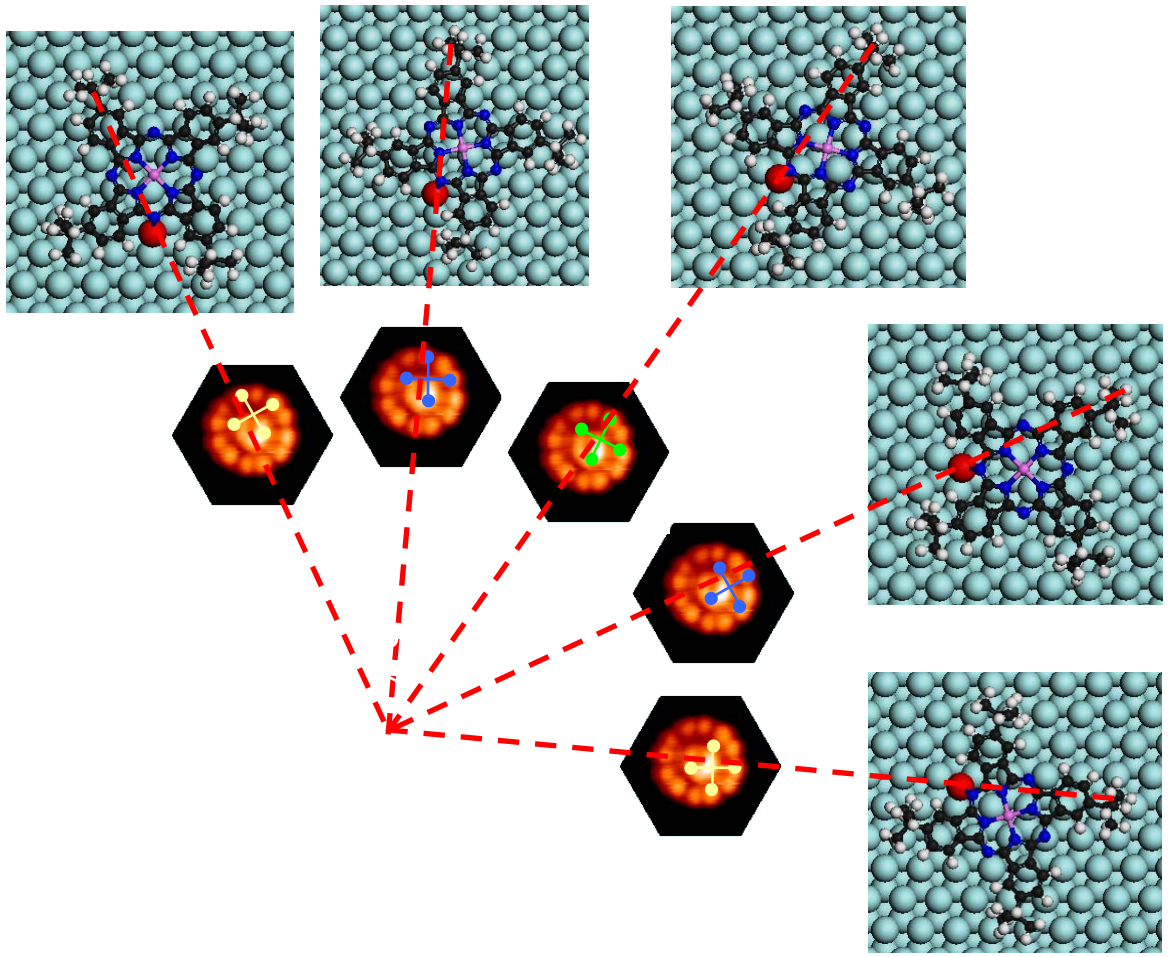


Conclusions and Outlook

Constructing Anchored Single Molecular Rotor Array



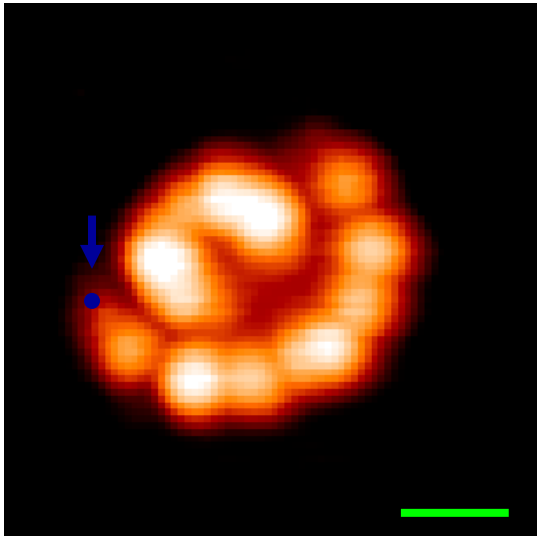


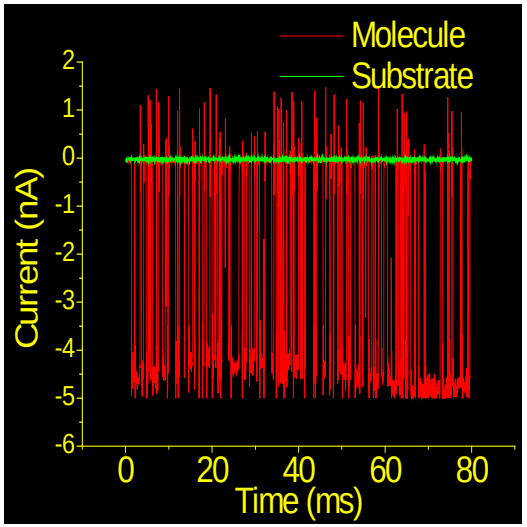


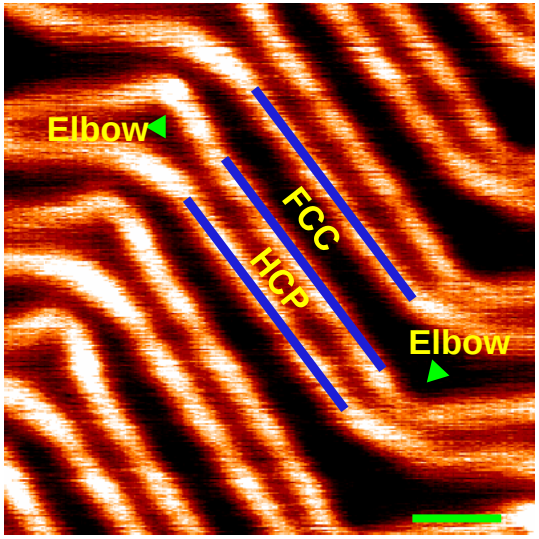
Meta-stable configurations

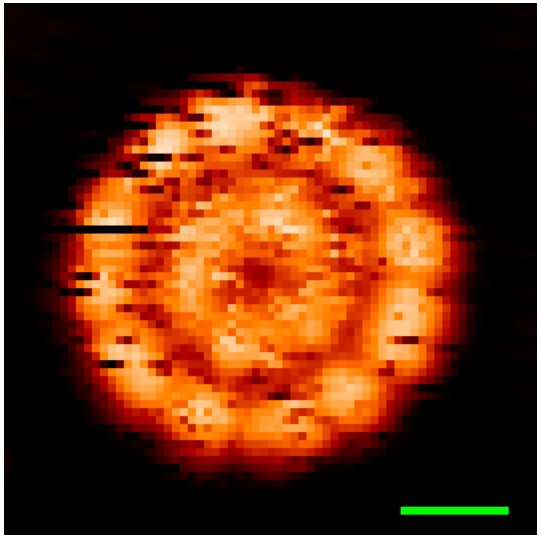
Conclusions and Outlook

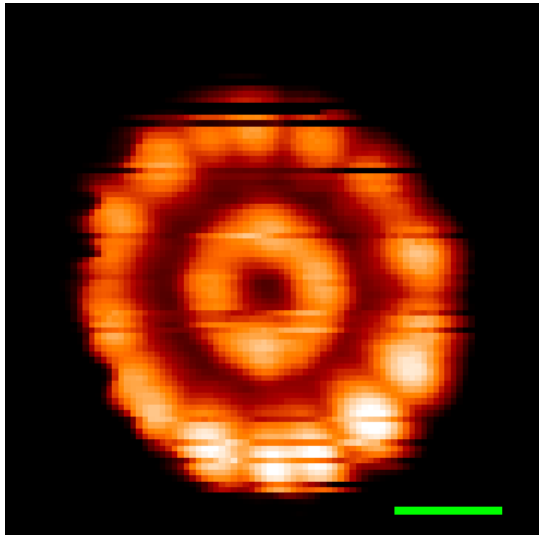
Different Rotation Behavior at Different Sites of Au(111)

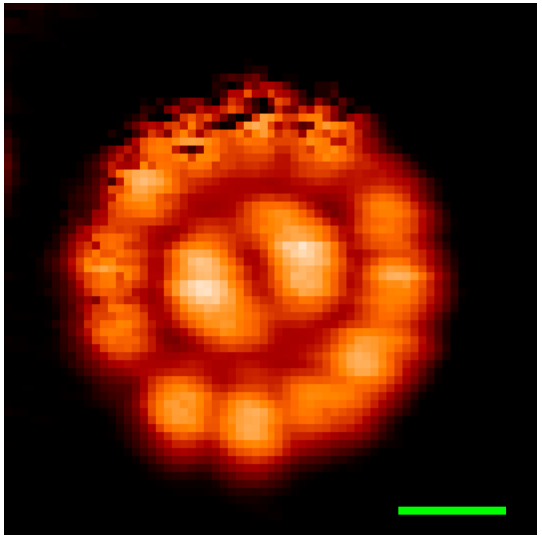




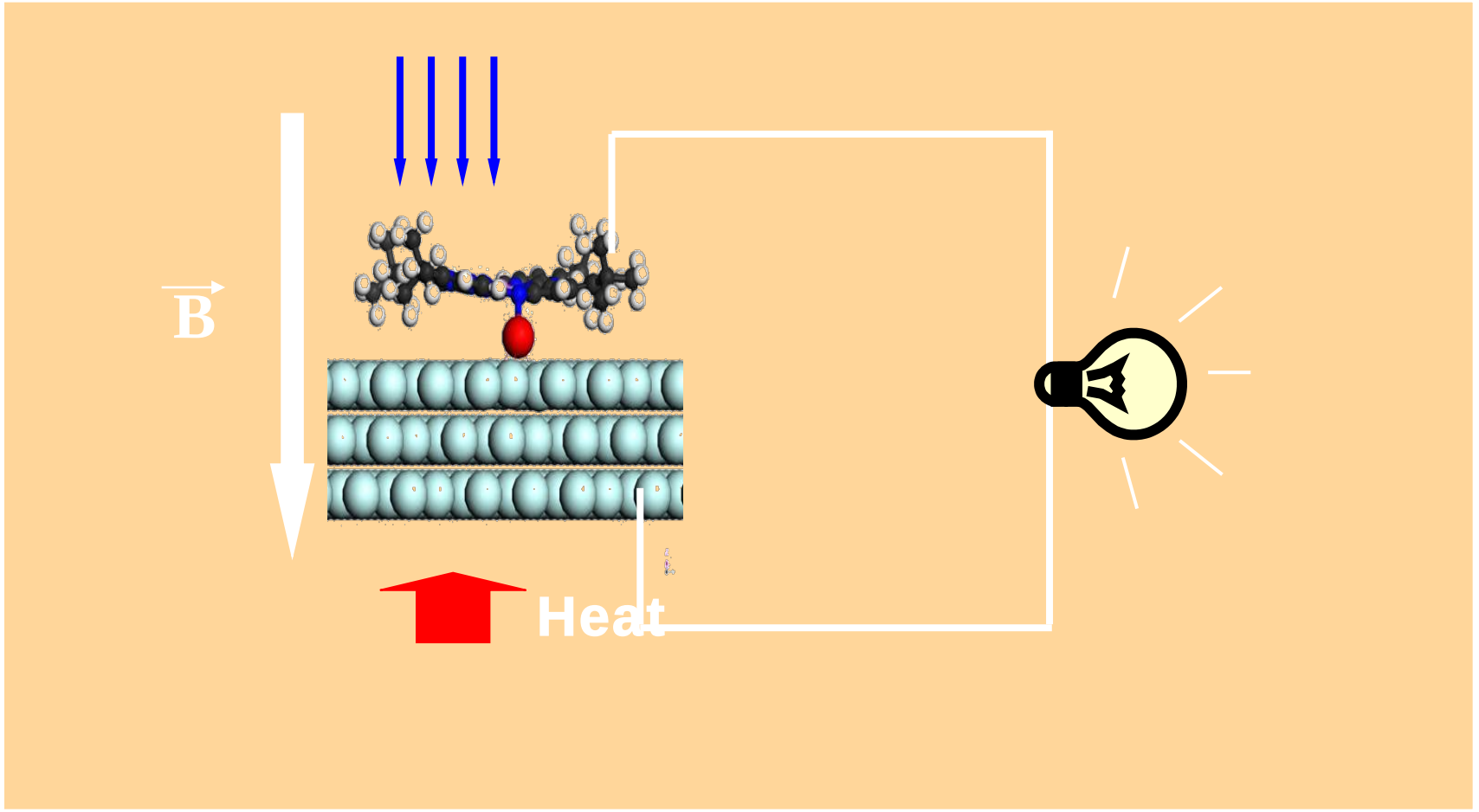






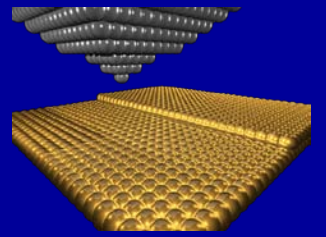


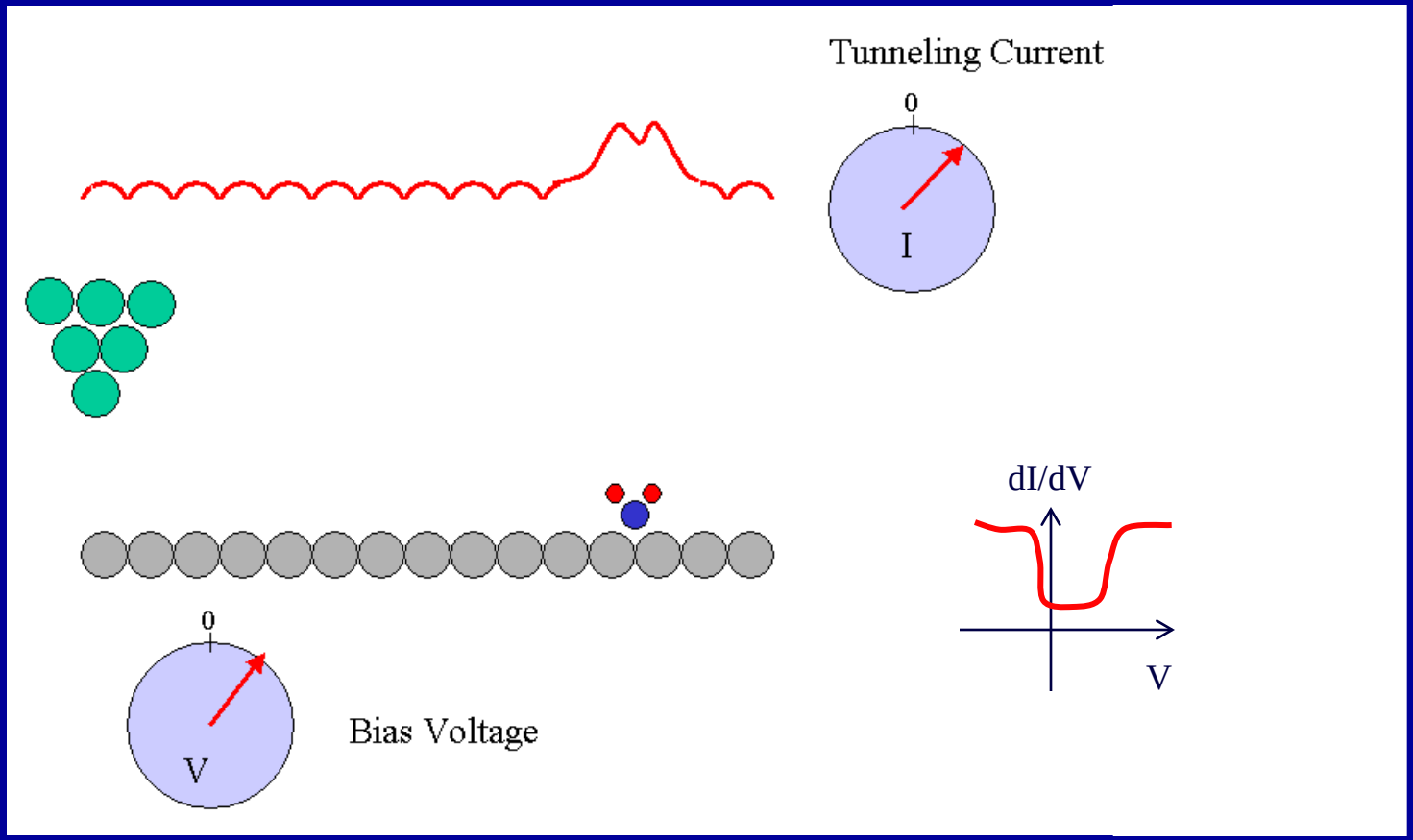
Electricity Generator of a single molecule



Site-specific Kondo Effect at Ambient Temperatures in PcFe Molecules

Scanning Tunneling Spectroscopy

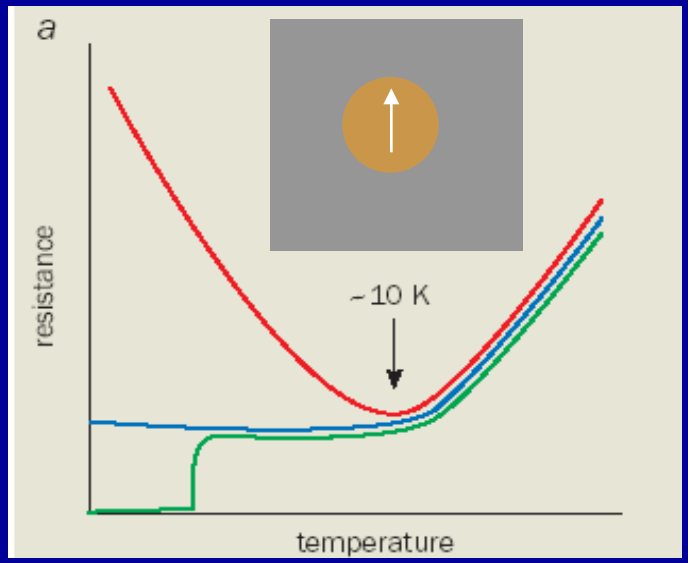




Differential Conductance (dI/dV) ~ LDOS(r, E)

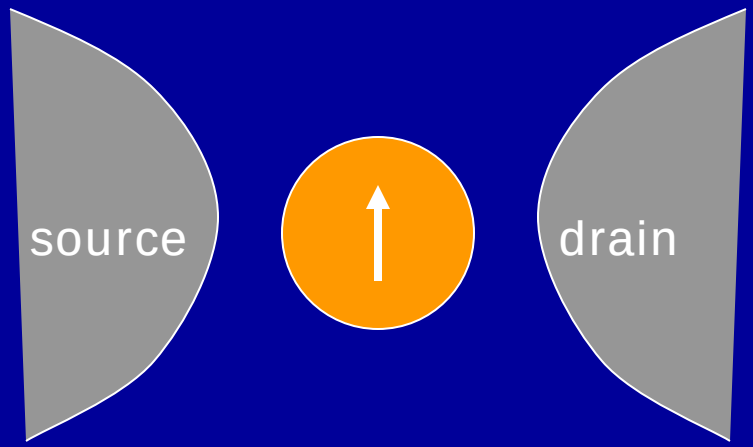
Kondo Physics

magnetic impurities in metals



low-T resistance minimum
anomalous χ, c, etc.
-> spin flip scattering

in quantum dots

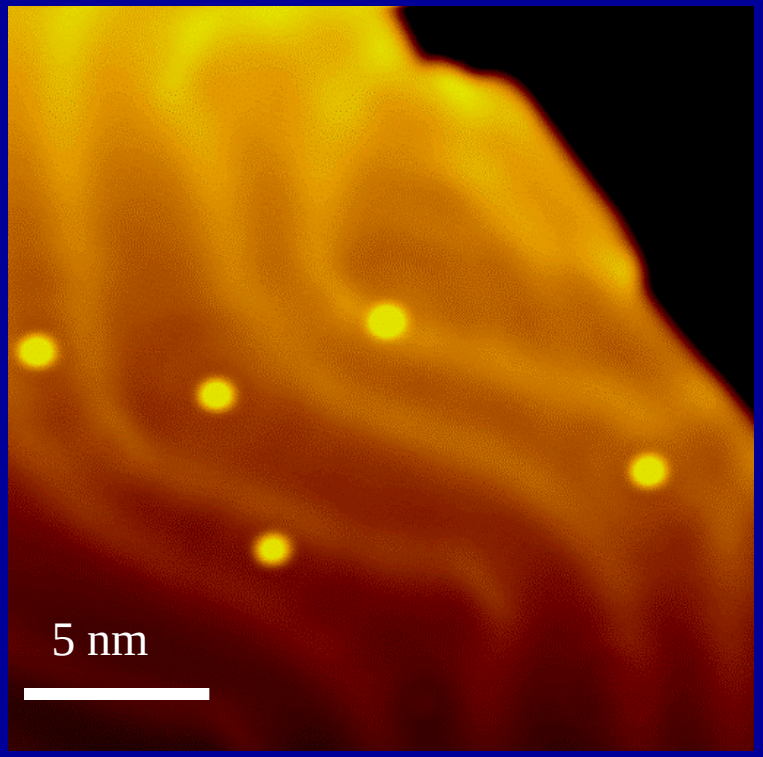


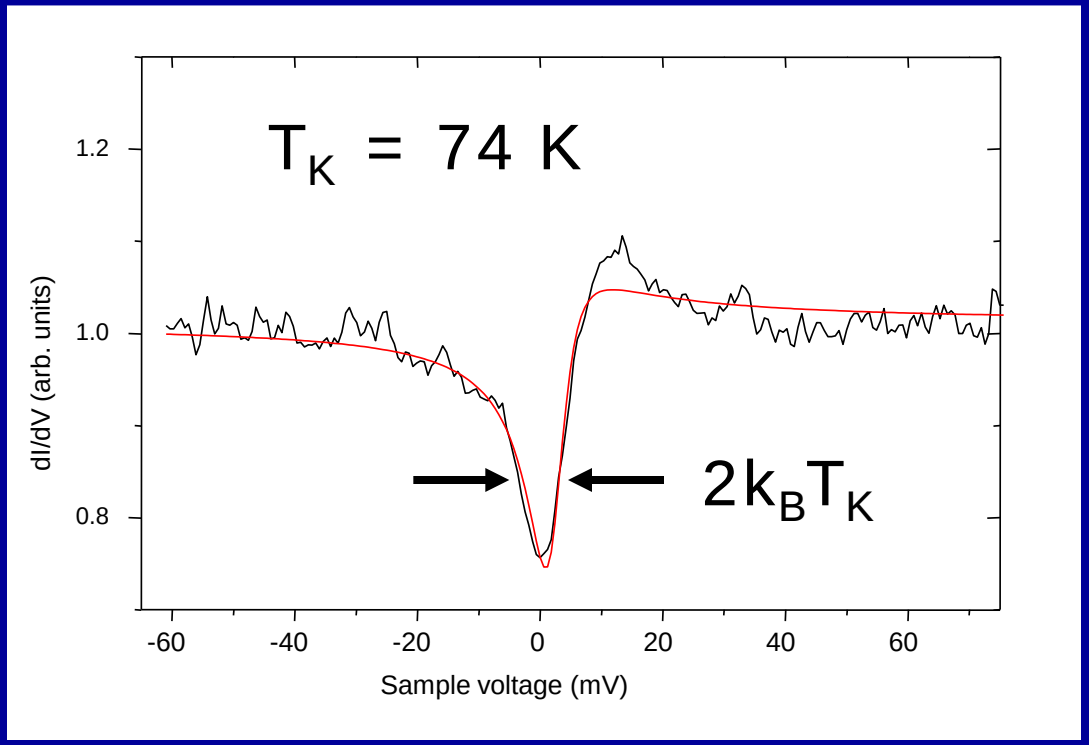
enhanced conductivity
at $V_{sd}=0$ for odd # electrons
on dot

„New“: at surfaces with STM: direct access

Single Magnetic Atom Spectra

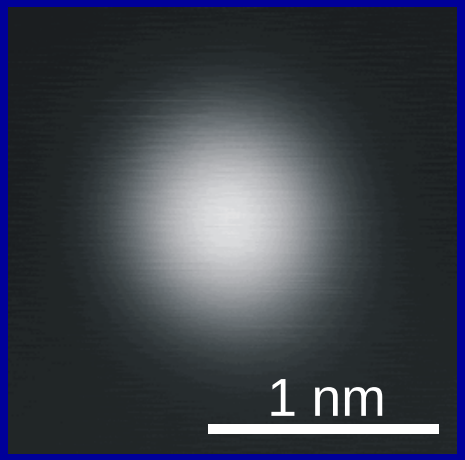
Co adatoms on Au(111)



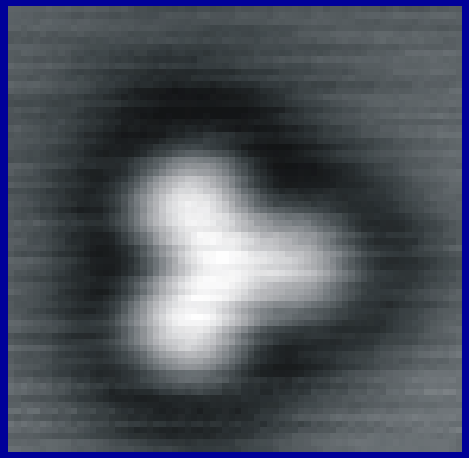


See also: V. Madhavan, et al., Science 280, 567 (1998)
V. Madhavan, et al., PRB 64, 165412 (2001)
J. Li et al., PRL 80, 2893 (1998) (Ce on Ag(111))

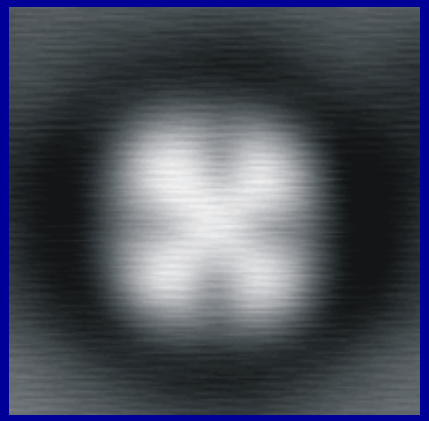
Cobalt - Carbonyls



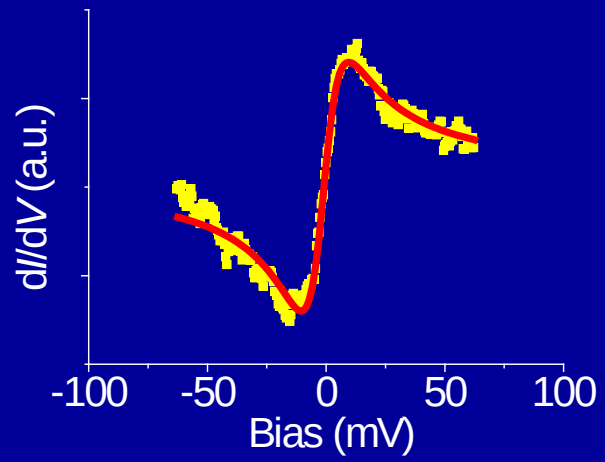
Co



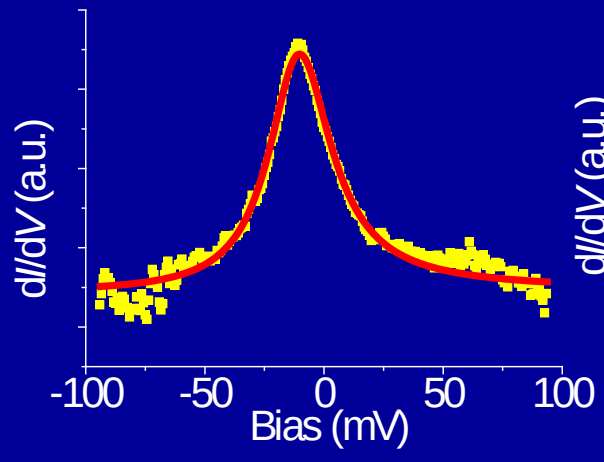
$Co(CO)_3$



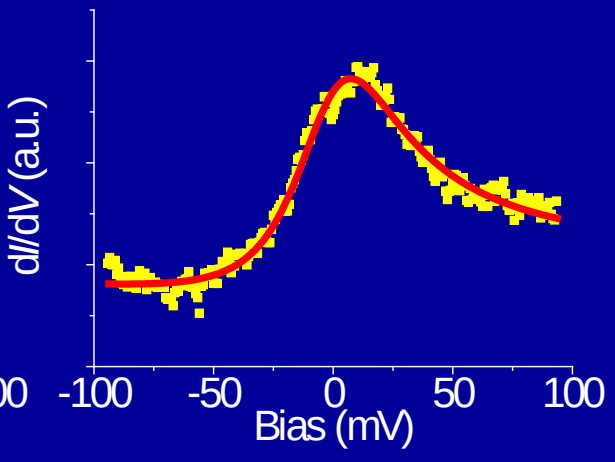
$Co(CO)_4$



$T_K = 88 \pm 4K$



$T_K = 166 \pm 16K$



$T_K = 283 \pm 36K$

P. Wahl, PhD Thesis, U Konstanz

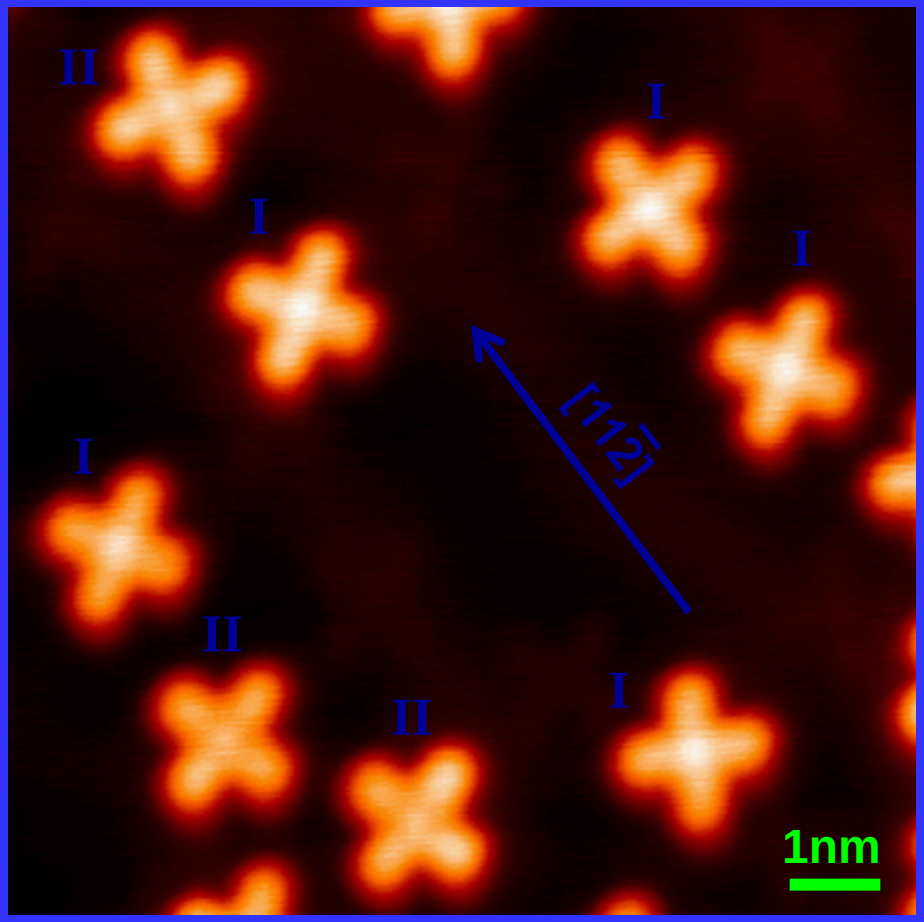
Controlling Kondo Effect

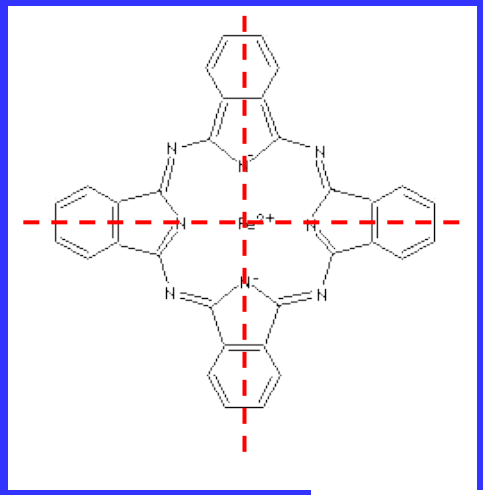
- Molecular structure of the magnetic impurities.
  - cut off ligands from impurities.
  - attach ligands to impurities.
- Changing the substrate properties.
  - different materials.
  - film thickness, Pb/Si(111).

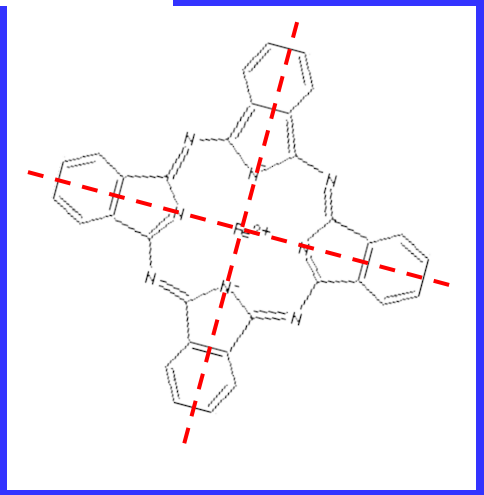
nondestructive and reversible control

A. Zhao *et al.*, *Science* **309**, 1542 (2005).
P. Wahl *et al.*, *Phys. Rev. Lett.* **95**, 166601 (2005).
V. Iancu *et al.*, *Nano Lett.* **6**, 820 (2006).
P. Wahl *et al.*, *Phys. Rev. Lett.* **98**, 056601 (2007).
Y. S. Fu *et al.*, *Phys. Rev. Lett.* **99**, 256601 (2007).

Two Molecular Orientations





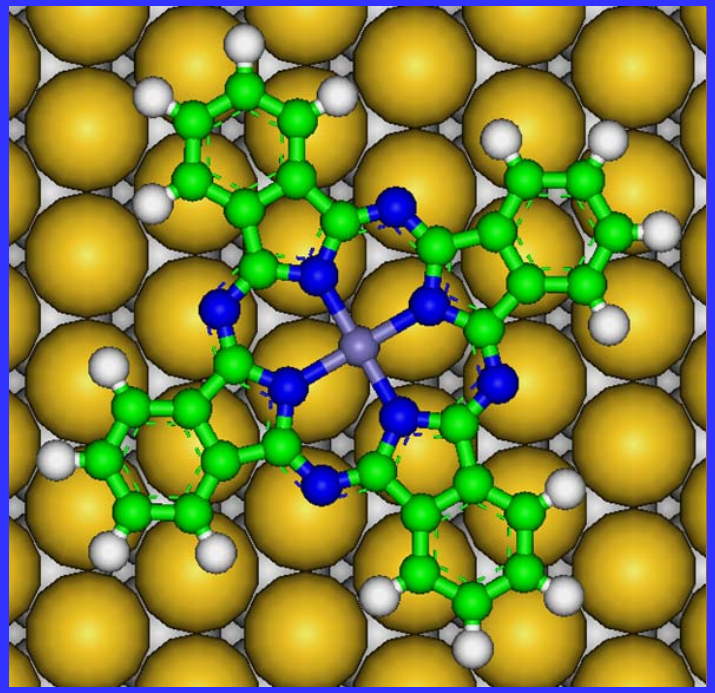


5 K

L. Gao *et al*. *Phys. Rev. Lett.* **99**, 106402 (2007).

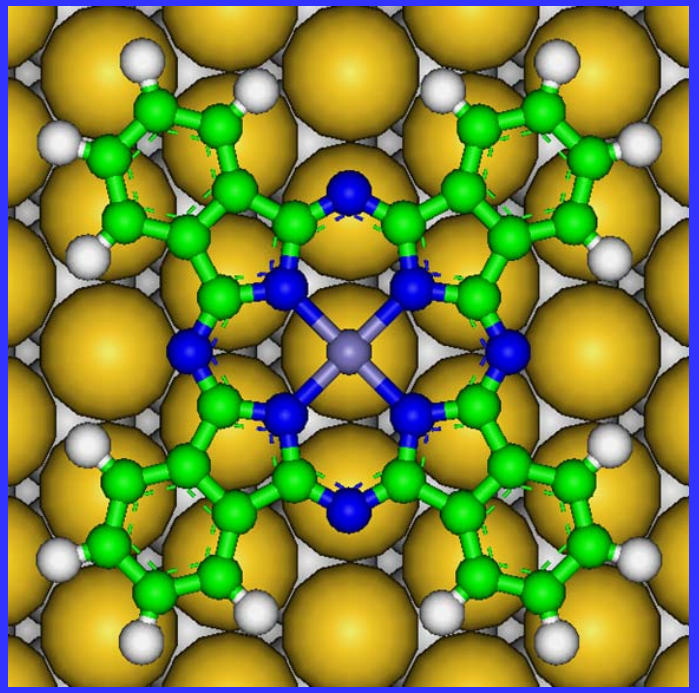
Isolated FePc Molecules on Au(111)

Orientation I



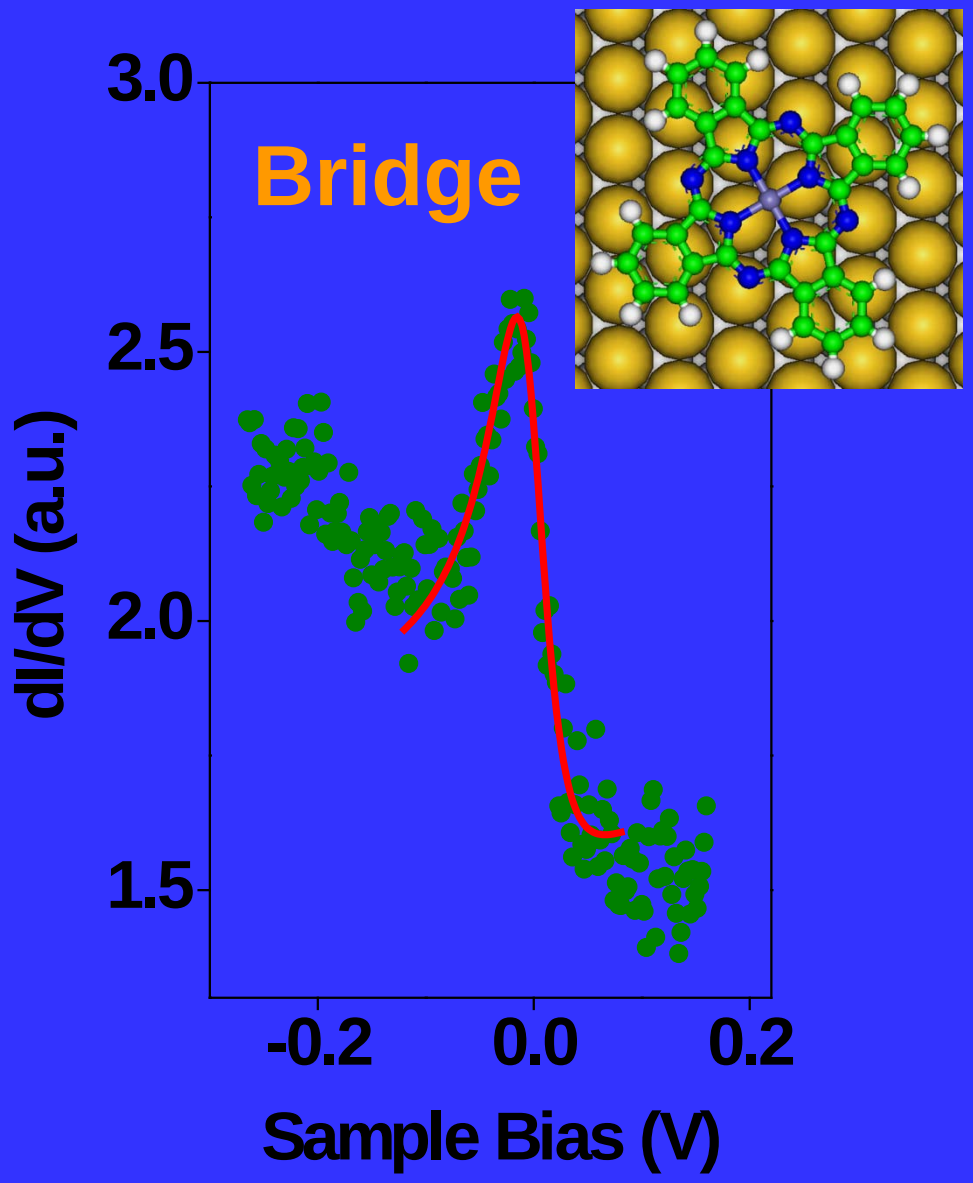
Bridge Site

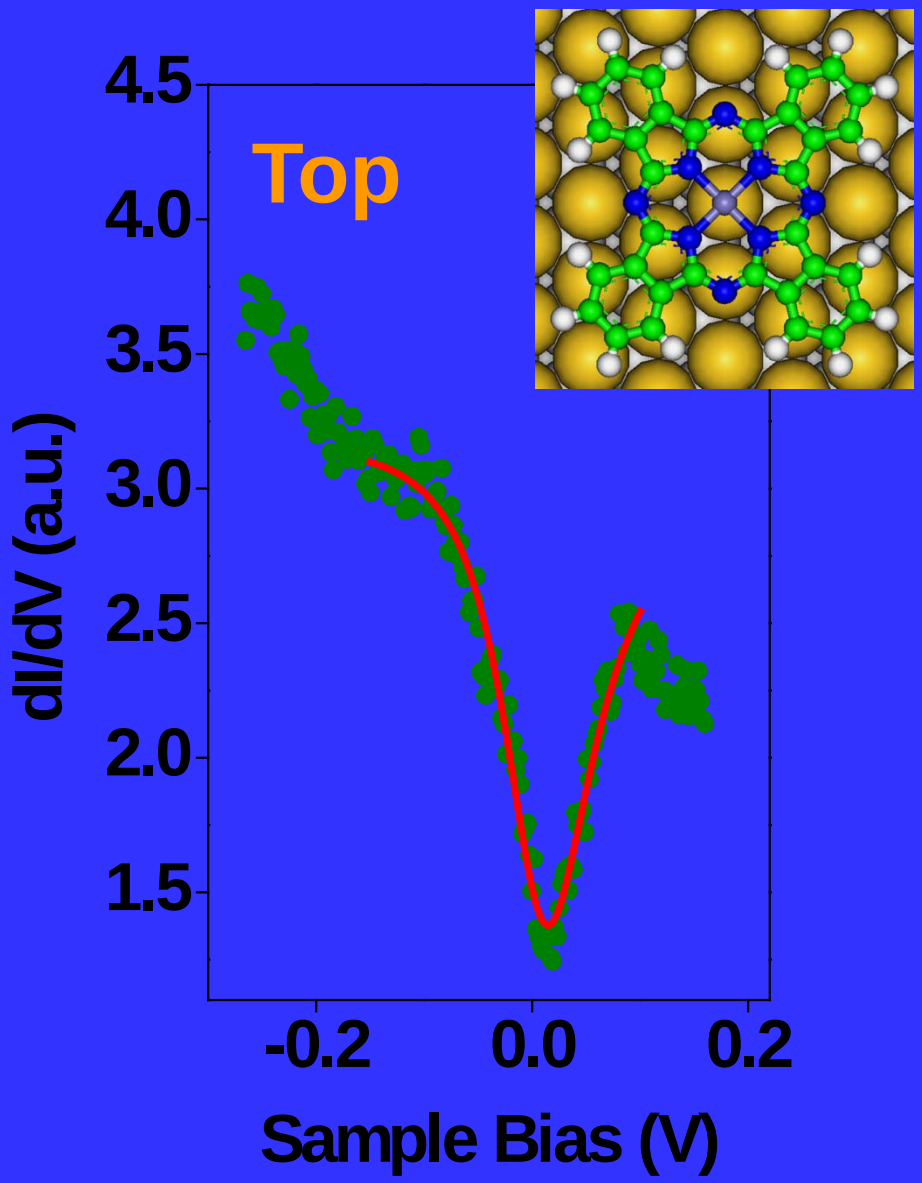
Orientation II



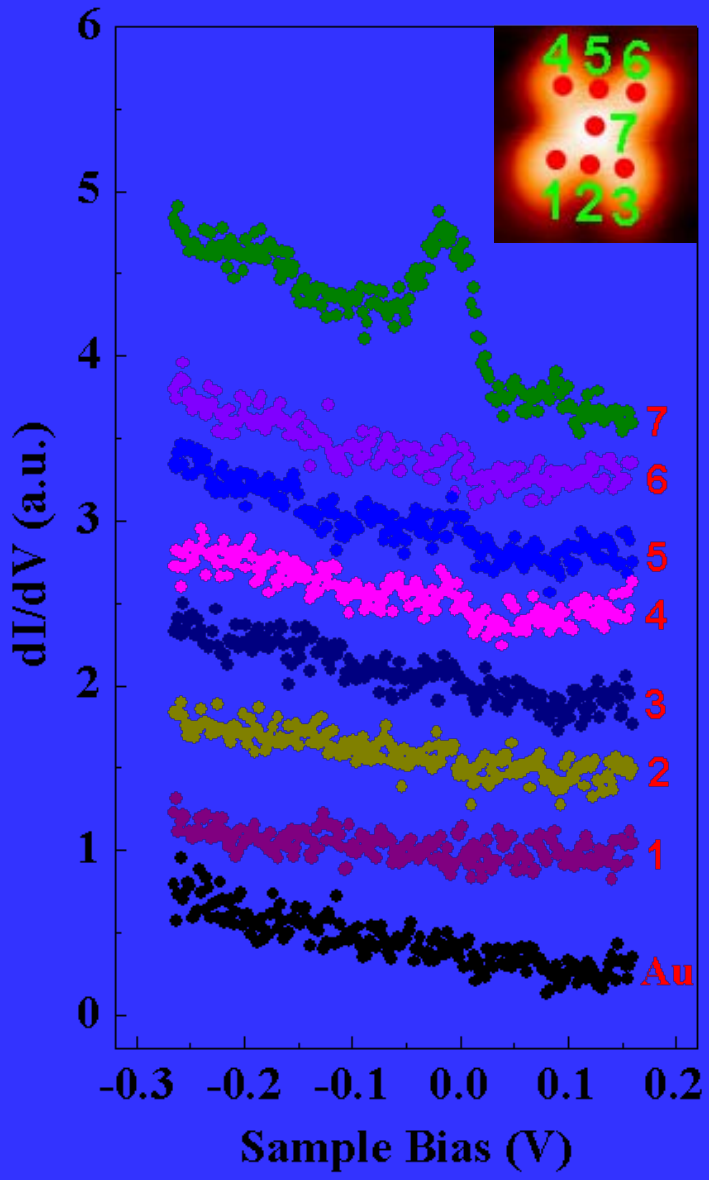
Top Site

dI/dV Spectra at Molecular Center

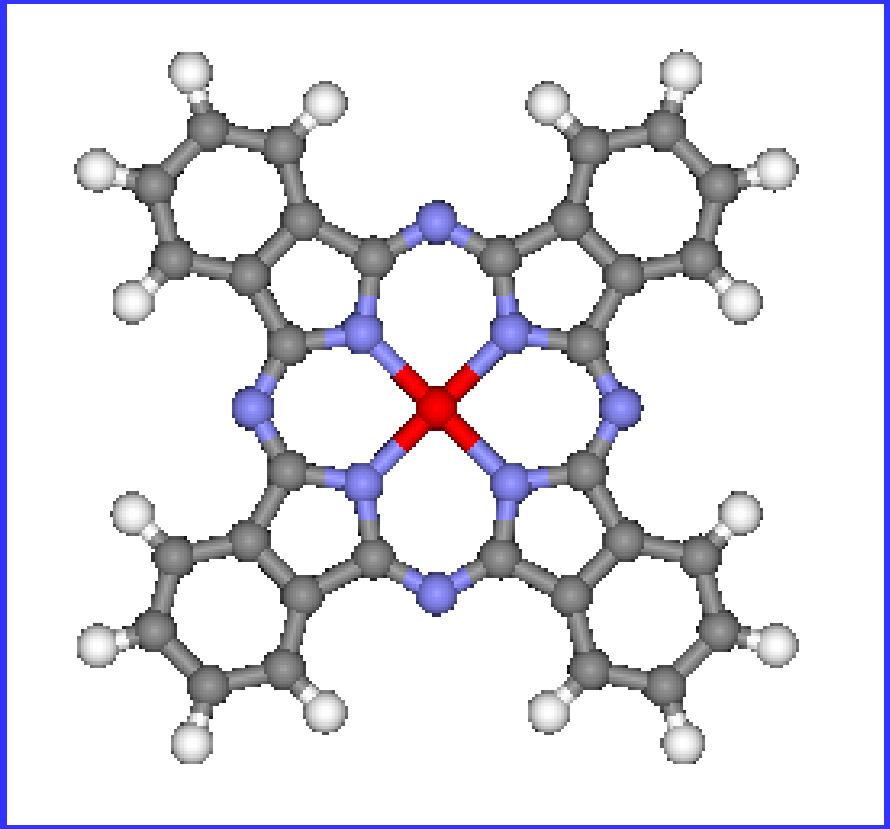




Spatial dI/dV Spectra

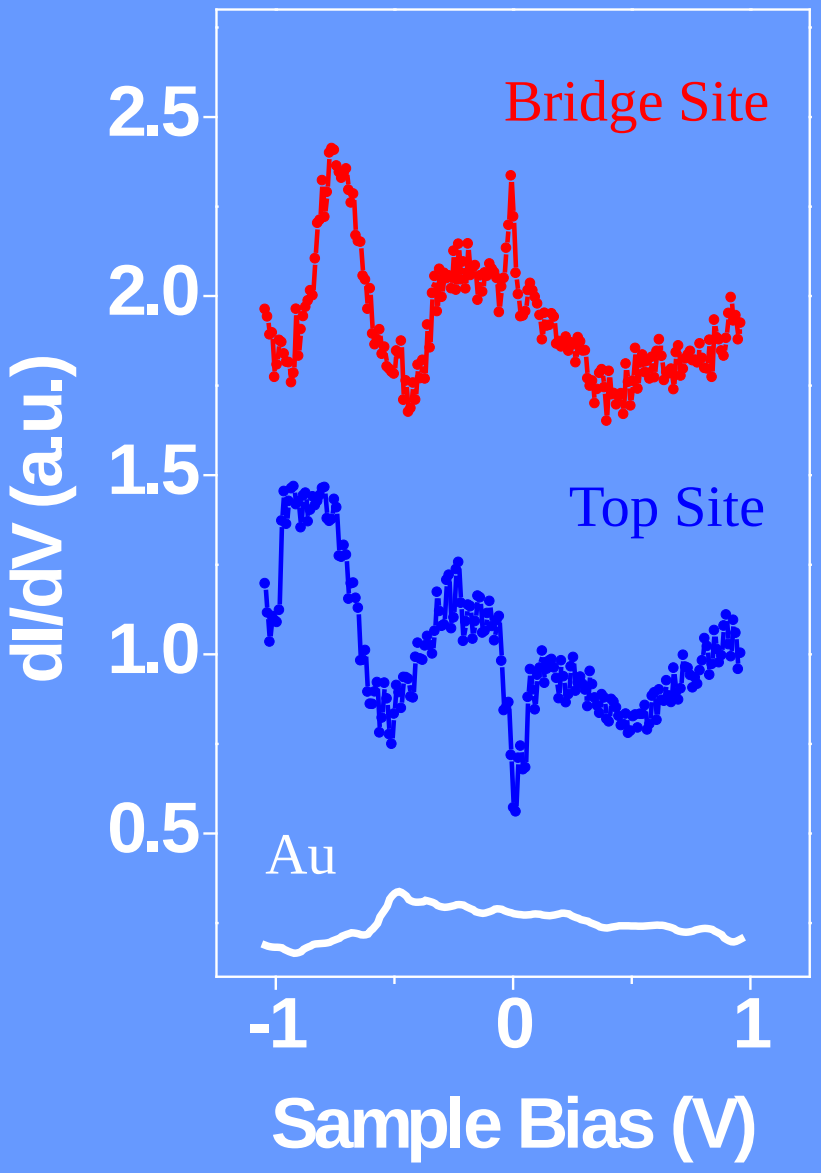


Fe: $3d^6 4s^2$



● Fe ● N

Kondo Effect



- Related to central Fe atom
  - unpaired *d* electrons
  - local magnetic moment
- Line shape
- Energy position: Fermi level
- Small FWHM

Fano Function Fit

$$\frac{dI}{dV}(V) = A \cdot \frac{(\varepsilon' + q)^2}{1 + \varepsilon'^2} + B$$

$$k_B T_K = \Gamma$$

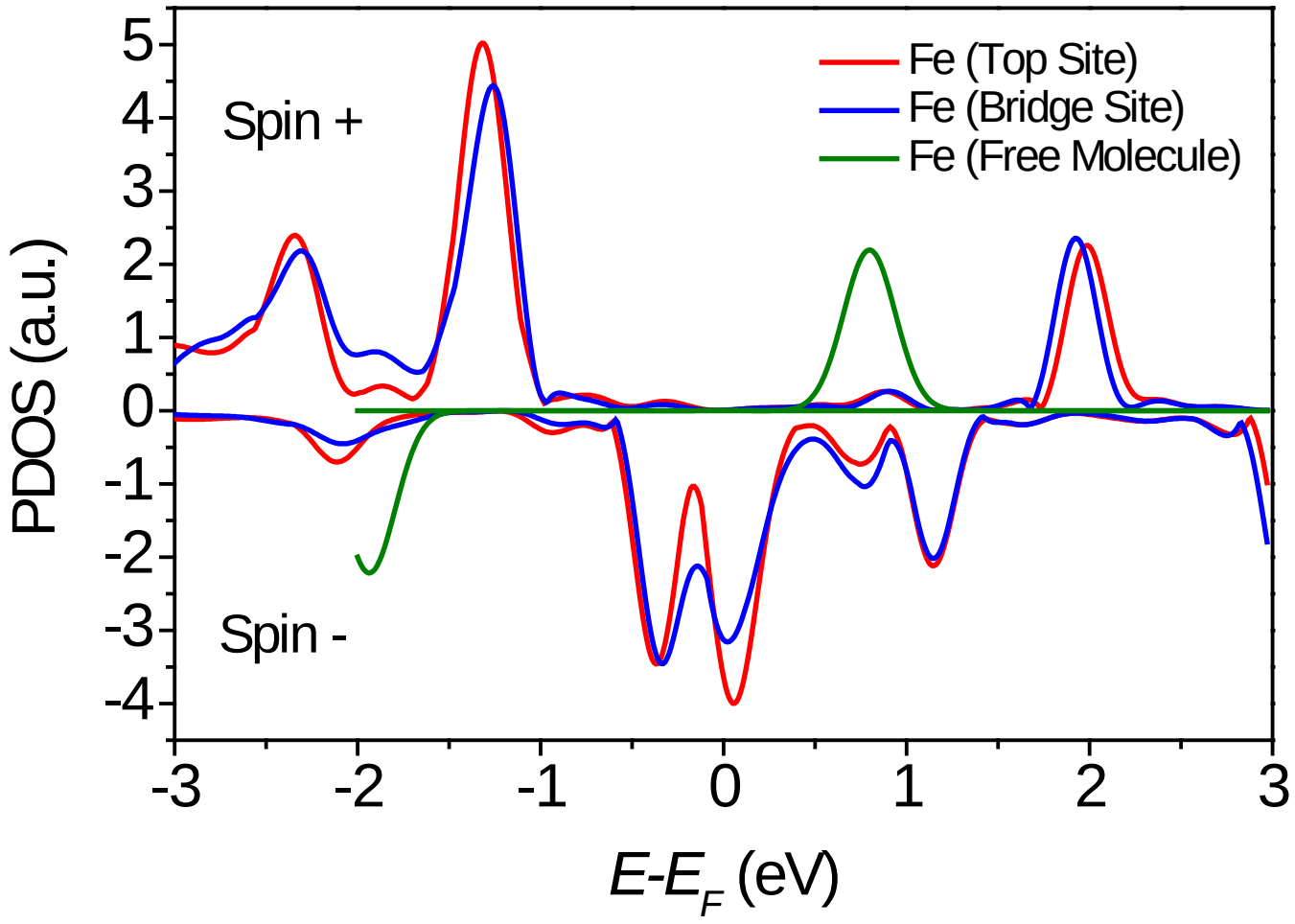
$$\varepsilon' = (eV - \varepsilon_0)/\Gamma$$

$$k_B T_K = D \exp\left(-\frac{1}{2|J|g_F}\right)$$

	Bridge Site	Top Site
q	**2.20** ± 0.19	**0.12** ± 0.03
ε_0	1.58 ± 0.82 meV	-8.39 ± 0.63 meV
Γ	**30.73** ± 1.77 meV	**51.52** ± 1.60 meV

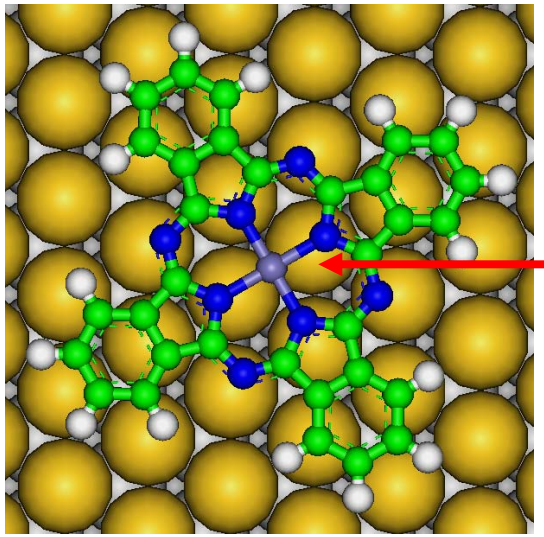
U. Fano, *Phys. Rev.* **124**, 1866 (1961).

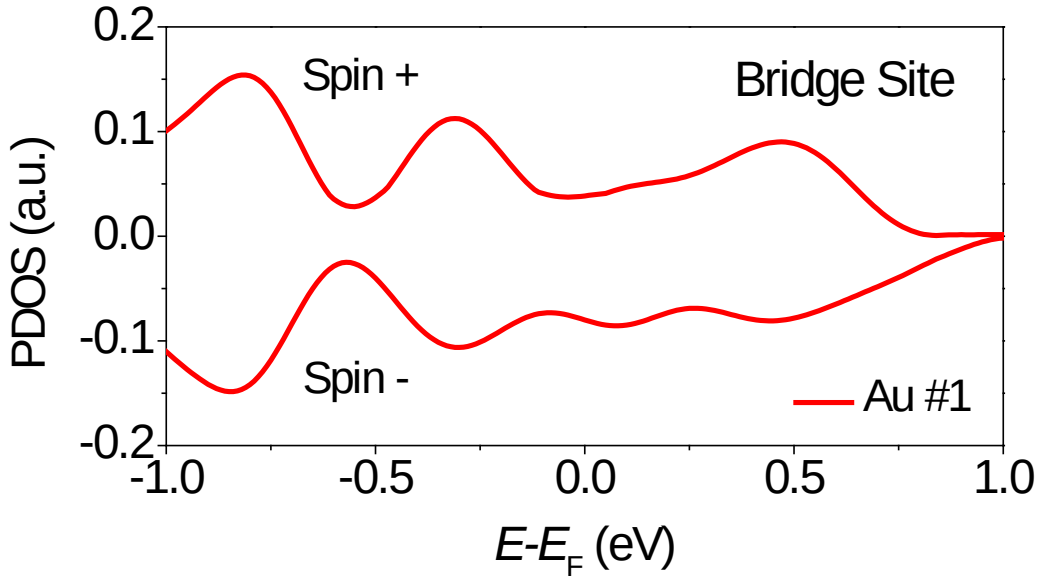
Spin Polarized PDOS of Fe(2+)

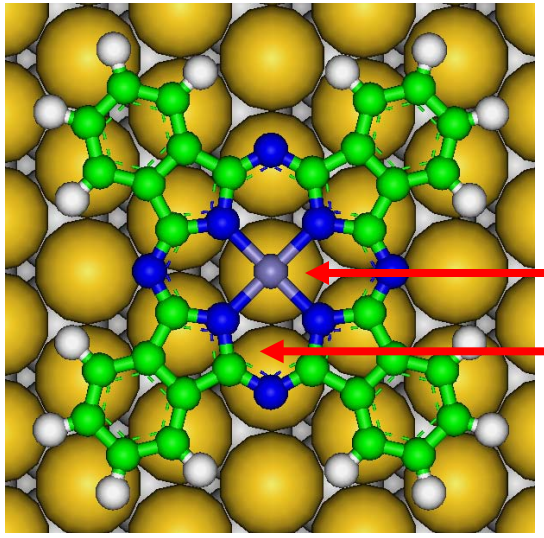


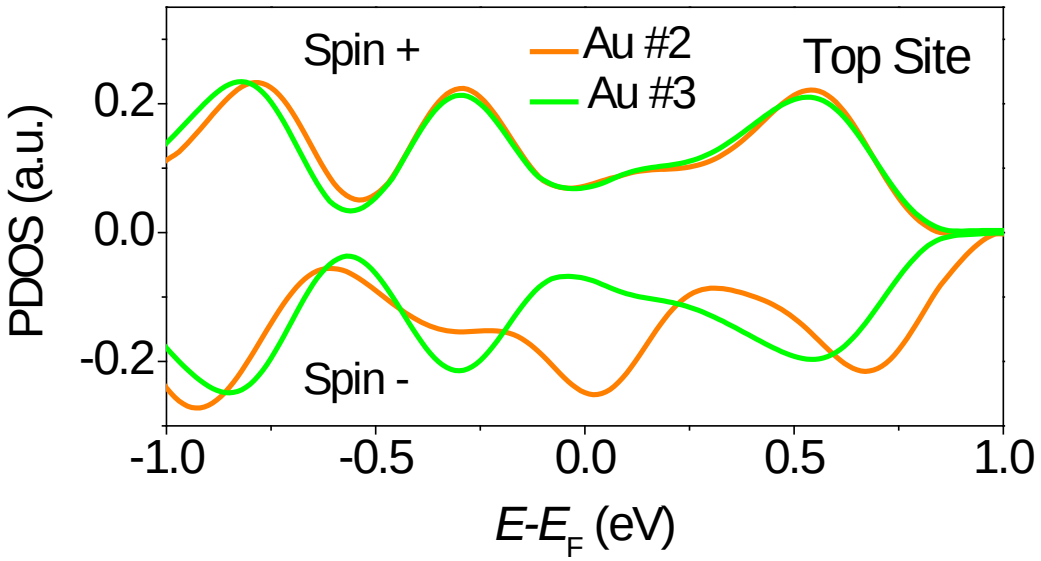
- Spin-polarized electronic structures lead to a local magnetic moment

PDOS of Neighboring Au Atoms

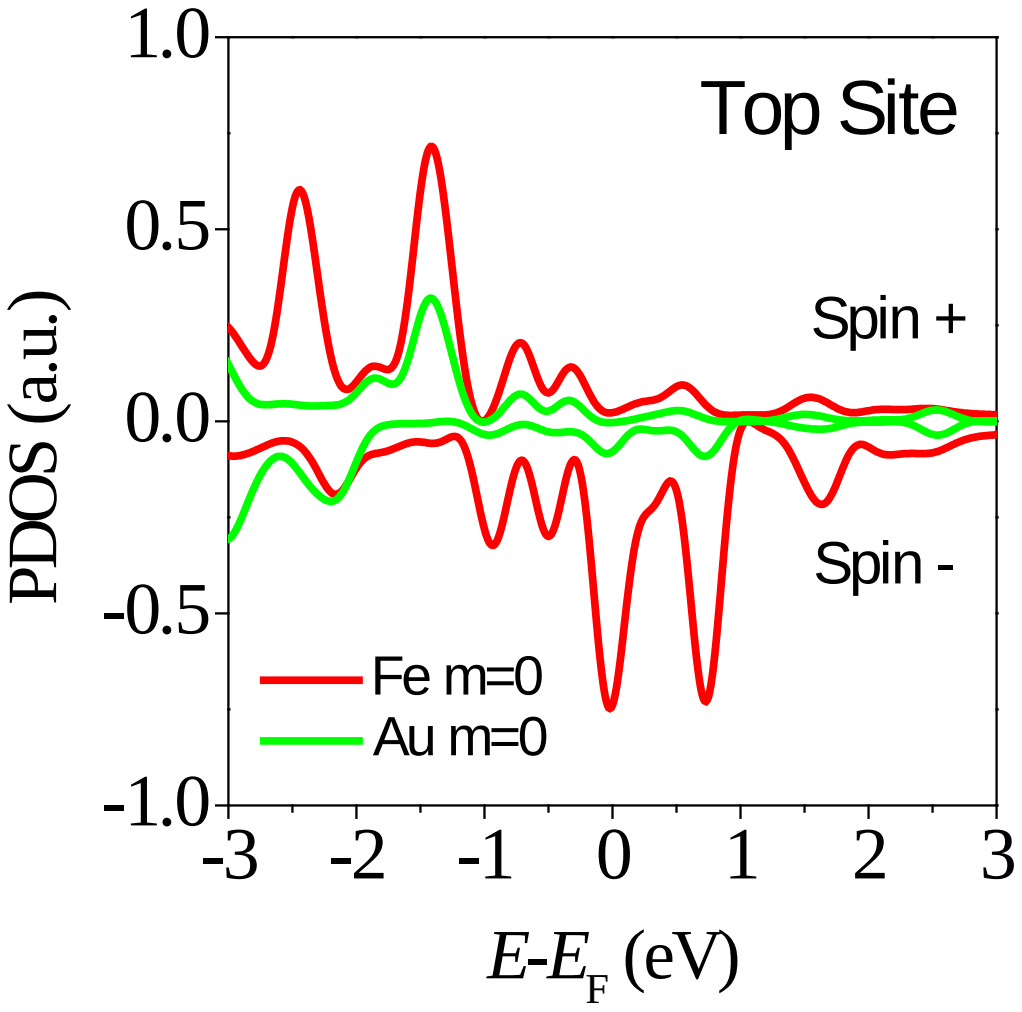




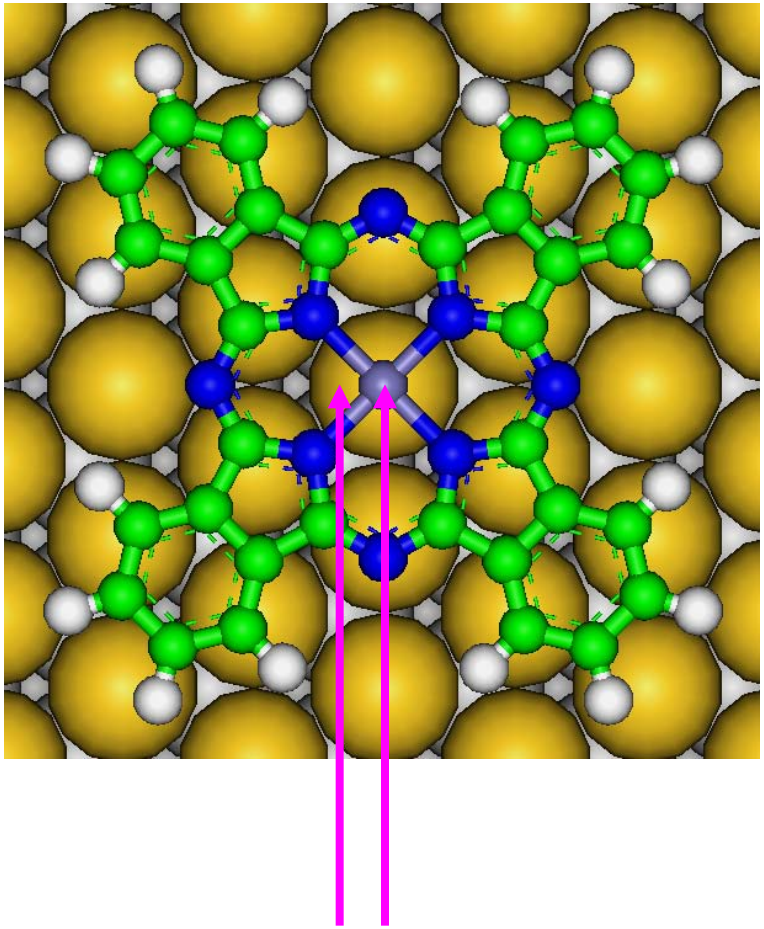




Top Site: d-level Hybridization



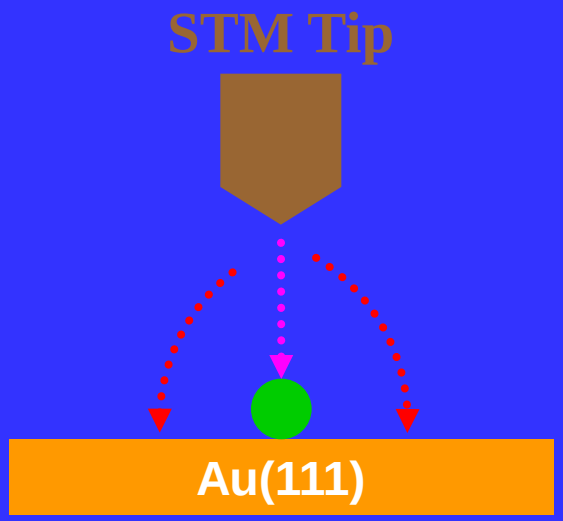
d_{z^2} orbital contribution

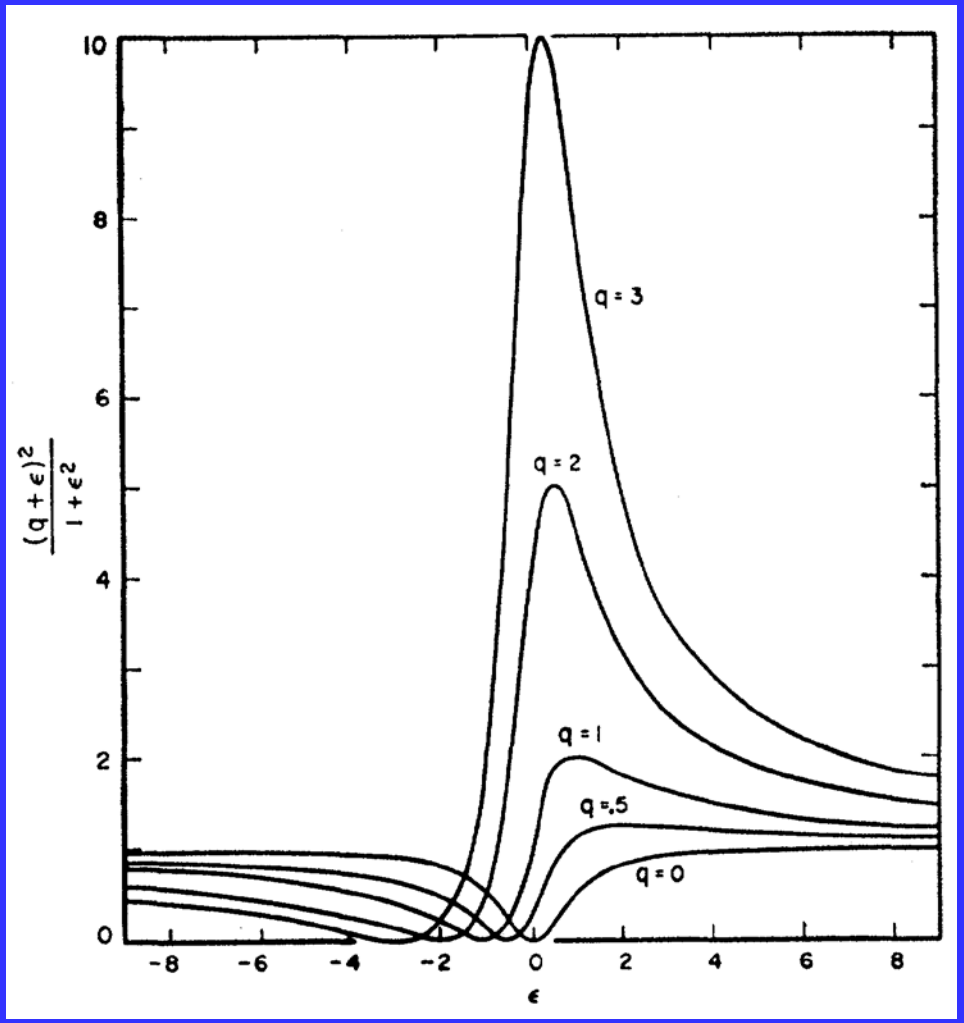


Line Shape of Kondo Resonance

- Bridge site: q = 2.20±0.19
- Top site: q = 0.12±0.03

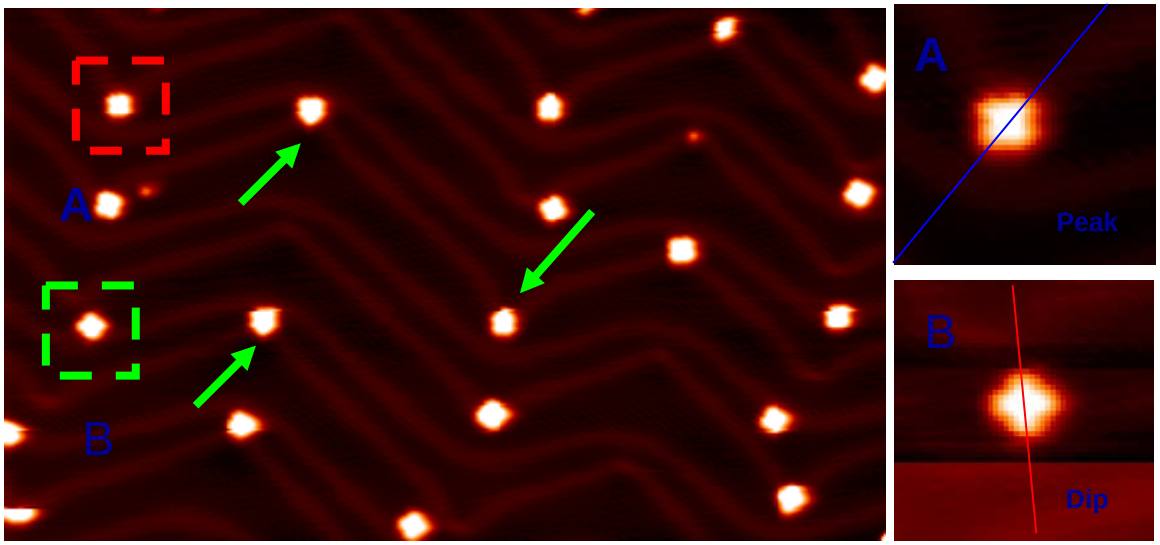
$$\frac{1}{2}\pi q^2 = \frac{\left|\left(\Phi\middle|T\middle|i\right)\right|^2}{\left|\left(\psi_E\middle|T\middle|i\right)\right|^2\Gamma}$$

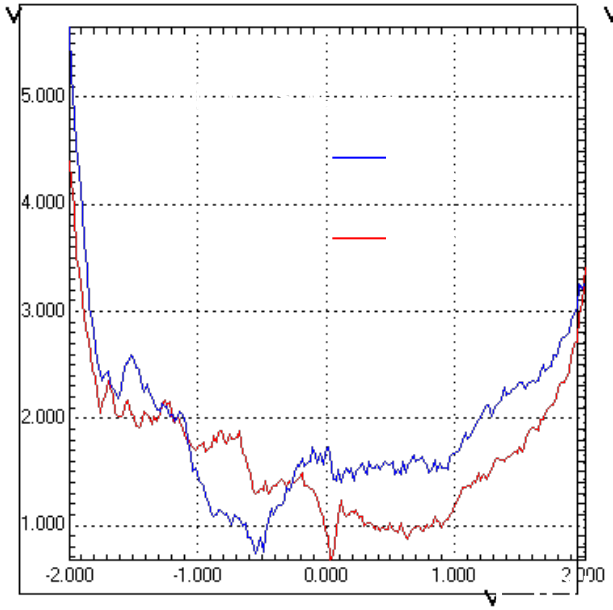


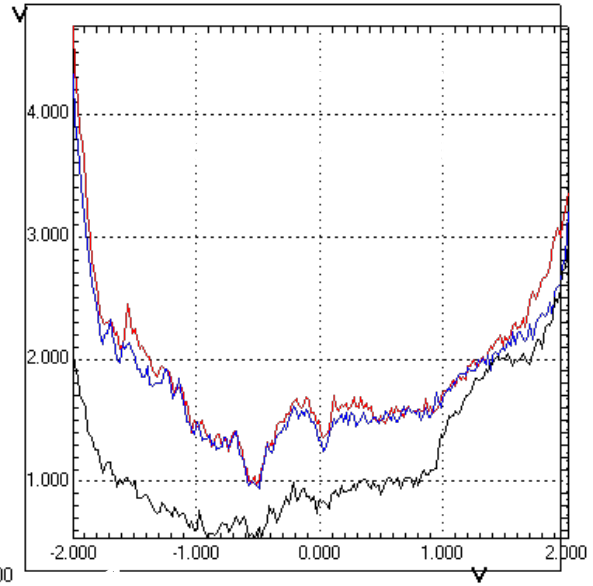


U. Fano, *Phys. Rev.* **124**, 1866 (1961).

Manipulation of Kondo Resonance Through Molecular Manipulation

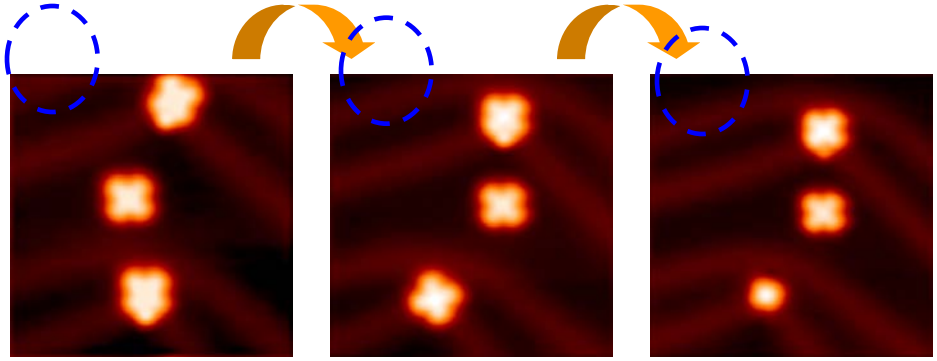




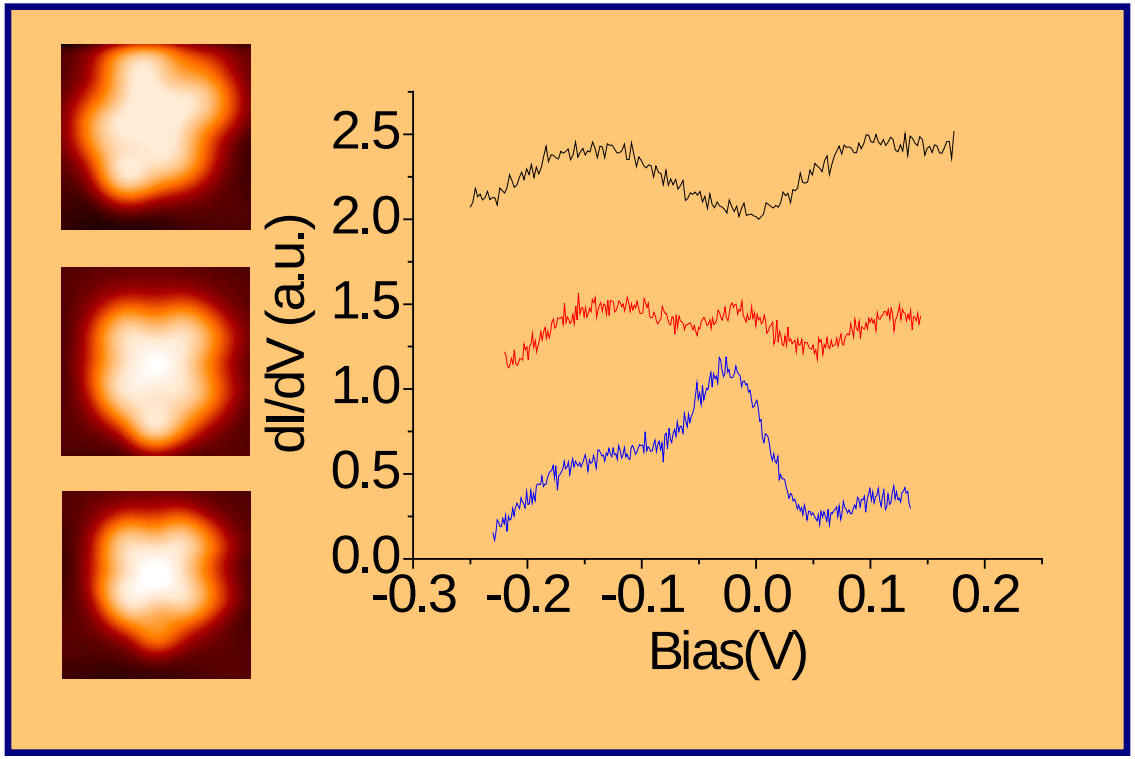


Manipulation of Kondo Resonance Through Molecular "Rotating"

Rotating

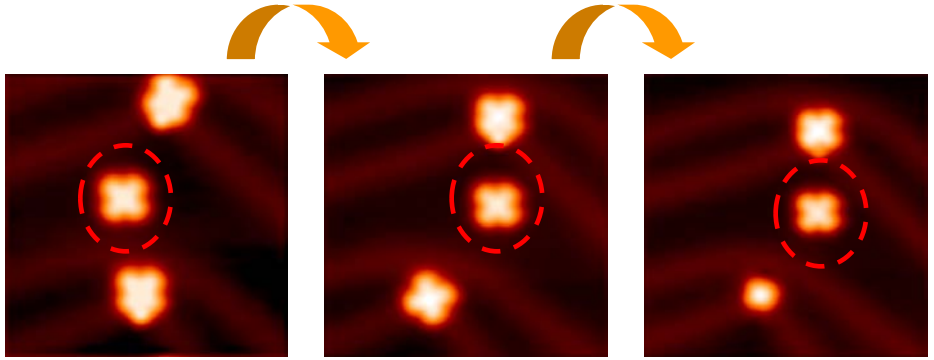


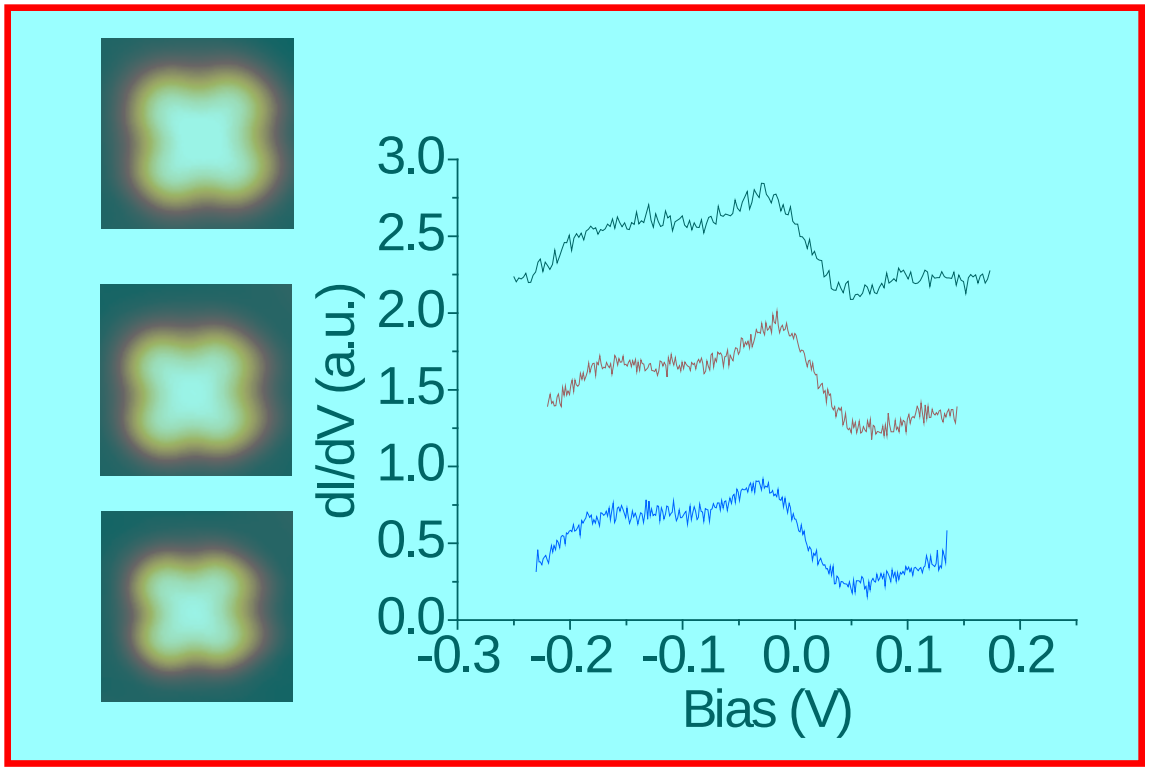
1.3 V, 0.1nA



Manipulation of Kondo Resonance Through Molecular "Shifting"

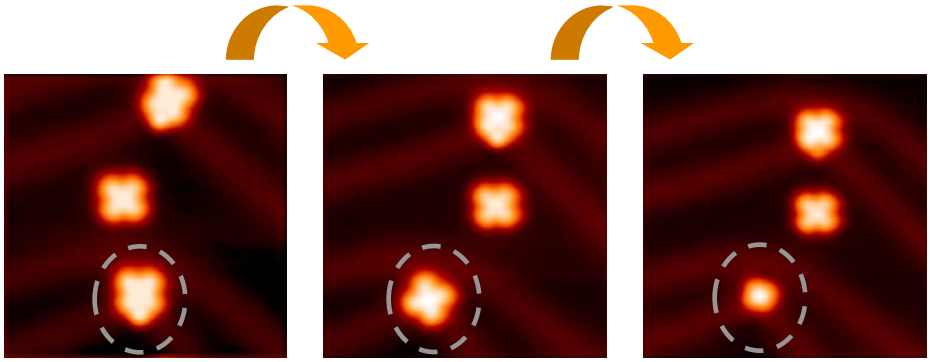
Shifting

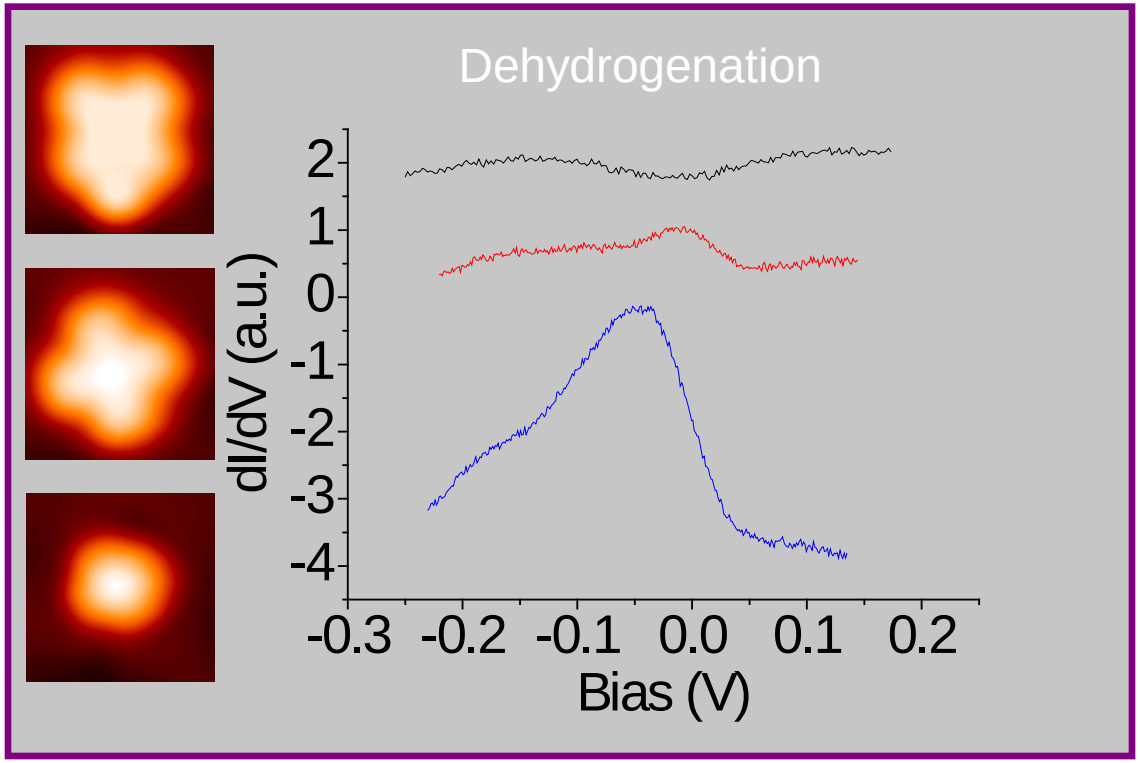




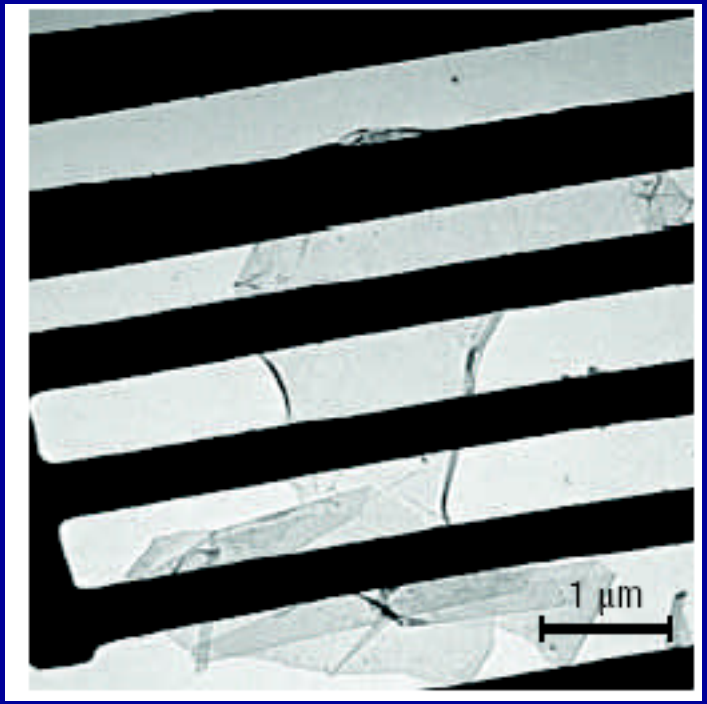
Manipulation of Kondo Resonance Through Molecular "Dehydrogenation"

Rydrogenation

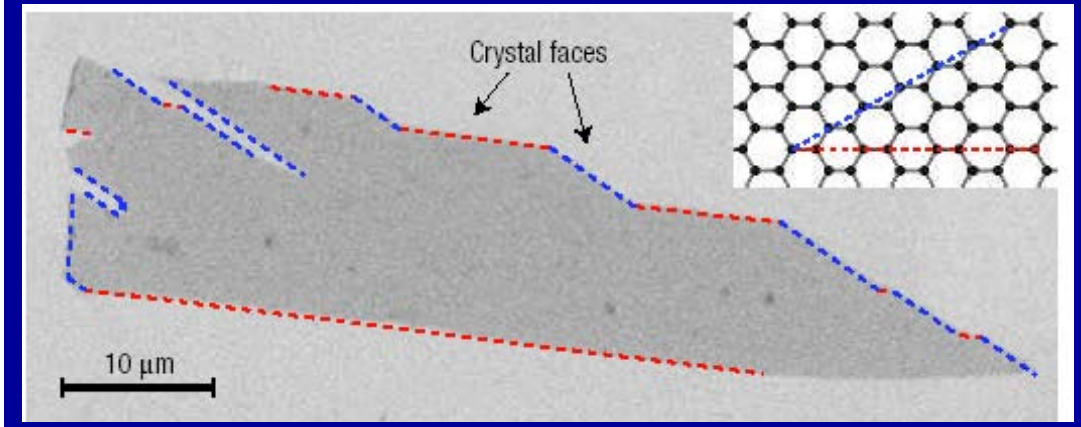




Fabrication Techniques: Peel Off
(Geim's Group)



A TEM image of a graphene sheet suspended on a µm size metallic scaffold

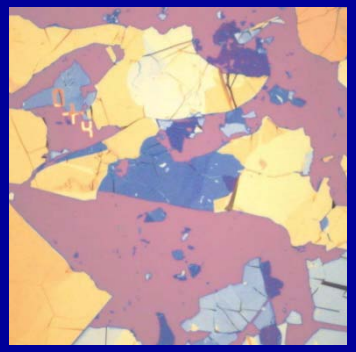


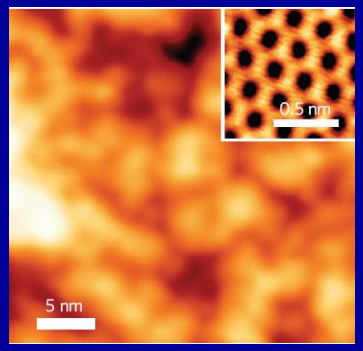
Scanning electron microscopy of a relatively large graphene

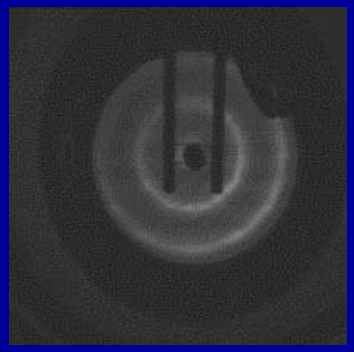
Science **36,** 666 (2004).
PNAS **102,** 10451 (2005).
Nature Materials, **6**,183(2007)
Nature, **446**, 60(2007)

HOPG Scraped

Graphene



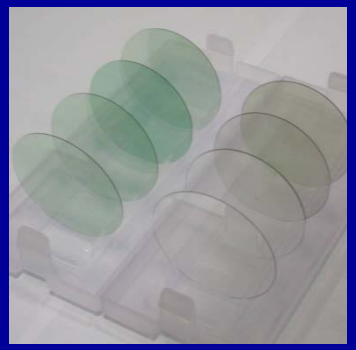


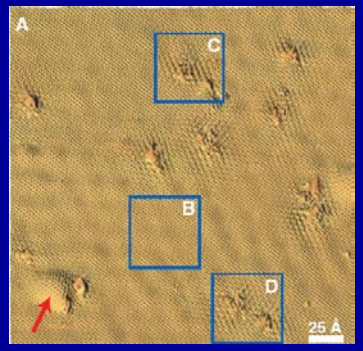


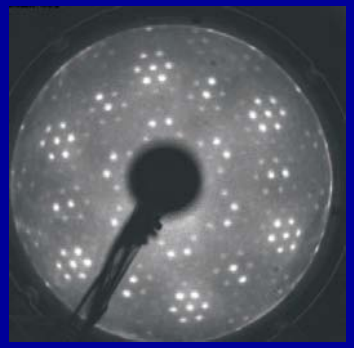
Polycrystalline!

SiC Epitaxial

Graphene





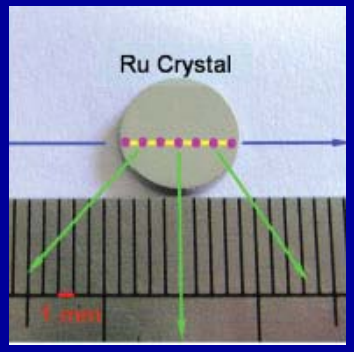


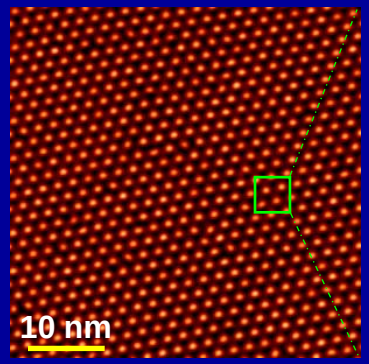
Single Crystalline,

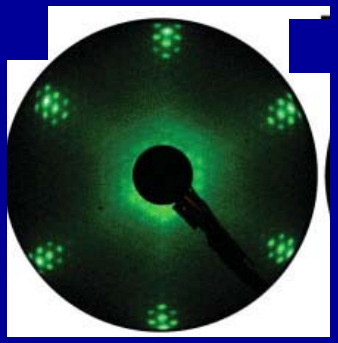
but Defects!

Metal Epitaxial

Graphene







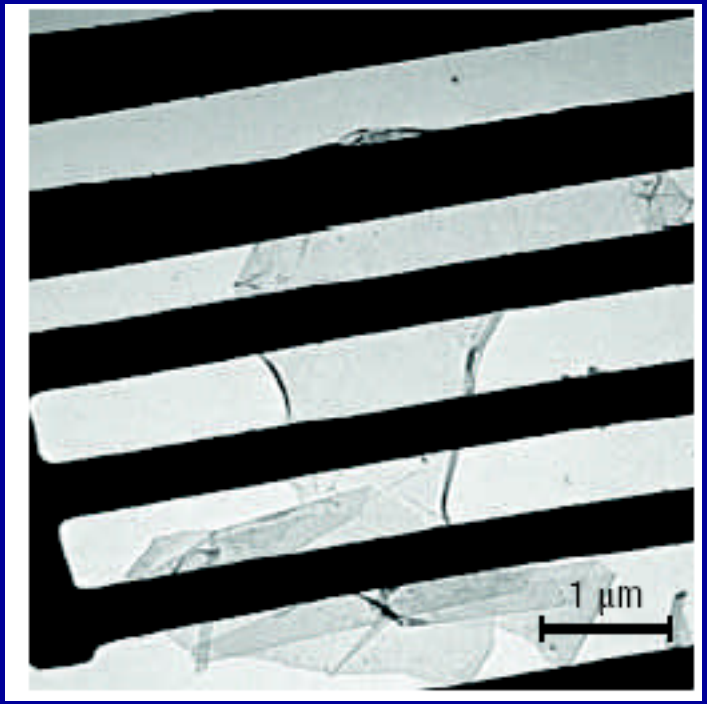
Perfect single crystalline, but strong interaction!

J. C. Meyer *et al. Nature* **446**, 60 (2007); Y. Zhang *et al. Nature Physics* **5**, 722 (2009); G. M. Rutter *et al. Science* **317**, 219 (2007);

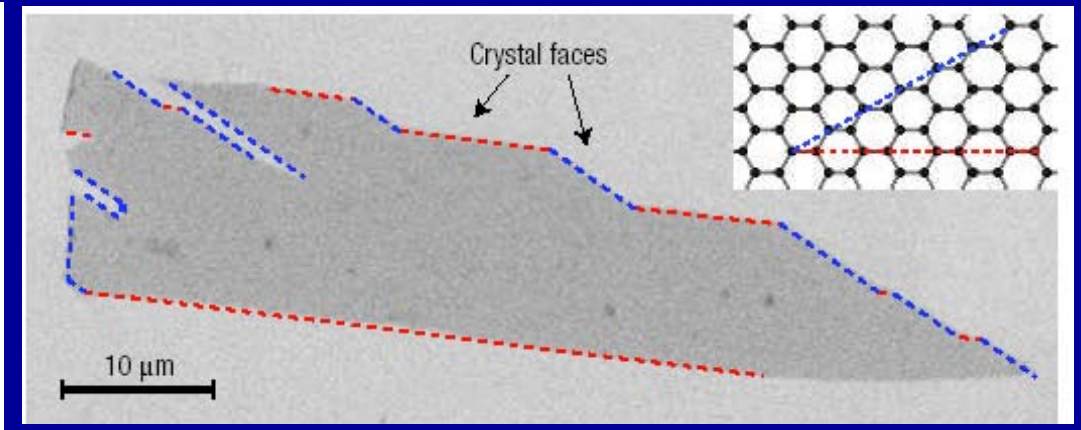
U Starke and C Riedl, *J. Phys.: Condens. Matter* **21,**134016 (2009); Y. Pan *et al. Adv. Mater.* **21**, 2777 (2009)

Main Challenges
from
Experimental Aspect
for
Future Studies

Fabrication Techniques: Peel Off
(Geim's Group)



A TEM image of a graphene sheet suspended on a micrometer-size metallic scaffold



Scanning electron microscopy of a relatively large graphene

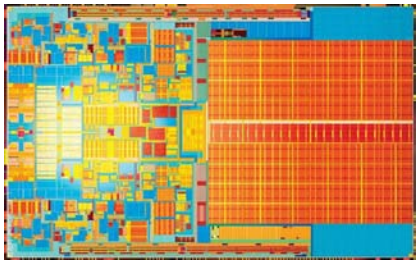
Science **36,** 666 (2004).

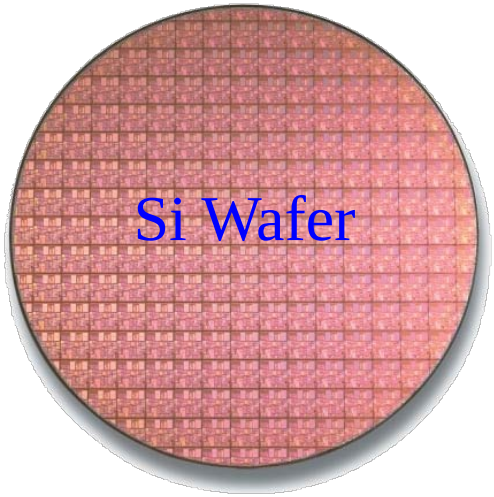
PNAS **102,** 10451 (2005).

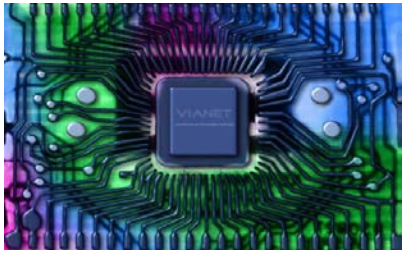
Nature Materials, **6**,183(2007)

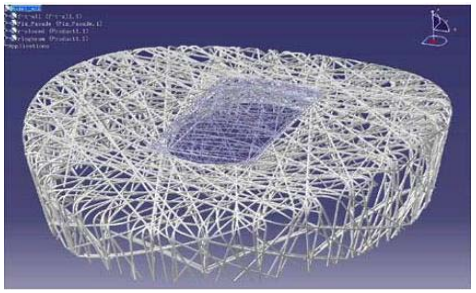
Nature, **446**, 60(2007)

Single Crystal Si Based Industry and Application







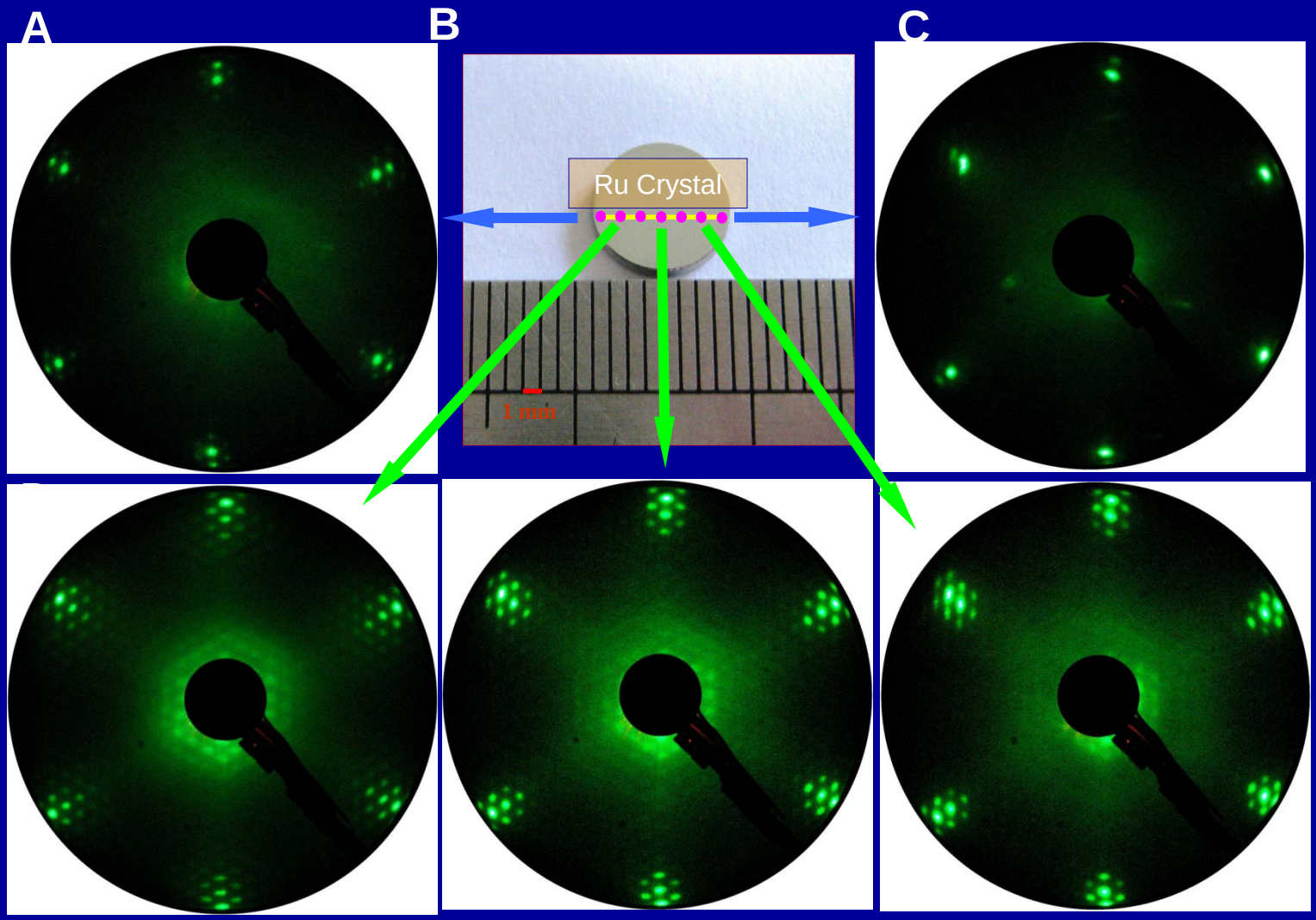


Limited grain size in HOPG, and thus the size of the single crystalline graphene

Highly Ordered, Millimeter-scale, Continuous, Single Crystalline Graphene Monolayer Formed on Ru (0001)

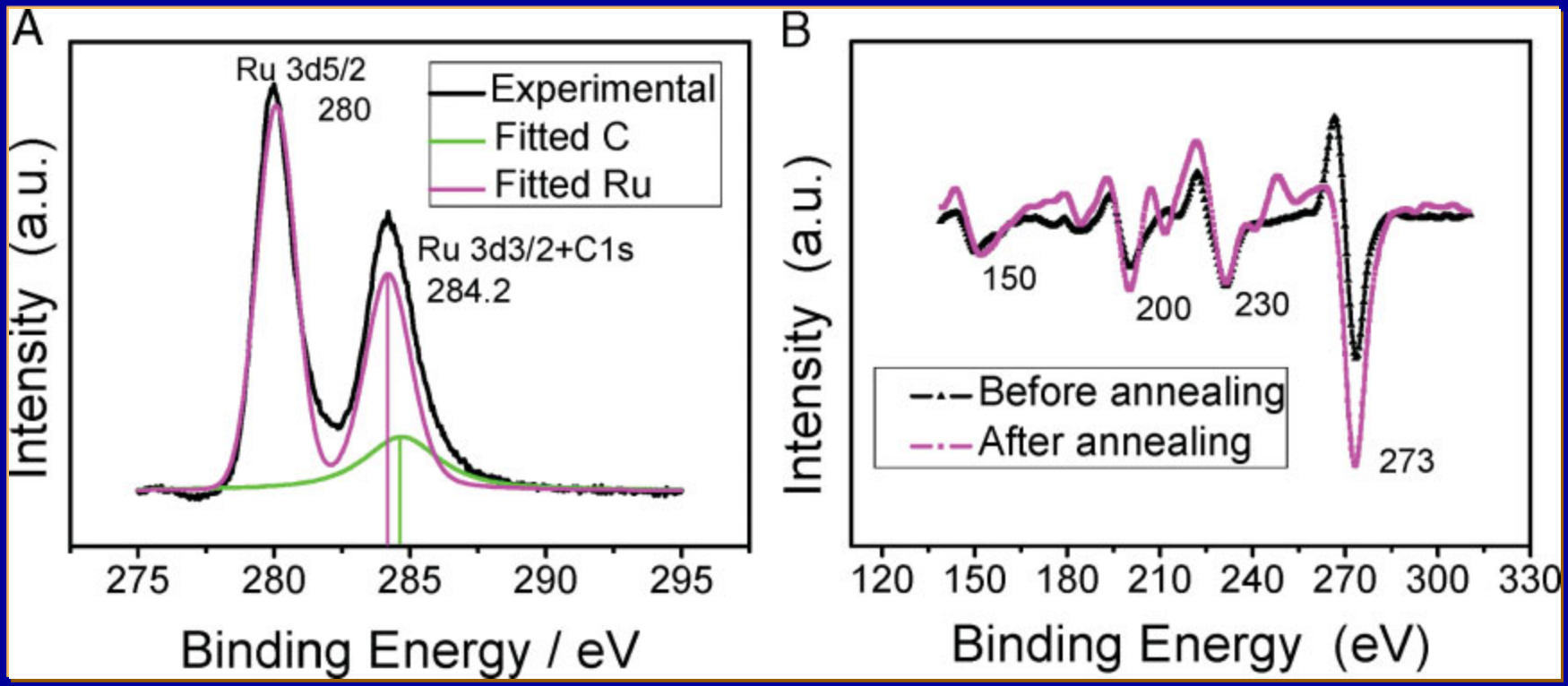
Y. Pan/H.J. Gao et al., Adv. Mater., 2009

LEED Patterns of the Graphene/Ru(0001)



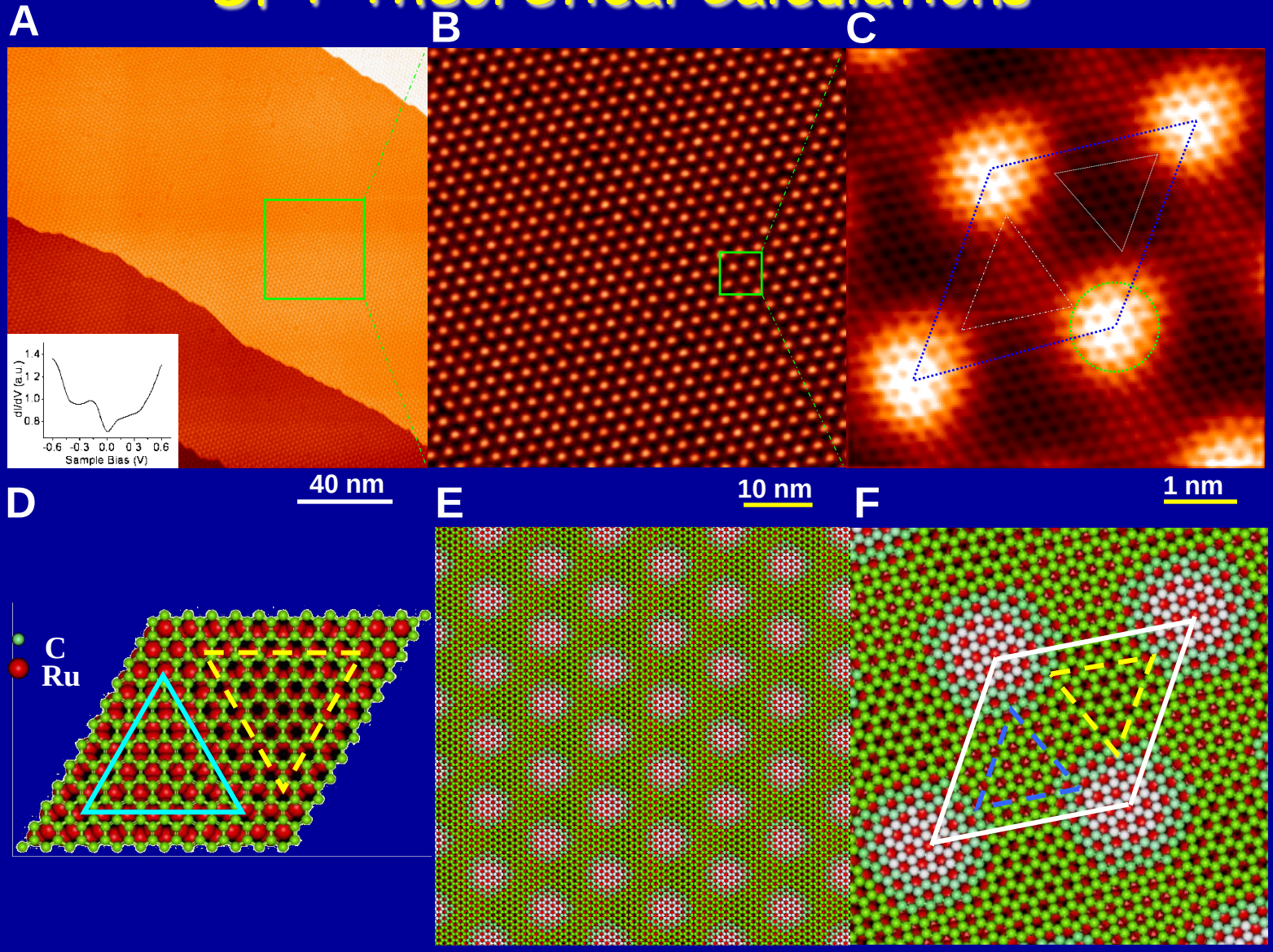
Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

XPS and AES Demonstration of C Adlayer on Ru (0001)



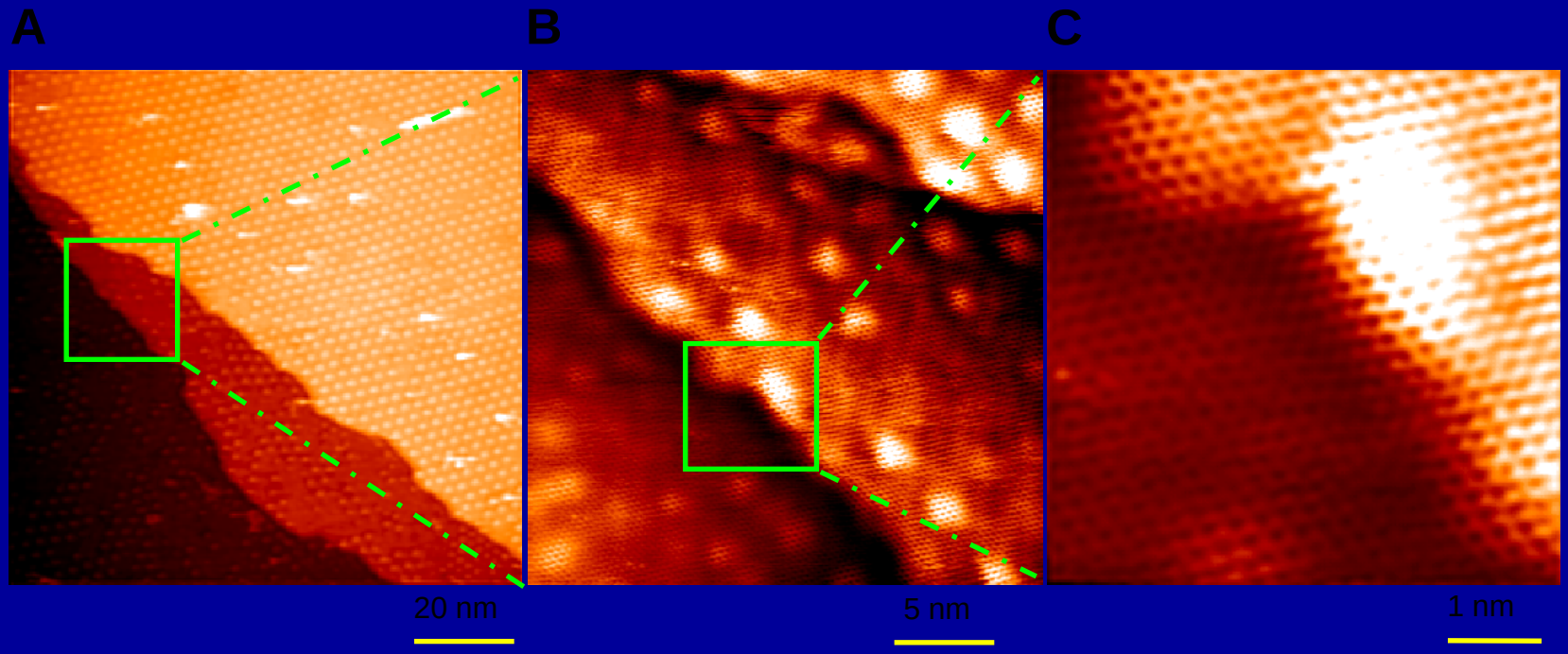
- XPS spectrum of the Ru(0001) surface with the graphene adlayer (black curve), which can be decomposed into the standard Ru spectrum (pink curve) and the low-intensity C spectrum (green curve).
- AES spectra of the Ru(0001) surface before (black curve) and after (pink curve) adlayer formation.

STM Images of Graphene/Ru(0001) and DFT Theoretical Calculations



Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

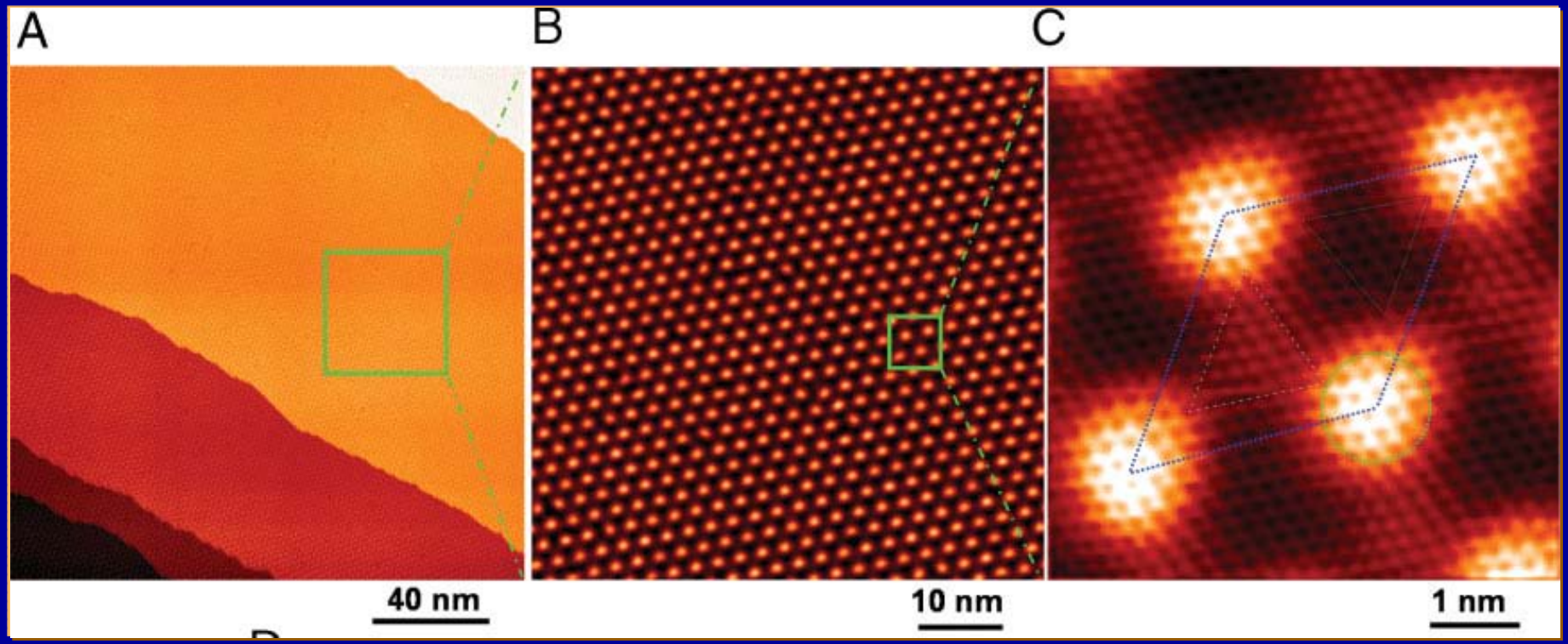
STM images of Graphene/Ru(0001) at Surface Steps: Continuous and Ordered Graphene



Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

Following Work:

- Can we employ the Ordered Moire Pattern of the Graphene on Metals?
- To grow Functional Quantum Structures?

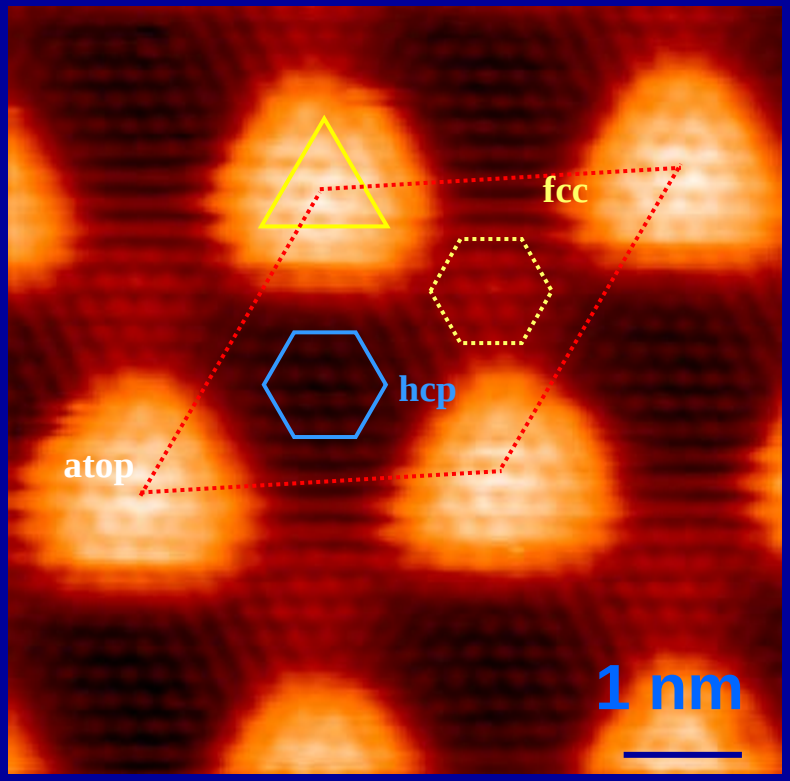


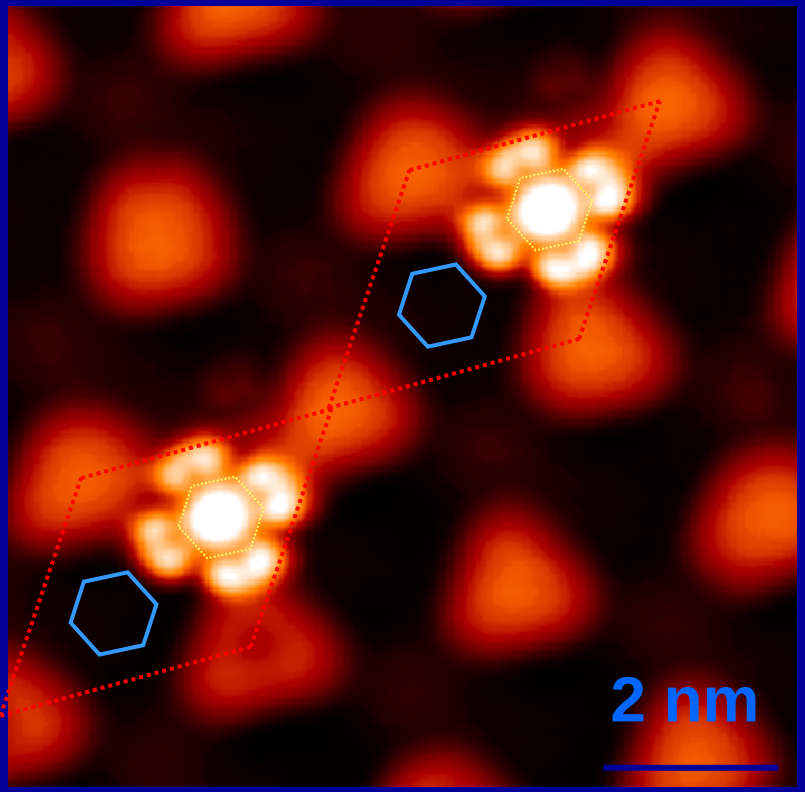
Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

Supramolecular Kagome lattices of magentic phthalocyanines using graphene based Morie templates: Formation and tunability

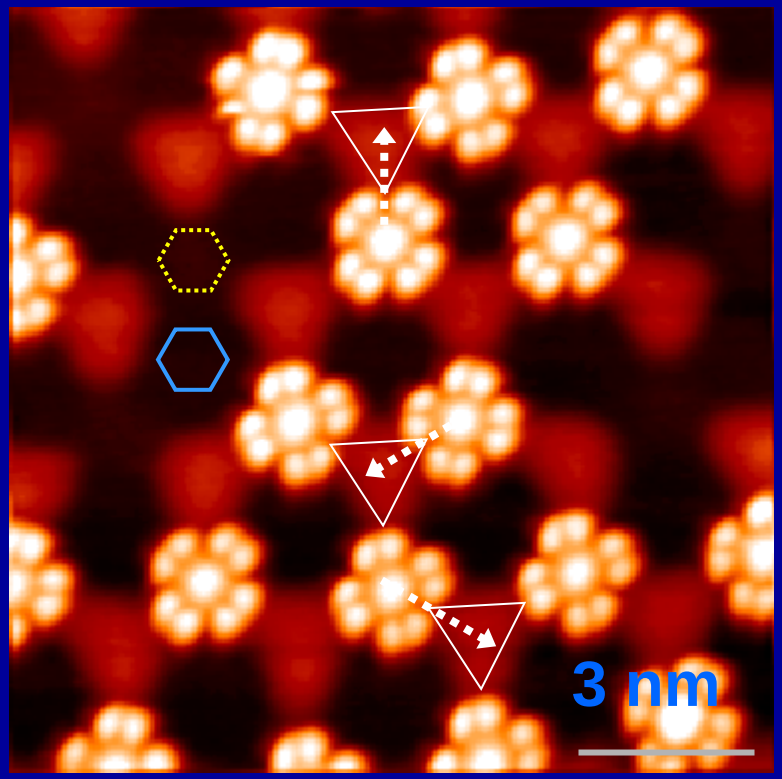
(J.H. Mao/H.J. Gao et al., JACS, 2009)

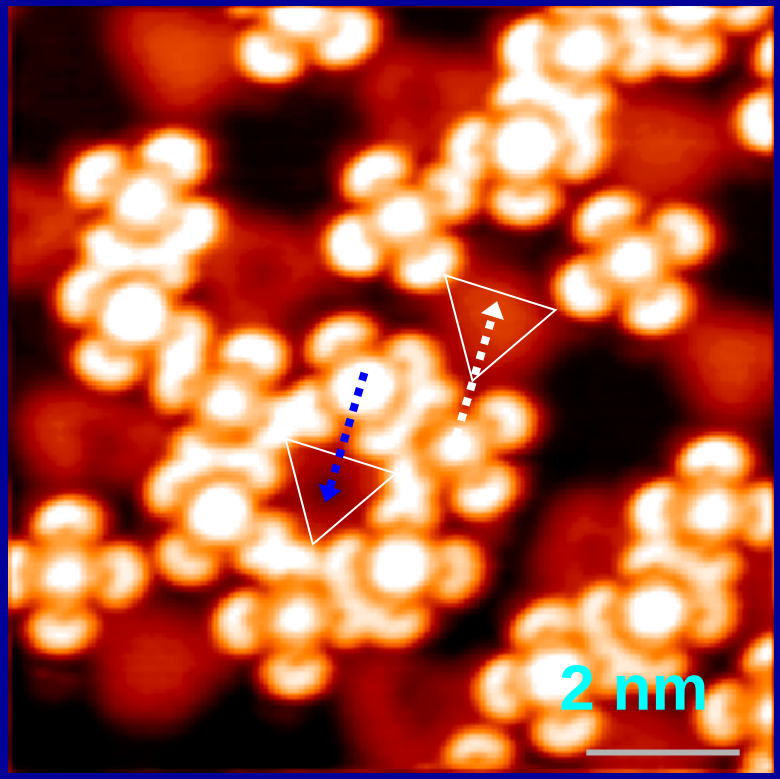
Selective Adsorption: FePc/MG/Ru(0001)



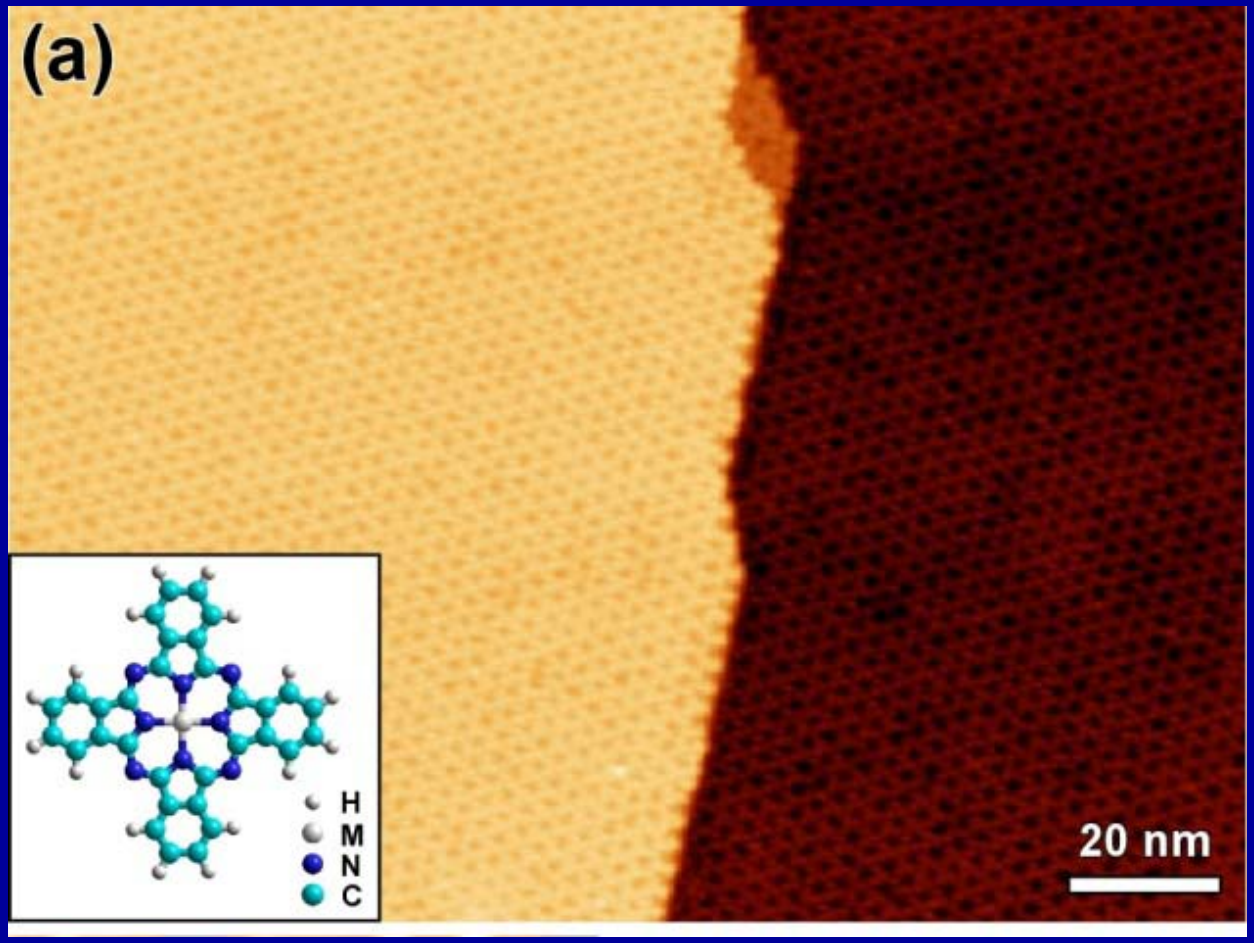


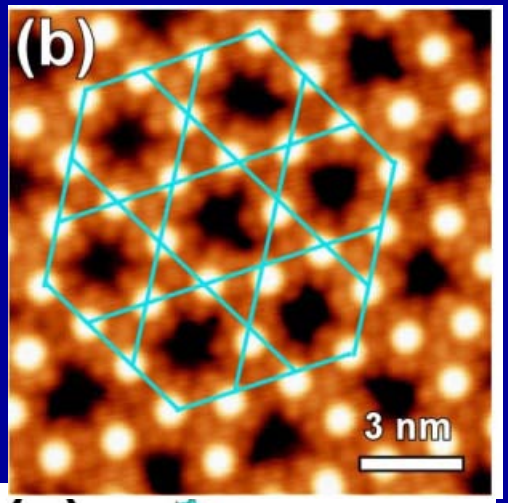
Selective Adsorption: FePc/MG/Ru(0001)

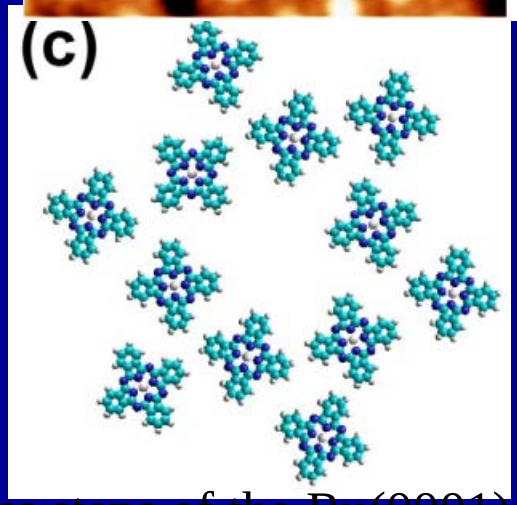




Kagome Lattice: FePc/MG/Ru(0001)

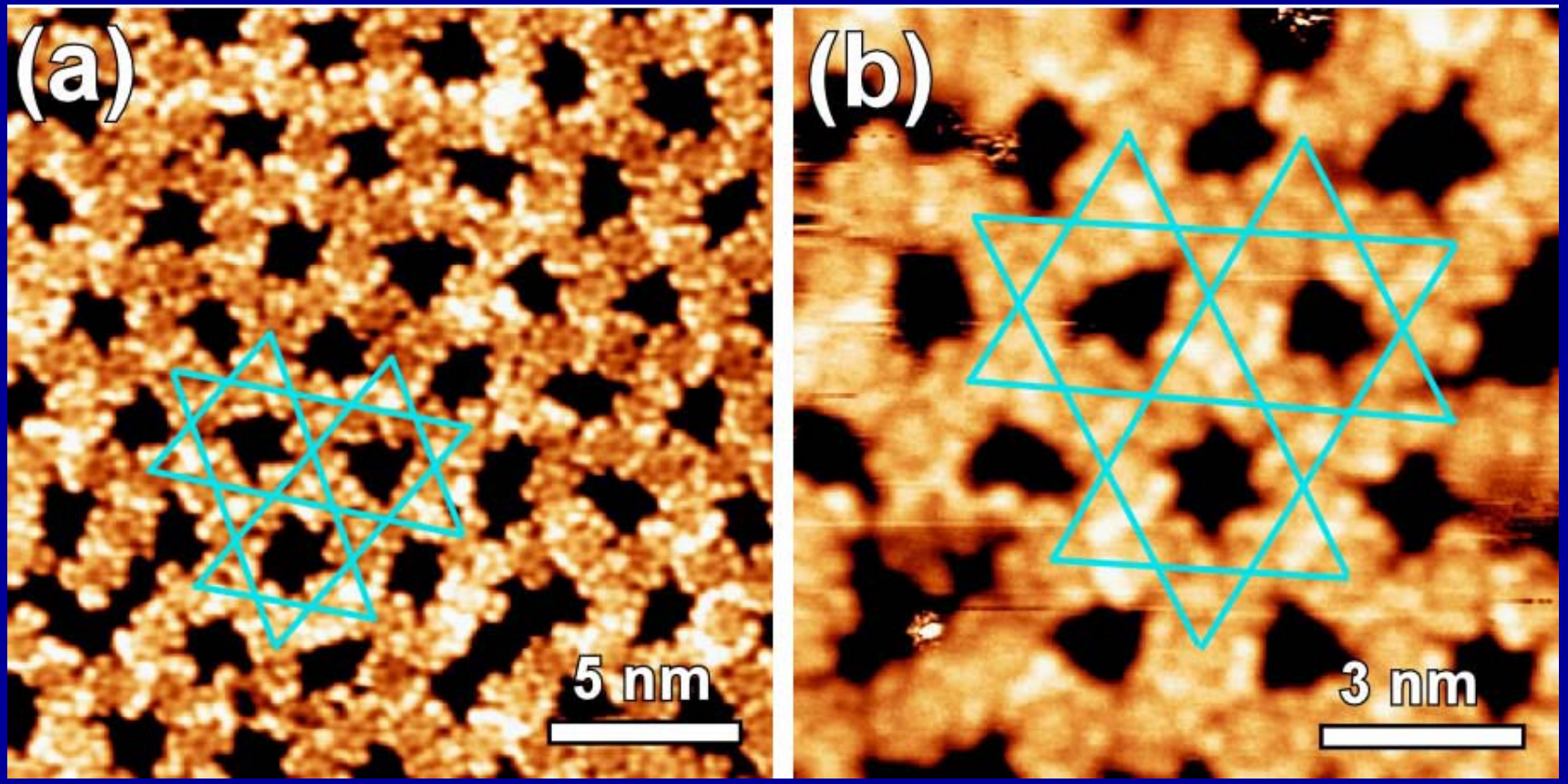






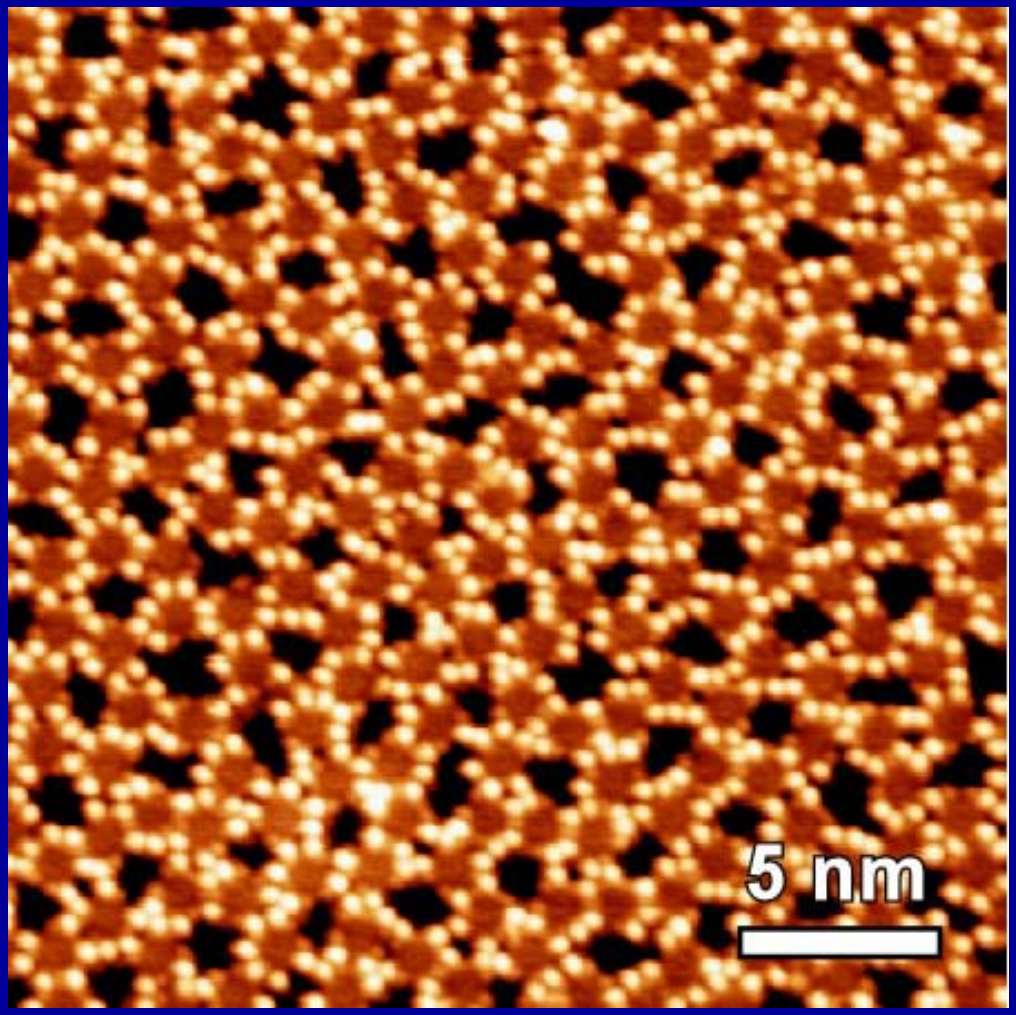
(a) Identical orientation of the Kagome lattice of FePc across steps of the Ru(0001) substrate.
(b) Details of the Kagome lattice of FePc.
(c) Structural model of the Kagome lattice showing molecular orientation disorder.

Kagome Lattice:
$H_2Pc(NiPc)/MG/Ru(0001)$



H_2Pc NiPc

Kagome Lattice: $(t\text{-}Bu)_4$-ZnPc/MG/Ru(0001)



STM images of (t-Bu)4-ZnPc on MG/Ru(0001). A distorted Kagome lattice with slight local disorder is visible.

Conclusions

- Formation of “Anchored” Single Molecular Rotor Array
- Molecular adsorption site influences Kondo resonance

  - Kondo temperature (strength of spin-electron coupling)

  - Line shape (tunneling channels)

- Large scale, highly ordered, single crystalline graphene formation and the ordered molecular formation

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IOP CAS, China

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Feng LIU
Utah U., USA
X.C. Xie
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Thank you for your attention!