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

Characterization of the Magnetism and Conformation of Single Porphyrin Molecules Adsorbed on Surfaces, and Artificial Graphene Nanoflakes

Presenter: Zhang Qiushi

Supervisor: Prof. Lin Nian

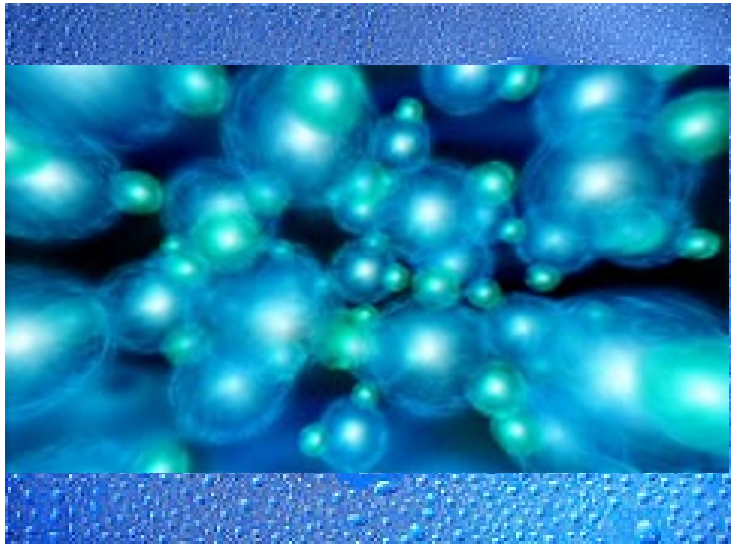
Department of Physics, The Hong Kong University of Science and Technology,
Clear Water Bay, Hong Kong

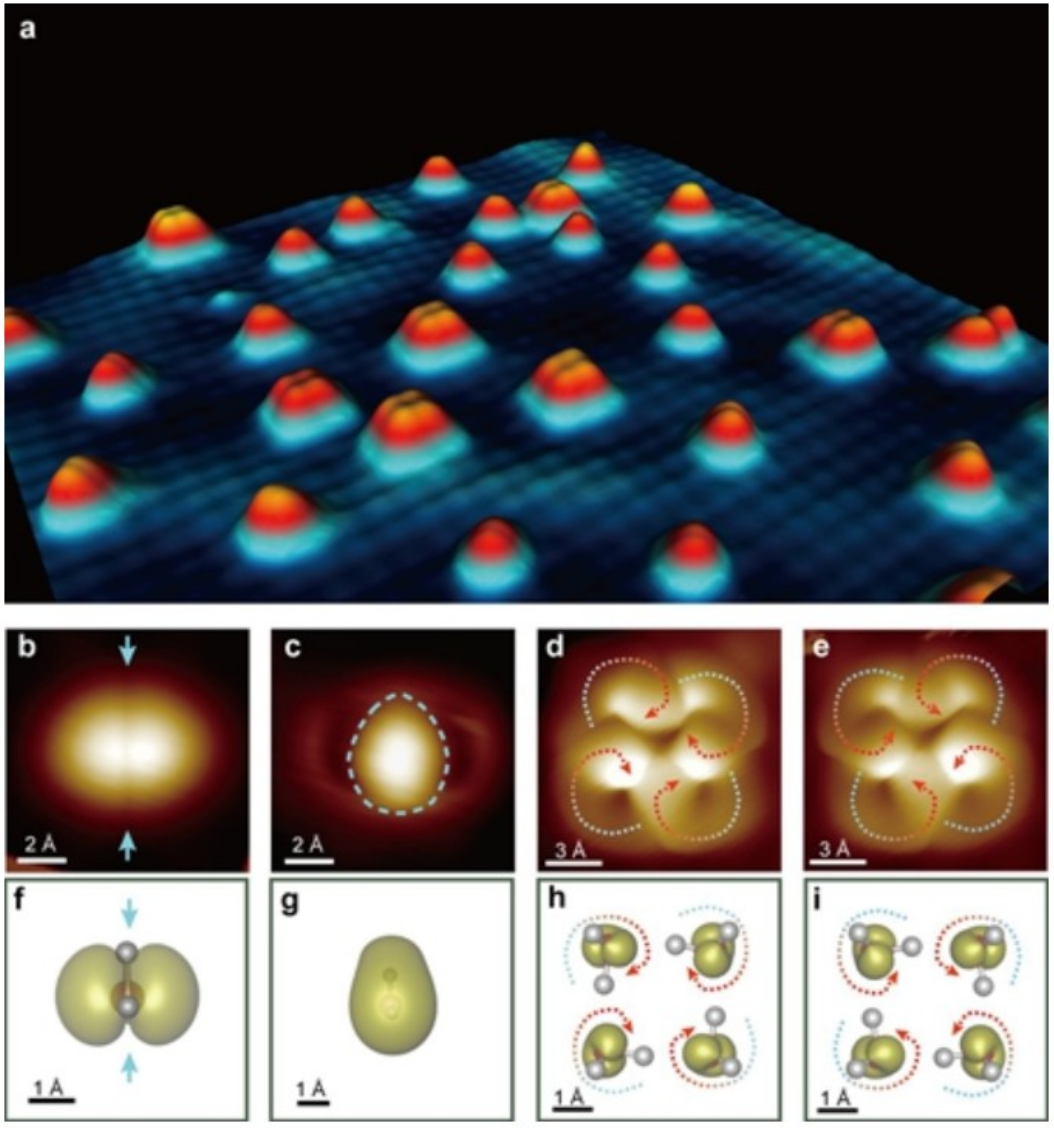
Outline

- Introduction
  - -> Introduction to single molecular study
  - -> Introduction to the experimental setups
  - -> Introduction to porphyrin molecules
- Single-molecule investigations of conformation adaptation of porphyrins on surfaces
- Switching molecular Kondo effect via supramolecular interaction
- The electronic properties of artificial graphene nanoflakes
- Conclusion

Single molecular study

- Chemical and biological proces
  structures.
- Many phenomena and proper
  molecular level.
- Single molecular properties ar
  properties.
- Bottom-up techniques in nanc

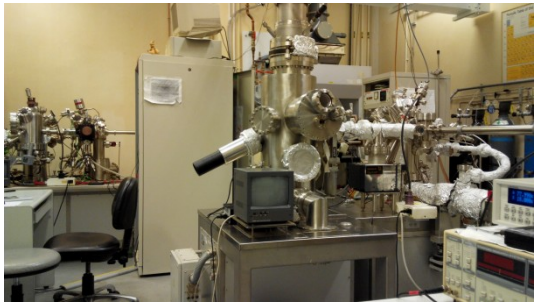




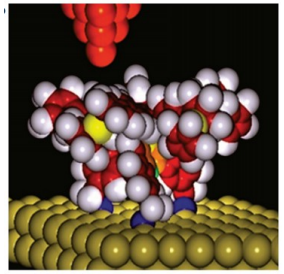
a) STM image of water monomers and tetramers adsorbed on the NaCl film.
(b) (c) water monomer images.
(d) (e) water tetramers with different H-bonding.
(f)-(i) orbital calculations.

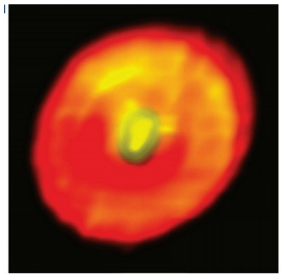
http://flickrhivemind.net/User/Marco%20Braun/Interesting
https://www.pinterest.com/dobevaeva/atomic-structure-and-bonding/
http://www.microscopy-analysis.com/editorials/editorial-listings/stm-

Scanning probe techniques for single molecular study

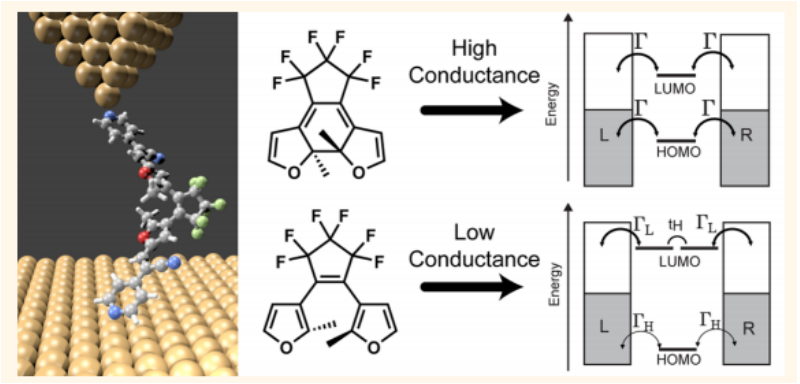


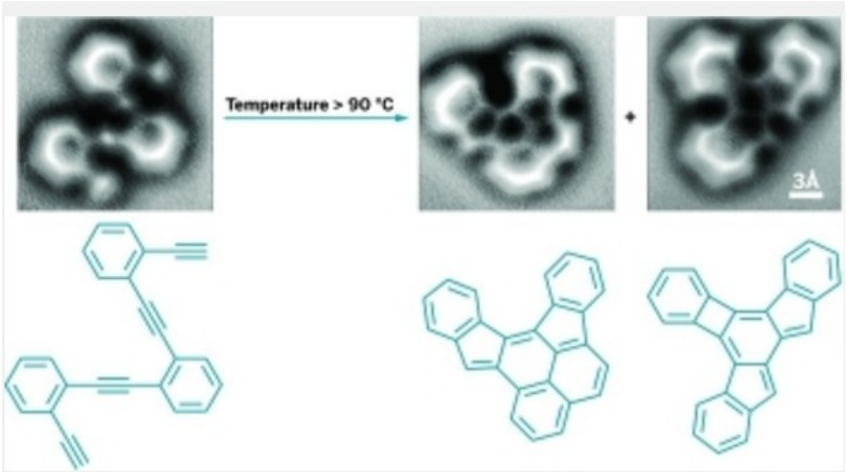
Molecular rotors





Charge transistor

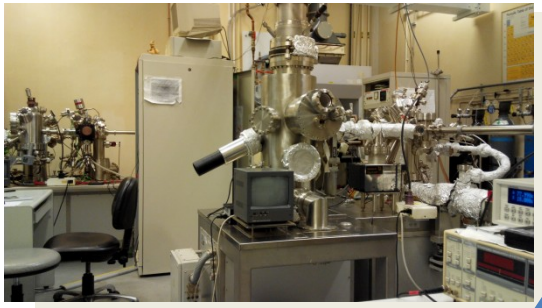




PRODUCT PORTRAIT
AFM images show cyclization of an enediyne compound on a silver surface to form fused-ring polycyclic aromatic products.
Credit: Science

ACS Nano, 2016, 10 (11),
http://www.chem.ed.ac. *:ott-l-cockroft*
http://www.nanounity.com/atomic-force-microscopy.php
Nature Nanotechnology **8**, 46–51 (2013)
http://cen.acs.org/articles/91/i51/Atomic-Force-Microscopy-Provides-Astonishing.html

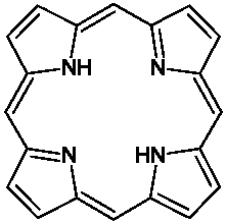
Introduction to the experimental setups



Phys. Rev. B. 88, 245430 (2013)

Introduction to porphyrin molecules

- Among the systems of organic molecules, porphyrin molecules are one of the most studied cases --- **structures and properties**.
- Chemical and biological processes, such as oxygen transport in heme, electron transfer and oxidation reactions in photosynthetic chlorophyll.



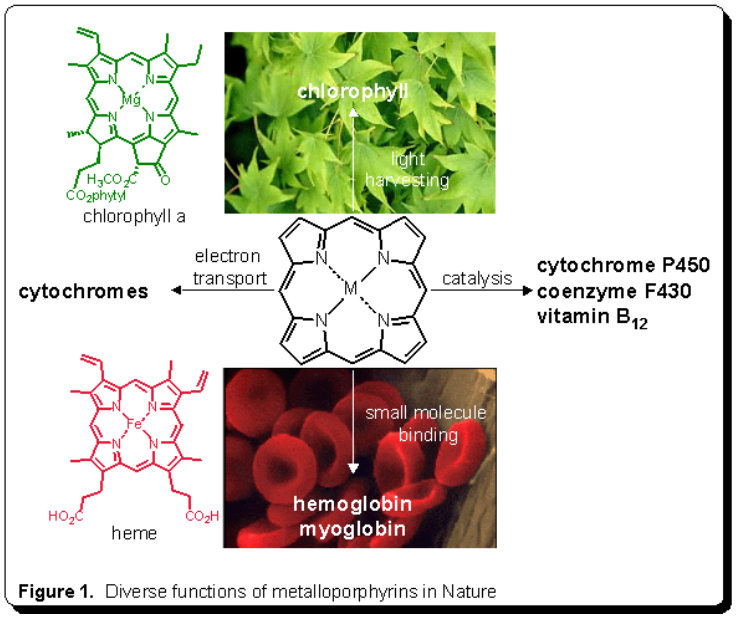
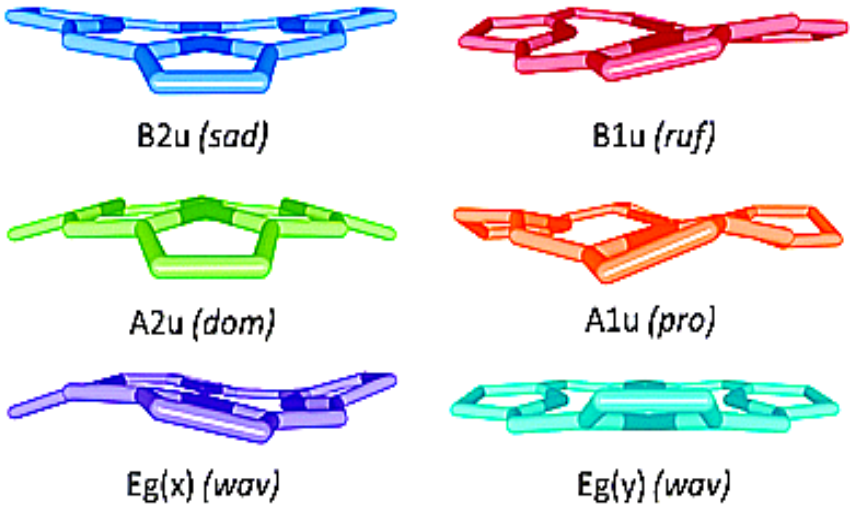


Figure 1. Diverse functions of metalloporphyrins in Nature

Porphyrins can adapt different conformations upon environmental conditions. The electronic and magnetic properties are always related to structural conformations.



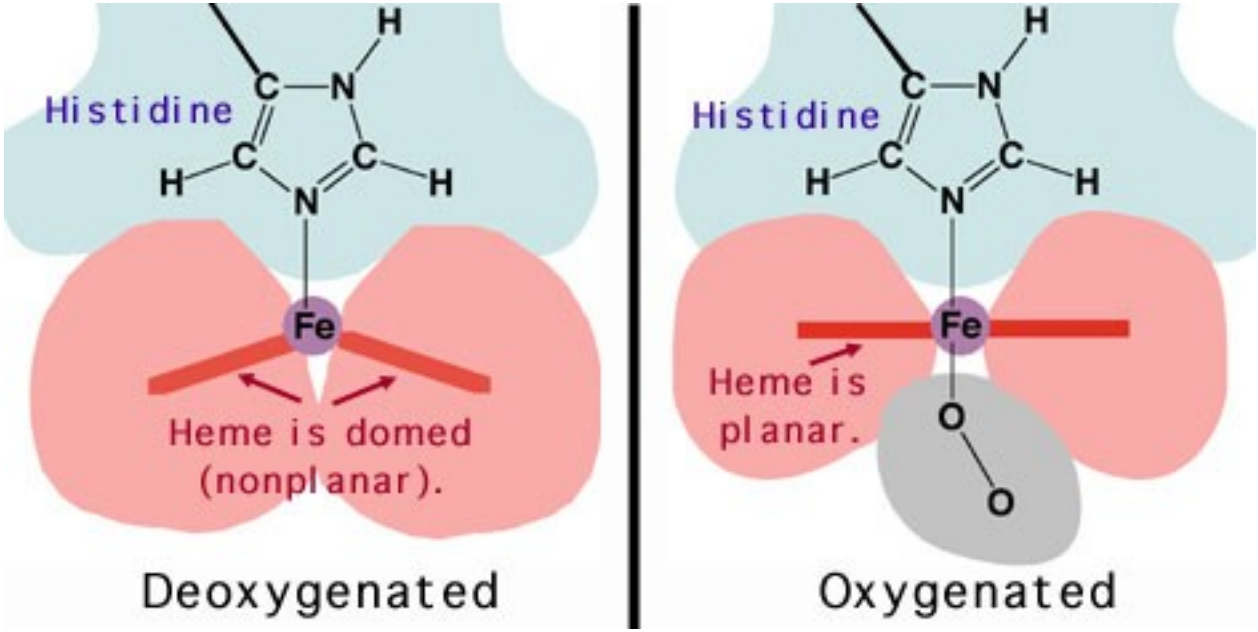
www.chemistry.usf.edu

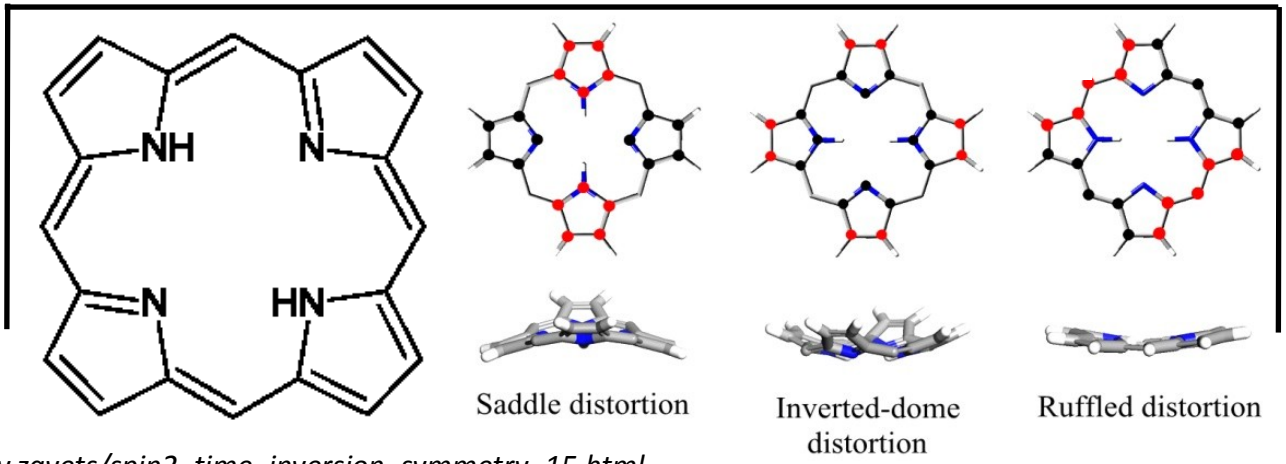
M. O. Senge, S. A. MacGowan, J. M. O'Brien, Chem. Commun. 51, 17031-17063 (2015).

Outline

- Introduction
  - -> Introduction to single molecular study
  - -> Introduction to the experimental setups
  - -> Introduction to porphyrin molecules
- Single-molecule investigations of conformation adaptation of porphyrins on surfaces
- Switching molecular Kondo effect via supramolecular interaction
- The electronic properties of artificial graphene nanoflakes
- Conclusion

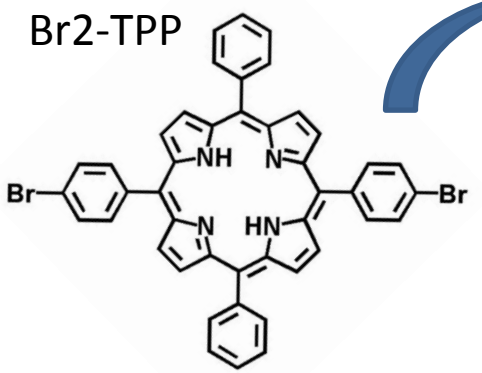
Porphyrin --- Properties and Conformations

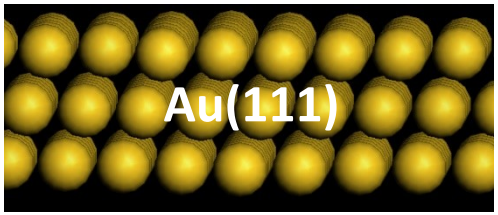


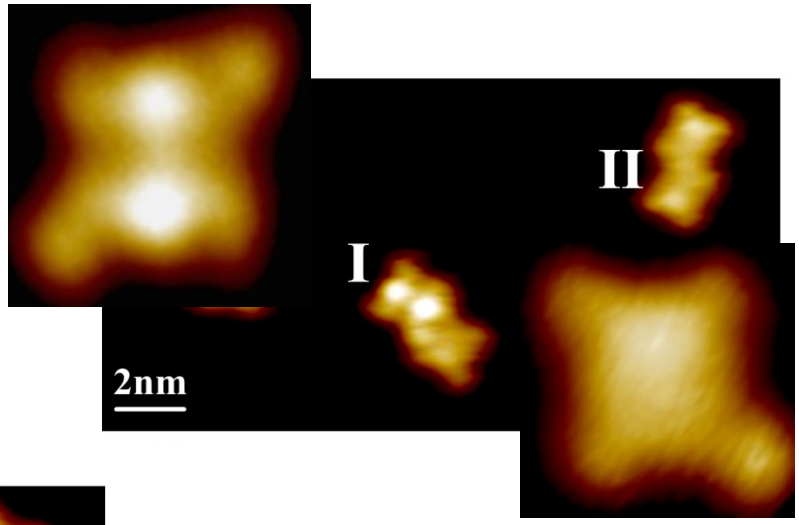


https://staff.aist.go.jp/v.zayets/spin2_time_inversion_symmetry_15.html
http://www.bethehealthyu.com/healthy-blog/2
http://www.chemistry.wustl.edu/~edudev/LabTutorials/Hemoglobin/MetalComplexinBlood.html

Br2-TPP on Au(111)

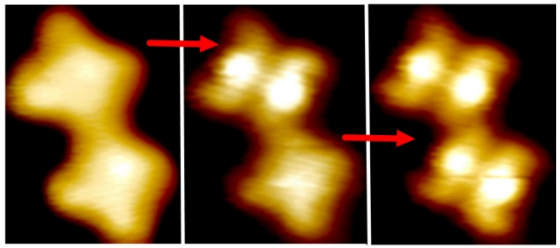






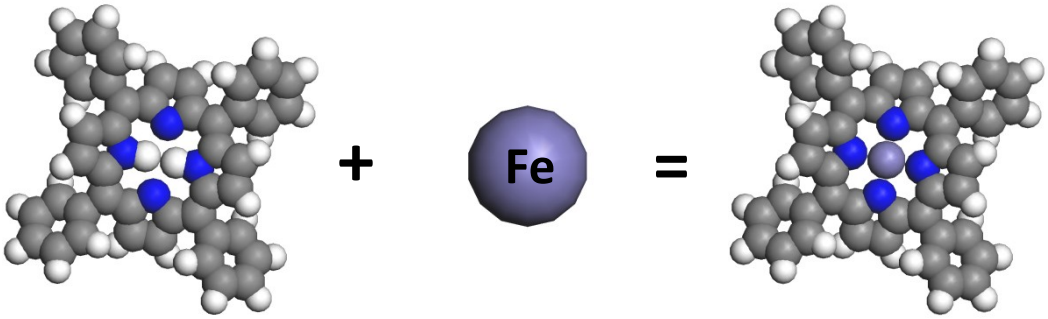
Dimer connected by covalent bond

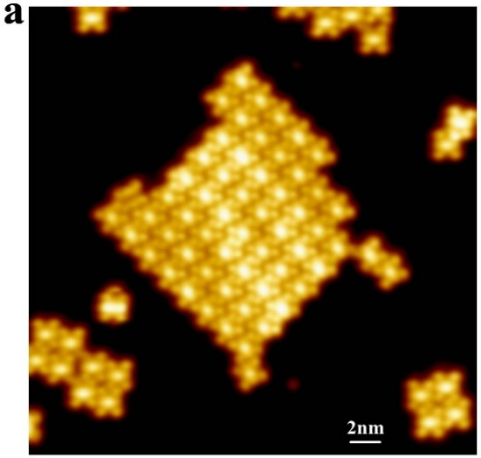
Voltage pulse



Type I is more stable than II

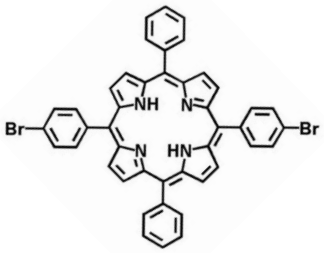
Fe atom metalation

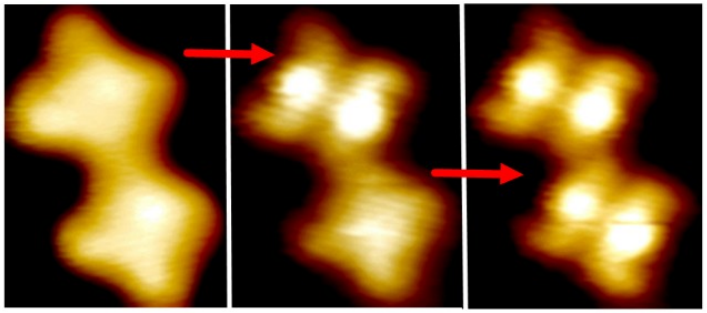


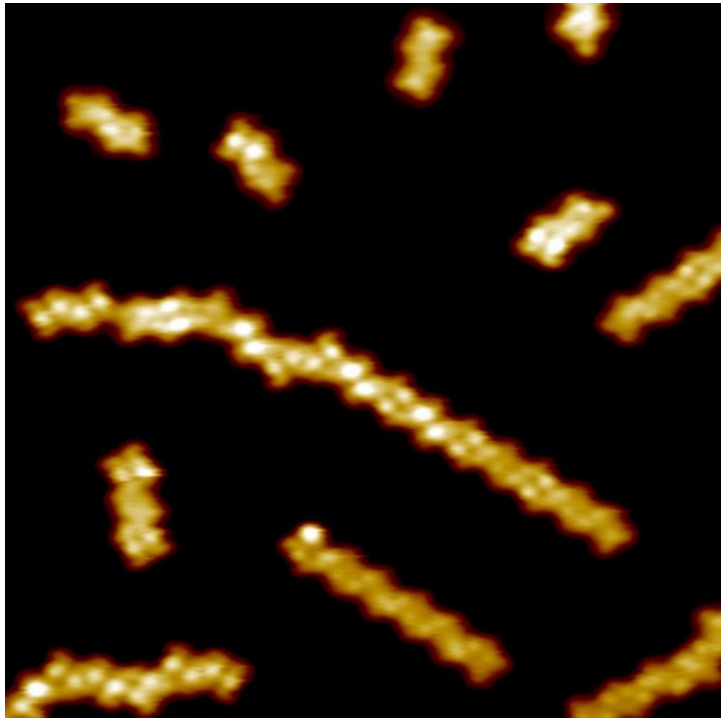


The cause of the two types of molecules

Debromination

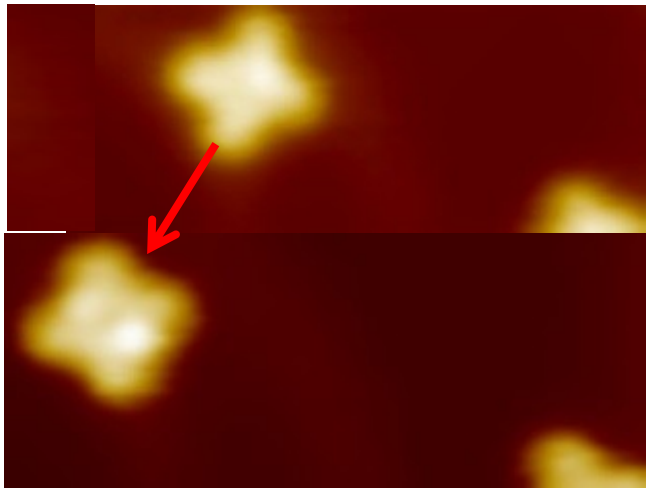




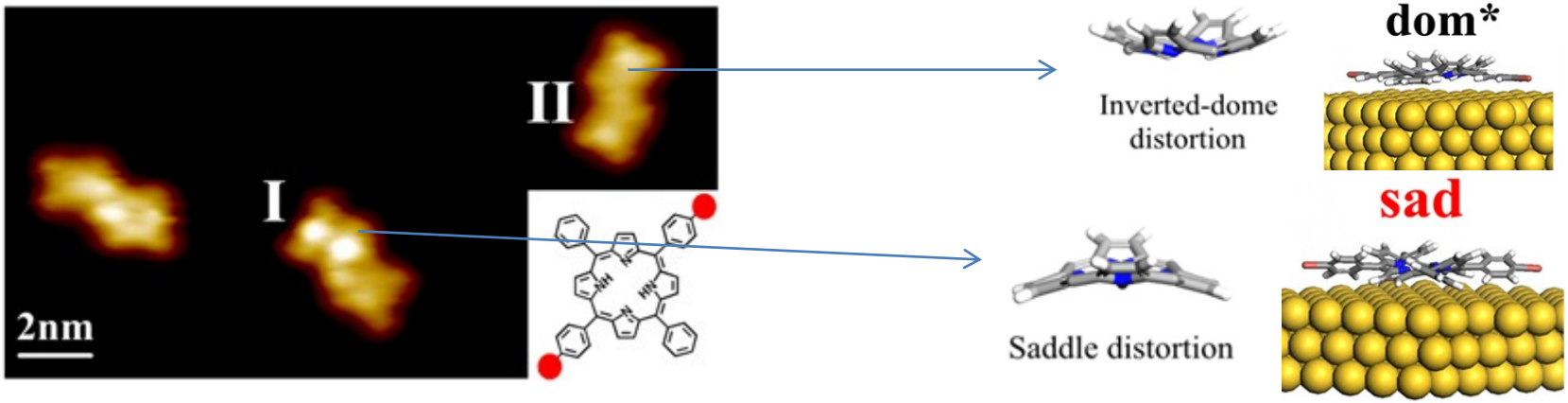


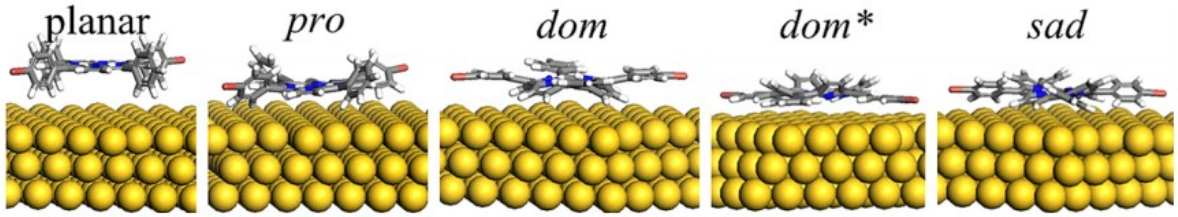
Adsorption sites

Adatoms



Two conformations --- Different geometry structure





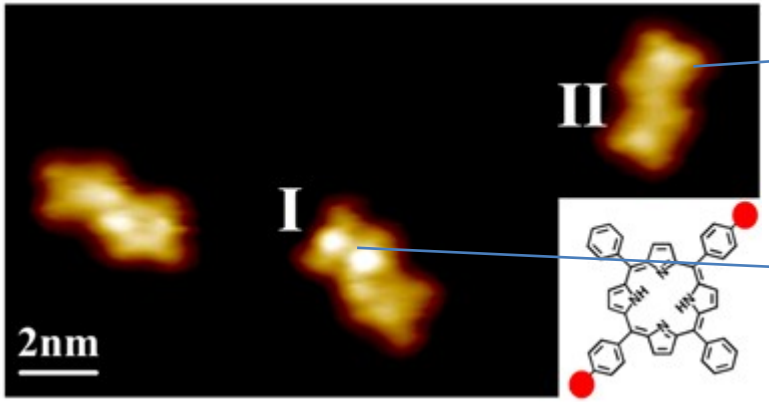
conformation	planar	*pro*	*dom*	*dom**	*sad*
adsorption height (Å)	3.95	3.80	3.80	3.50	3.75
adsorption energy (eV)	0.91	1.21	0.73	1.35	2.16
distortion energy (eV)	0.08	0.38	0.45	0.41	0.49

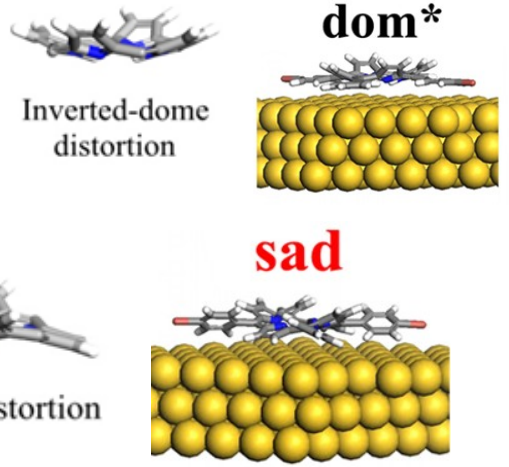
$E_{adsorption} = E_{Au} + E_m - E_{total}$

$E_{distortion} = E_m - E_{planar}$

$E_{distortion}$ thus quantifies the cost of distorting a planar molecule to a specific conformation in free space.

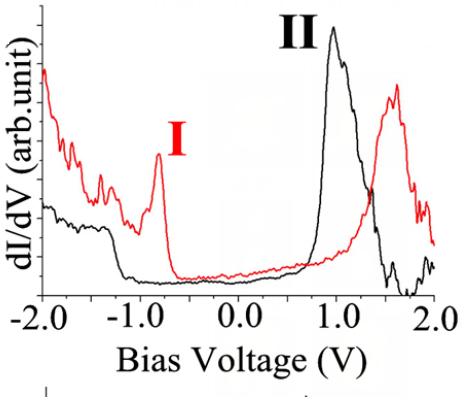
Two conformations --- Different geometry structure



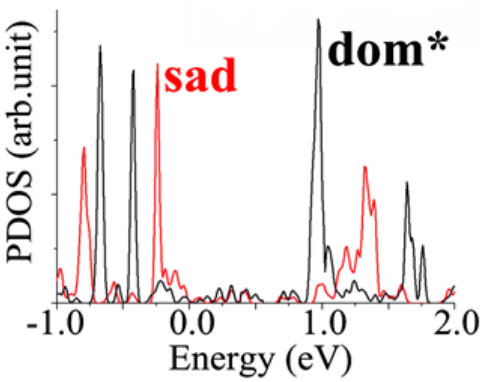


Conformation	Planar	Dom	Dom*	Ruf	Sad
HOMO (eV)	-0.19	-0.09	-0.46	-	-0.23
LUMO (eV)	1.49	1.10	0.95	-	1.33

Experimental STS



DFT calculated DOS

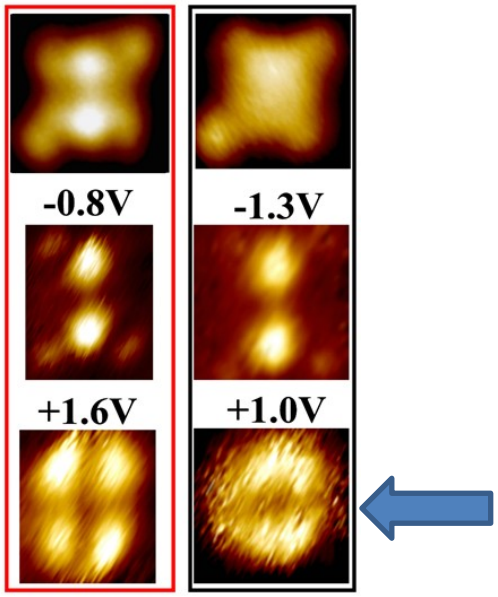


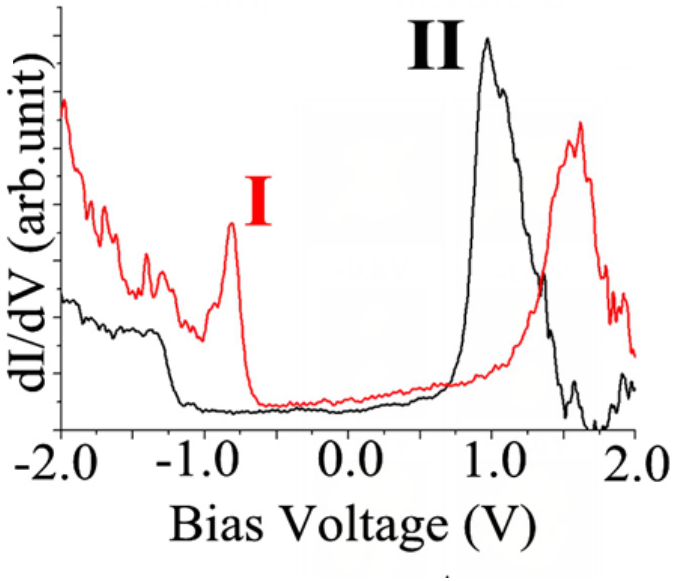
The distribution of HOMOs and LUMOs of two Conformations

STM

HOMO

LUMO

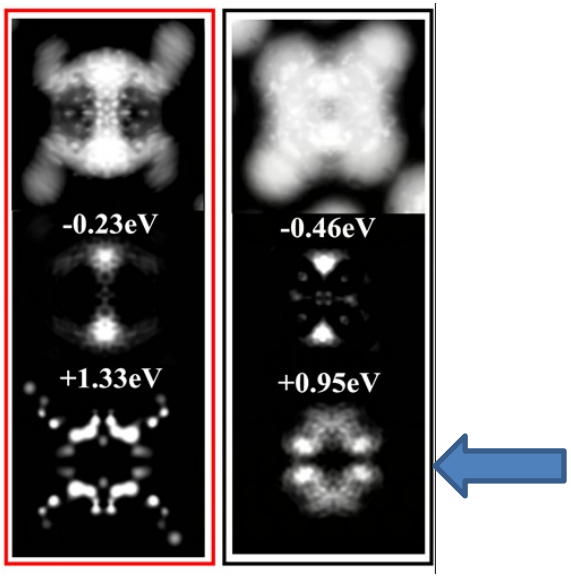


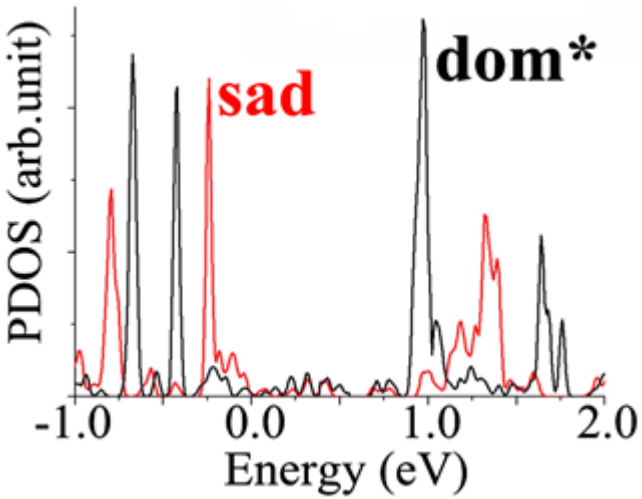


Simulated STM

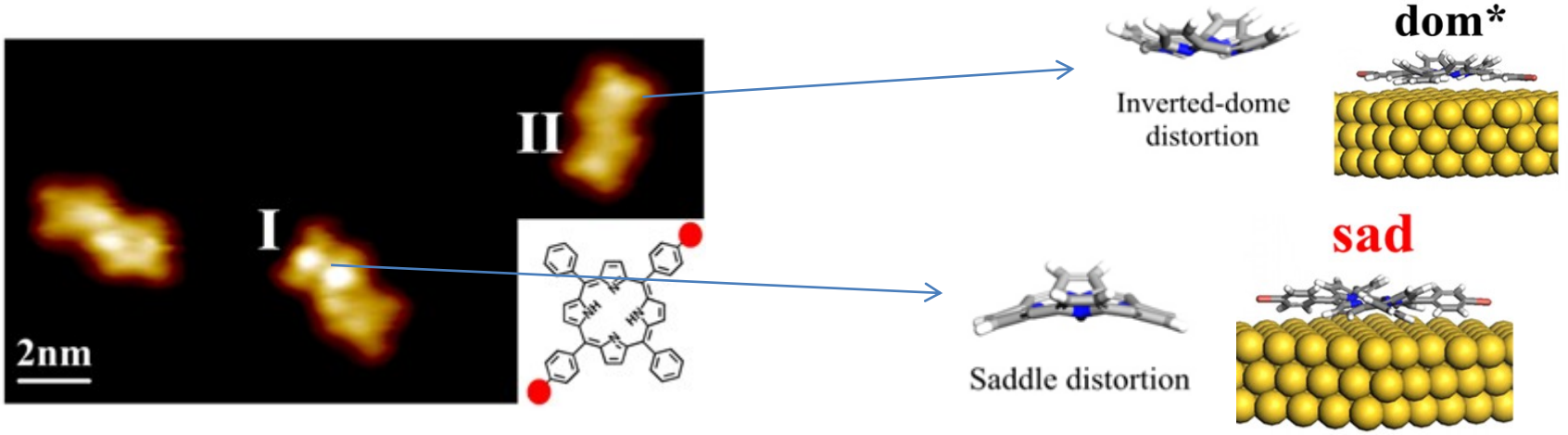
HOMO

LUMO





Two conformations --- Different geometry structure

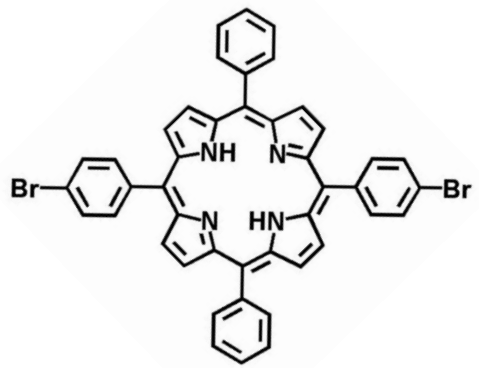


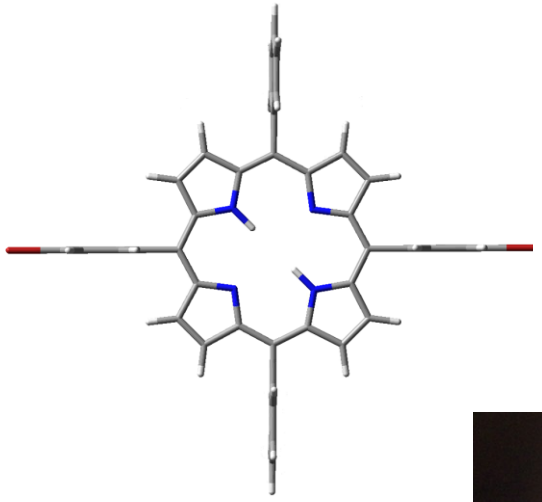
What is the mechanism of forming these two different conformations?

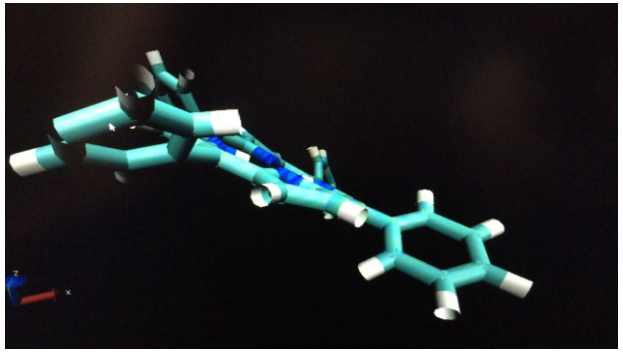
The effects of substrates.

The gas phase of Br2-TPP

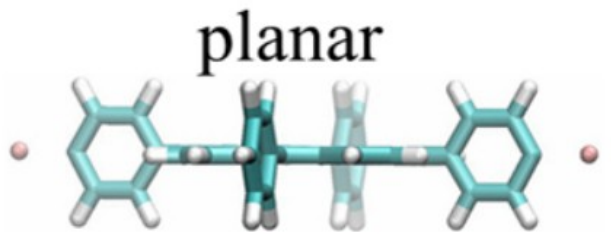
At temperature 0 K

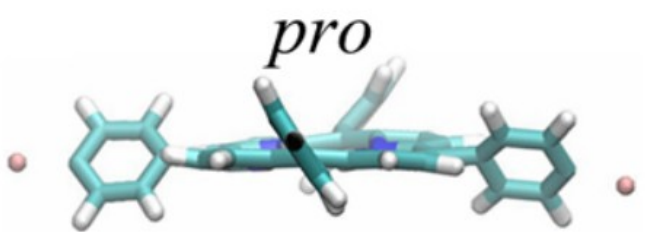


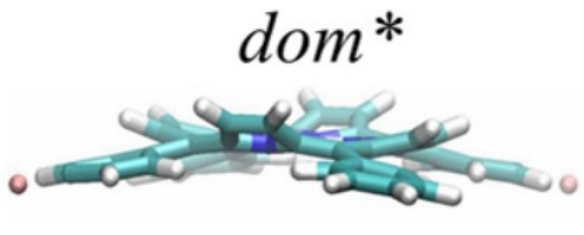




The MD simulations revealed that the molecule was transformed alternatively among planar, pro, and dom (dom*) conformations at 550K.



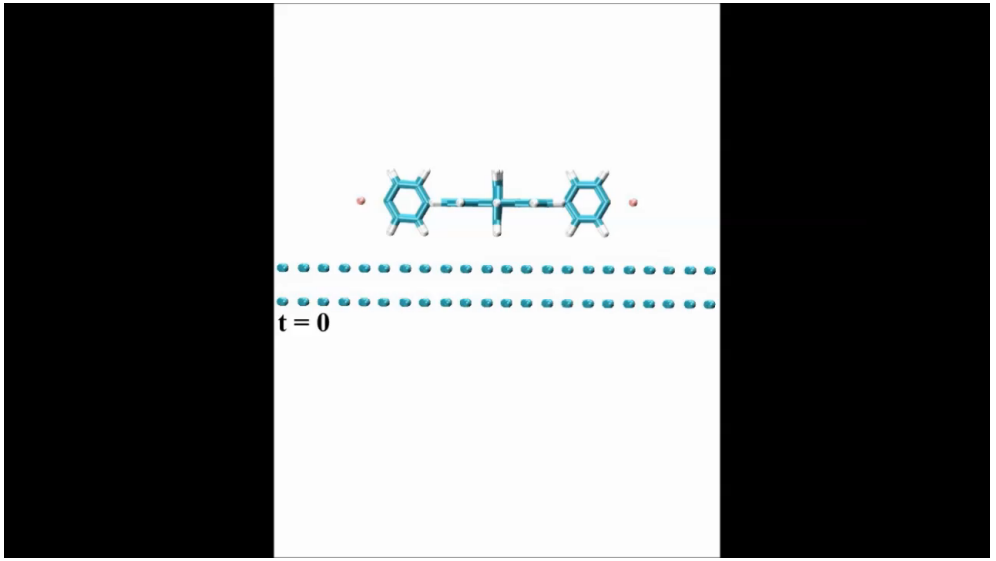




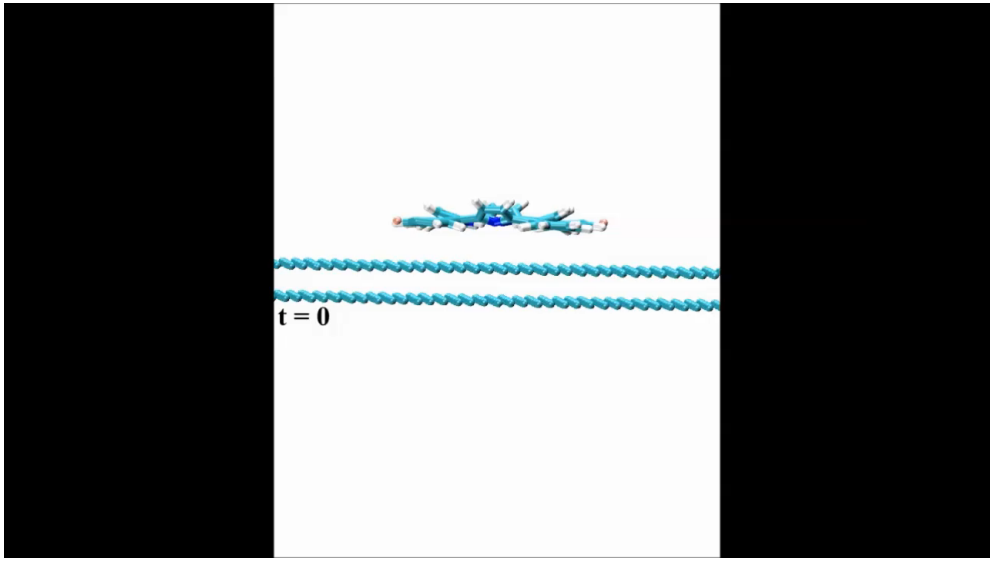
After adsorbed on Au(111) surface

At 250K

planar

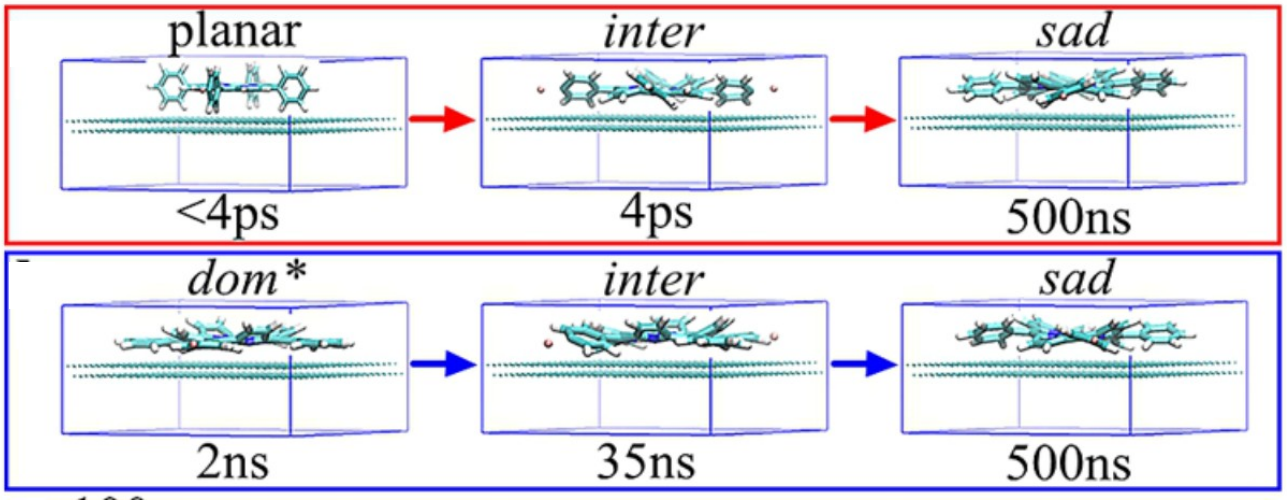


*dom**

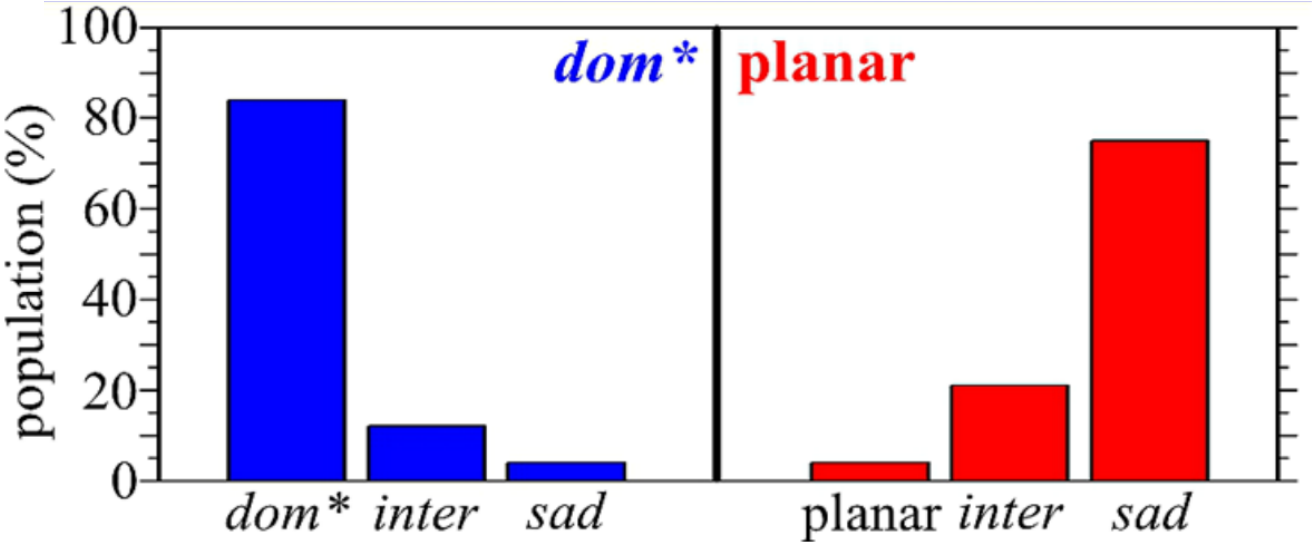


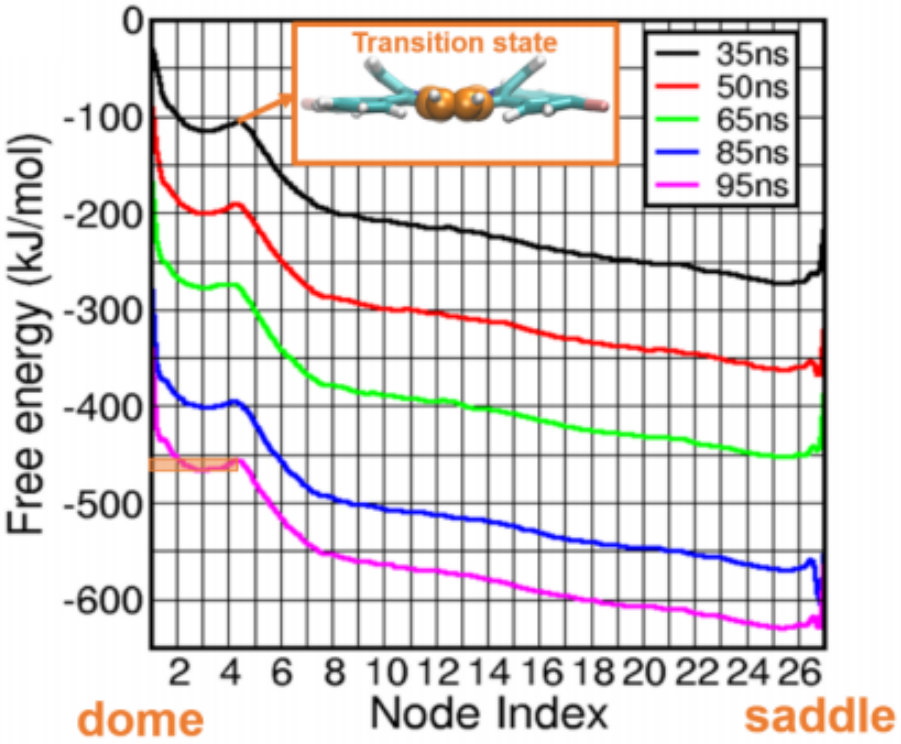
After adsorbed on Au(111) surface

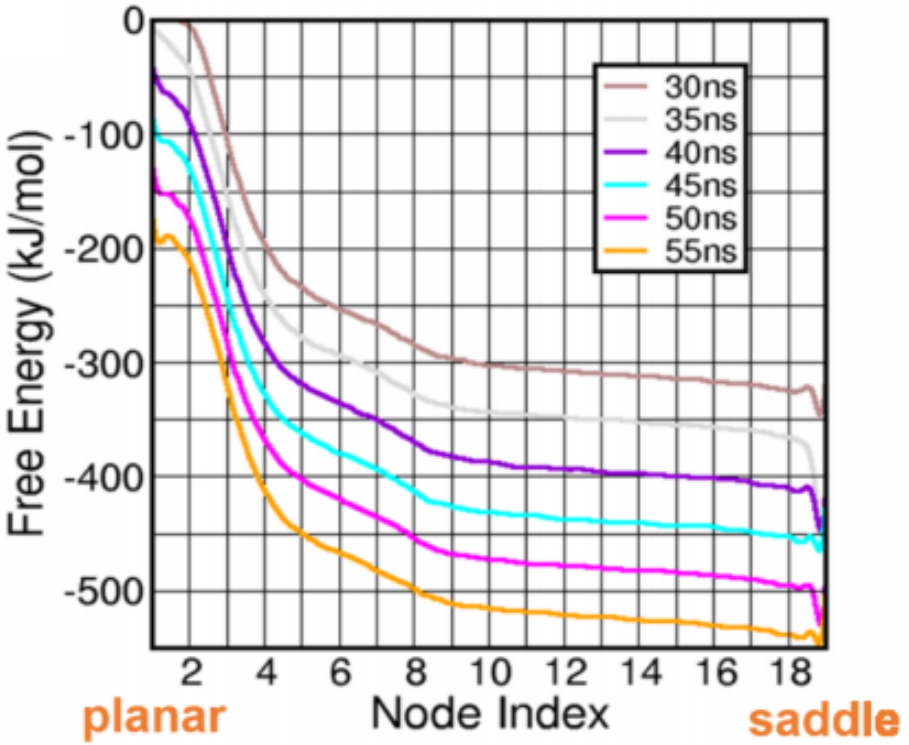
At 250K

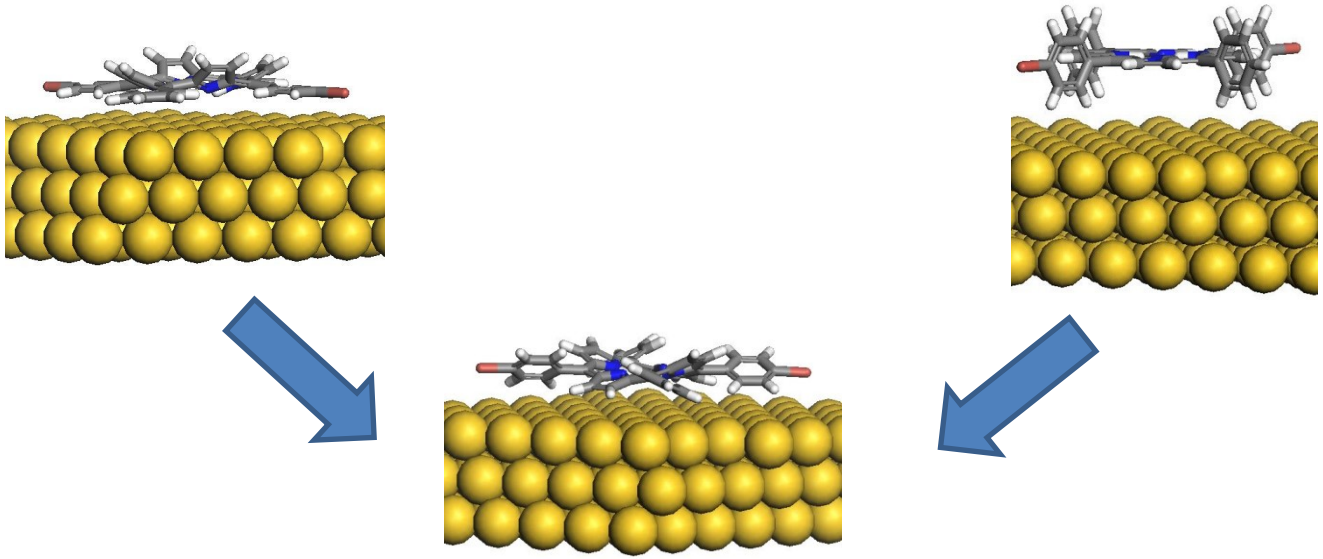


The final products after the ***dom**** /**planar** conformer cools from 250 to 5K (5K is the STM imaging temperature)




Transition state
35ns
50ns
65ns
85ns
95ns
Free energy (kJ/mol)
0
-100
-200
-300
-400
-500
-600
2 4 6 8 10 12 14 16 18 20 22 24 26
Node Index
dome
saddle

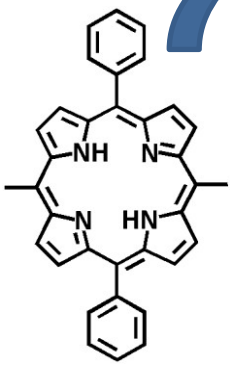

30ns
35ns
40ns
45ns
50ns
55ns
Free Energy (kJ/mol)
0
-100
-200
-300
-400
-500
2 4 6 8 10 12 14 16 18
Node Index
planar
saddle

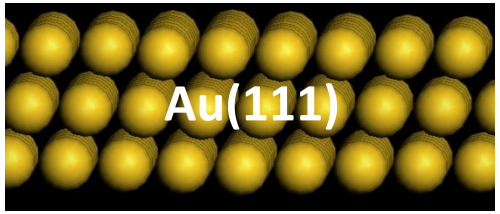


Dpp on Au(111)

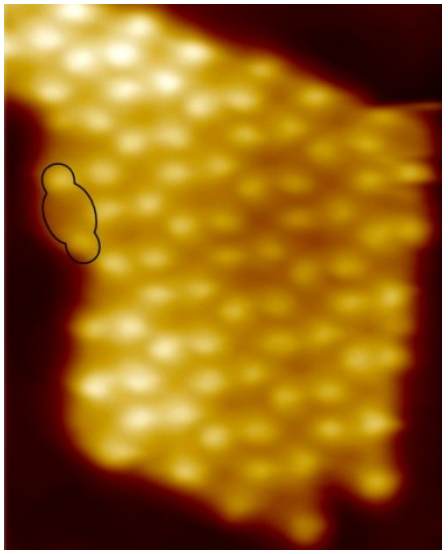
Affect of Functional group

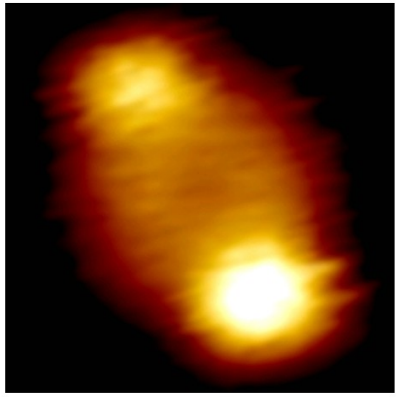
DPP

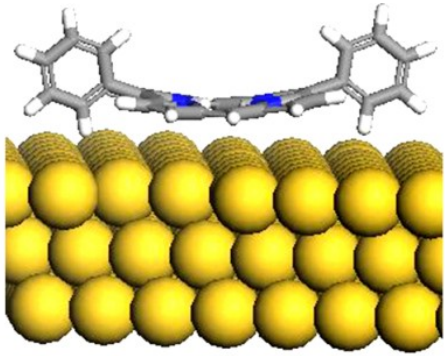




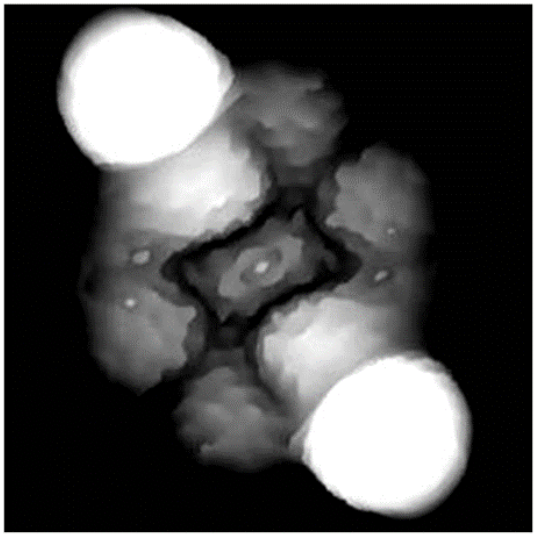
Only one type



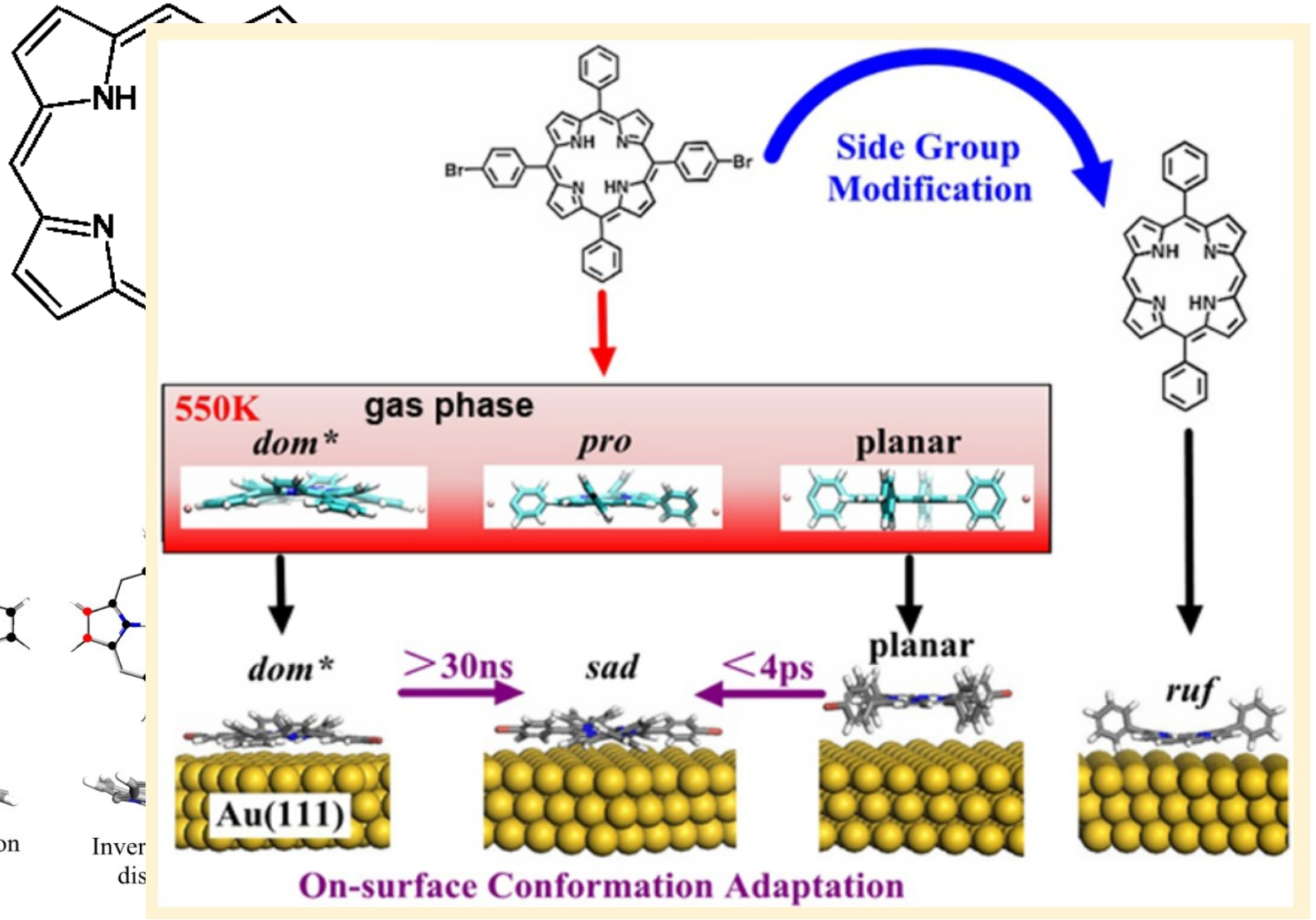




Ruffled distortion



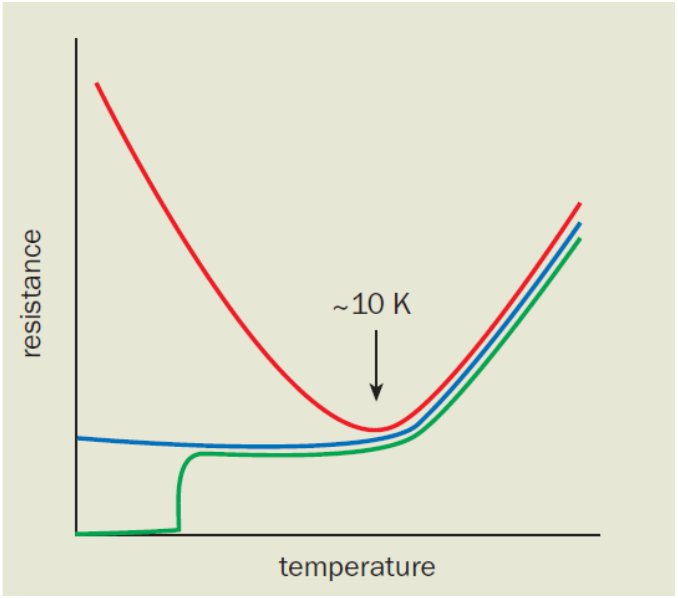
Summary

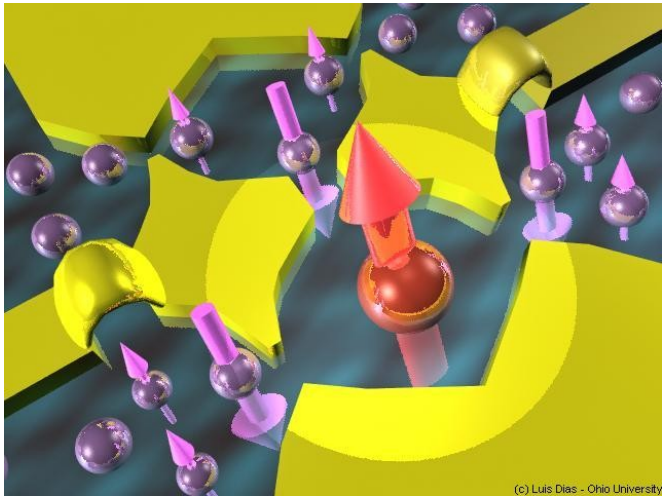

NH
N
Br
Br
Side Group
Modification
550K
gas phase
dom*
pro
planar
dom*
>30ns
sad
<4ps
planar
ruf
Au(111)
On-surface Conformation Adaptation
Saddle distortion
Inver
dis

Outline

- Introduction
  - -> Introduction to single molecular study
  - -> Introduction to the experimental setups
  - -> Introduction to porphyrin molecules
- Single-molecule investigations of conformation adaptation of porphyrins on surfaces
- Switching molecular Kondo effect via supramolecular interaction
- The electronic properties of artificial graphene nanoflakes
- Conclusion

Kondo Effect

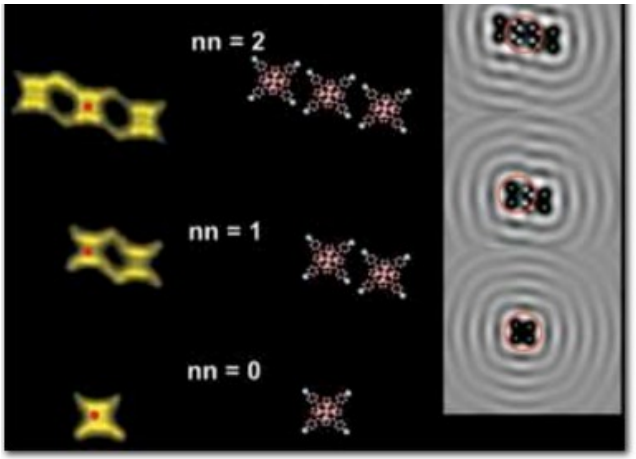


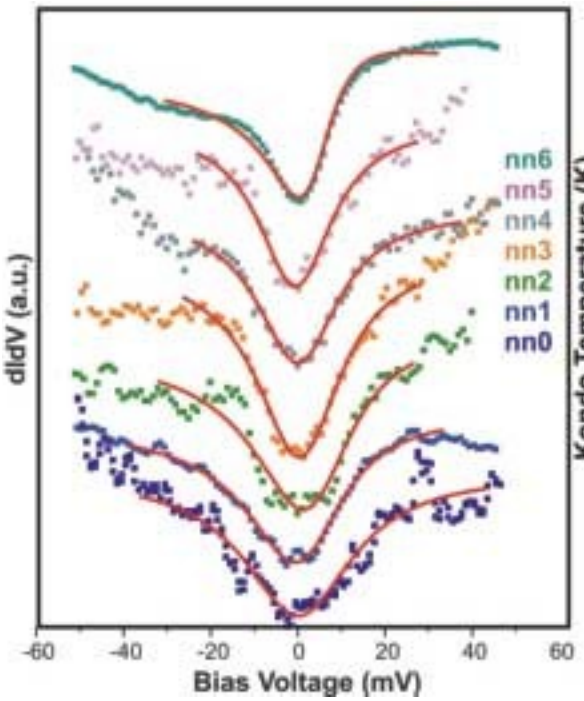


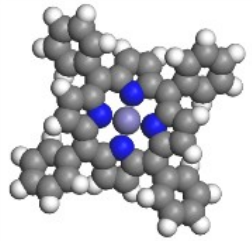
- Low temperature behavior. (Below the Kondo temperature)
- The electrical resistance increases as the temperature is lowered
- Kondo Effect was first explained by Japanese theorist Jun Kondo in 1964.
- The Kondo effect: The exchange interaction between the localized spins of magnetic impurities and the conducting electrons in the host metal.
- For future applications such as in spintronics and quantum information processing.

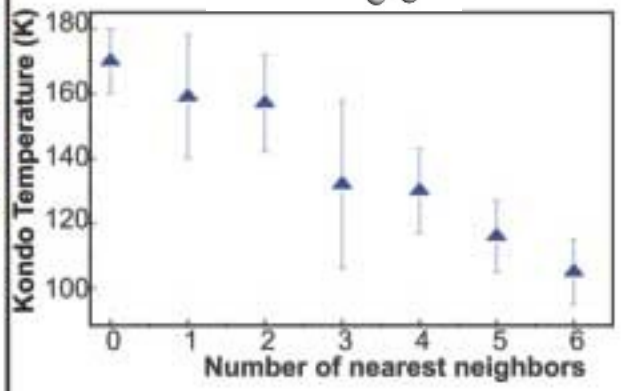
Physics World, Volume 14, Number 1
http://www.fmt.if.usp.br/~luisdias/KondoPage/kondo.html

Molecular Kondo system









The Fano function：

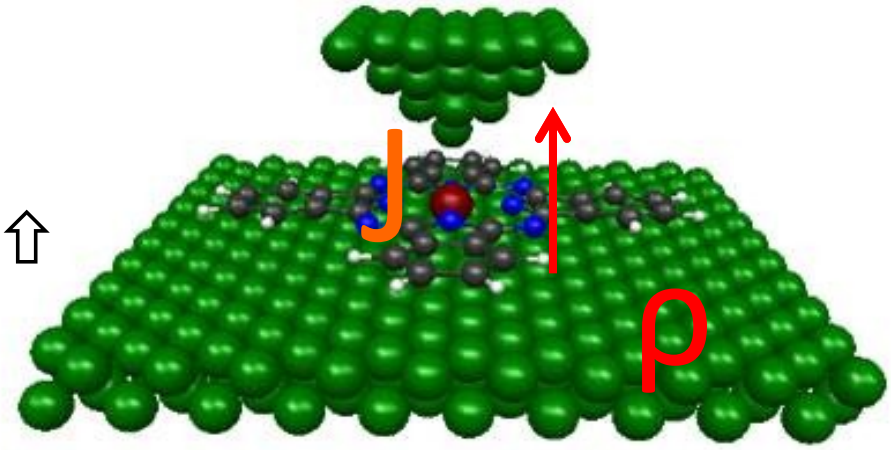
$$\frac{dI}{dV} \propto \frac{[q+(V-V_0)/\Delta]^2}{1+[(V-V_0)/\Delta]^2} + G_{EL}$$

$$\Delta = k_B T_K$$

Phys. Rev. Lett. **97**, 266603

Qualitative Model (J and ρ) for molecular system

$J\Uparrow, \rho\Uparrow \longrightarrow T_K\Uparrow$



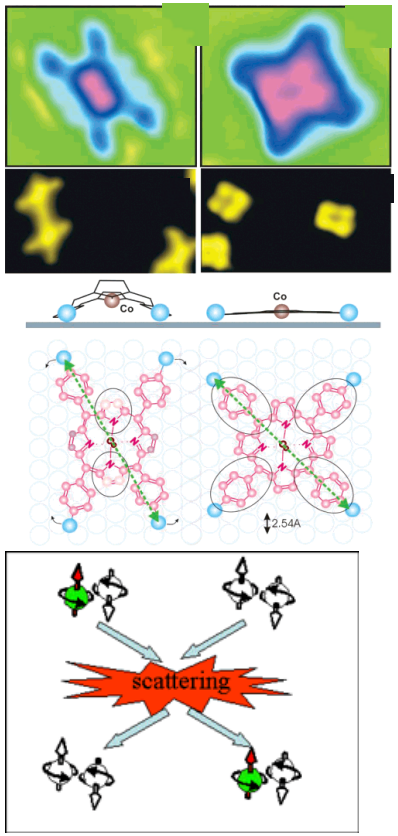
- Qualitative correlation $k_B T_K \propto e^{-1/\rho J}$
- The host density of states ‘‘ρ’’ and spin-electron coupling ‘‘J’’
- The magnetic moment of center spin also contributed to the magnitude of ρ

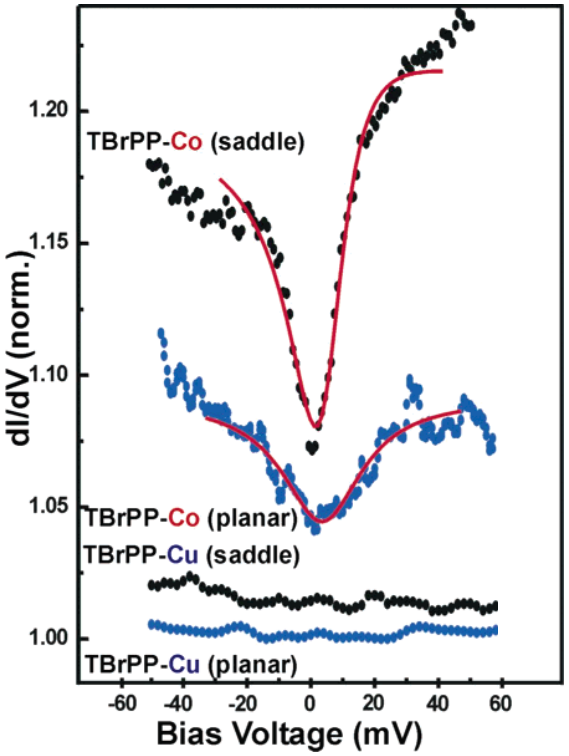
Nanoscale Modeling Group, Chair Materials Science and Nanotechnology, TU Dresden

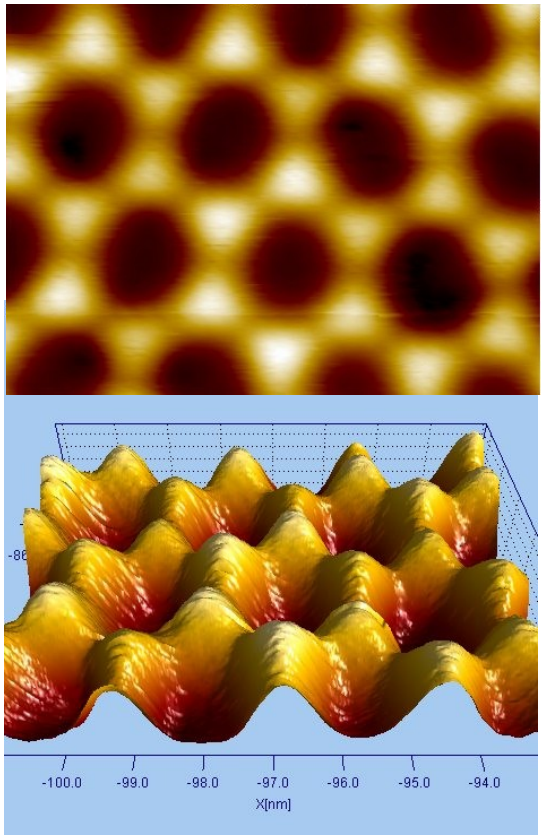
Controls of molecular Kondo Resonance

Changing conditions (molecular, environment)
Distinct properties (structural, magnetic)
Spin screen and exchange process
Controlling of Kondo effect

Metal-organic coordination poles can be used to modify the environment of magnetic impurities

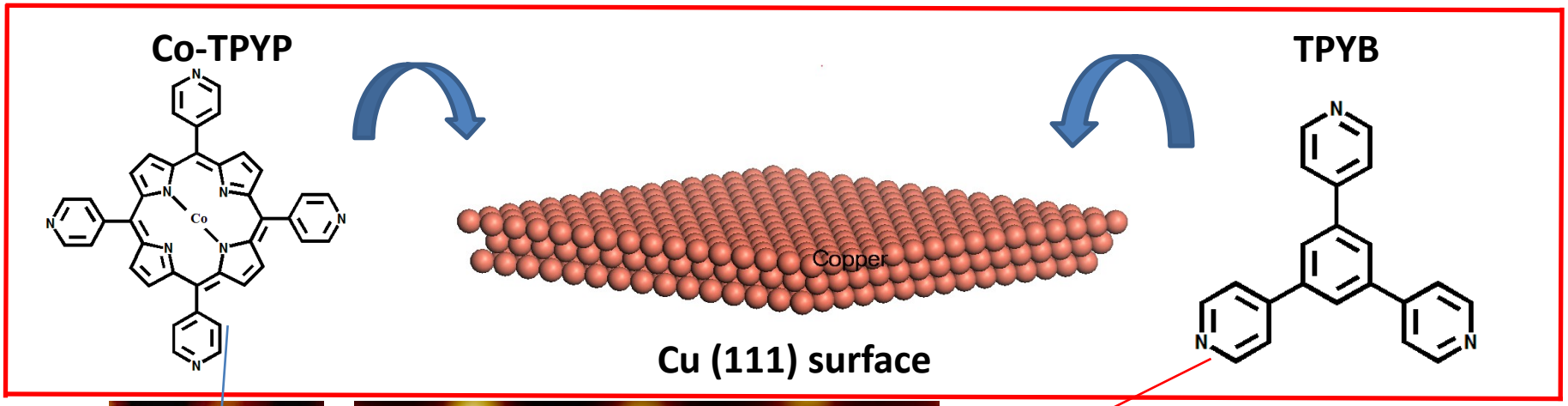


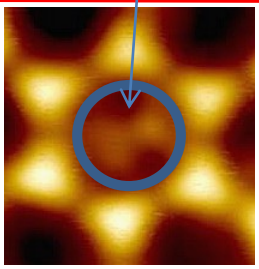


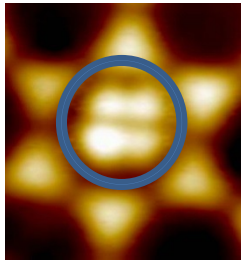


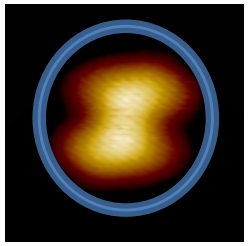
Nano Lett., Vol. 6, No. 4, 2006

Experimental Results-Cu(111)

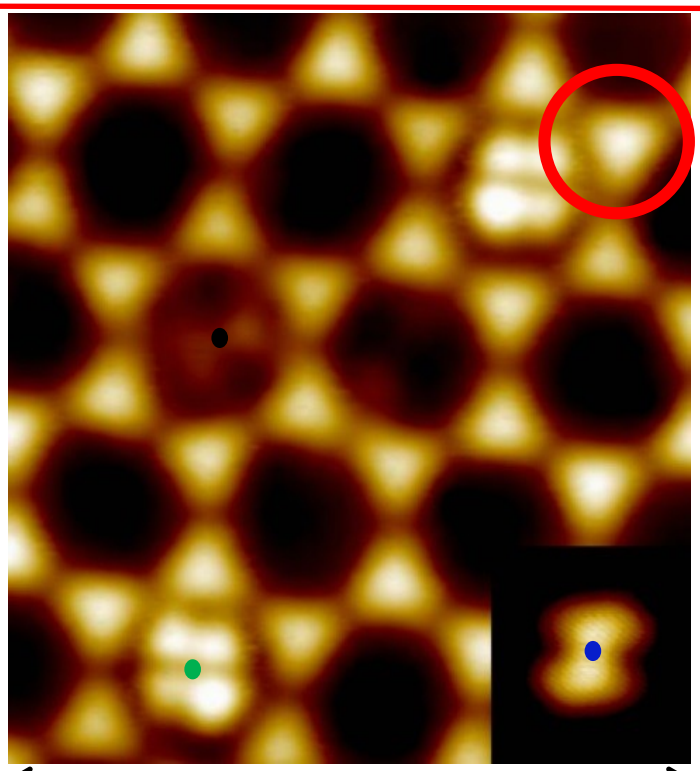




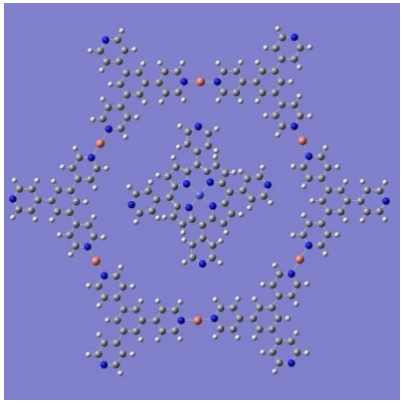


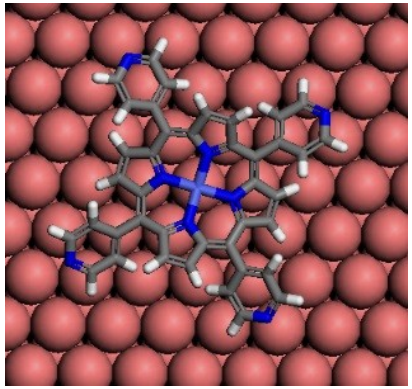


-1V, 0.3nA



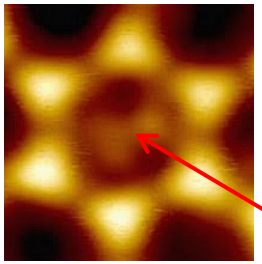
9nm



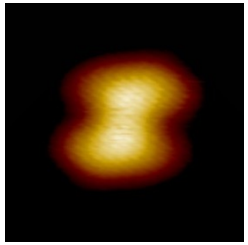


Experimental Results

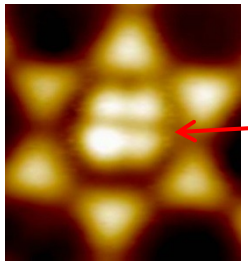
Kondo

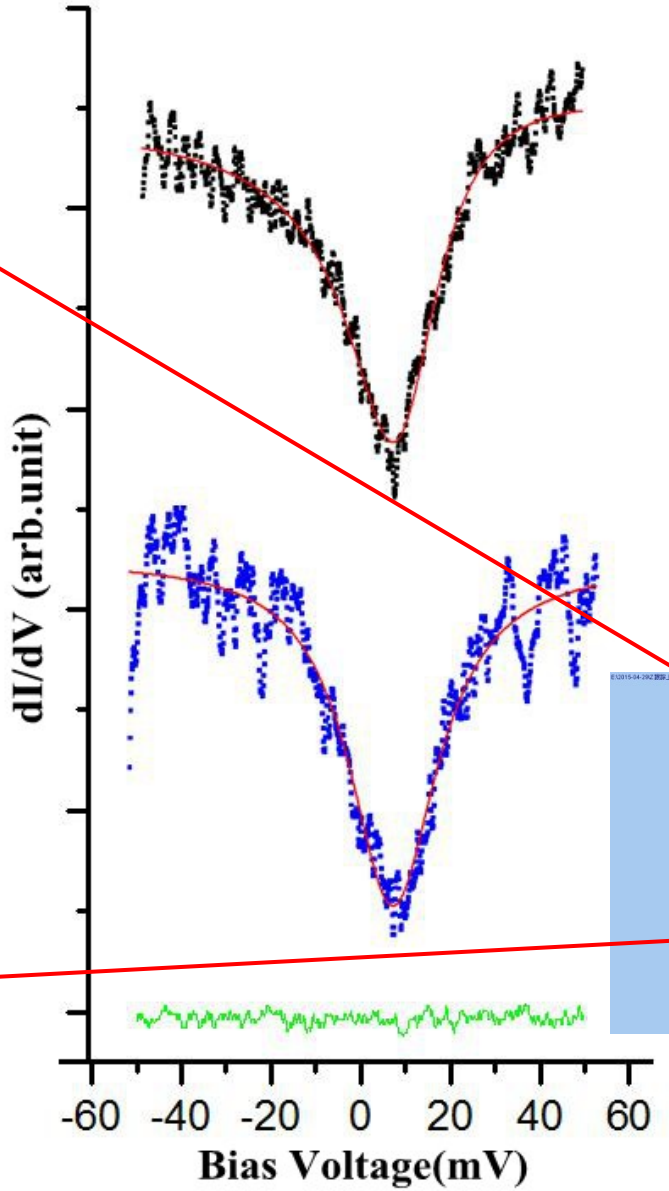


Kondo

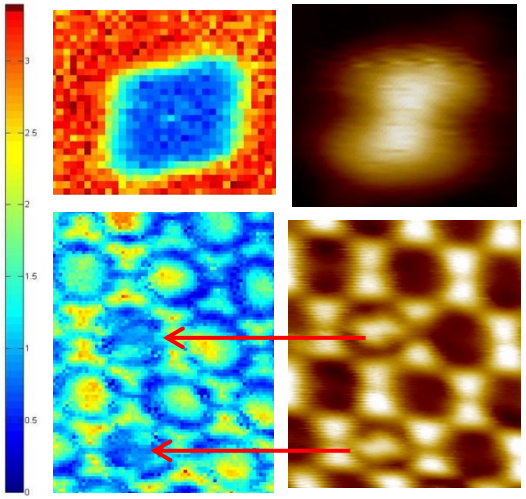


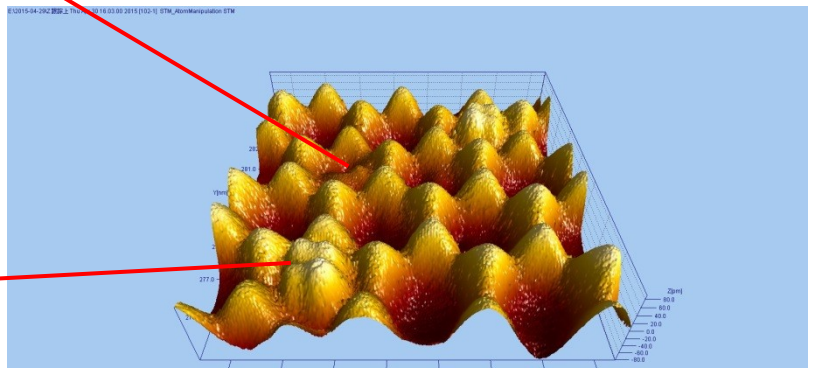
No Kondo



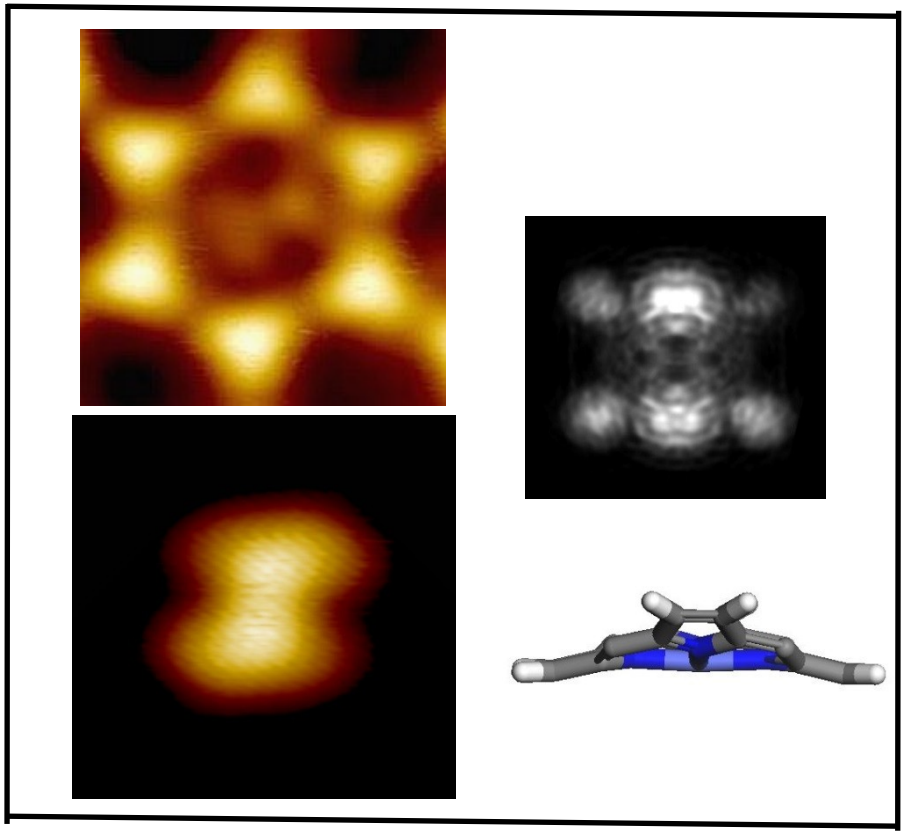


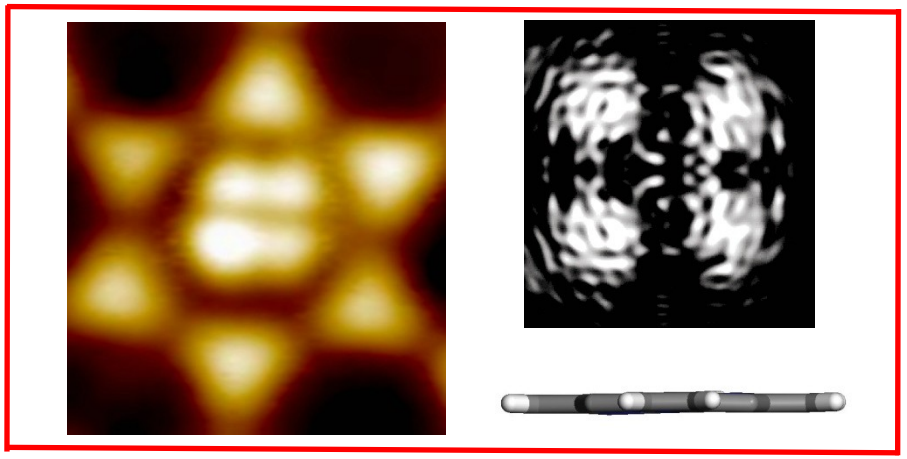
dI/dV distribution at the Fermi level



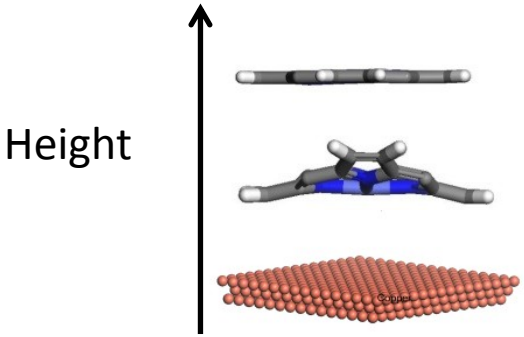


Experimental explanation





Coordination Selection



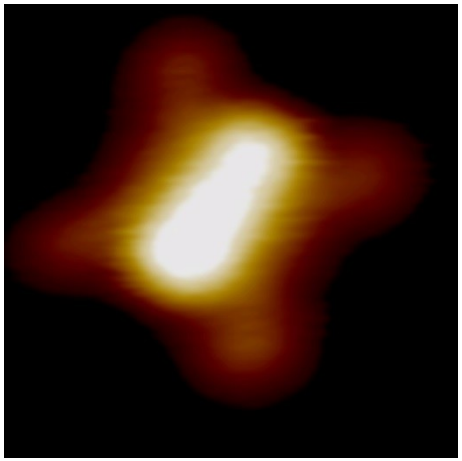
Lift up --- Gas phase

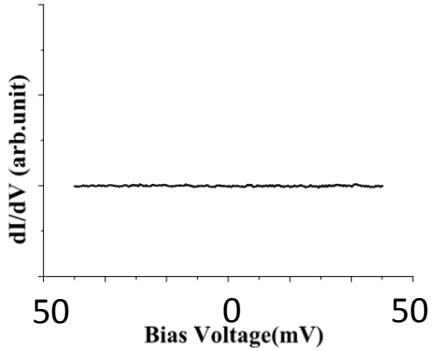
Substrate	Environment Conditions	Experimental T_K Range (K)	Height Related to substrate surface (Å)
Cu (111)	Single molecule	141.73~151.81	2.52/2.6(DFT)
Cu (111)	Inside coordination hole	106.96~268.16	**2.31**
Cu (111)	Above coordination hole	No Kondo Resonance	**3.46**

Indications: For the gas-phase molecules, the absence of substrate-molecule coupling leads to NO KONDO RESONNANCE.

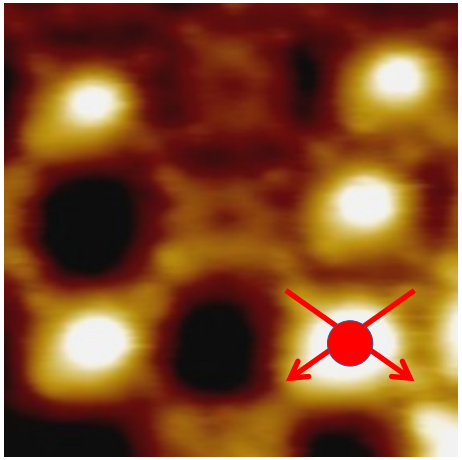
Experimental Results-Au(111)

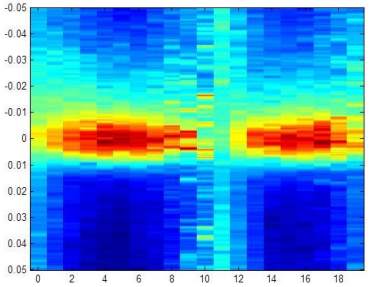
Co-TPYP on Au (111) surface

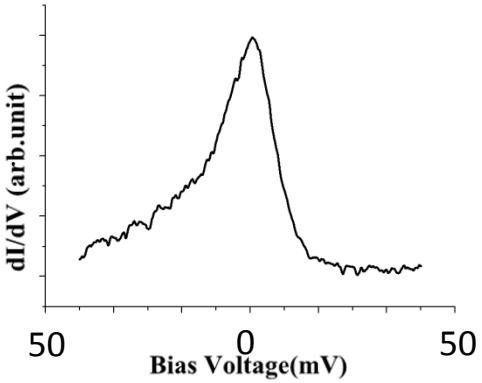


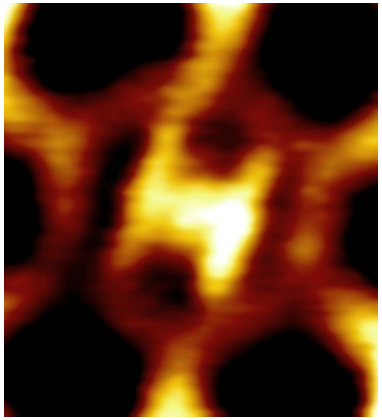


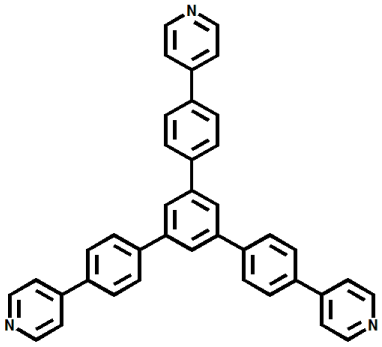
Kondo Effect can only exist if there is molecular array/coordination



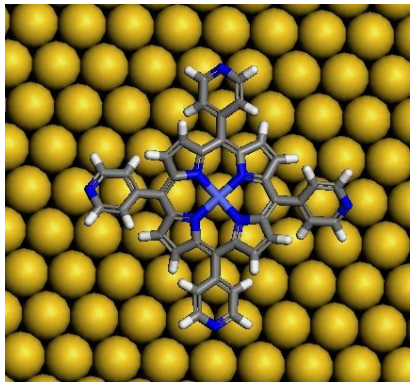


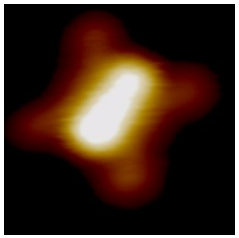


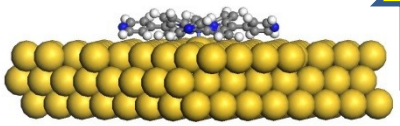




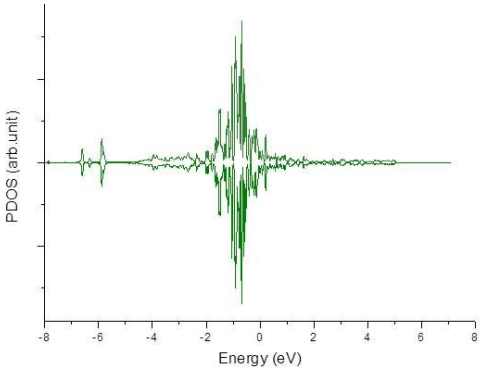
Experimental explanation





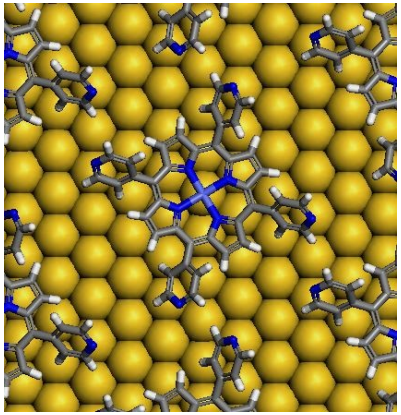


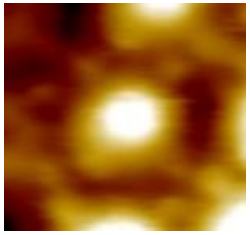
Substrate	Environment Conditions	Experimental T_K Range (K)	Height Related to substrate surface (Å)
Au (111)	Single molecule	No Kondo Resonance	1.96/2.3 (DFT)
Au (111)	Close packing	100.01~118.21	2.62/2.8 (DFT)

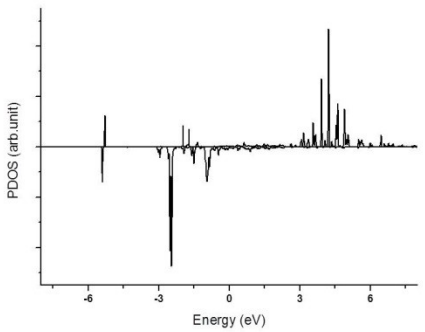


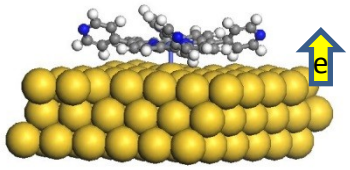
Coordination Selection

Lift up --- weaken the coupling strength and reduce charges transferred





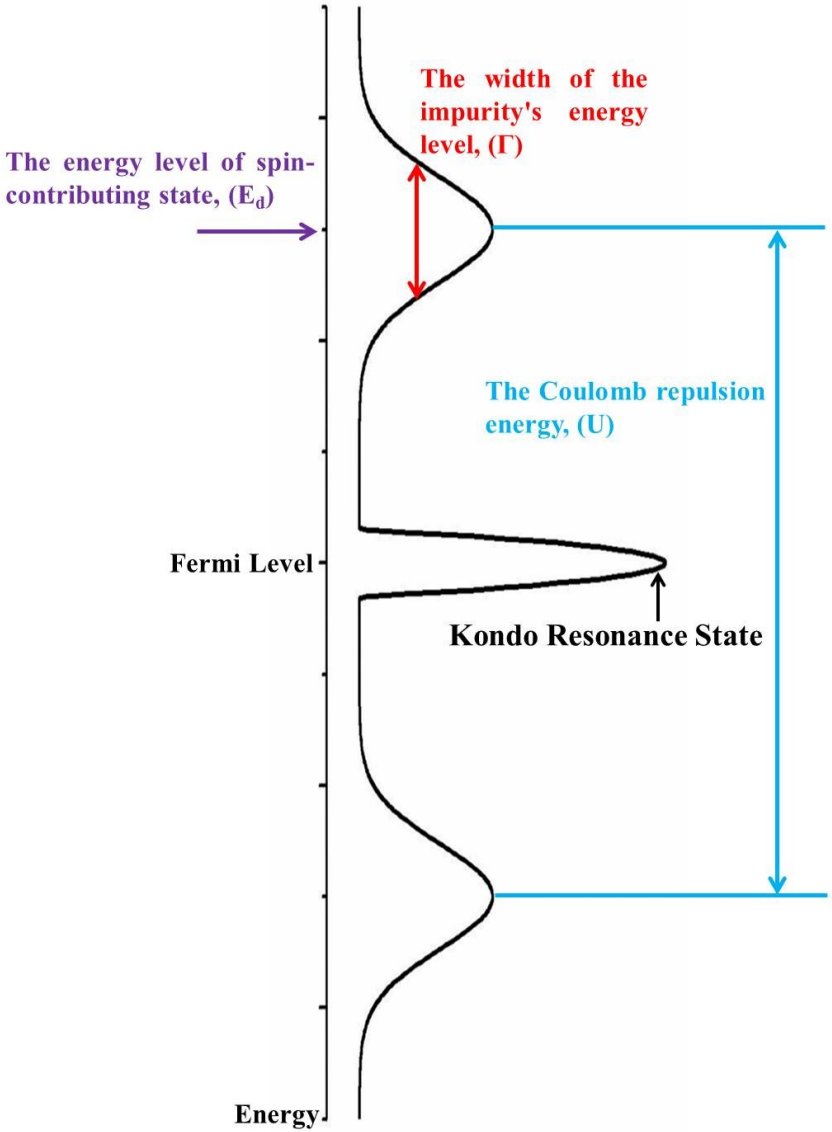




<u>Indications</u>: For the strongly adsorbed molecules, the substrate-molecule charge-transfer process leads to NO KONDO RESONNANCE.

0.9e (single adsorbed) 0.3e (close packing) from Au atom to Co atom

The Anderson model for molecular system

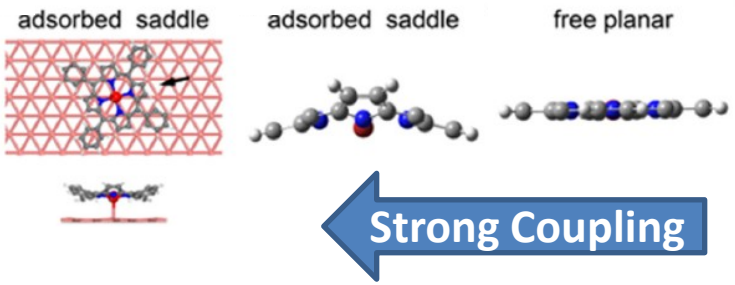


The Anderson model is:

$T_K = ½ (ΓU)^{1/2} \exp[\pi E_d(E_d + U)/ΓU]$

U ---- the magnetic moment

Γ ---- the strength of molecule-substrate coupling

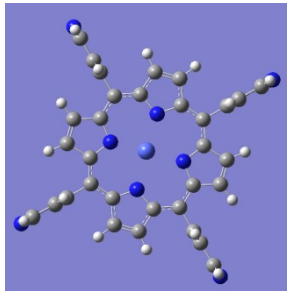


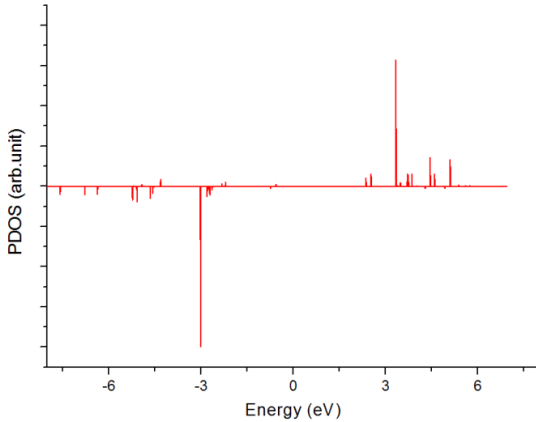
The amount of charges transferred between substrate and molecules increasing; the magnetic moment reducing

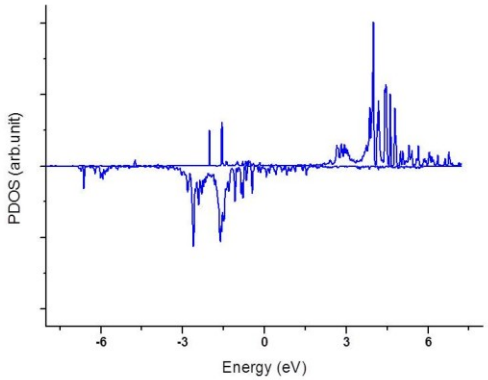
(i) the Coulomb repulsion energy U decreasing
(ii) the Gaussian broadening Γ increasing
(iii) the energy level of spin-contributing state E_d moving closer to the Fermi level

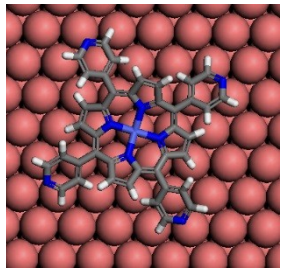
PHYSICAL REVIEW B ***91****, 045440 (2015)*

Calculate the Kondo Temperature

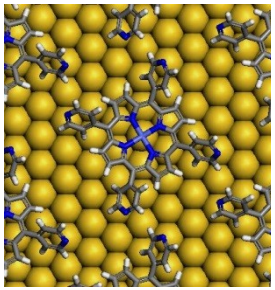


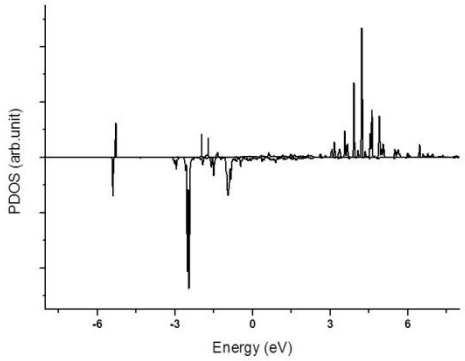


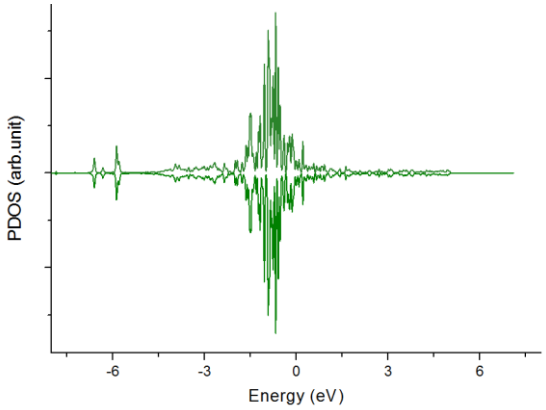


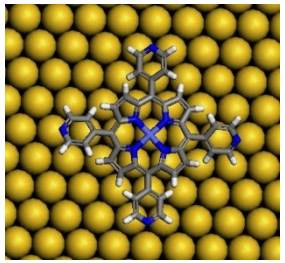


$$T_K = \tfrac{1}{2}(\Gamma U)^{1/2}\exp[\pi E_d(E_d + U)/\Gamma U]$$







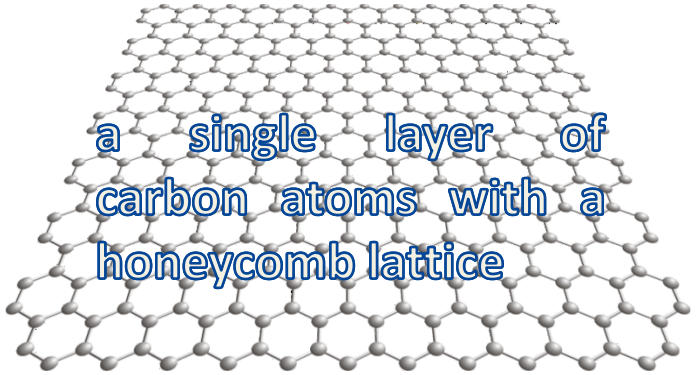


Type of Molecules	E_d (eV)	U (eV)	Γ (eV)	Calculated/Experimental T_K (K)	Magnetic Moment (μ_B)
Gas Phase	-3.052	6.317	~0	N/A	1.07
Single Adsorbed (Cu)	-1.784	6.147	0.85	122.88/146	0.78
Close-packing (Au)	-1.811	6.052	0.81	92.24/109	0.64
Single Adsorbed (Au)	-0.723	~0	1.02	N/A	0.01

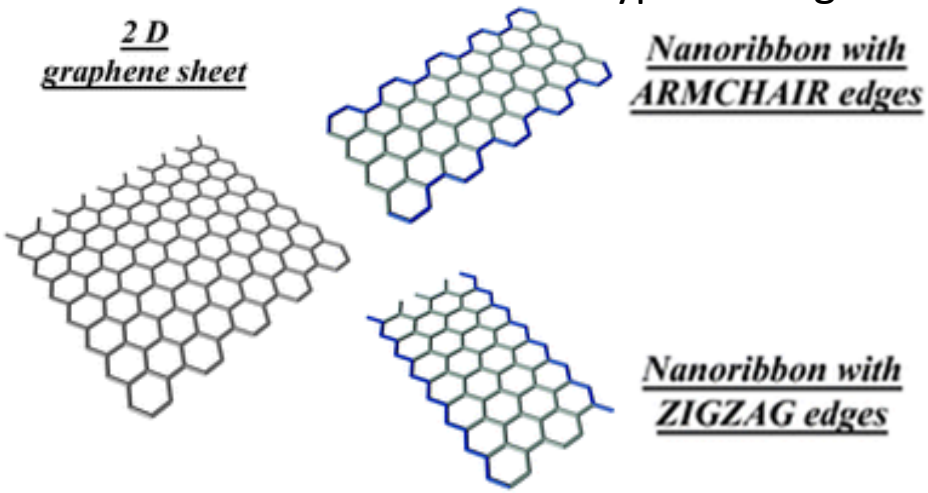
Outline

- Introduction
  - -> Introduction to single molecular study
  - -> Introduction to the experimental setups
  - -> Introduction to porphyrin molecules
- Single-molecule investigations of conformation adaptation of porphyrins on surfaces
- Switching molecular Kondo effect via supramolecular interaction
- The electronic properties of artificial graphene nanoflakes
- Conclusion

Graphene

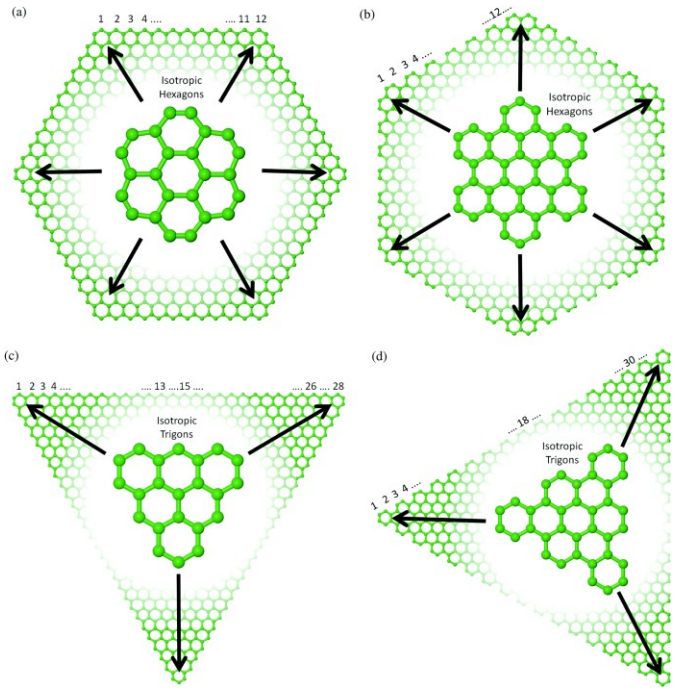


Two fundamental types of edge



Graphene nano-flake:

1. Has a large number of configurational degrees.
2. Graphene quantum dots hold the extremely long spin relaxation and decoherence time. **long coherence times and fast operating times, Solid –state spin qubits**

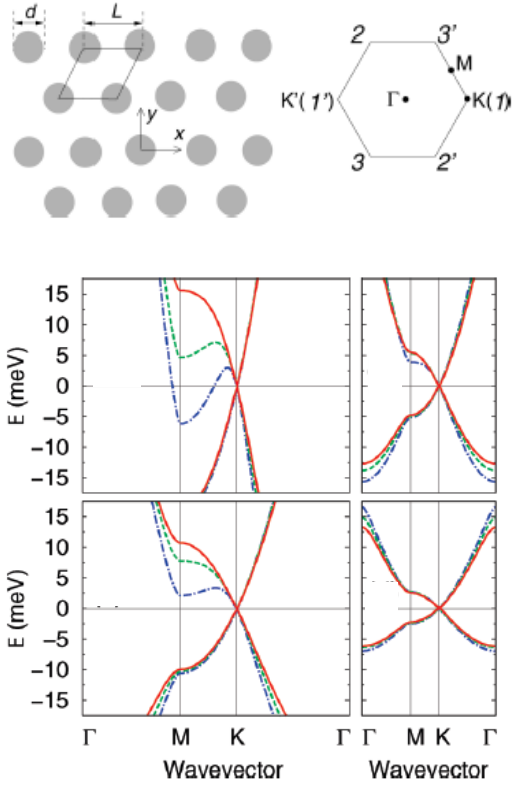


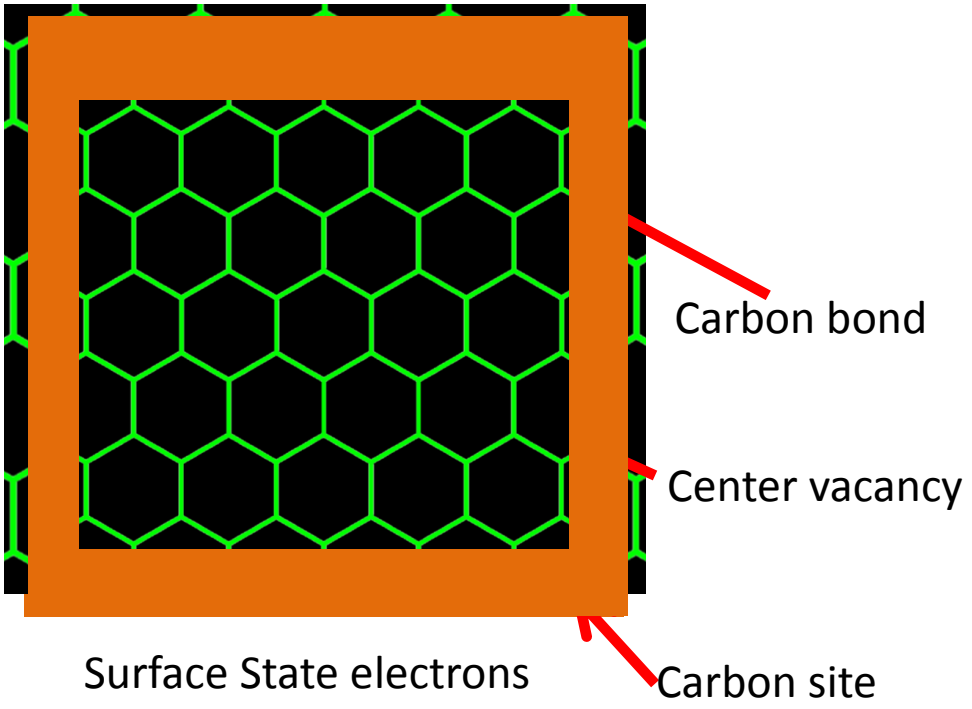
http://www.nanocarbon.cz/research.html
Nature Phys. 3, 192 (2007).
Nanoscale, 2011, **3**, 86-95
Nanoscale, 2015, **7**, 1864-1871

Artificial graphene

- ***Artificial graphene: A system shows similar electronic structures as graphene***

Making Massless Dirac Fermions from a Patterned Two-Dimensional Electron Gas

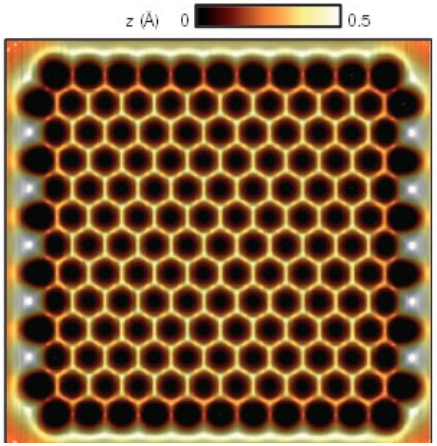




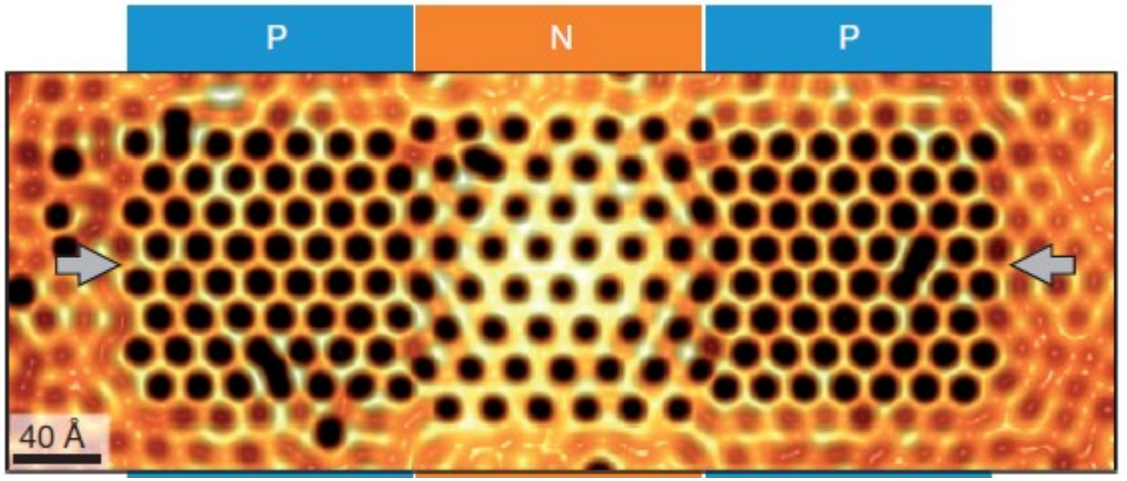
C. Park and S. G. Louise, **Nano Letter**, **7**, 1973 (2009)

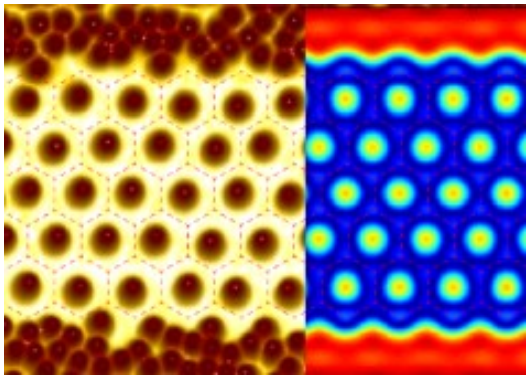
Artificial graphene

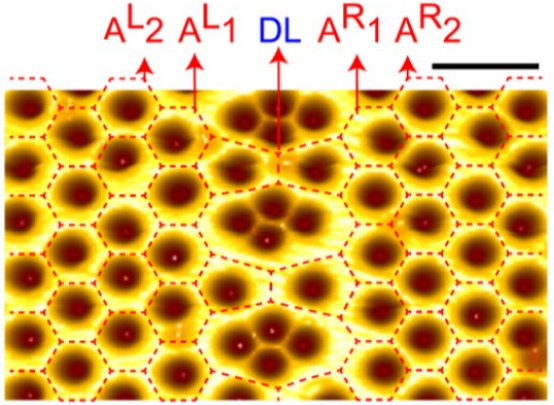
- The lattice constant (hopping parameters) is tunable



CO on Cu(111)



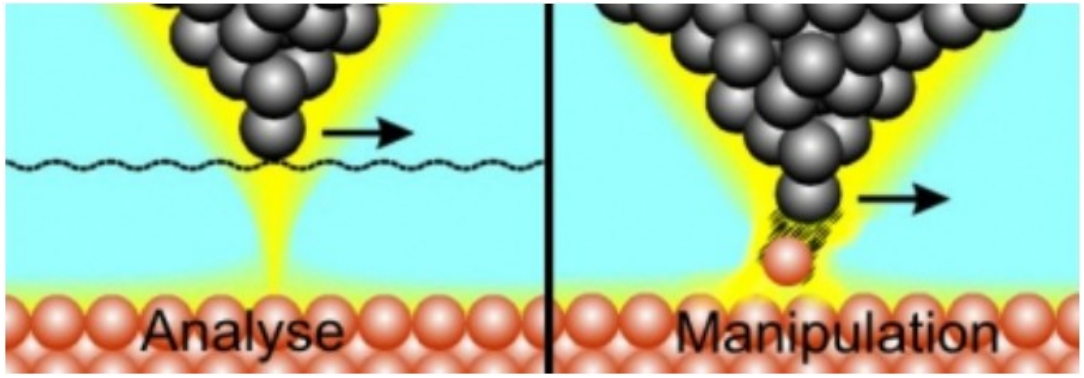




Coronene on Cu(111)

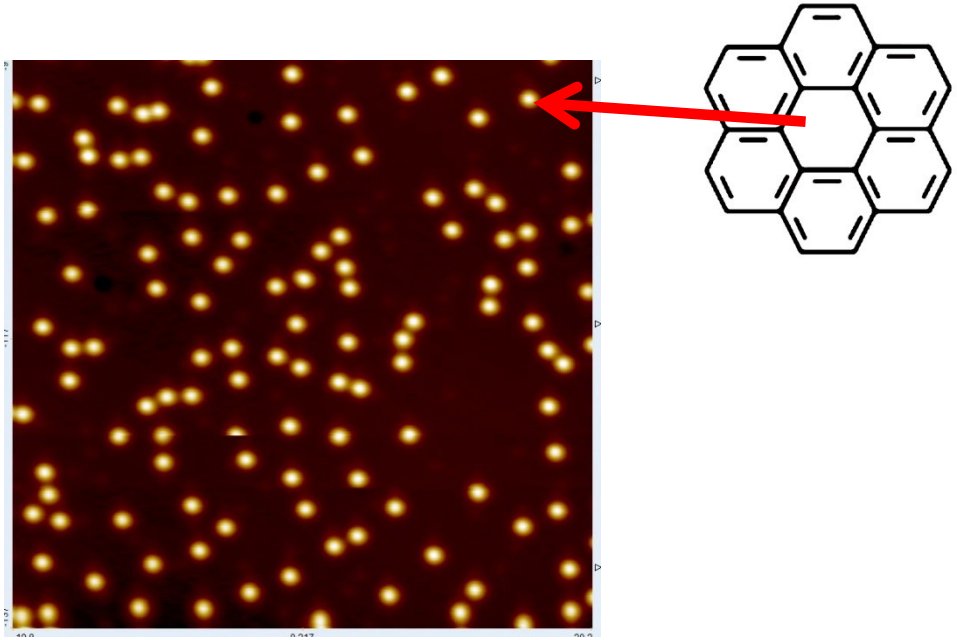
K. Gomes et al., **Nature**, **483**, 306 (2012)
PRL 113, 196803 (2014)

STM Manipulation



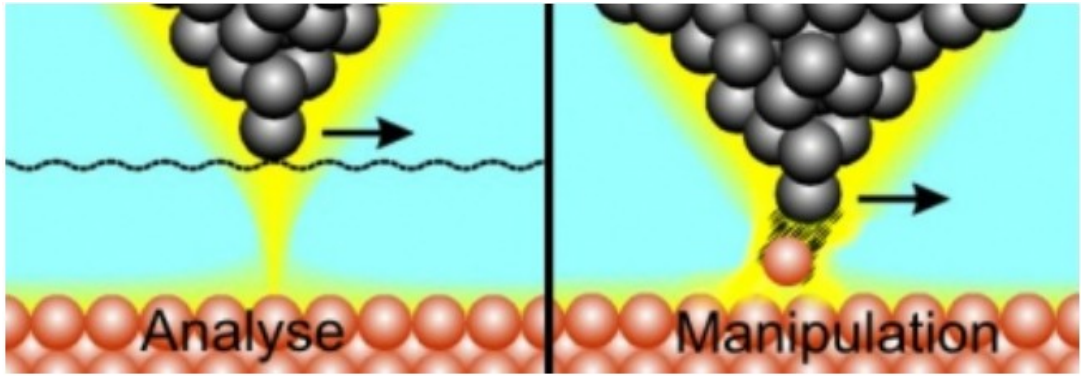
- Lateral manipulation

1. Approach STM tip to the molecule with ~ 2 Å
2. a bias voltage of -2V
3. Laterally move the tip



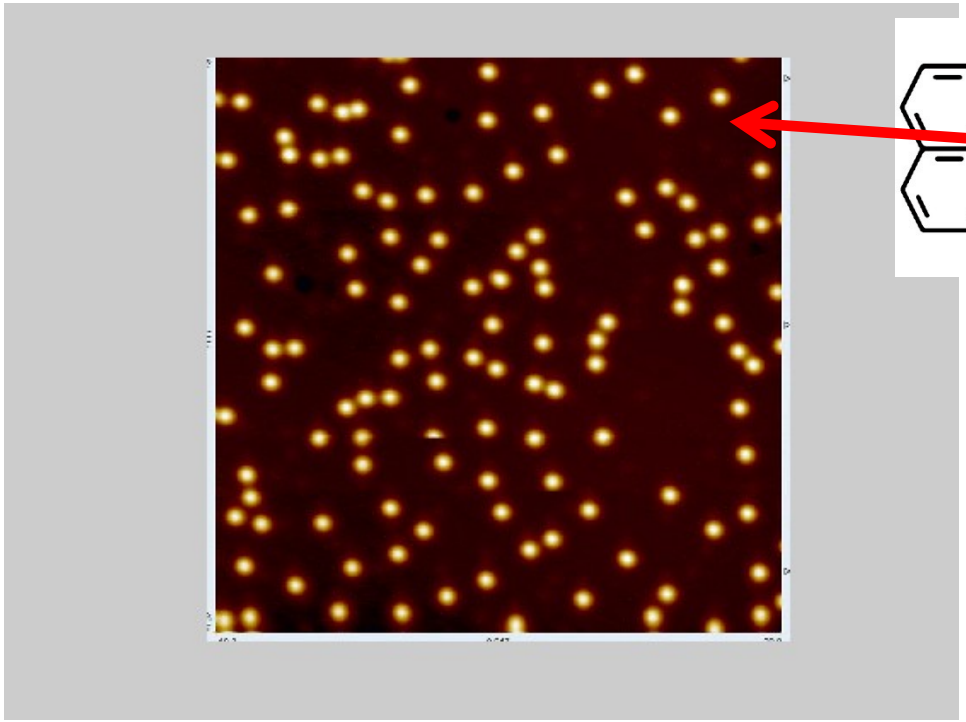
Nature 344, 524–526 (1990)

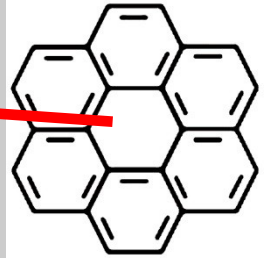
STM Manipulation

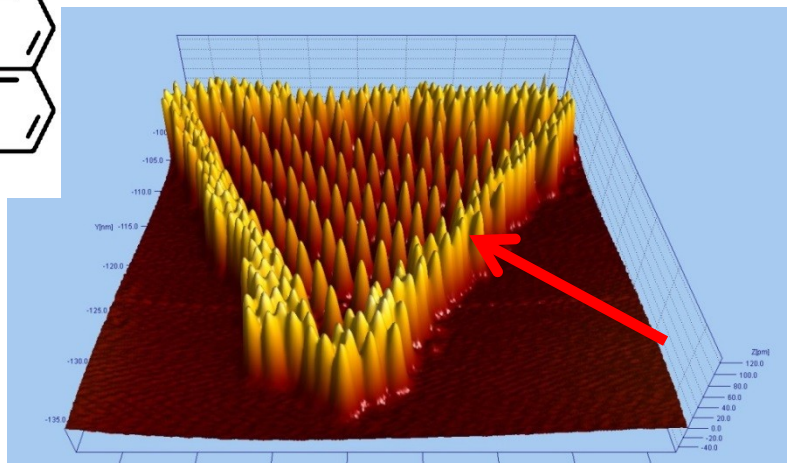


- Lateral manipulation

1. Approach STM tip to the molecule with ~ 2 Å
2. a bias voltage of -2V
3. Laterally move the tip







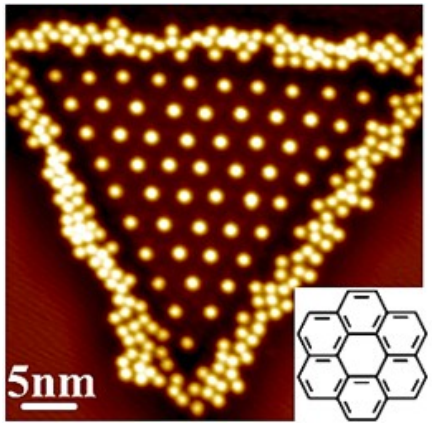
Nature 344, 524–526 (1990)

Artificial graphene nano-flakes

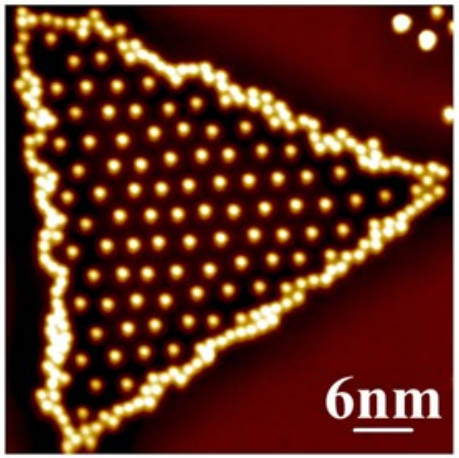
Boundary conditions

Shape of the nano-flake

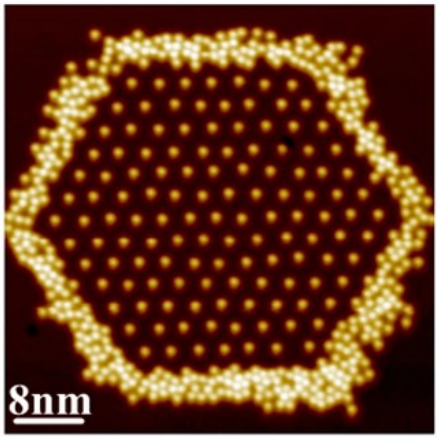
Zigzag Triangle



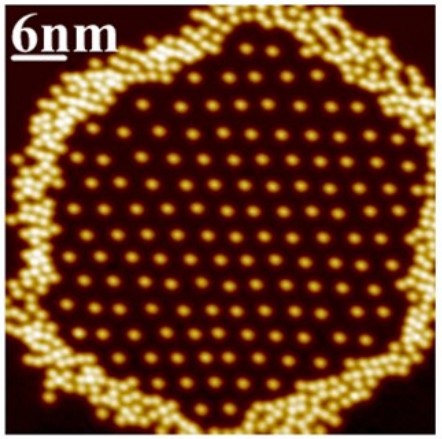
Armchair Triangle



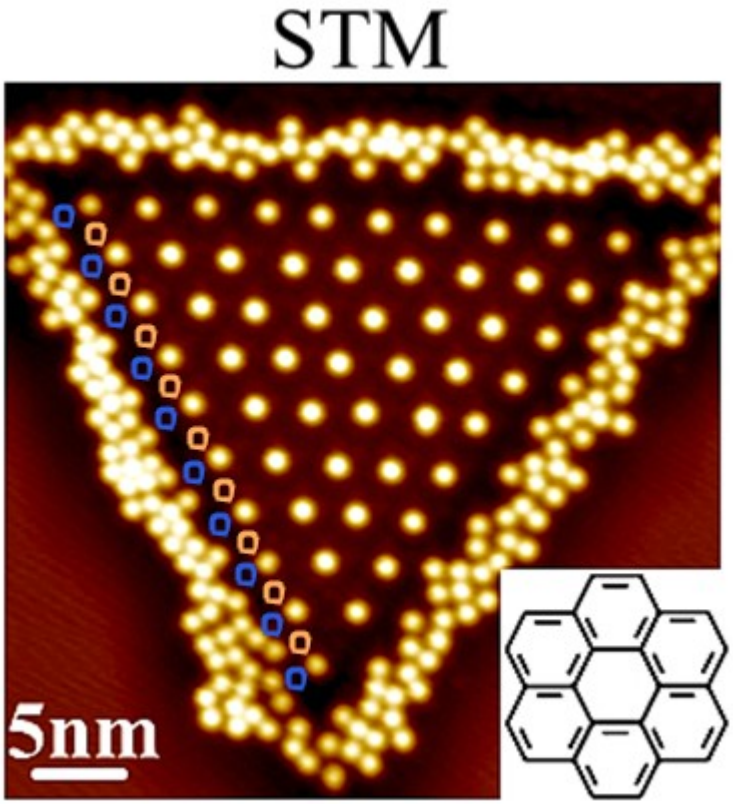
Zigzag Hexagonal

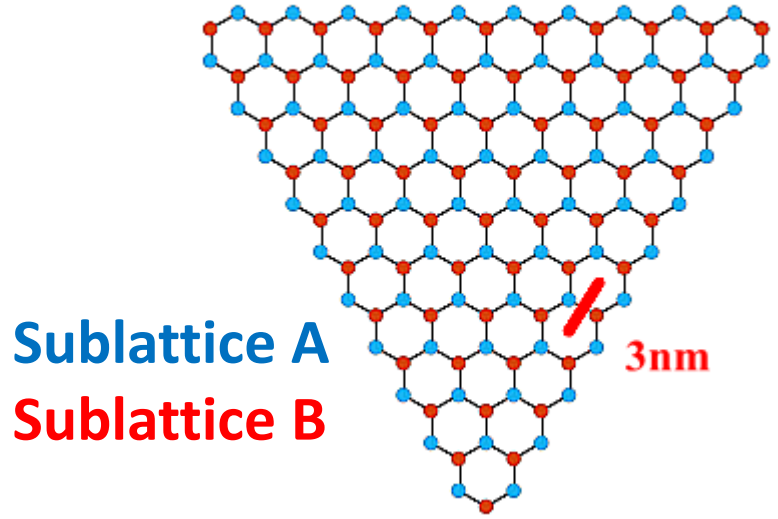


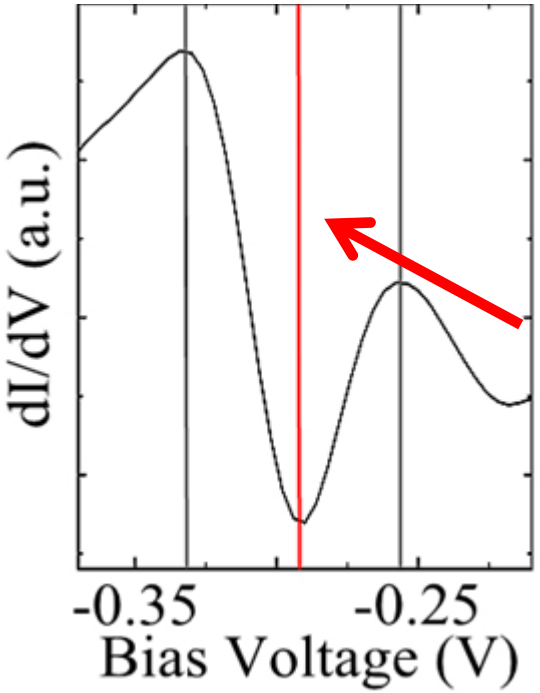
Armchair Hexagonal



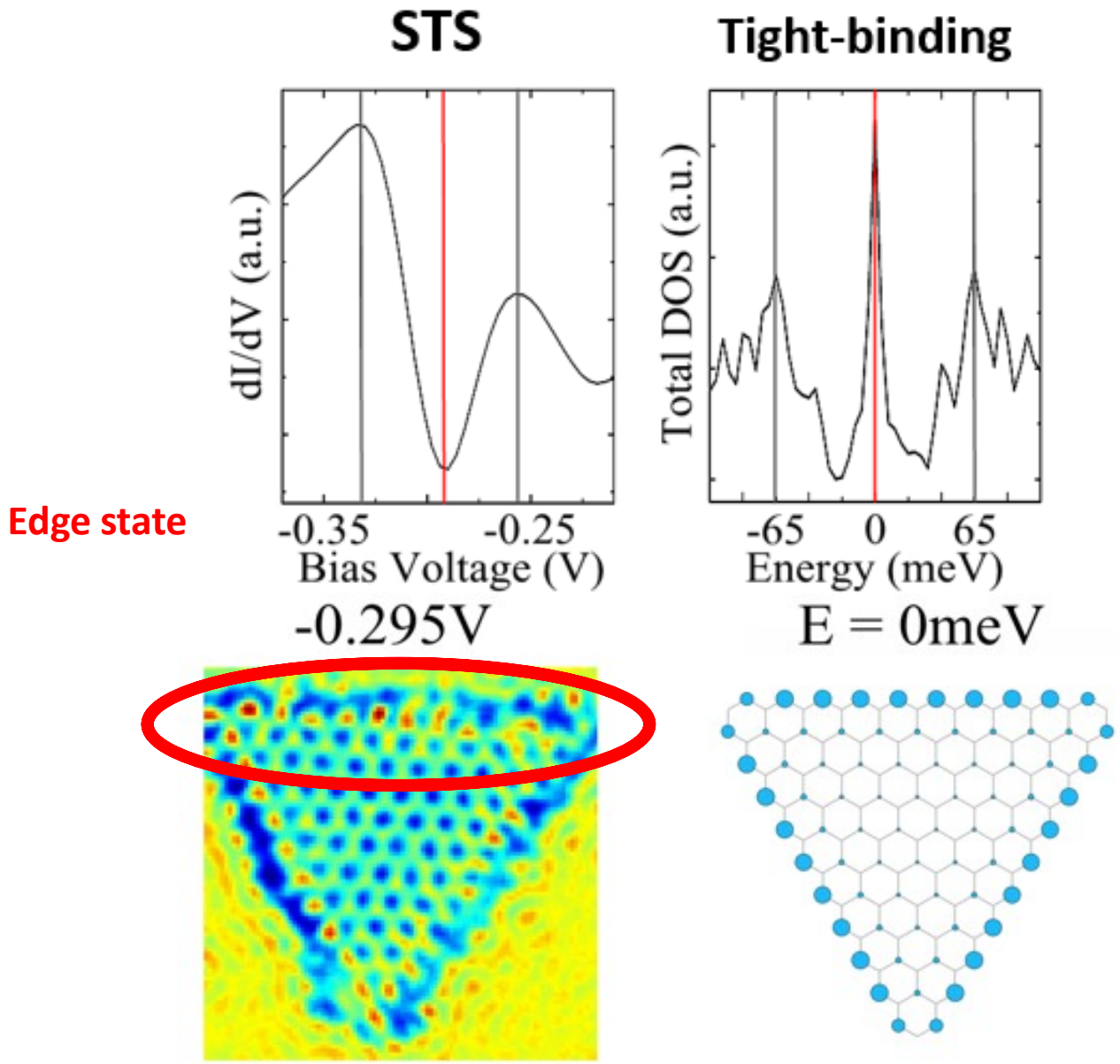
Zigzag Triangle



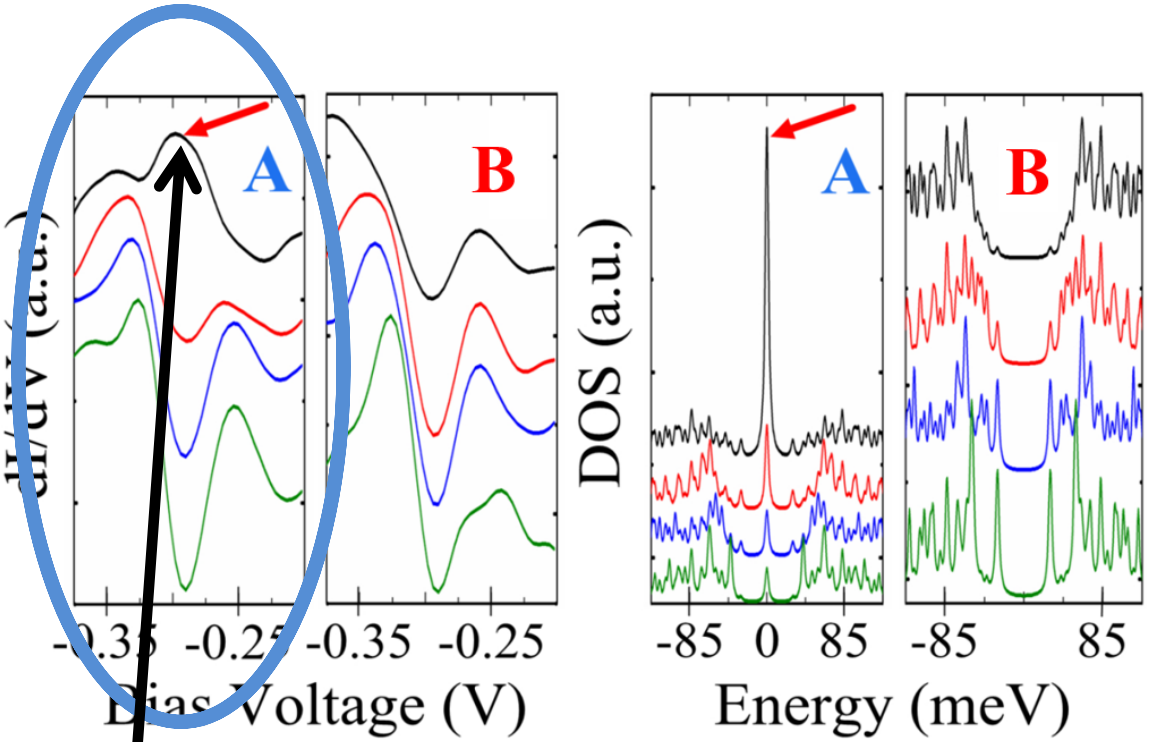


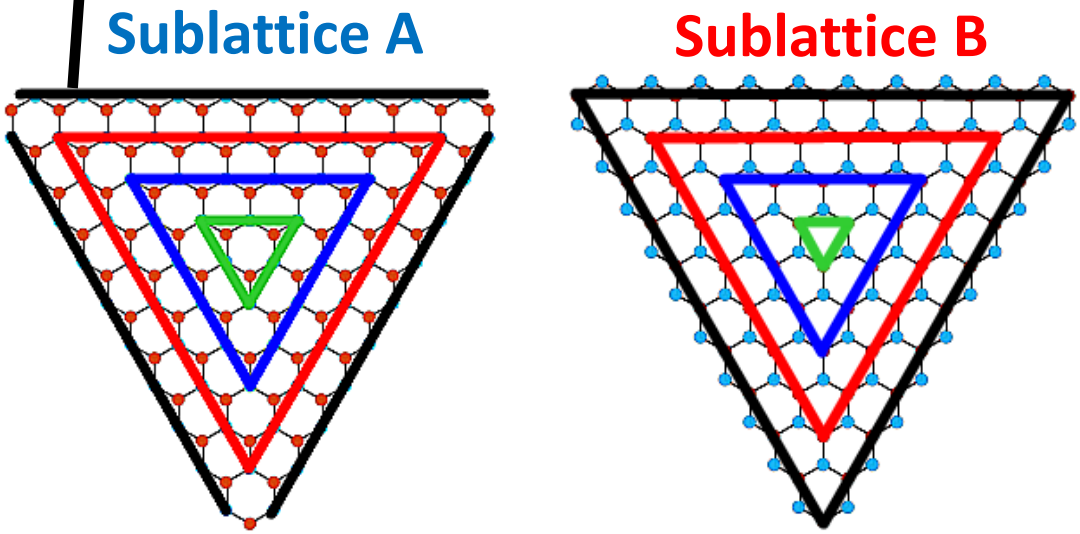


This zero-energy edge state is caused by the states confined at the edges

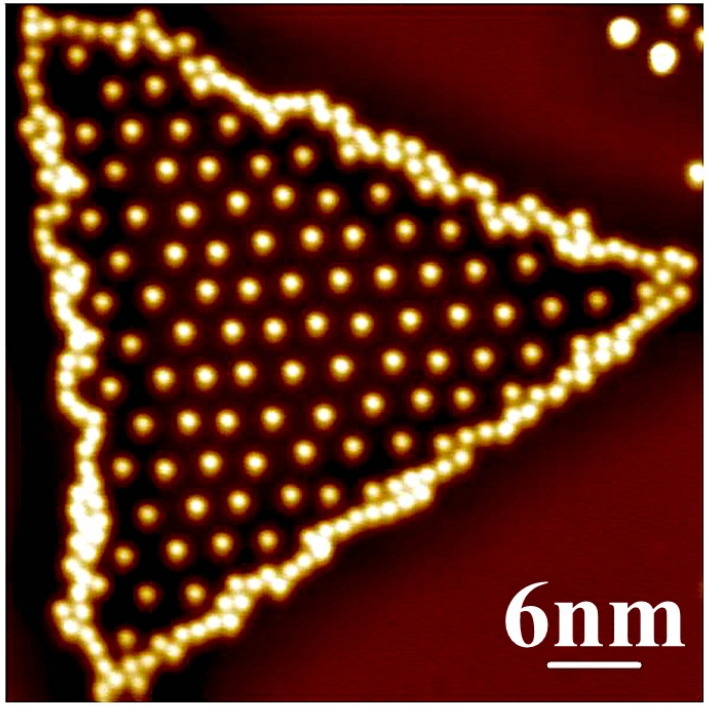


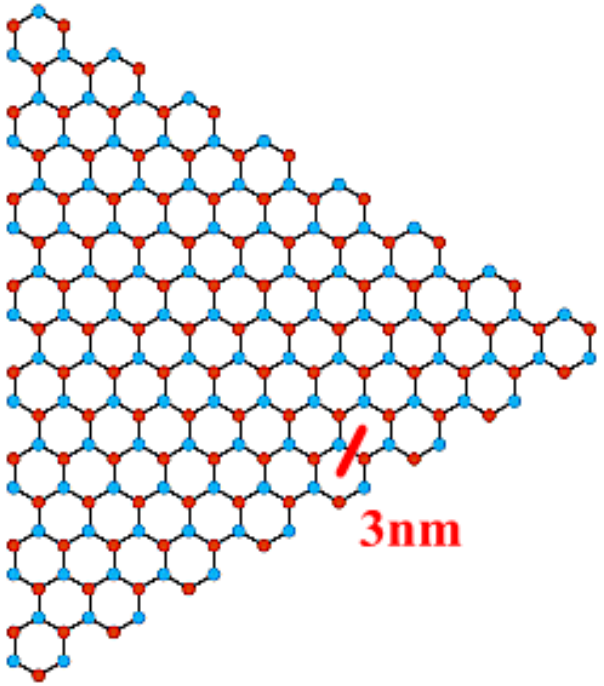
Line-averaged DOS

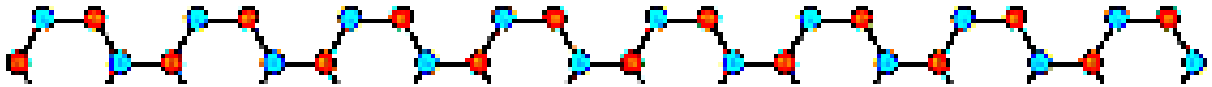




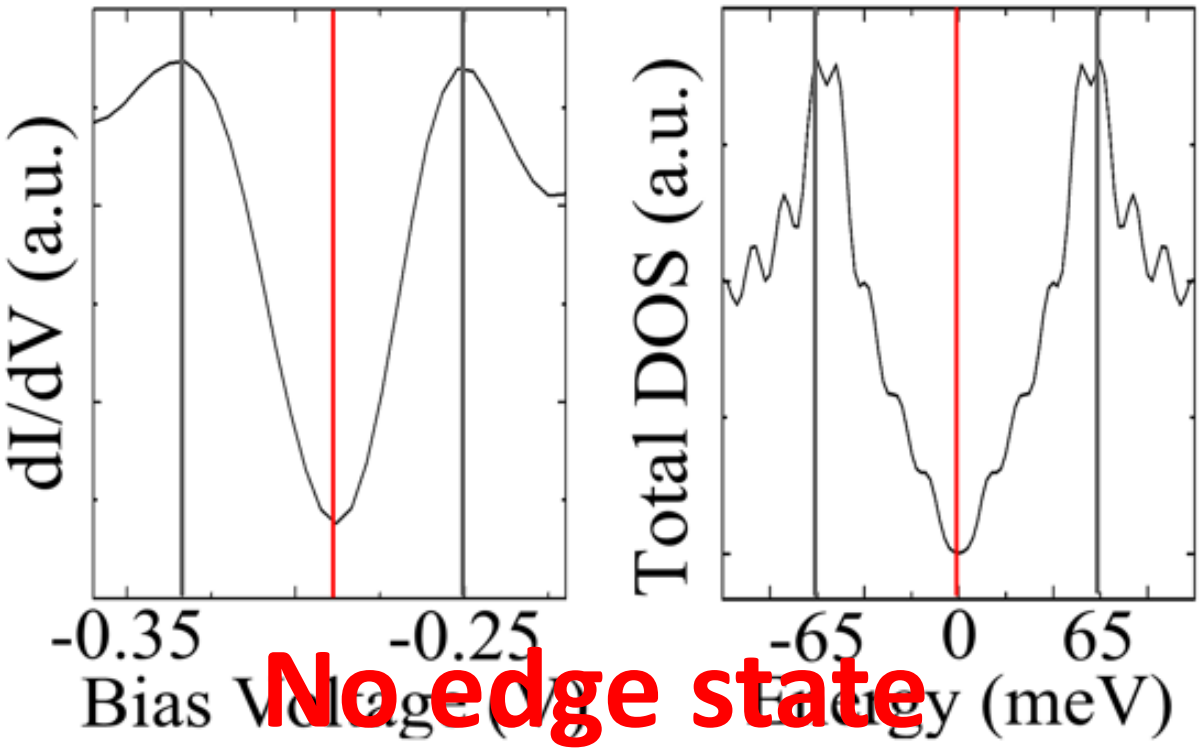
Armchair Triangle



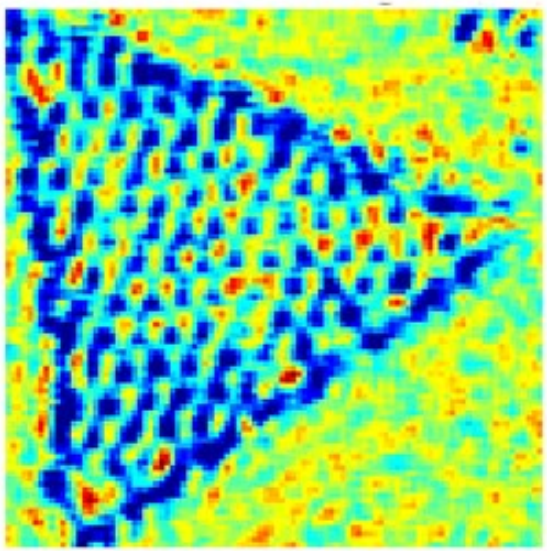




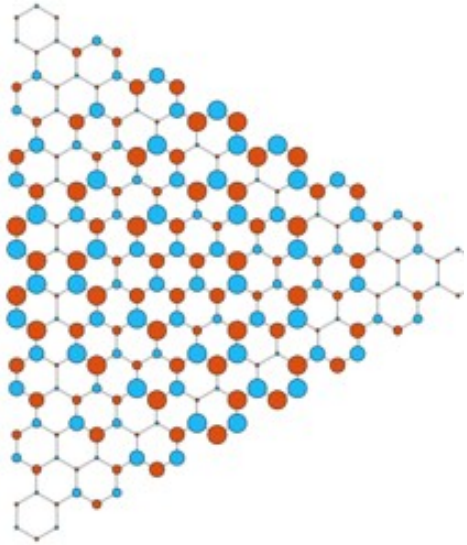
Two sublattices are equivalently distributed at each edge



No edge state



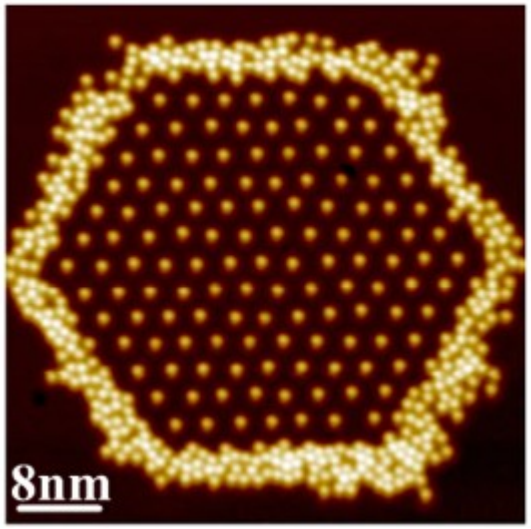
-0.29V

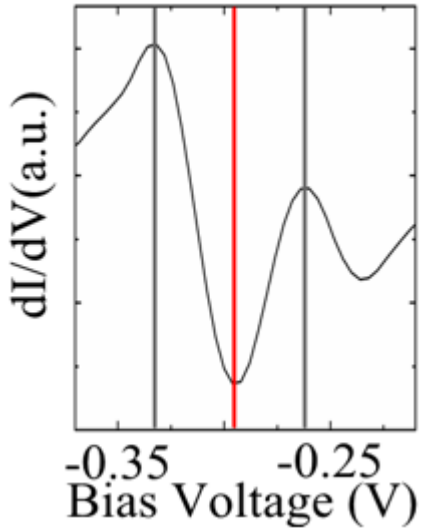


E = 0meV

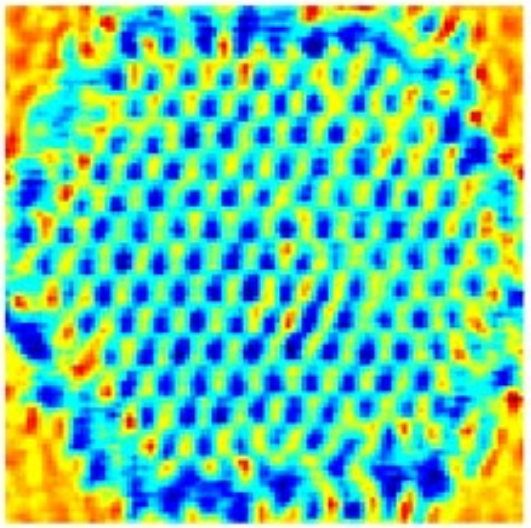
Hexagonal nanoflakes

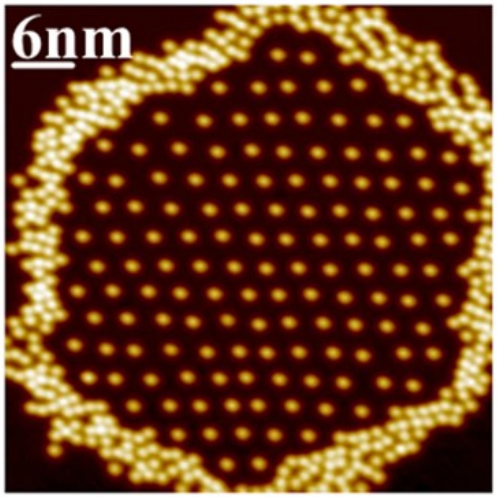
STM

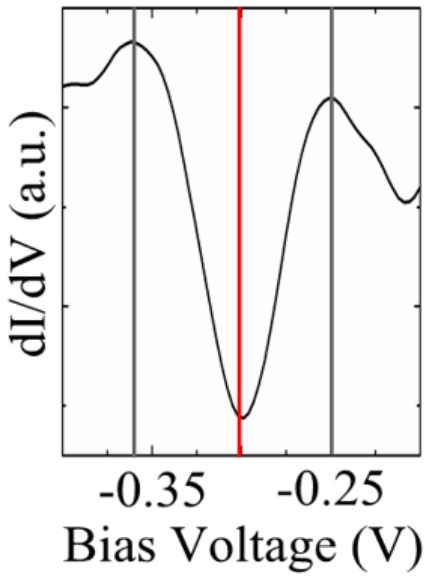


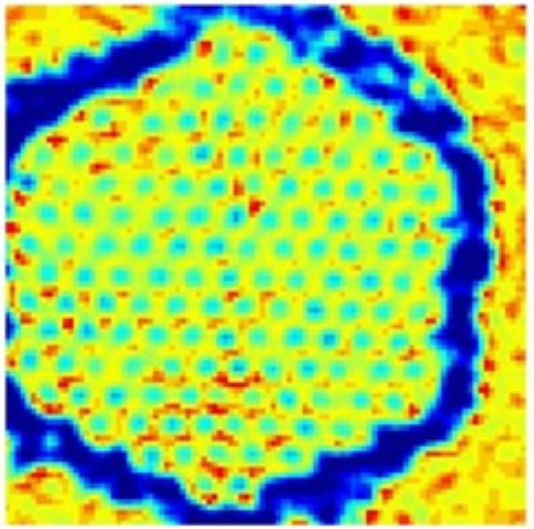


-0.29V





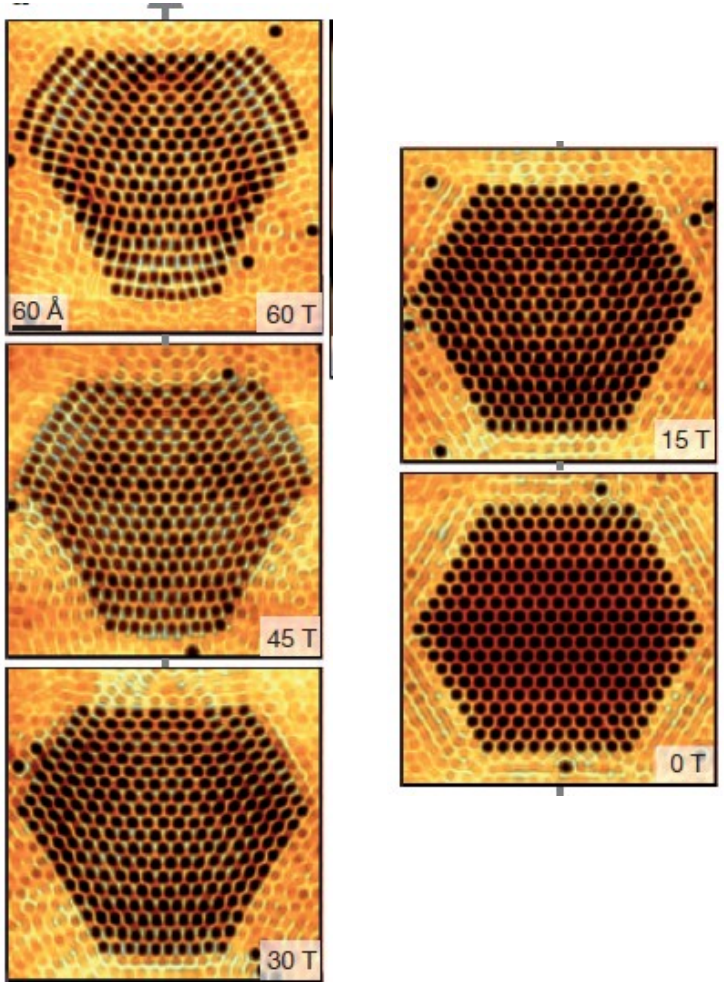


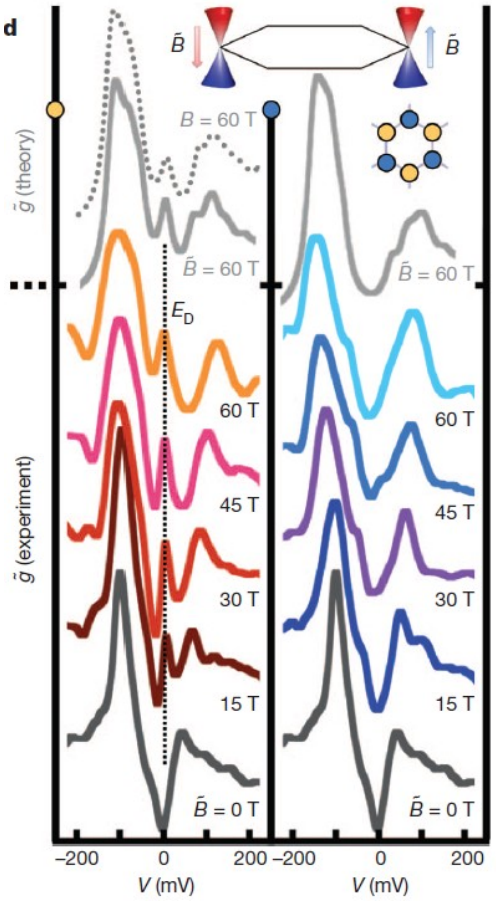


-0.3V

Deformed graphene nano-flake

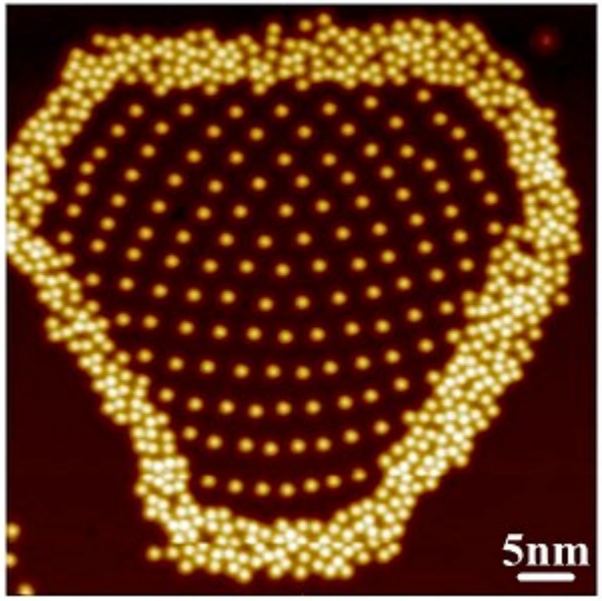
- Deformation by LT-STM manipulation
- Interestingly, this deformed artificial graphene system can behave like the real graphene flakes under the elastic strain.
- Graphene layer under large pseudo-magnetic field

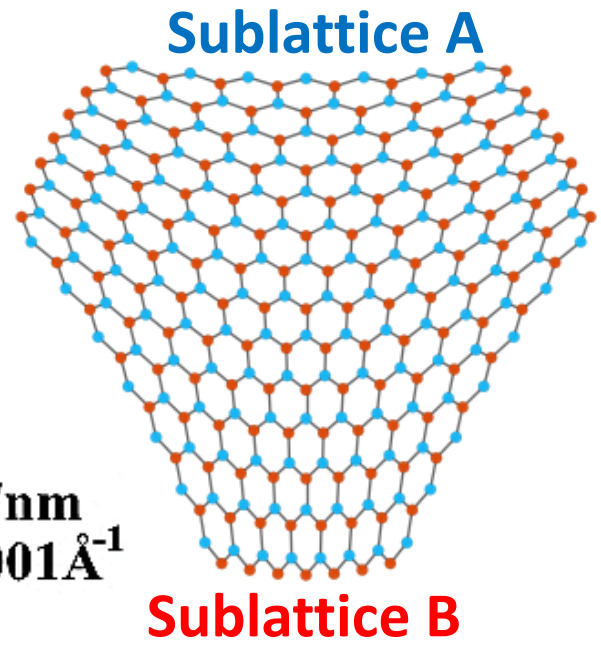




Nature Volume: 483, Pages:306–310

Deformed graphene nano-flake





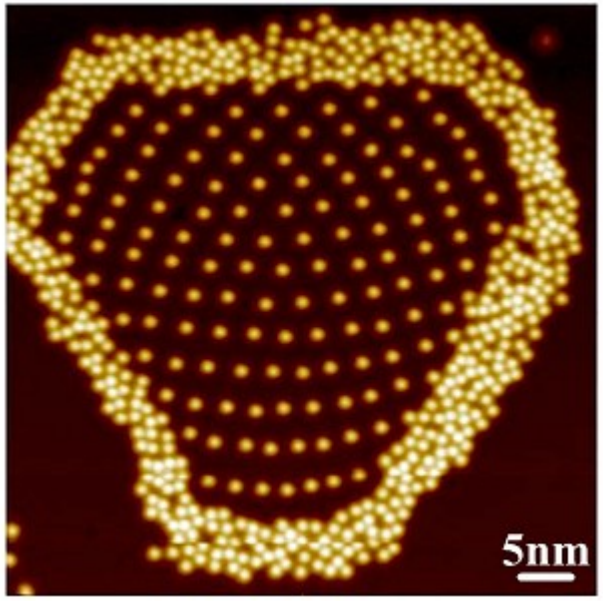
In the radial representation, the following displacements:

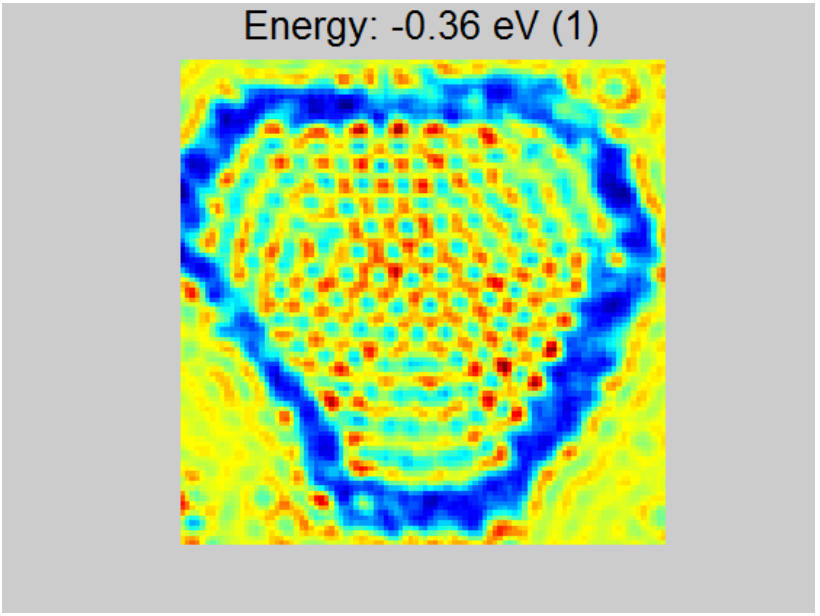
$$u_r = qr^2 \sin(3\theta);\ u_\theta = qr^2 \cos(3\theta)$$

$B_s = (16\pi/3)\ q/d$ (given in the unit of $\hbar/e$ =1).

Thus, the induced pseudo-magnetic field of our sample is about **45T**.

Deformed graphene nano-flake

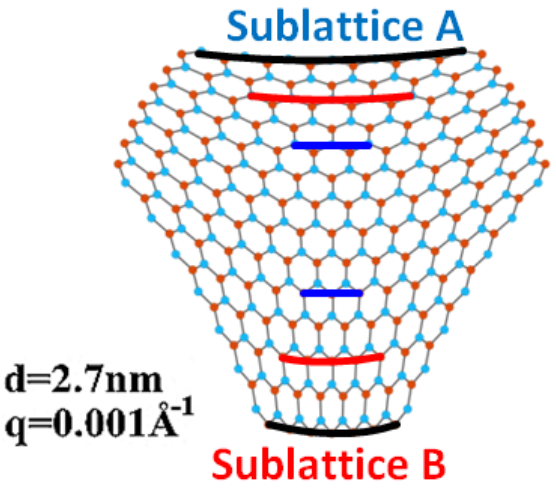


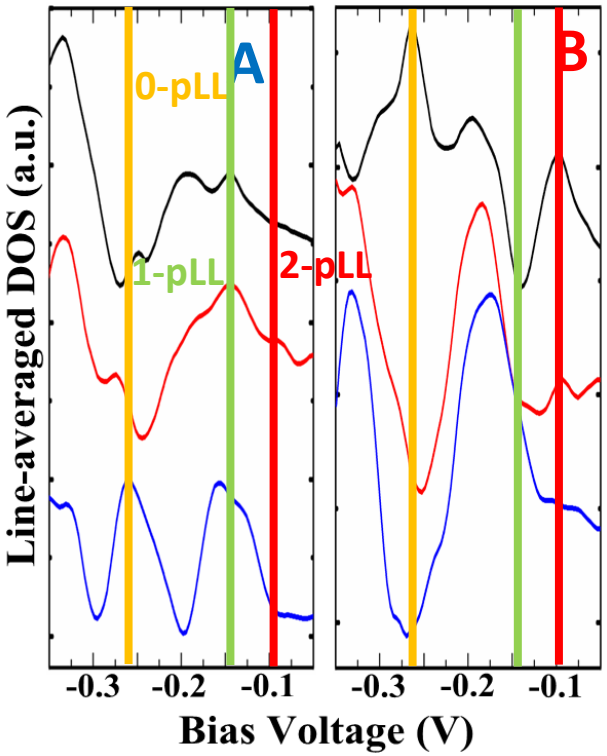


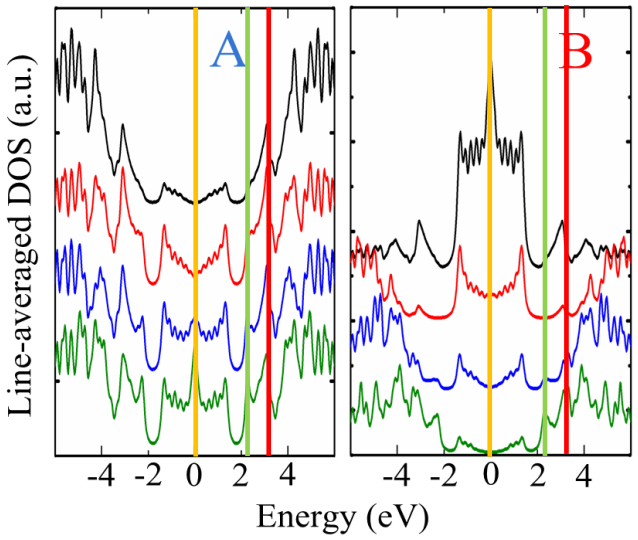
$u_r = qr^2 \sin(3\theta)$; $u_\theta = qr^2 \cos(3\theta)$

1. **The distribution of pseudo Landau levels (pLL) in real space.**
2. **The role of flake edges.**
3. **Sublattice-dependence of pLL.**

pseudo Landau Level (pLL)

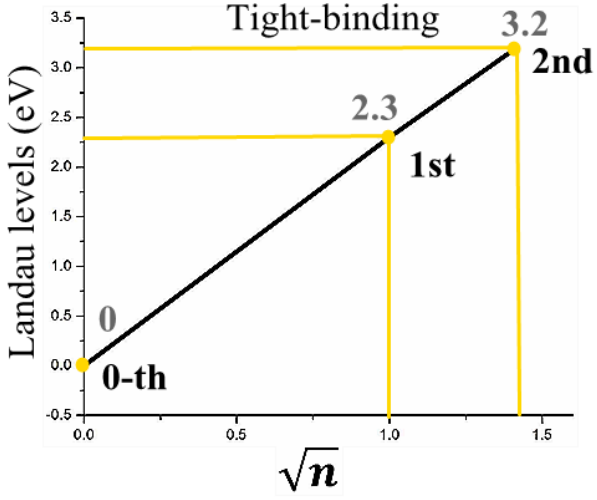


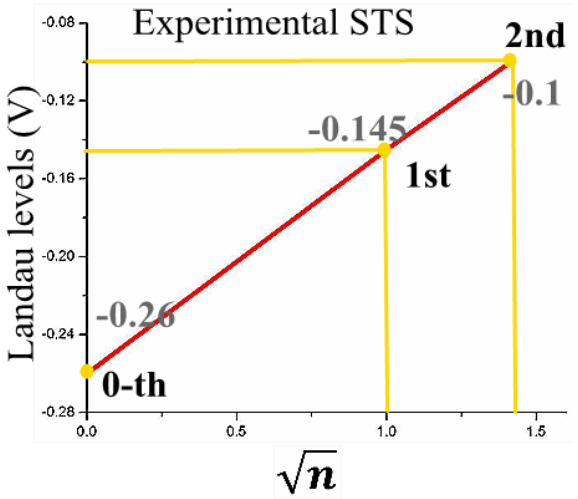




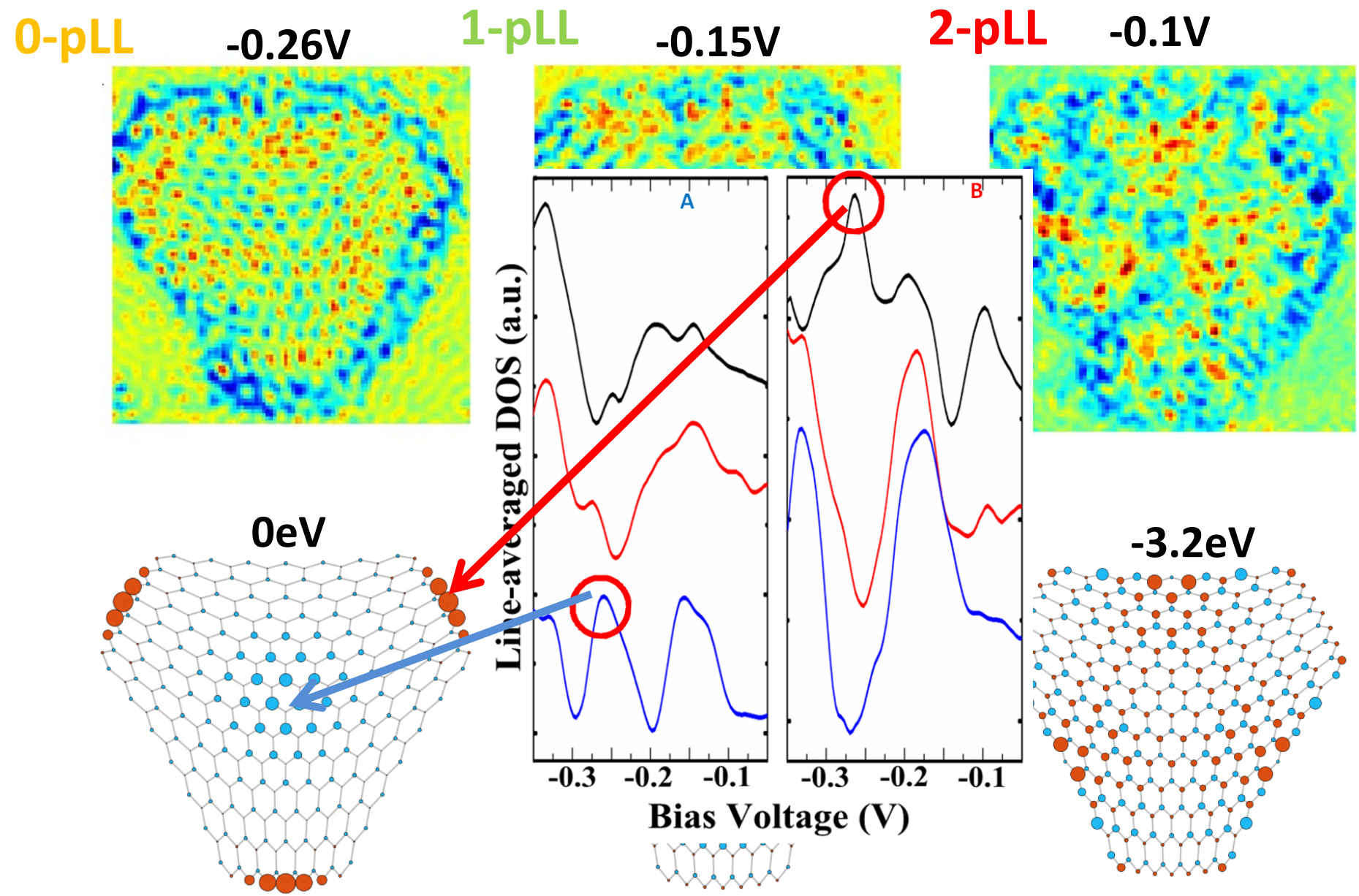
Energy scales of Landau levels:

$$dE_{(Ln-L0)} \sim v_F \times \sqrt{nB}$$





Distrobution of each pLL

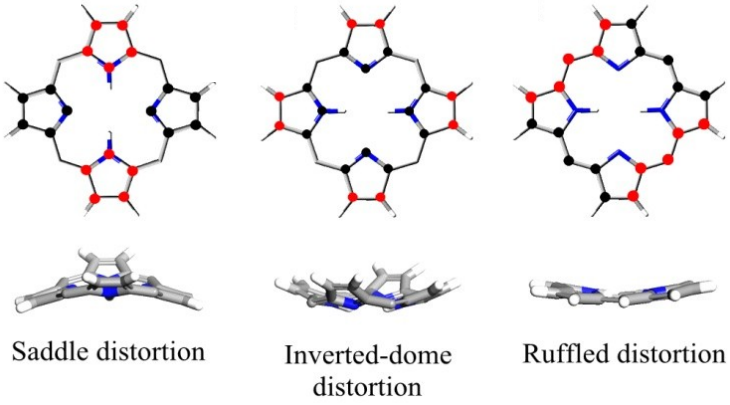


Outline

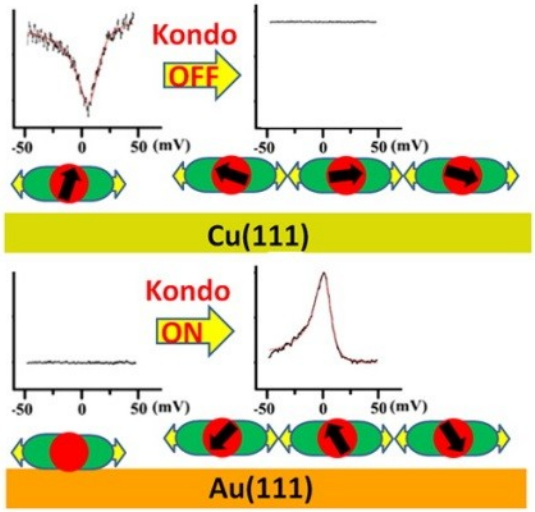
- Introduction
  - -> Introduction to single molecular study
  - -> Introduction to the experimental setups
  - -> Introduction to porphyrin molecules
- Single-molecule investigations of conformation adaptation of porphyrins on surfaces
- Switching molecular Kondo effect via supramolecular interaction
- The electronic properties of artificial graphene nanoflakes
- Conclusion

Conclusion

- Different adsorption conformations of porphyrins



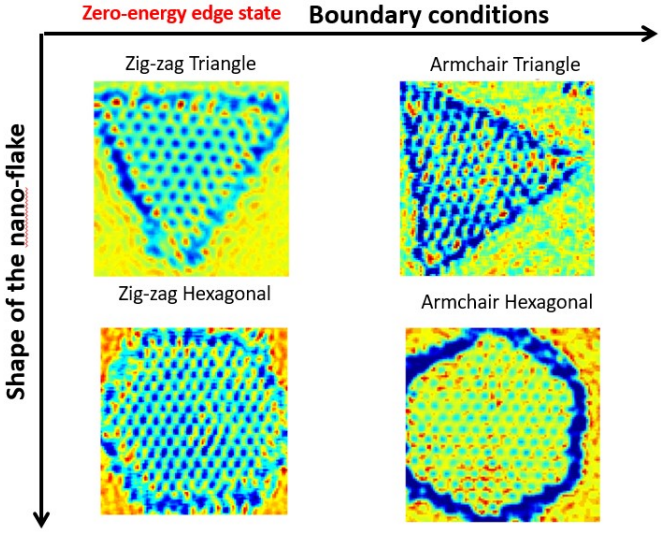
- Switching molecular Kondo effect via supramolecular interaction



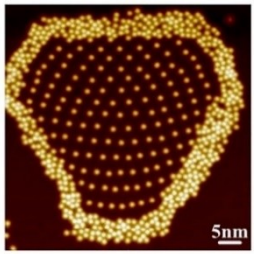
ACS Nano, 2015, 9 (12), pp 12521–12528

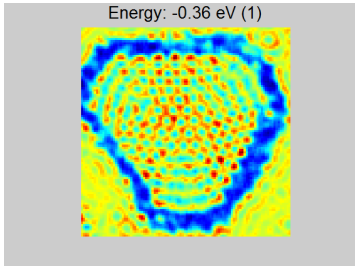
Conclusion

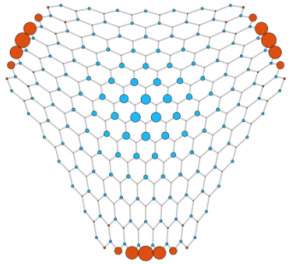
- The electronic properties of triangle artificial graphene nanoflakes

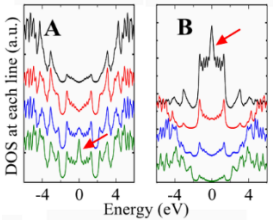


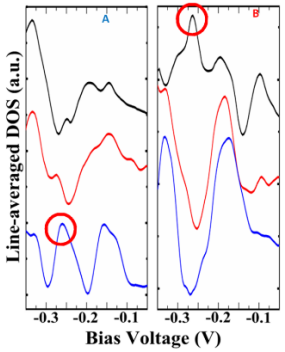
- The electronic properties of deformed artificial graphene nanoflakes











Acknowledgements

◆**Collaborators:**

Prof. Lin Nian

Prof. Liu Peinian

Prof. Michel A. Van Hove

Prof. Shi Xingqiang

Prof. Huang Xuhui

Prof. Xu Hu

Dr. PANG Rui

Dr. Zheng Xiaoyan

Mr. Wu Tszchun

Mr. Xie A'yu

◆**Current members:**

Dr. Yan Linghao

Dr. Liu Jing

Mr. Lyu Guoqing

Mr. Kuang Guowen

Ms. Zhang Ran

Mr. Gao Zi'ang

Mr. Xia Bowen

◆**Former members:**

Dr. Wang Weihua

Dr. Wang Shiyong

Dr. Lin Tao

Mr. Chen Cheng

Dr. Dong Lei

Dr. Zhao Wei

◆**MPhil Thesis Examination Committee Members:**

Prof. Lortz Rolf W (Chairman)

Prof. Pan Ding

Prof. Lin Nian (Supervisor)

Publications

1. G. Kuang*, **Q. Zhang***, X. T. Lin, R. Pang, X. Shi, H. Xu, N. Lin, ***ACS Nano.*** 11, 6295 (2017).
2. **Q. Zhang**, X. Zheng, G. Kuang, W. Wang, L. Zhu, R. Pang, X. Shi, X. Shang, X. Huang, P. N. Liu, N. Lin, ***J. Phys. Chem. Lett.*** 8, 1241 (2017).
3. **Q. Zhang**, G. Kuang, R. Pang, X. Shi, P. N. Liu, N. Lin, ***ACS Nano***. 9, 12521 (2015).
4. **Q. Zhang,** G. Kuang, T. Wu, A. Xie, L. Yan, N. Lin, "Manipulation and Characterization of the Electronic Properties in Artificial Graphene Nano-flakes", ***in preparation*** (2017).
5. L. Yan, G. Kuang, **Q. Zhang**, X. Shang, P. N. Liu, N. Lin, ***Faraday Discuss. - Royal Society of Chemistry***, Advance Article, DOI: 10.1039/c7fd00088j (2017).
6. G. Lyu, **Q. Zhang**, J. Urgel, G. Kuang, W. Auwärter, D. Ecija, J. V. Barth, Johannes, N. Lin, ***Chem. Commun***. 52, 1618 (2016).
7. G Kuang, **Q. Zhang**, D. Li, X. Shang, T. Lin, P. N. Liu, N. Lin, ***Chemistry - A European Journal***, 21, 8028 (2015).
8. Q. Miao, J. Wang, M. Hu, F. Zhang, **Q. Zhang**, C. Xia, ***Eur. Phys. J. Plus***, 8, 129 (2014).
9. L. Yan, **Q. Zhang**, G. Kuang, P. N. Liu, N. Lin, "Self-assembly of two-dimensional superlattice Bi micro clusters-organic networks on Cu(111) surface", ***in preparation*** (2017).

Thanks For Your Attention