Characterization of electronic structures of single molecules, conjugated polymers and molecular nanostructures using low temperature scanning tunneling microscopy

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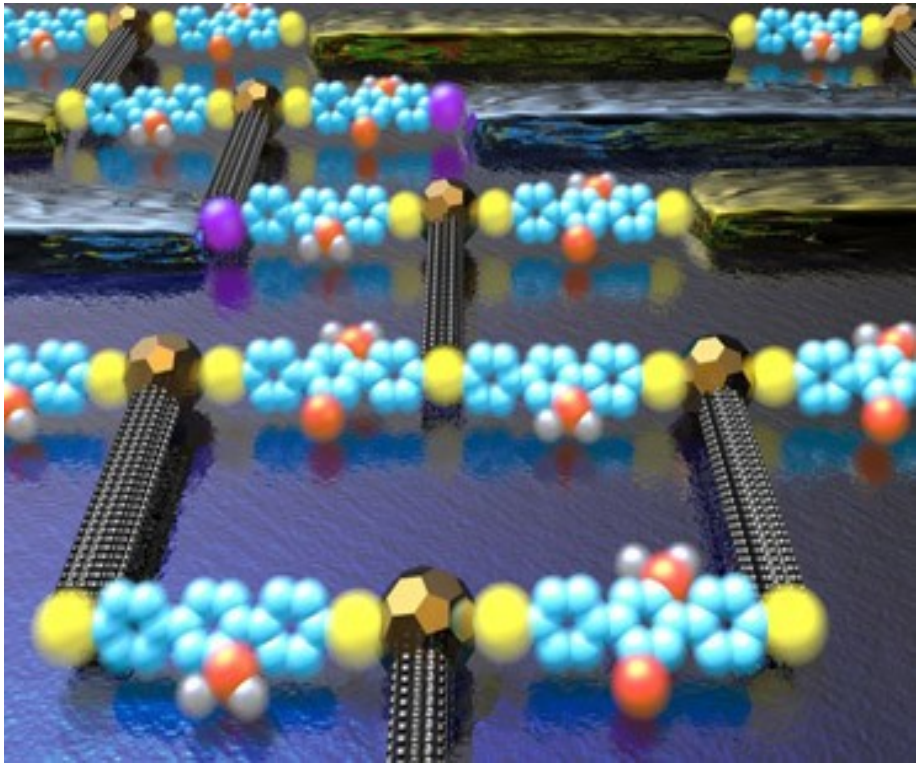
Introduction: Molecular electronics

Fabricate electronic devices with molecular building blocks



www.asdn.net

Advantages:

1. *further miniaturization*
2. *mechanically folding*
3. *Bottom-up technique*
4. *Artificial designed function*
5. *…*

Introduction: Molecular electronics

Objectives

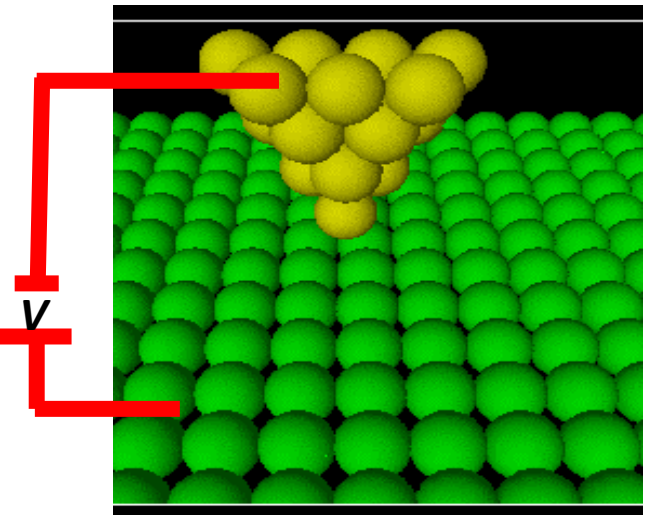
1. Intrinsic electronic structures
2. Charge transport properties
3. Molecule-metal hybridized systems

Experimental challenges

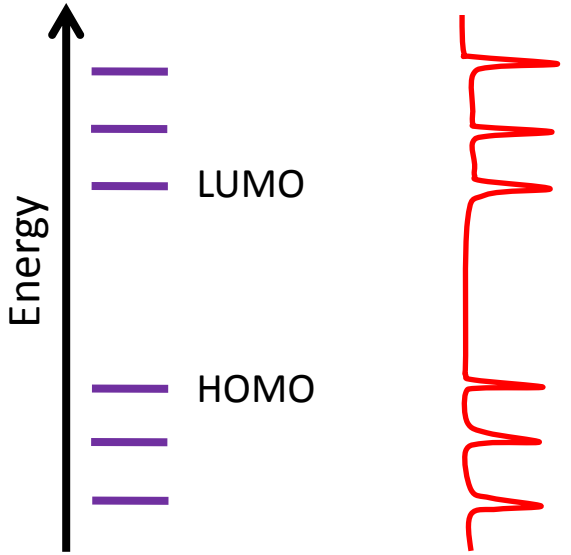
1. Simultaneously measure charge transport and structural details of molecular junctions
2. Study on single conjugated polymers at atomic resolution
3. Detect band structure of hybridized systems
4. …

Introduction: STM/STS

Tunneling



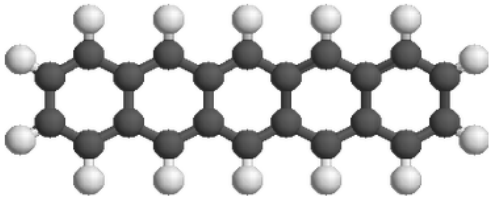
STS: $\frac{dI}{dV} \propto \rho_s(E_F - eV)$



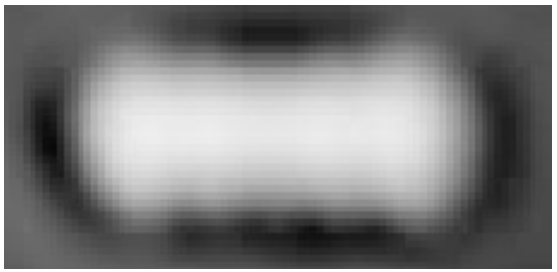
Levels

dI/dV spectra

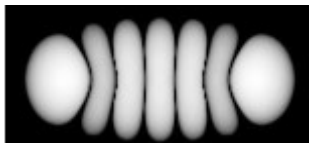
Pentacene



STM image



dI/dV mapping

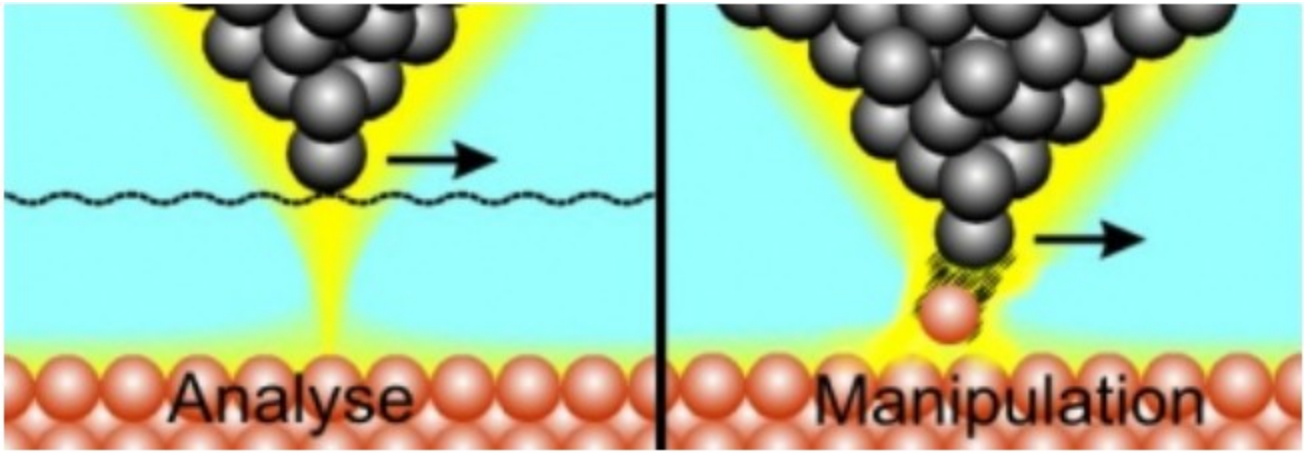


LUMO Orbital

dI/dV mapping

PRL **94,** 026803 (2005)

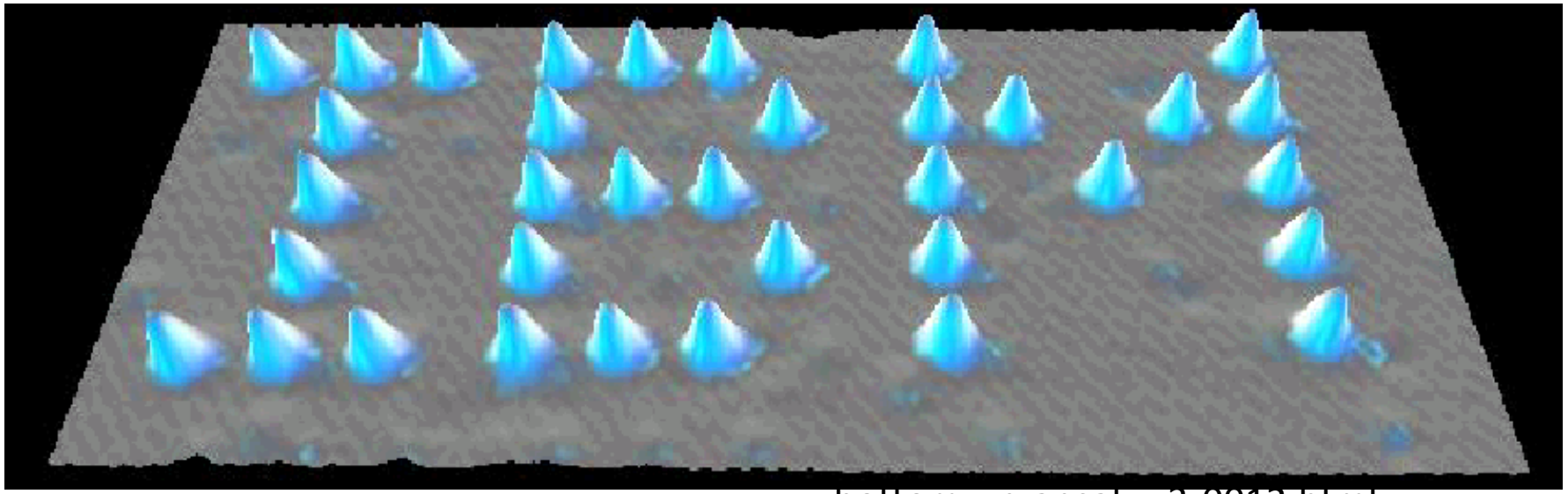
Introduction: STM manipulation



Lateral manipulation

Approach STM tip to the molecule with ~ 2 Å

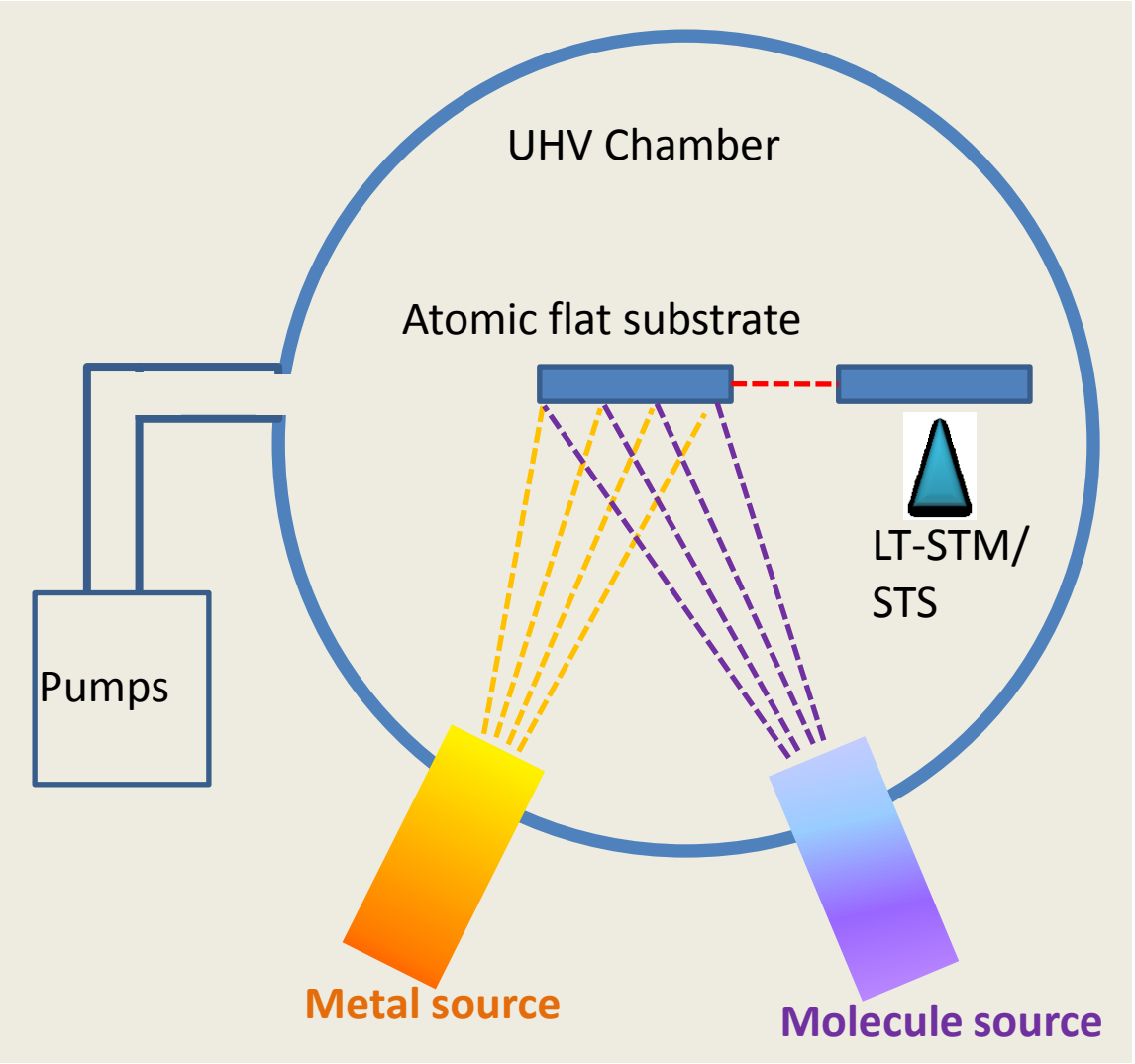
Laterally move the tip



bottom-up-ansatz--3-0012.html

NATURE · VOL 344 · 5 APRIL 1990

Introduction: Experiments



- **Sample preparation:**

1. OMBE
2. Supramolecular self-assemly
3. On-surface covalent coupling
4. STM manipulation

- **Characterization:**

1. STM: structural information
2. STS: electronic structure

Outline

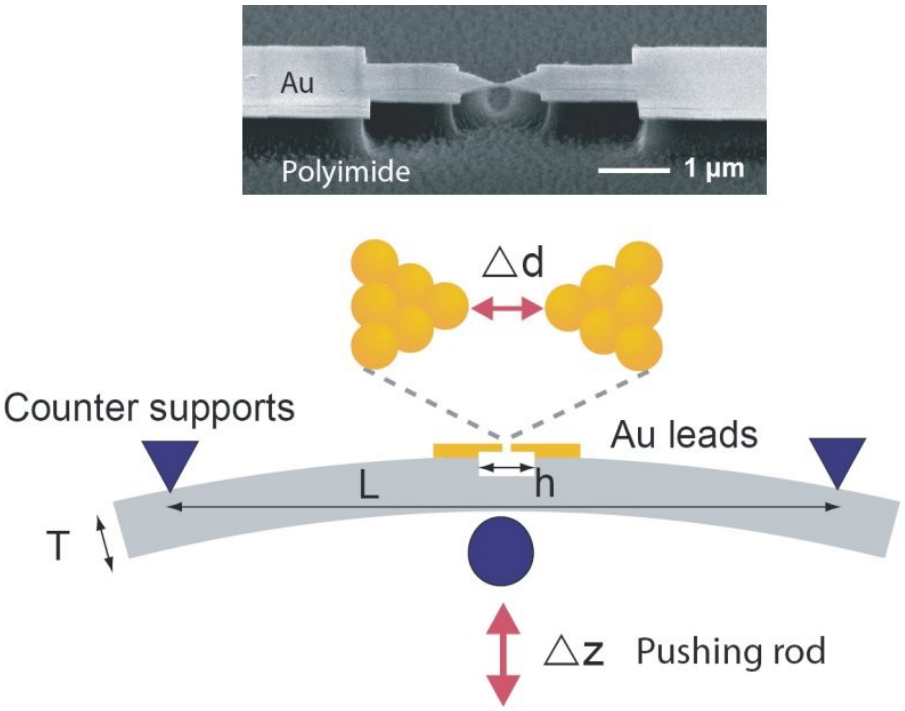
- Single molecular characterization:
  - Superexchange coupling
  - Molecular capacitance and conductance
  - Metal-atom contacts
- Conjugated poly-p-phenylene polymers
  - On-surface Ullmann reactions
  - Intrinsic electronic structures
  - Dopant states
- 2D molecular nanostructures
  - Modulation of Shockley surface-state by supramolecular self-assemblies
  - Fabrication and characterization of molecular graphene

Single molecule characterization

- STM/STS: Structural and electronic structures

~~Charge transport~~

- Charge transport measurement by break junction



Mechanical break technique

Unknown contact details!

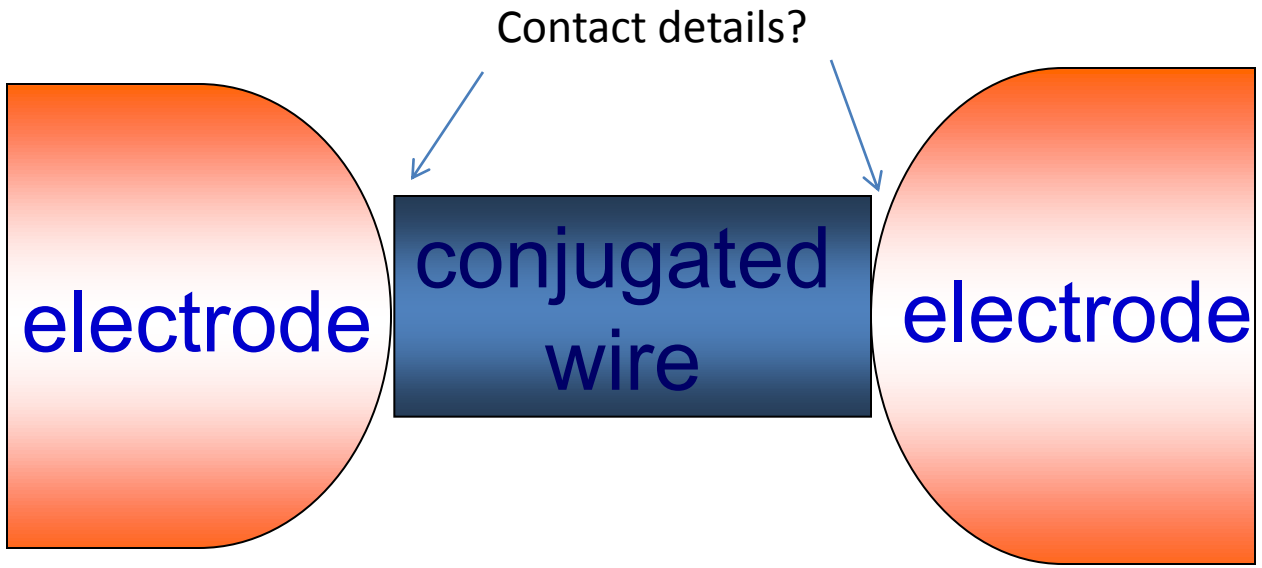
1. Number of molecules inside junction
2. Adsorption configurations of molecules

Exp. Challenge:

Simultaneously measure transport and contact details?

Supper-exchange coupling: T

Charge transfer mechanism of single molecular junction



Conductance

g

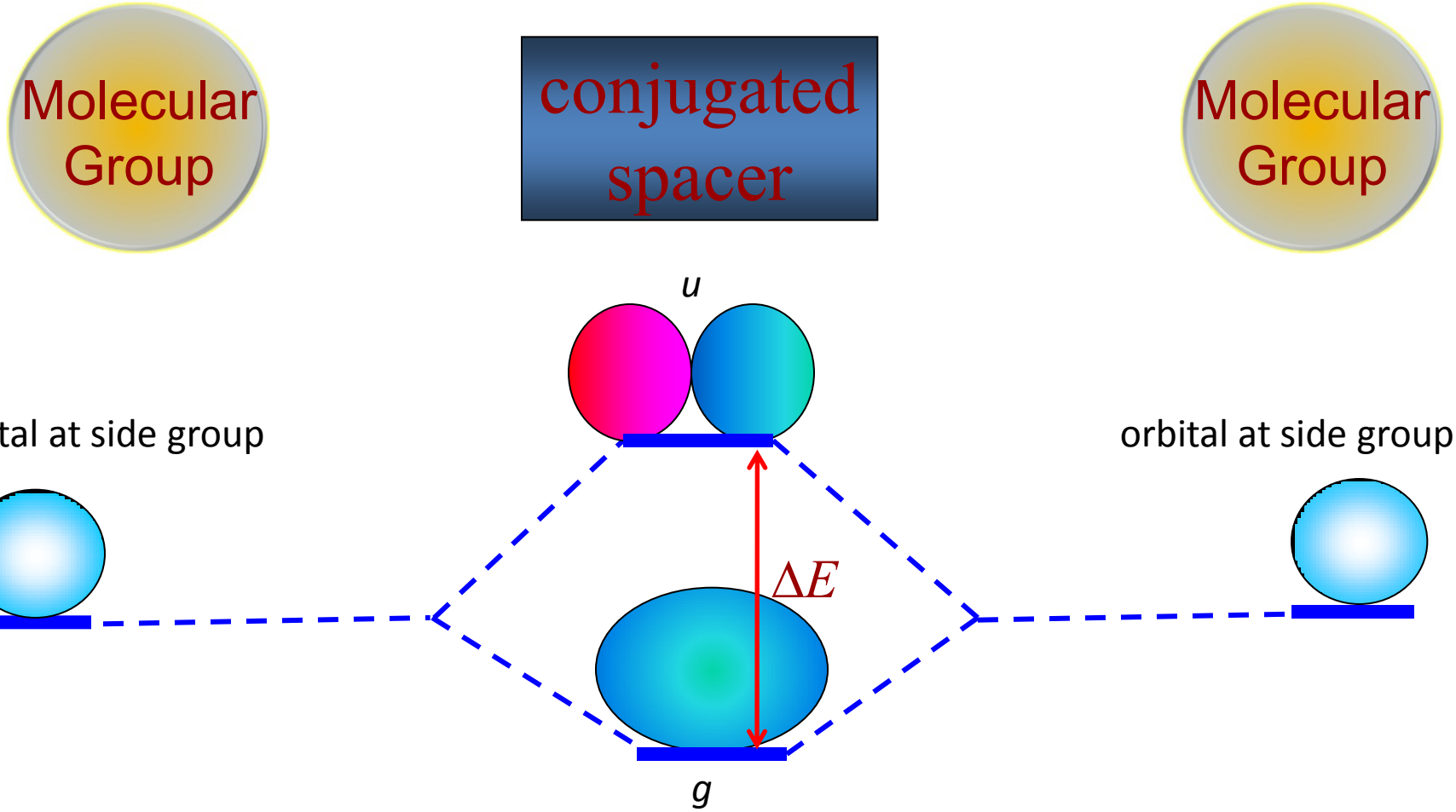
For short wire, superexchange coupling T dominates the charge transport process:

$$T \sim |g|^2$$

Break Junction: unknown contact details

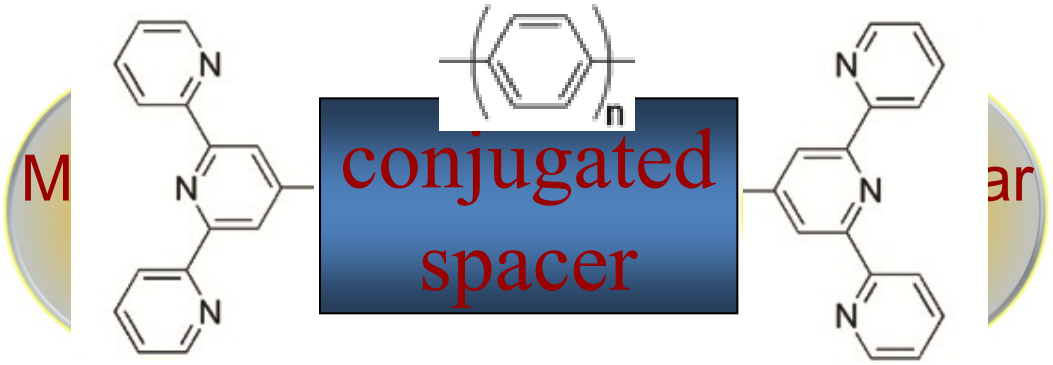
C. Joachim; M. A. Ratner, *Nanotechnology* 15, 1065 (2004)

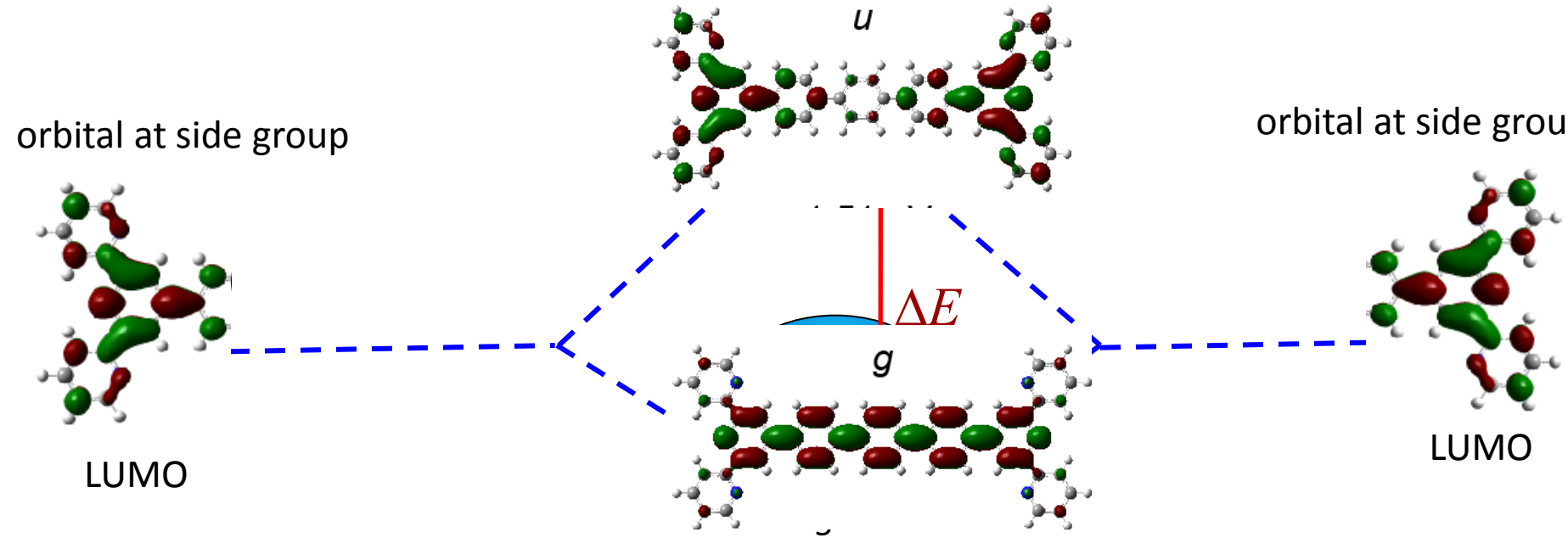
Our method



Superexchange coupling $T \sim \Delta E/2$

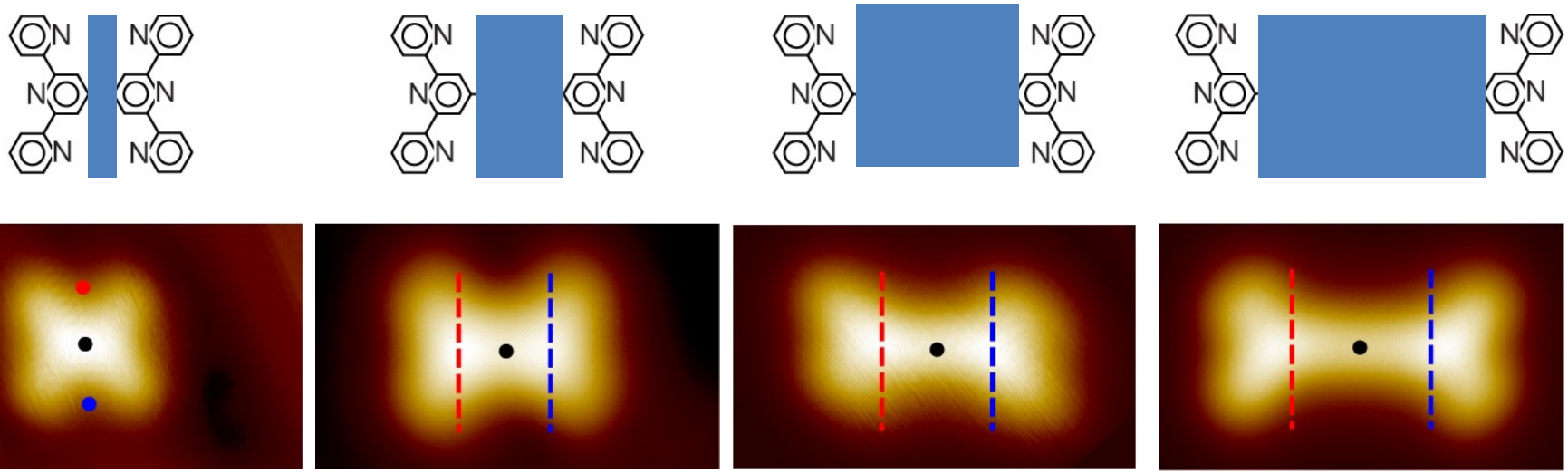
Our method

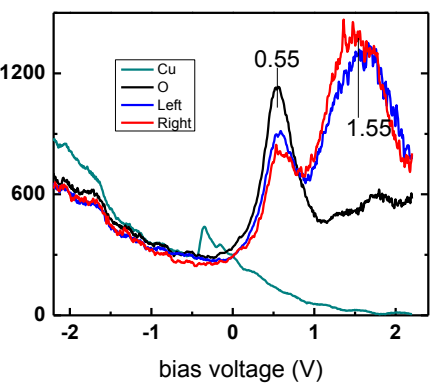


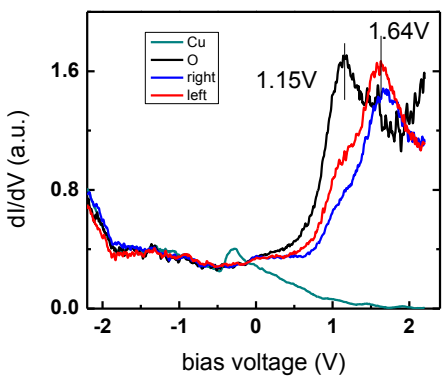


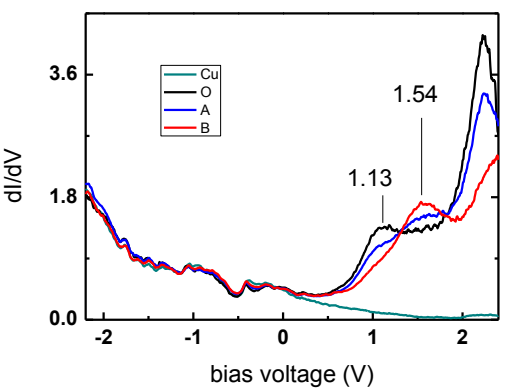
Superexchange coupling $T \sim \Delta E/2$

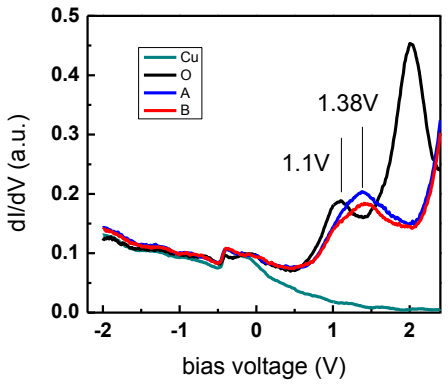
Dimerized Odd and Even States



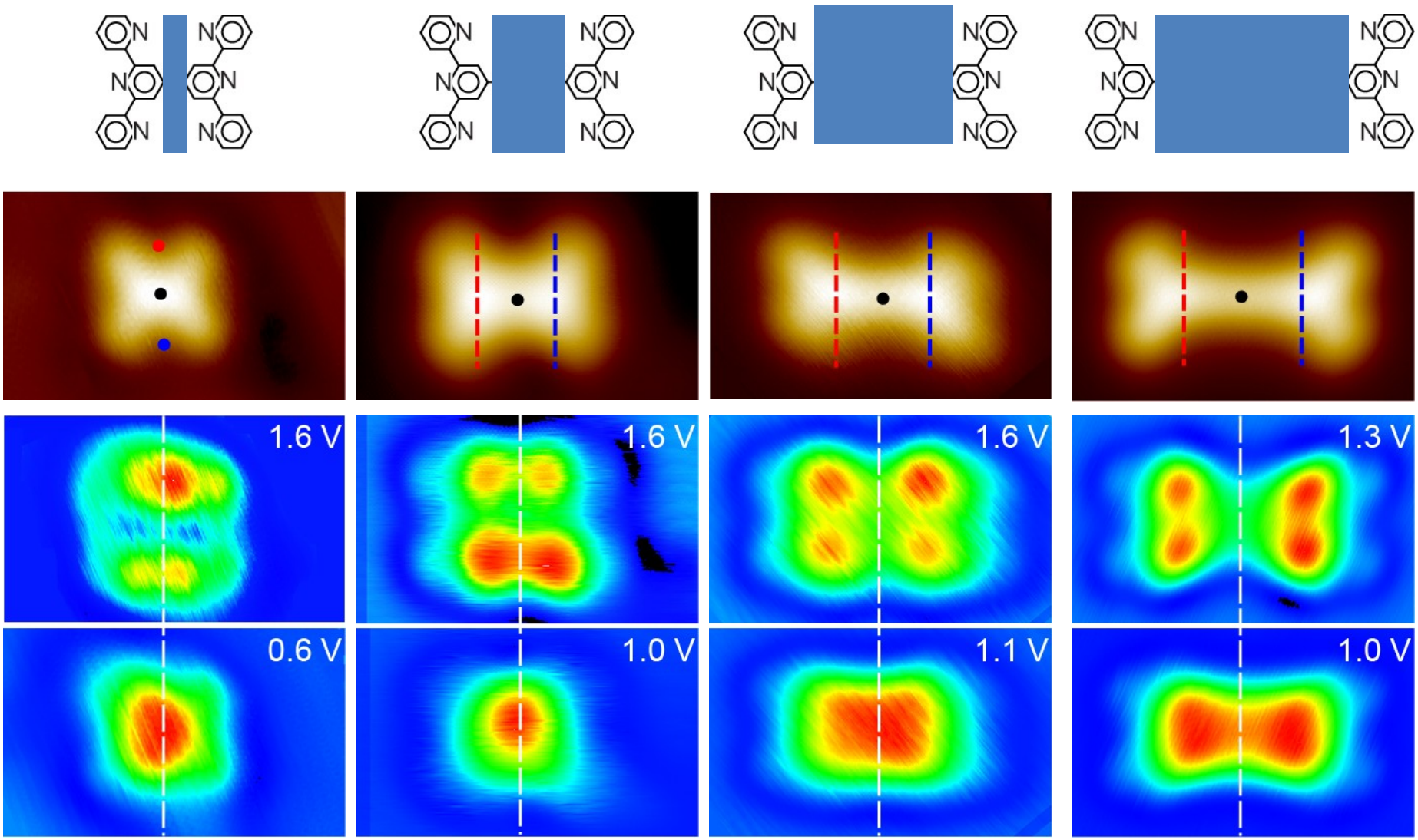




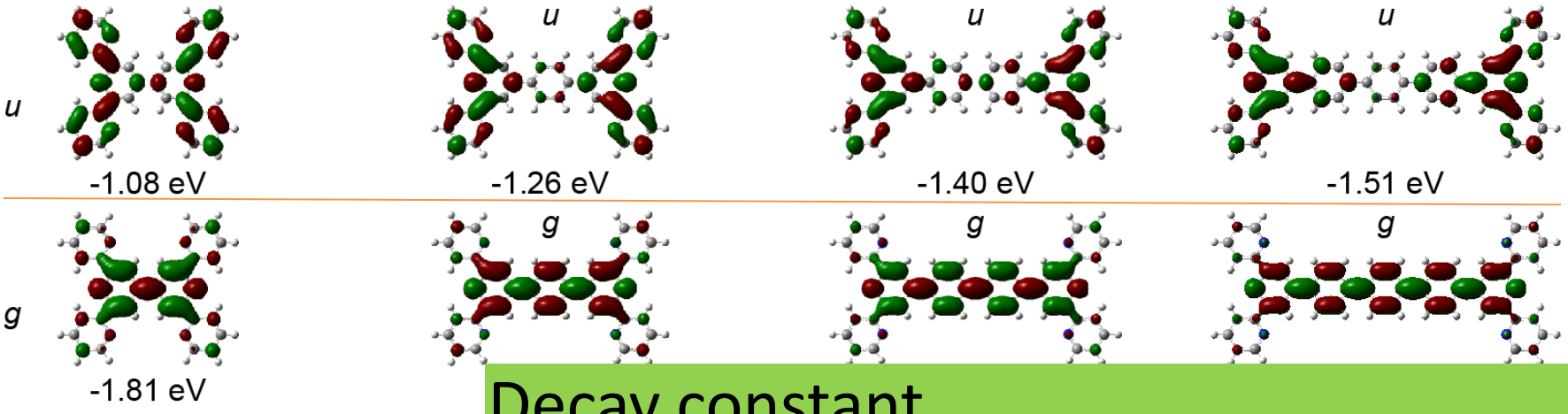


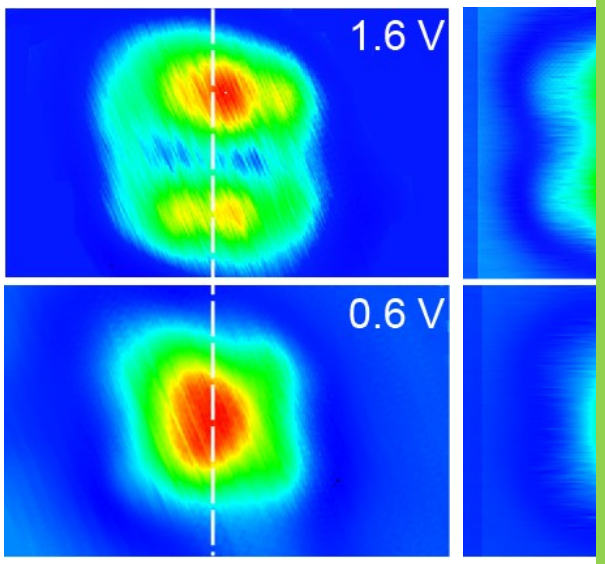


Dimerized Odd and Even States

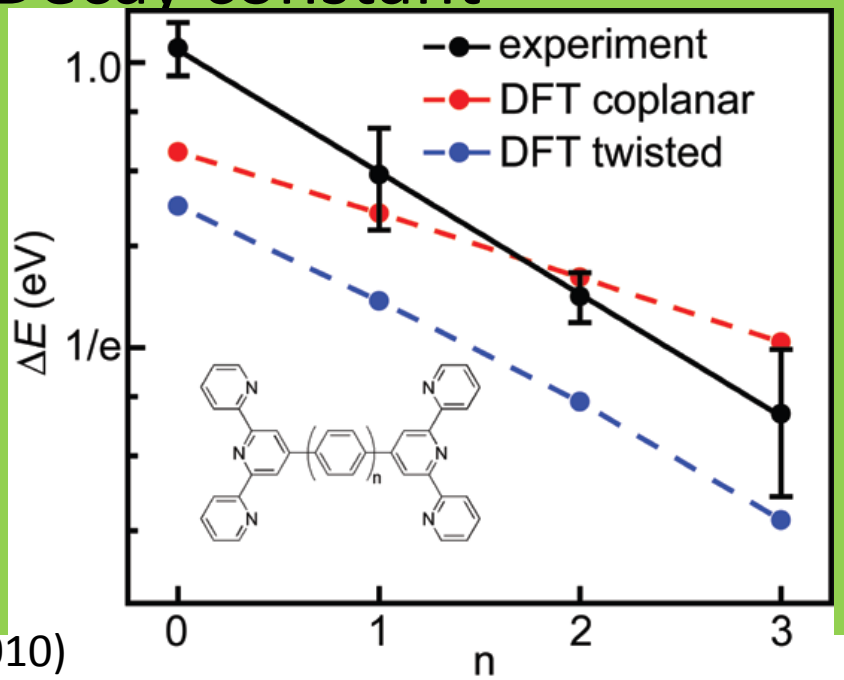


Dimerized Odd and Even States





Decay constant



$\Delta E \sim e^{-\beta d}$

$\beta = 0.10\ A^{-1}$

Theory:
0.08-0.2 A^{-1}

J. Am. Chem. Soc. 132, 8774 (2010)

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  - On-surface Ullmann reactions
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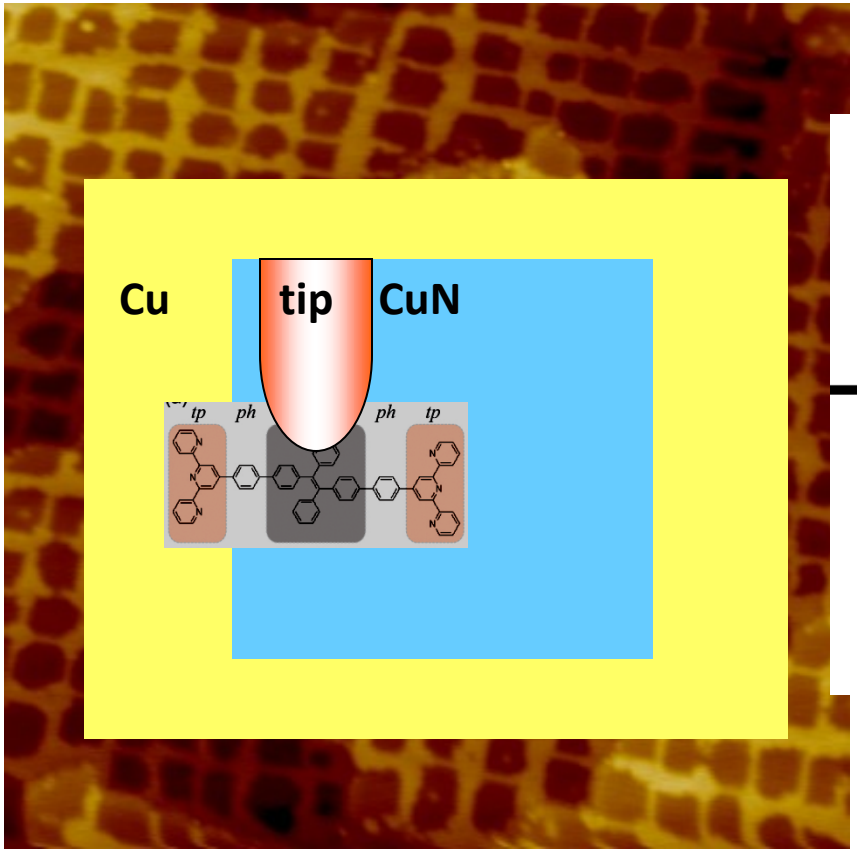
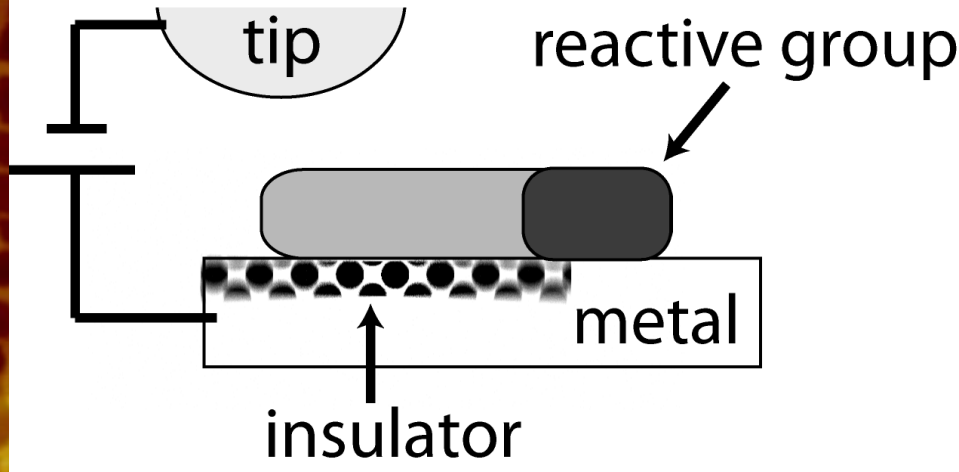
How to simultaneously measure molecular capacitance/conductance and contact details?

CuN/Cu(100) substrate

CuN: one atomic thick insulating film

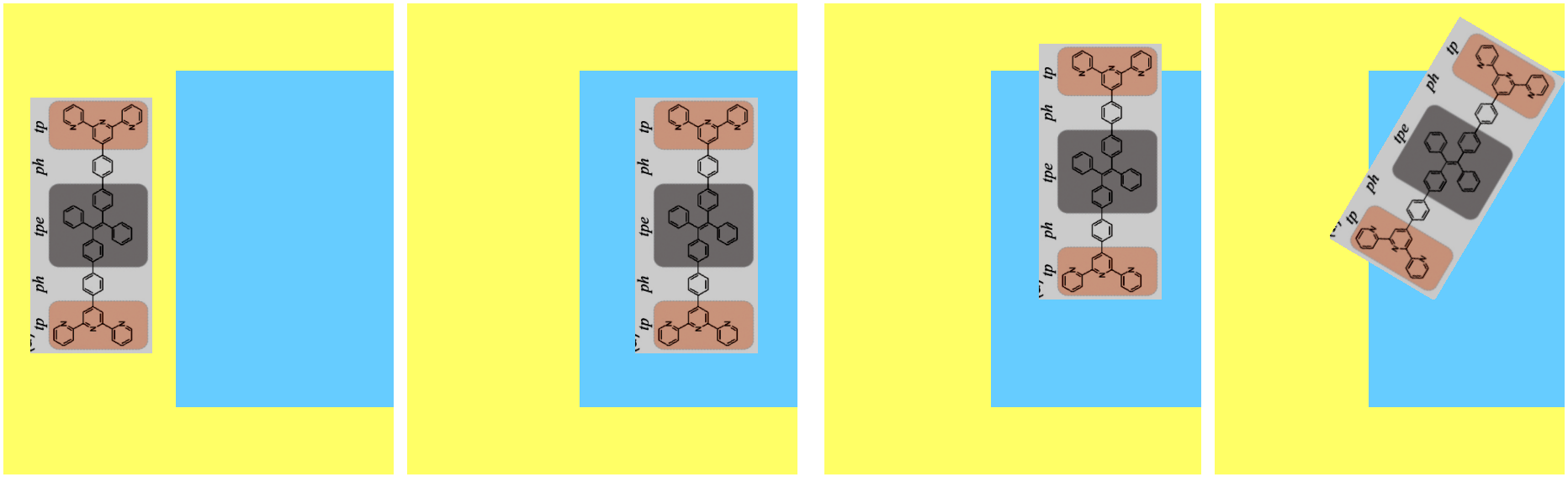


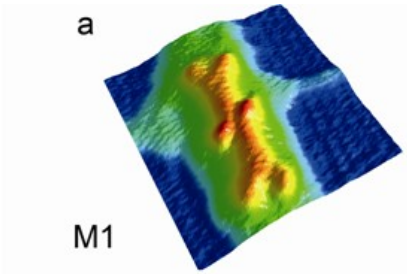
80 nm x 80 nm

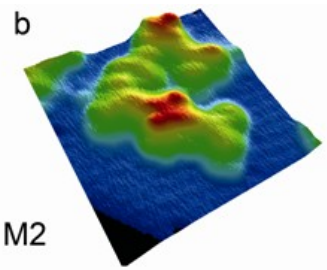


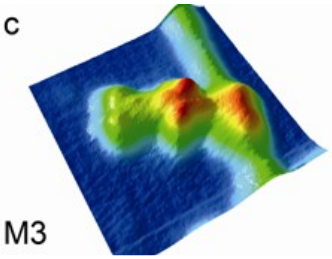
Chemically adsorbed on metal
Physically adsorbed on CuN

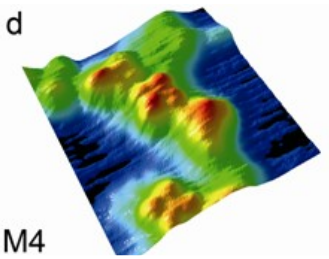
Adsorbed on CuN/Cu(100)

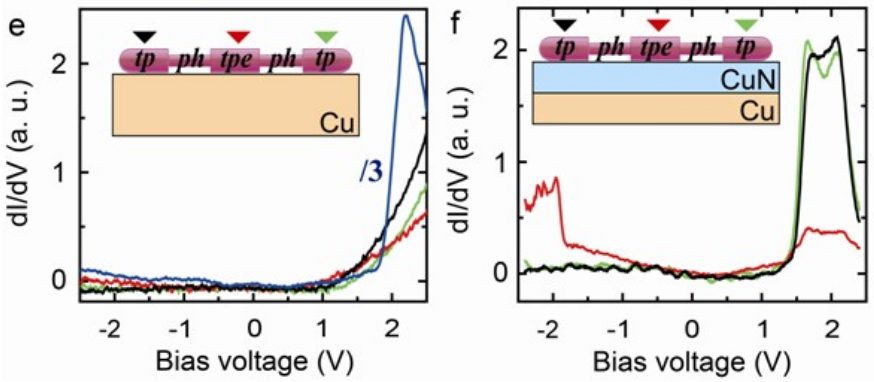




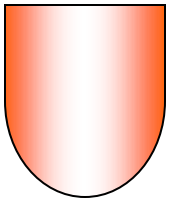


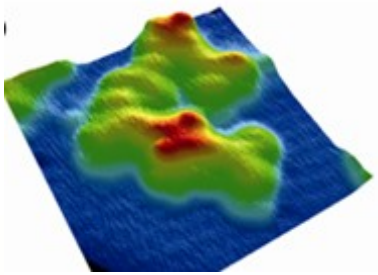




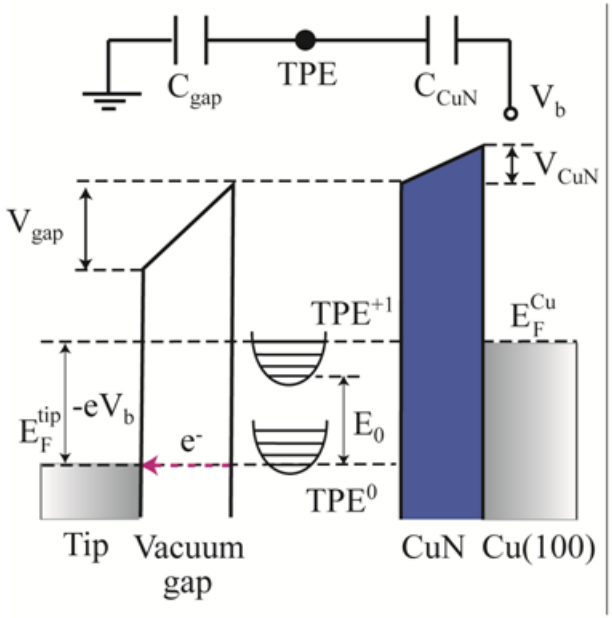


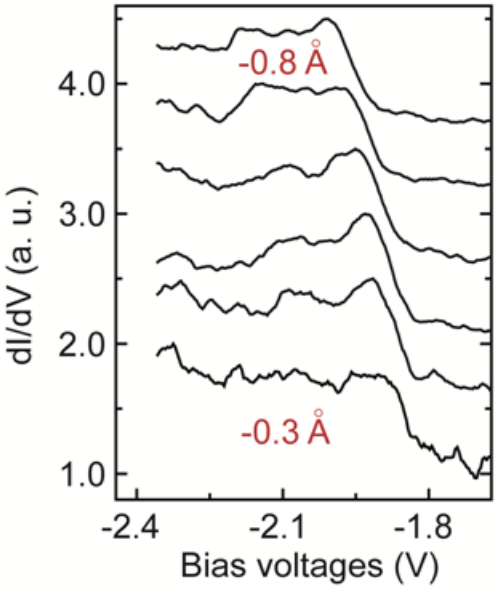
Double-Barrier-Tunneling Junction

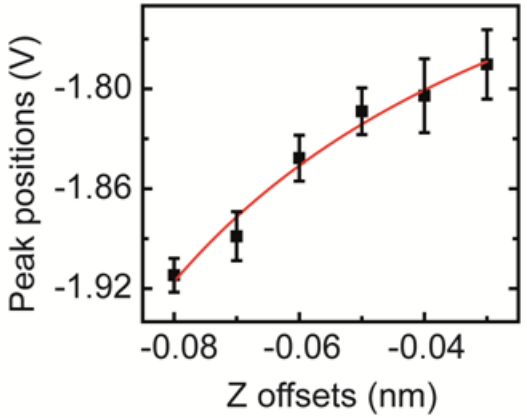




$$eV = -E_0\left[1 + \frac{\varepsilon_0 s}{zC_{CuN}}\right]$$





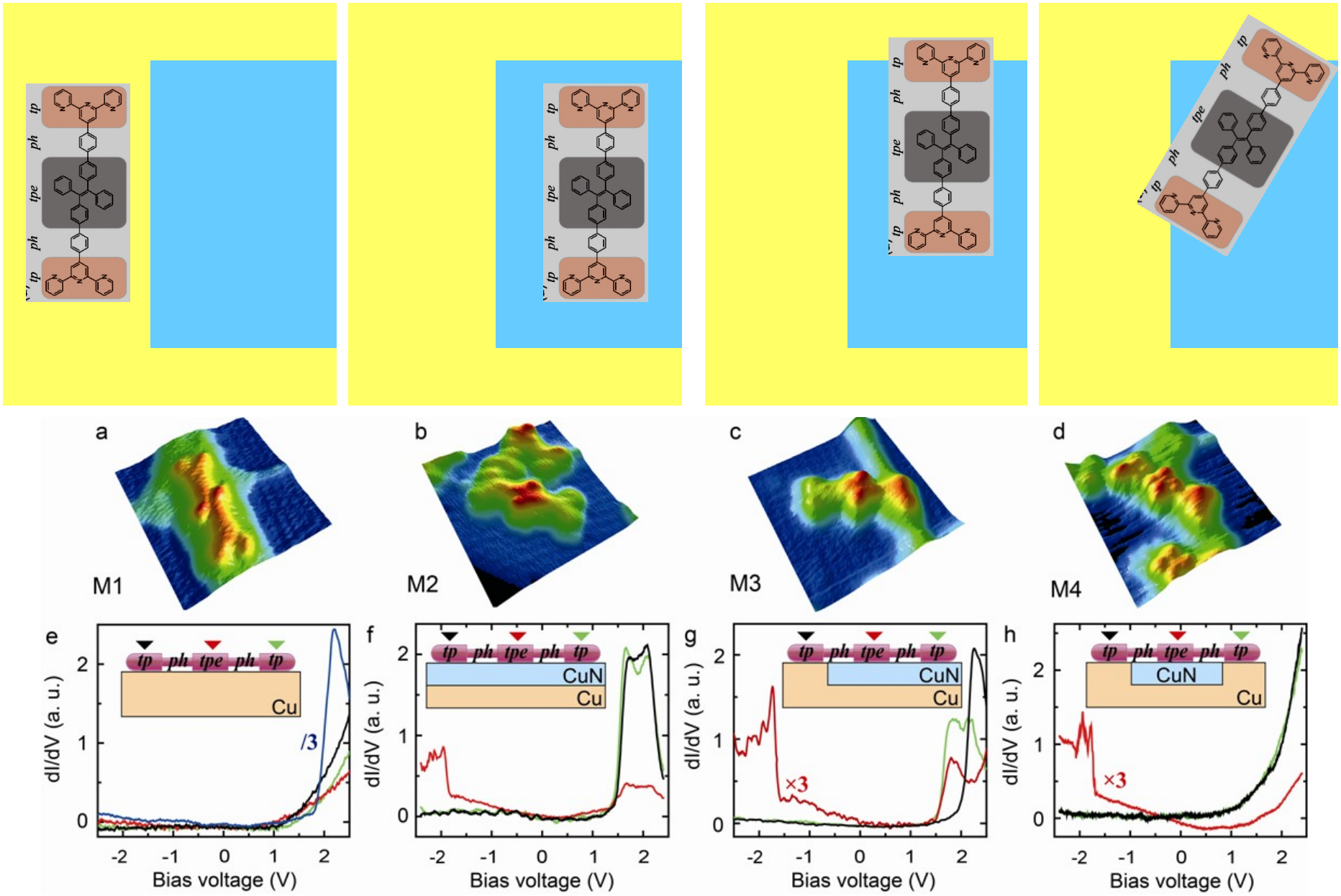


Single electron process

C_{CuN}=0.5 *aF*

ε_{CuN}= 11

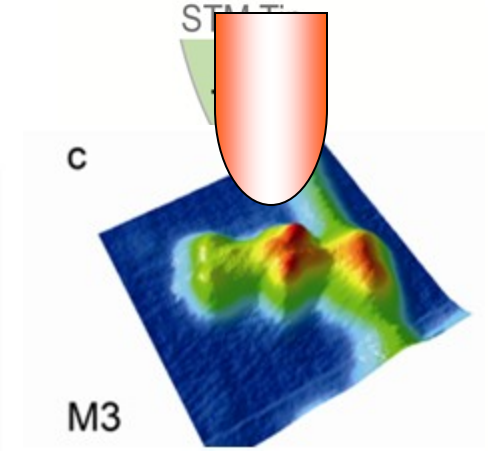
Adsorbed on CuN/Cu(100)

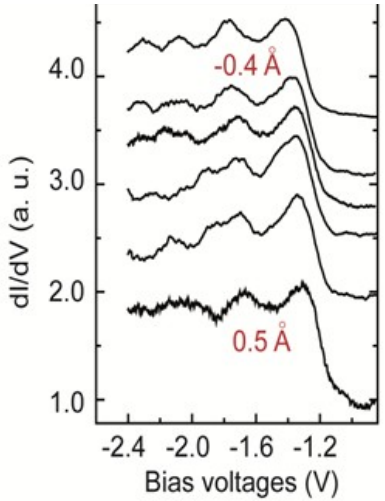


Molecular capacitance

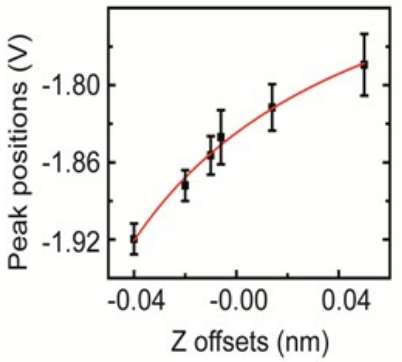
ΔE= *191±6 meV*

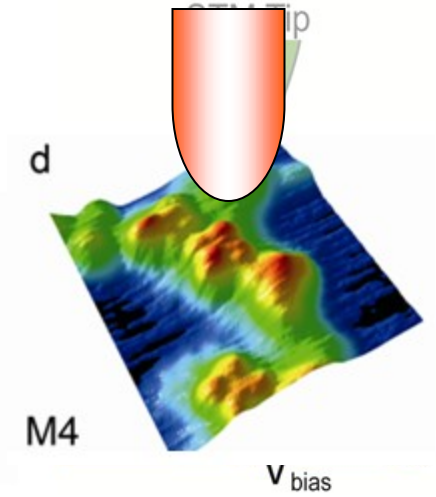
C=C stretching: *200 meV*

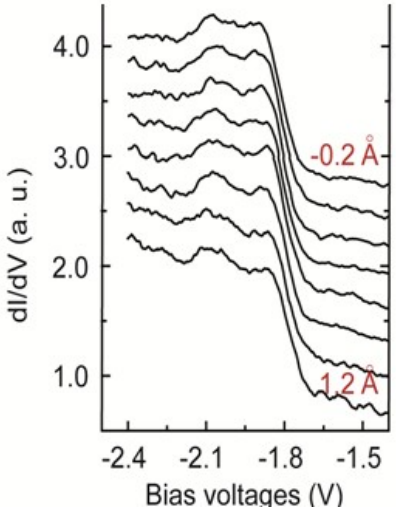




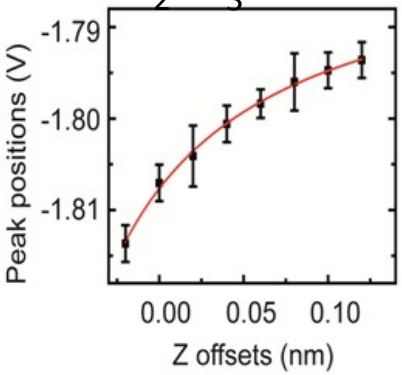
C_1=0.9 *aF*





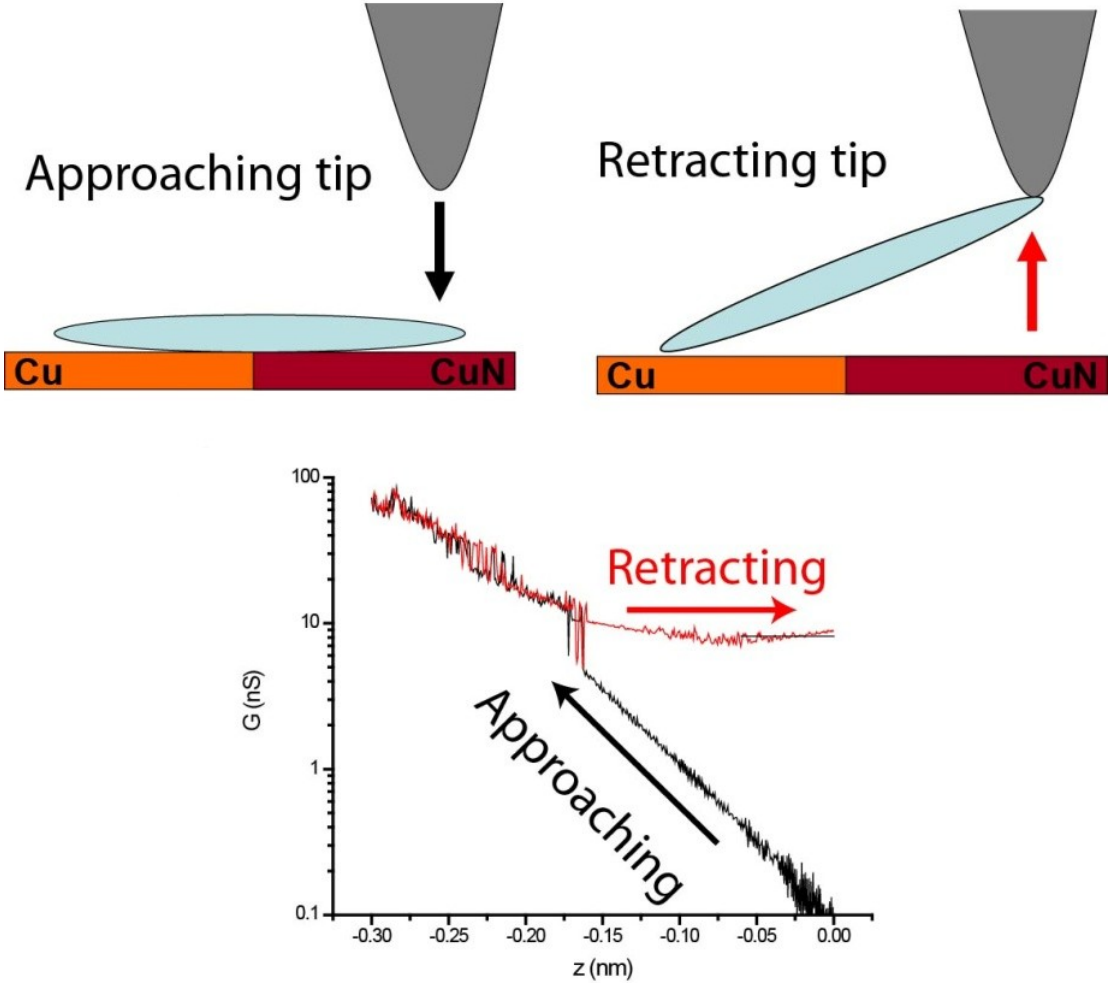


C_2+C_3=2.4 *aF*



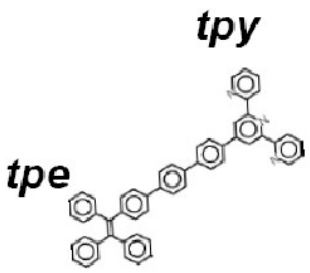
Phys. Rev. B 83, 115431 (2011).

Measure single molecular conductance

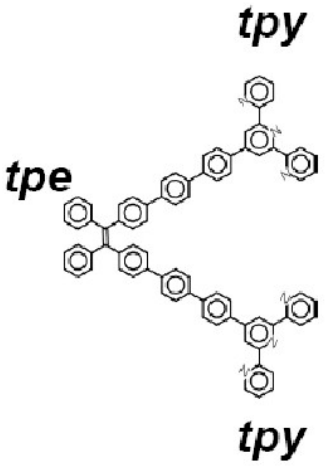


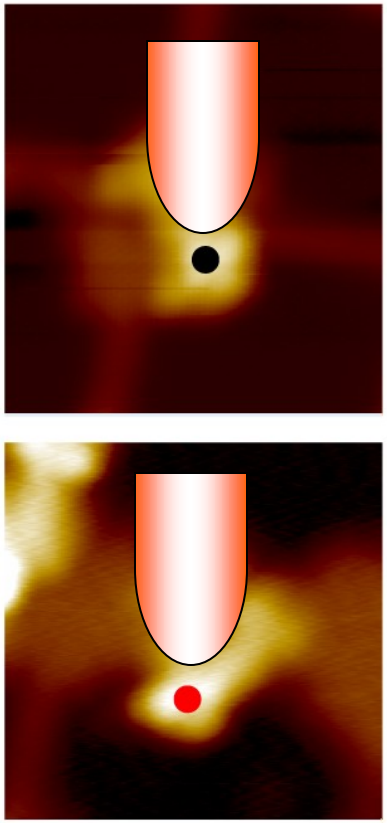
Molecular conductance

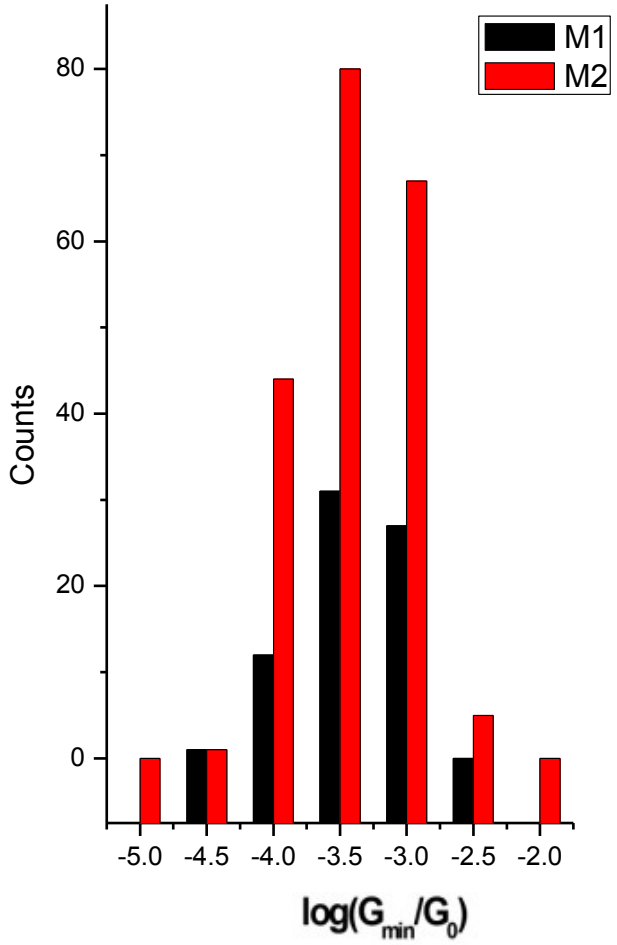
M1



M2







Both M1 and M2 have a typical conductance of 20 nS.

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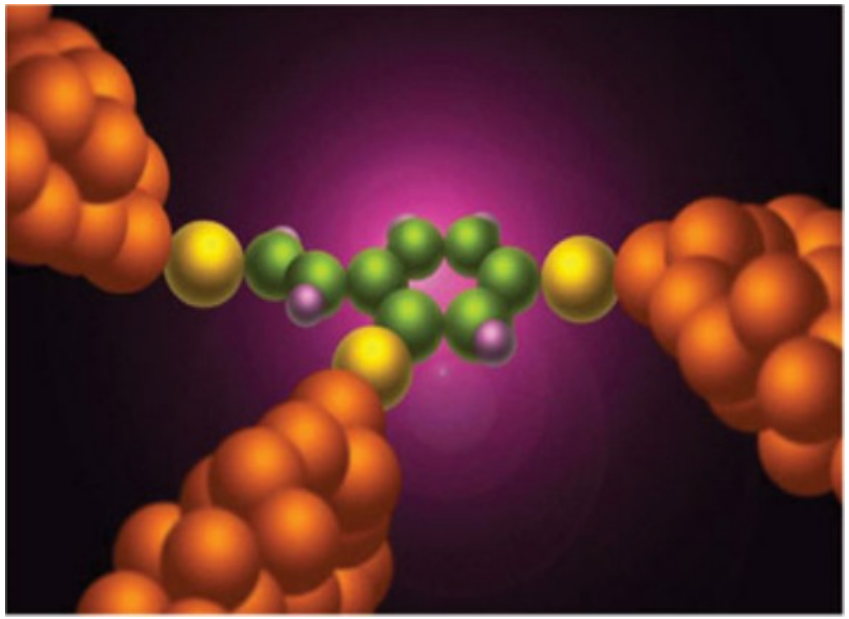
Motivation

- What happens to molecules when they contact to electrodes?

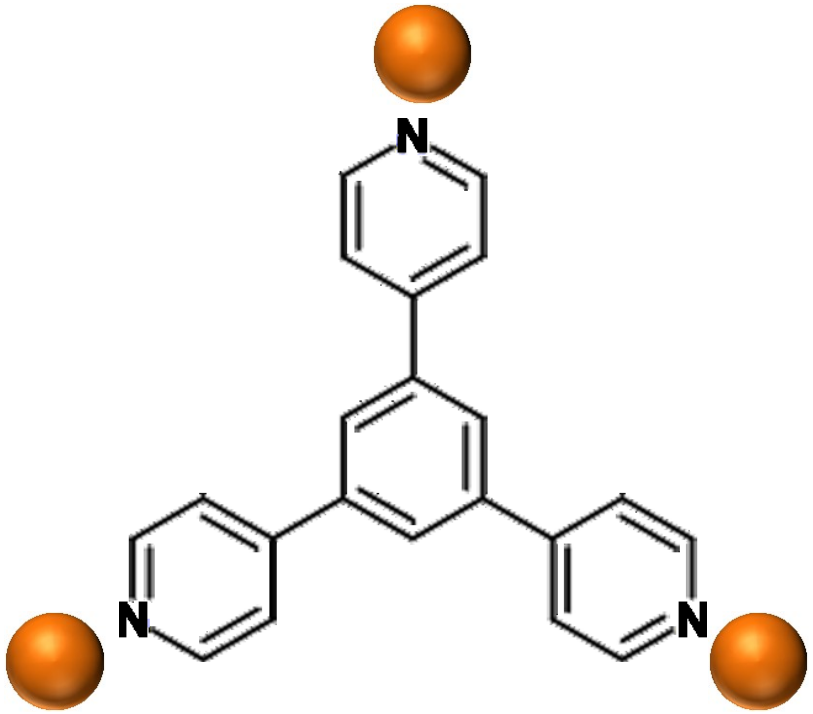
1. Molecular States modulate by multiple electrodes

2. In return influence charge transport properties

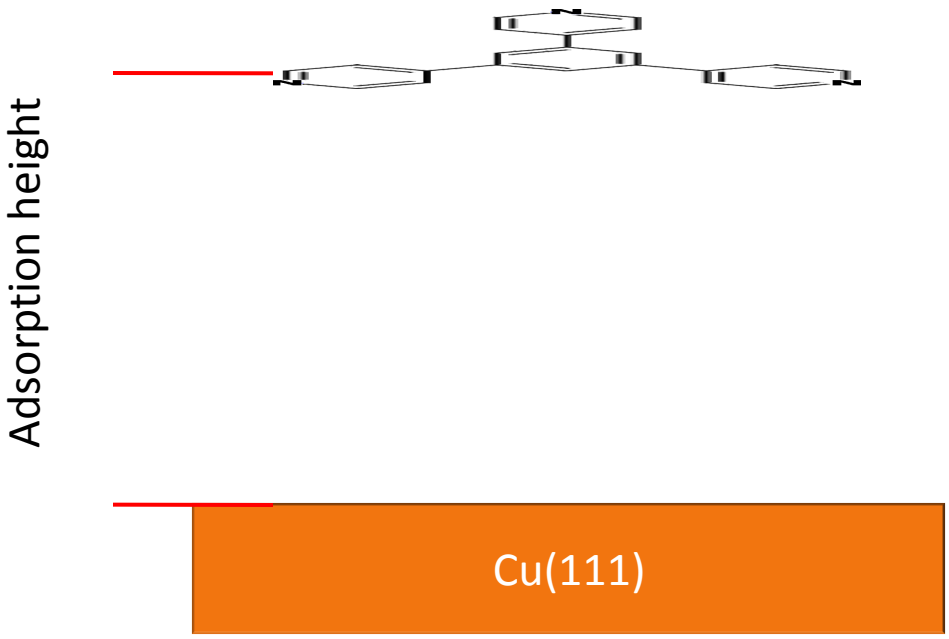


http://spie.org/x8437.xml

Modulation of molecular states by metal-atom contacts



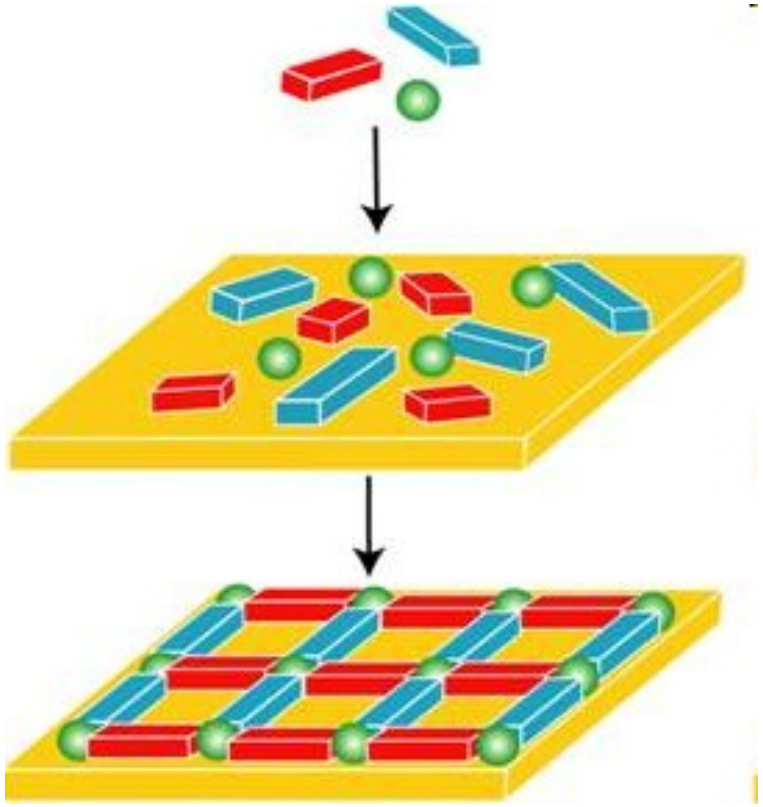
lateral modulation

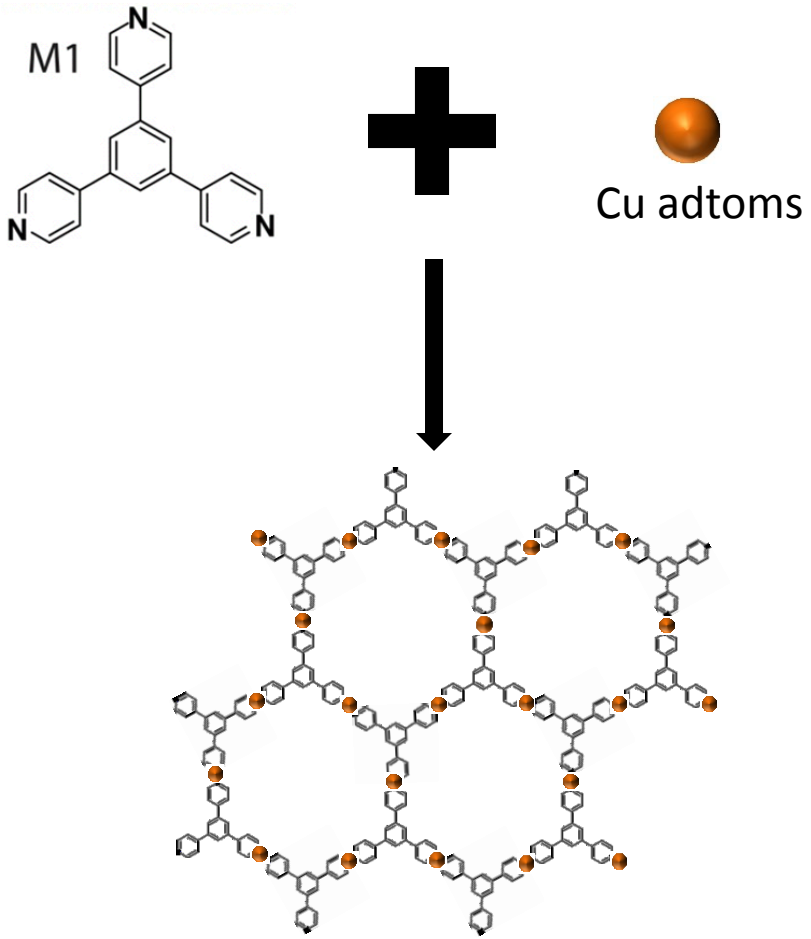


vertical modulation

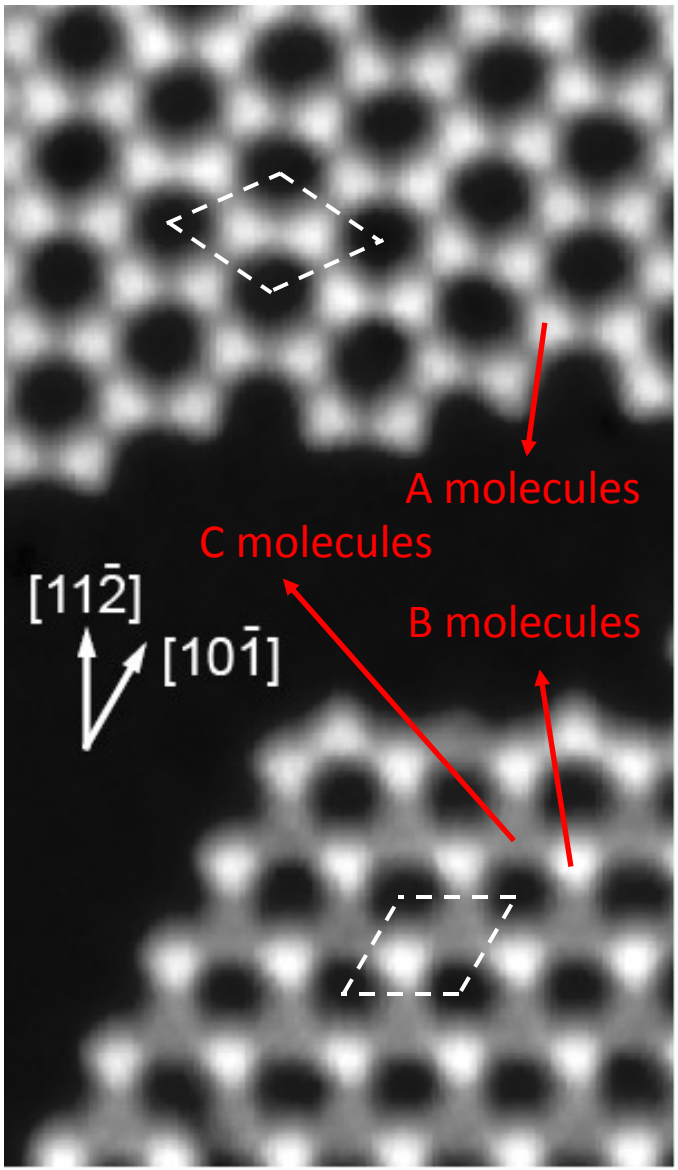
How to realize single atom contact?

- Supramolecular self-assembly strategy

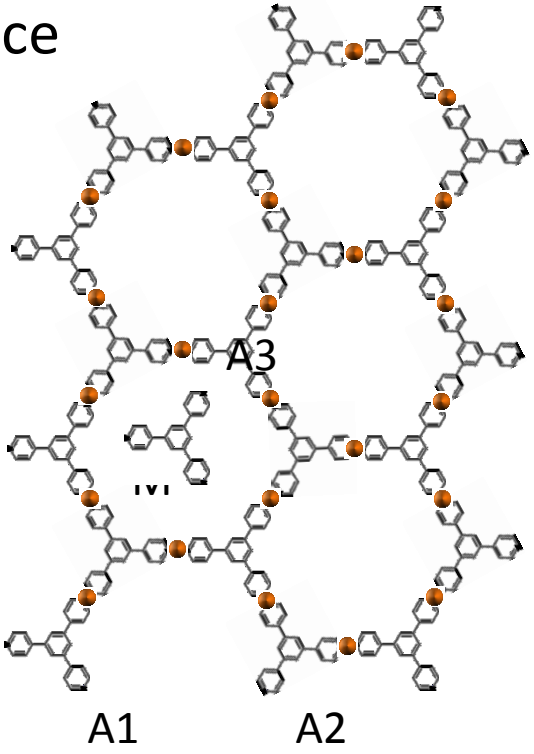




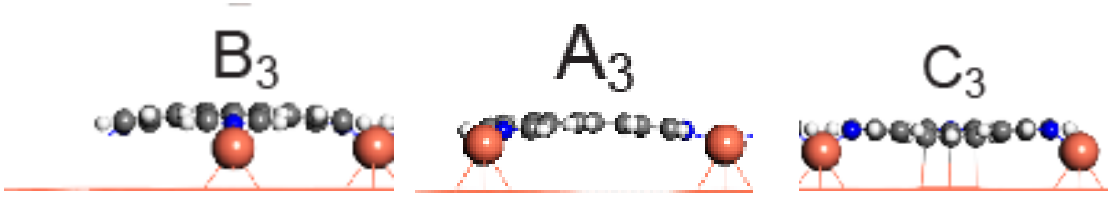
TPyB-Cu network on Cu(111) surface



Number of contacts
M: no contact
A1: one contact
A2: two contacts
A3: three contacts



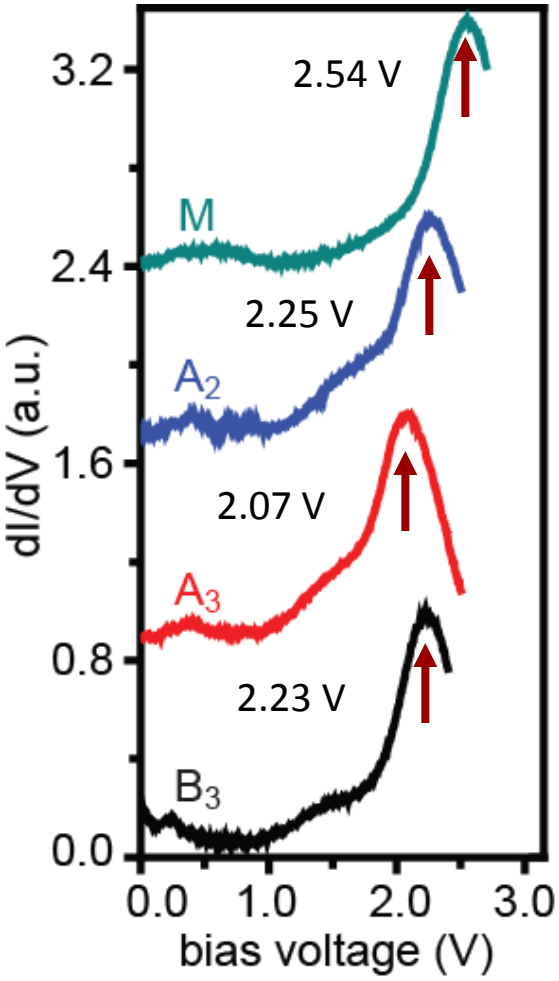
Different adsorption heights

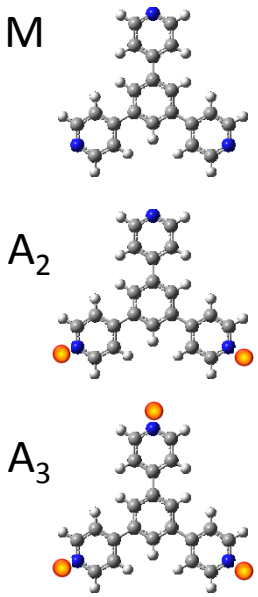


3.40 Å 3.29 Å 2.59 Å

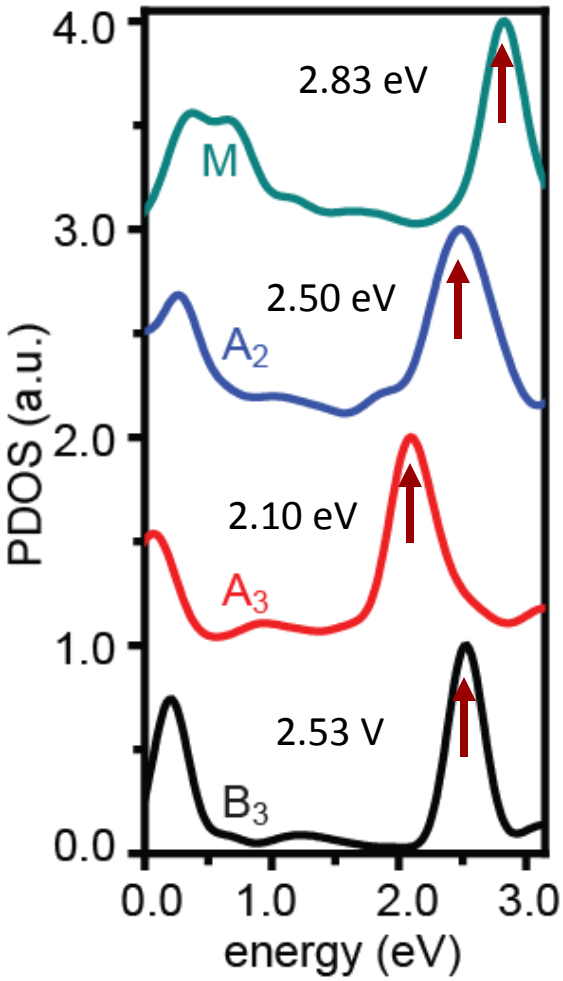
Definition:
A3/B3/C3: three contacts

Lateral and vertical modulation



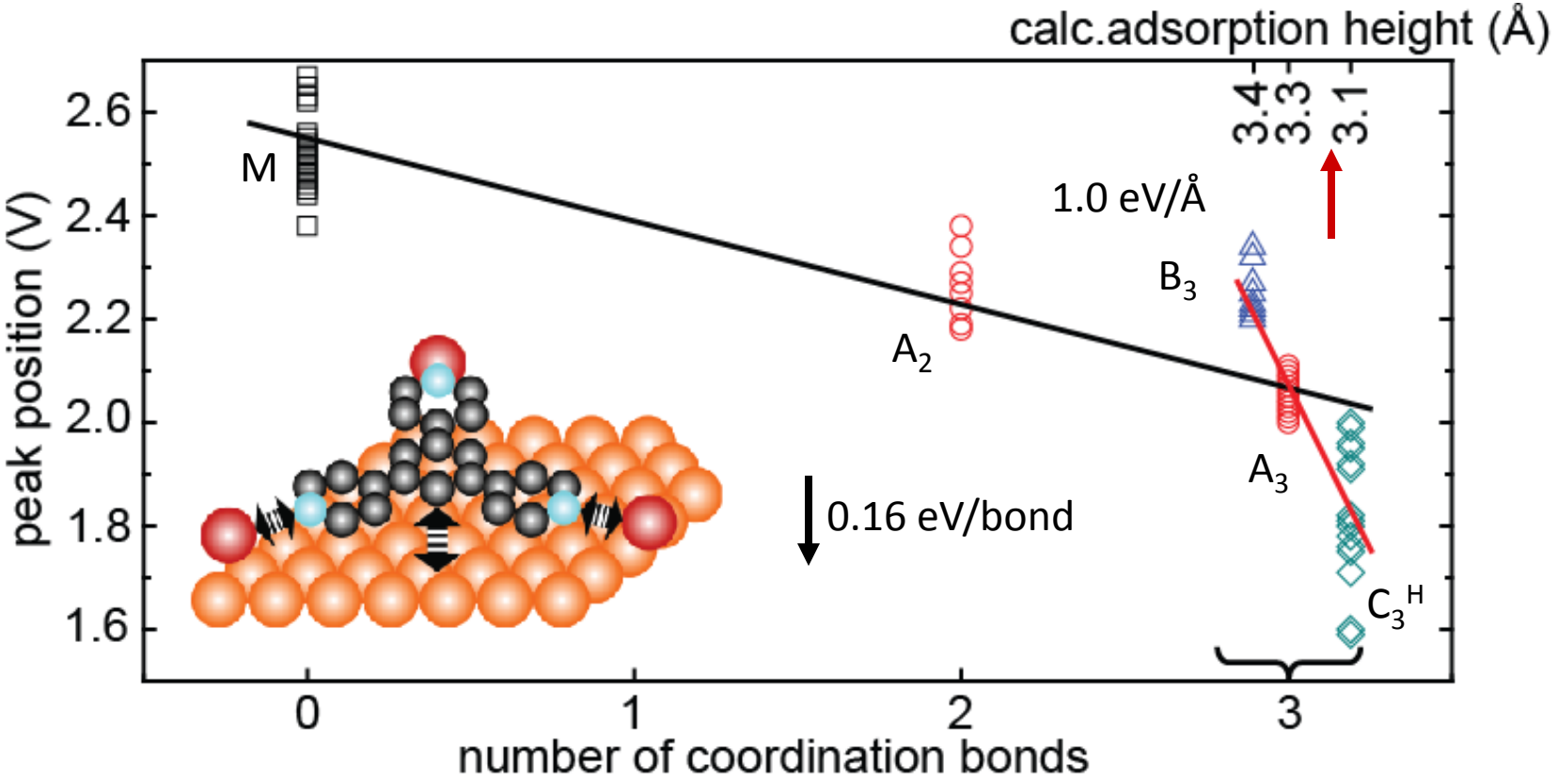


adsorption height
A_3 : B_3:
3.29 Å : 3.40 Å



Lateral: hybridization between the delocalized molecular orbital and the Cu states; Vertical: workfunction

Lateral and vertical modulation of electronic structures of TPyB molecules

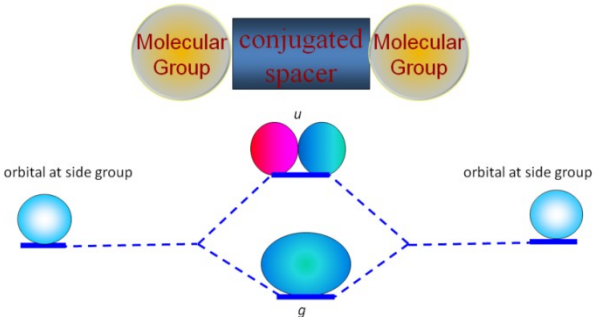


Phys. Rev. Lett. 110, 046802, (2012)

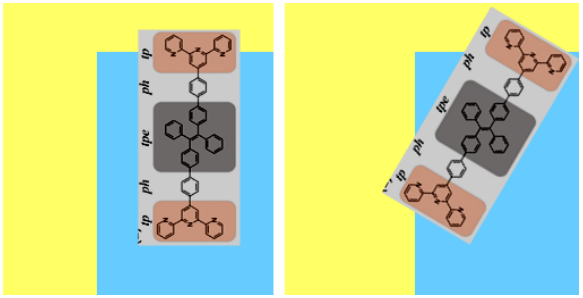
Summary

- Simultaneously measure transport and contact details

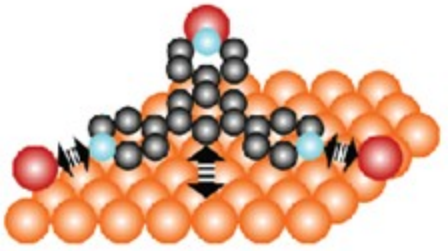
1. Superexchange coupling: energy splitting



2. Molecules on CuN/Cu(100) dual-functional substrate



- The modulation of molecular orbitals by metal atom contacts



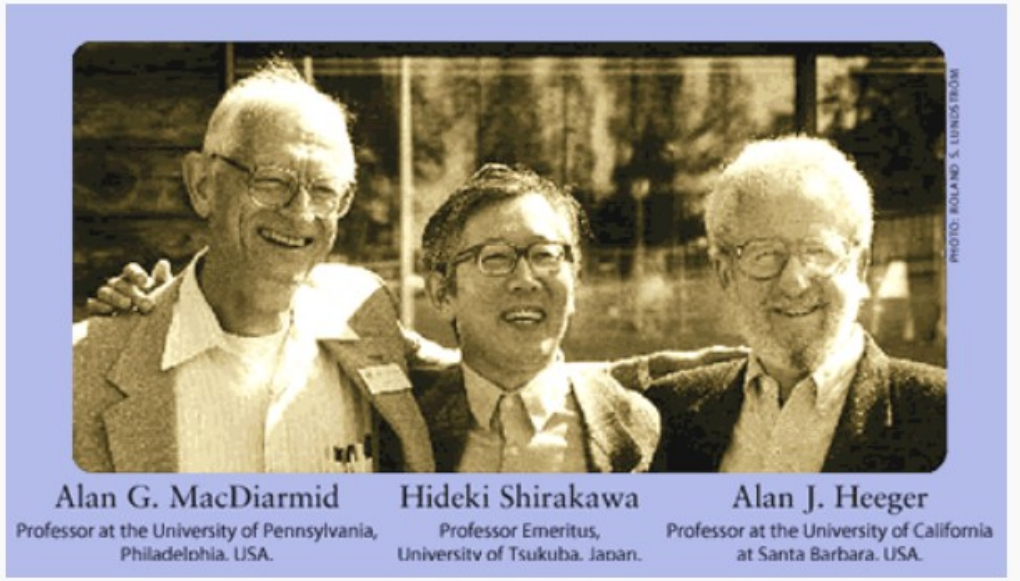
Outline

- Single molecular characterization:
  - Superexchange coupling
  - Molecular capacitance and conductance
  - Metal-atom contacts
- Conjugated poly-p-phenylene polymers
  - On-surface Ullmann reactions
  - Intrinsic electronic structures
  - Dopant states
- 2D molecular nanostructures
  - Modulation of Shockley surface-state by supramolecular self-assemblies
  - Fabrication and characterization of molecular graphene

Motivation

- Conjugated polymers are expected to used as molecular wires
- Doped conjugated polymers (Conductive polymers)

The Royal Swedish Academy of Sciences has awarded the Nobel Prize in Chemistry for 2000 jointly to ***Alan J. Heeger, Alan G. MacDiarmid*** *and* ***Hideki Shirakawa*** *"for the discovery and development of conductive polymers".*



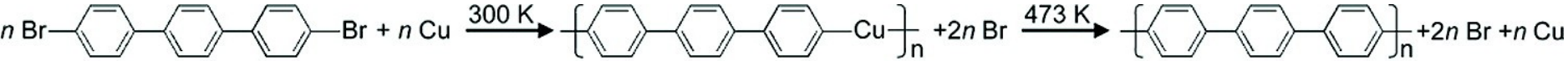
Exp. Challenge:

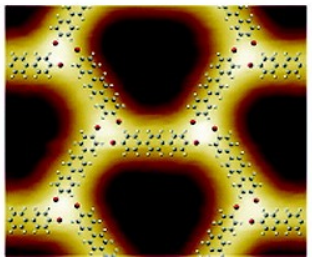
1. **Measure Single conjugated polymers**

2. **Visualize the predicated dopant states involved in conductive polymer**

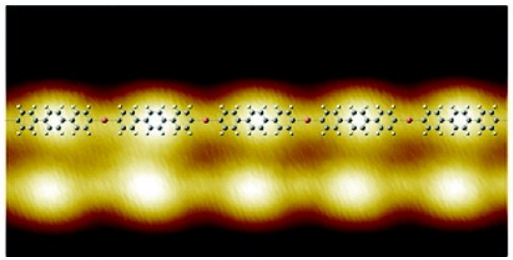
On-surface Ullmann coupling

- Substrate: Cu(111)
- Molecular precursor: 4, 4’’-dibromo-p-terphenyl

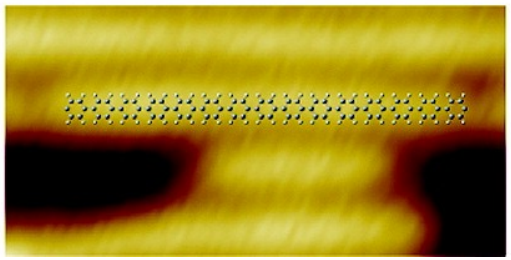




~150 K



300 K



470~500 K

J. Am. Chem. Soc. 133, 13264 (2011)

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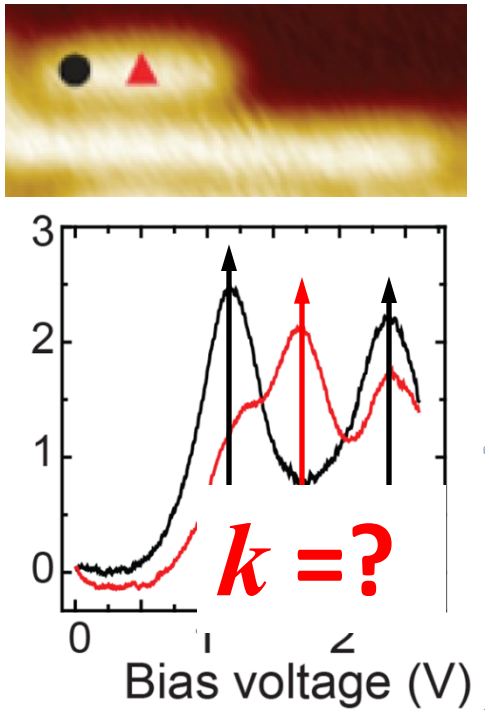
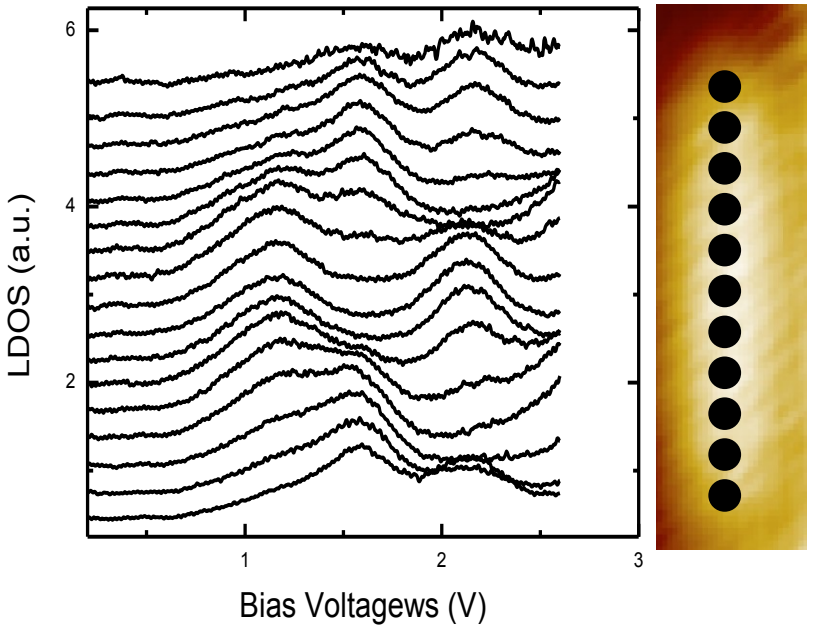
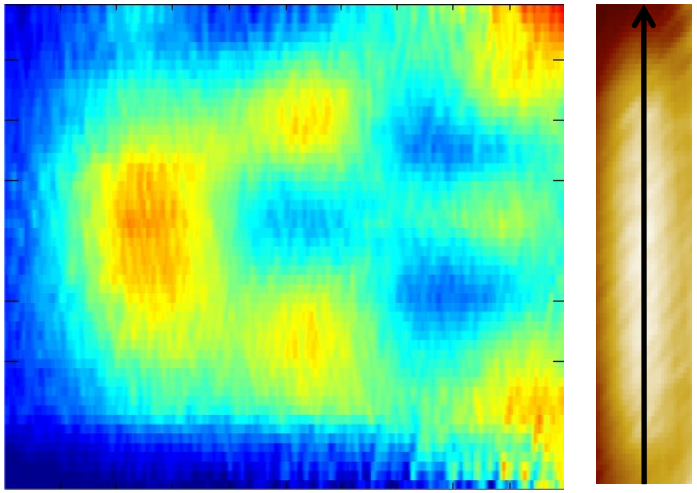
LDOS measurements







High

Low

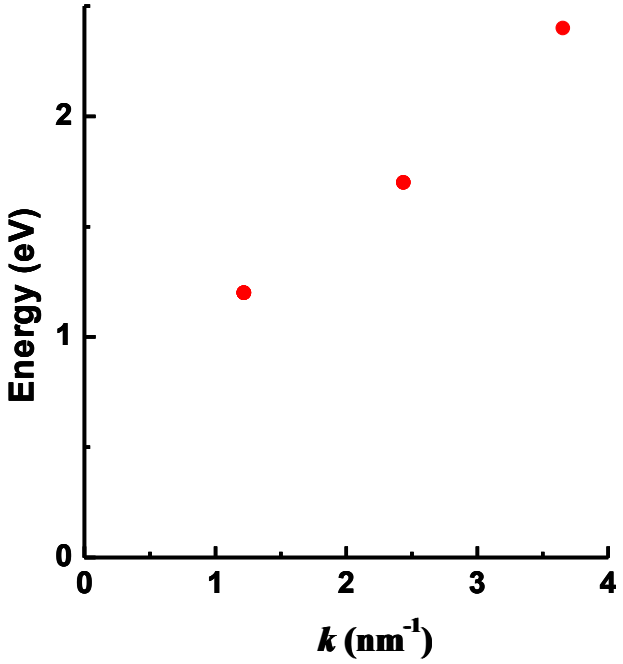
E-K relation

Dispersion relation

k: wave vector

$$k_m = m\pi/Na \quad (1 \le m \le N,\ N=3n)$$

a = 0.43 nm

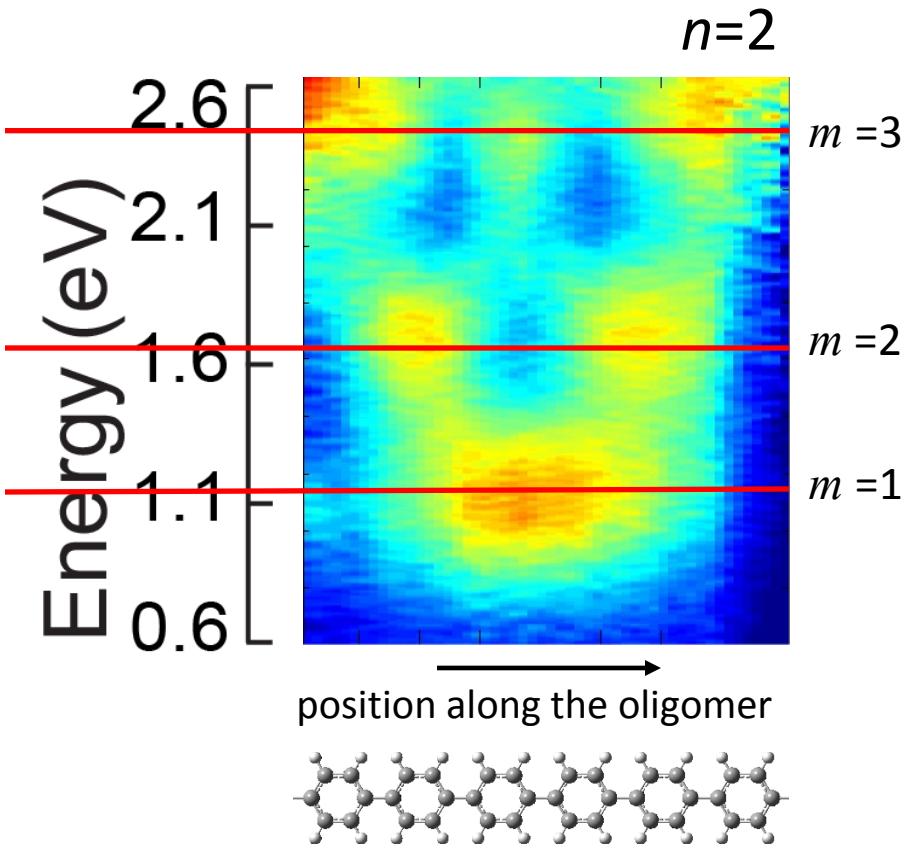


E-K relation

E =2.4 eV

E =1.7 eV

E =1.2 eV



LDOS plots and E-K relations (model)

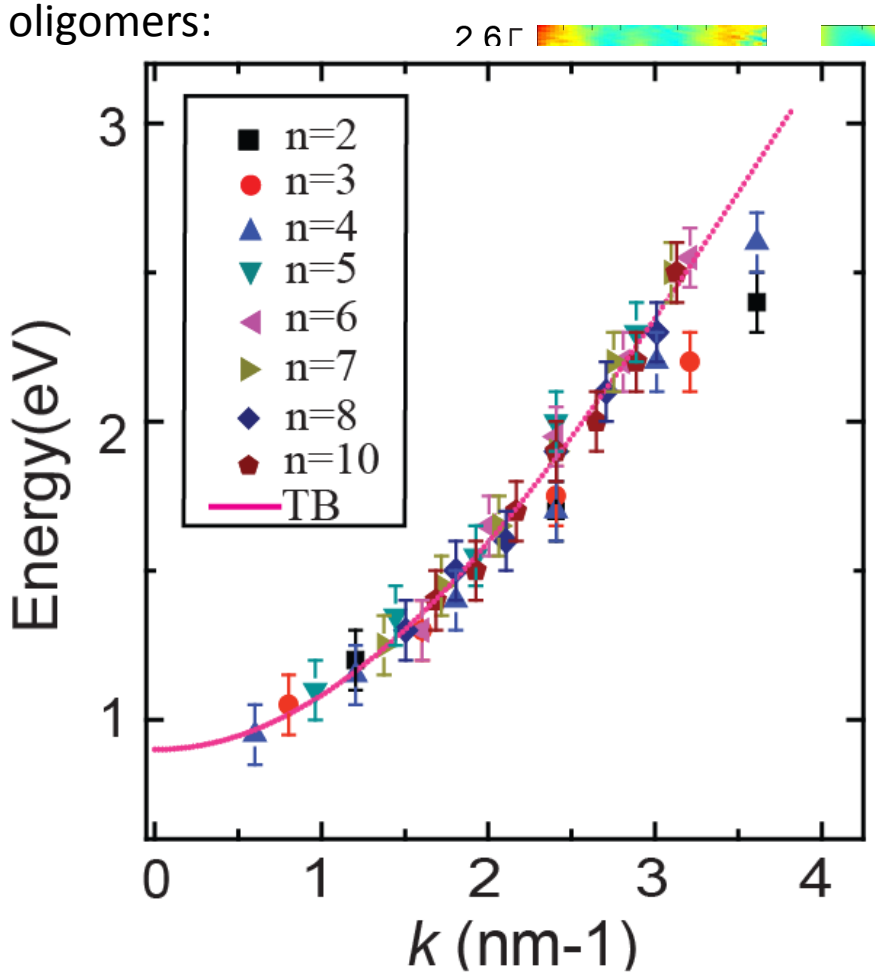
short oligomers:

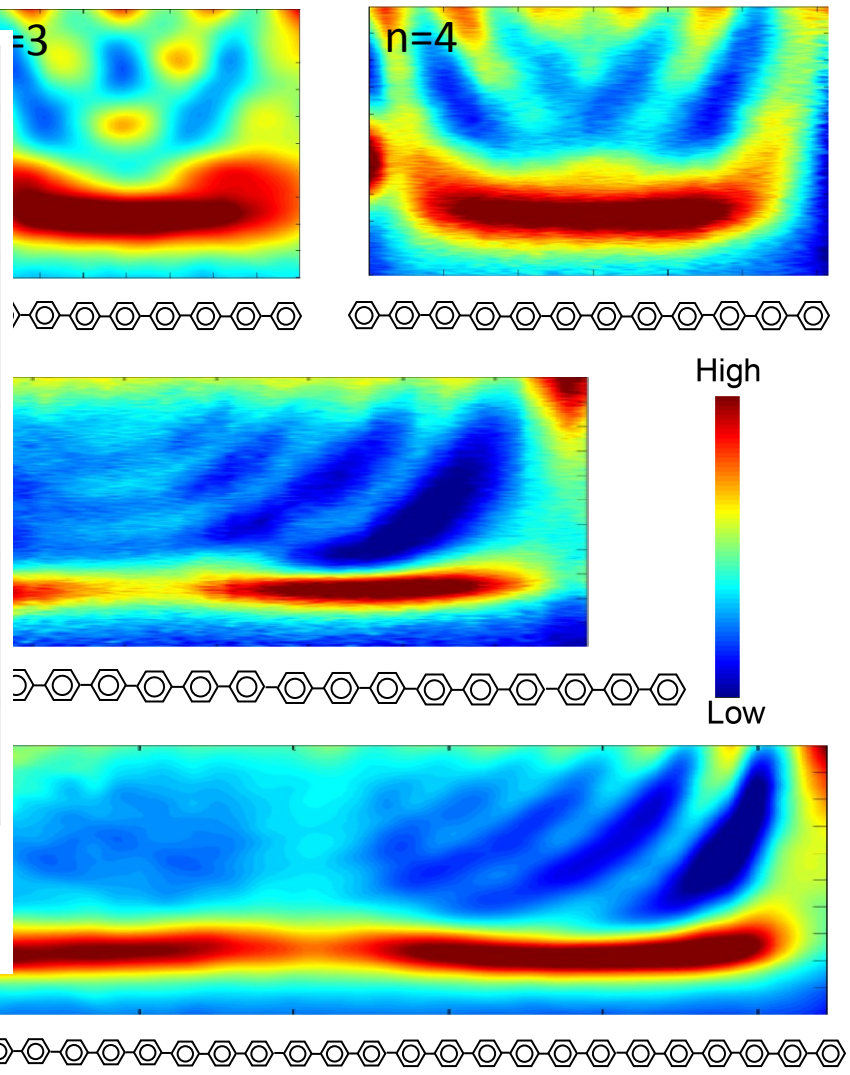
discr

long

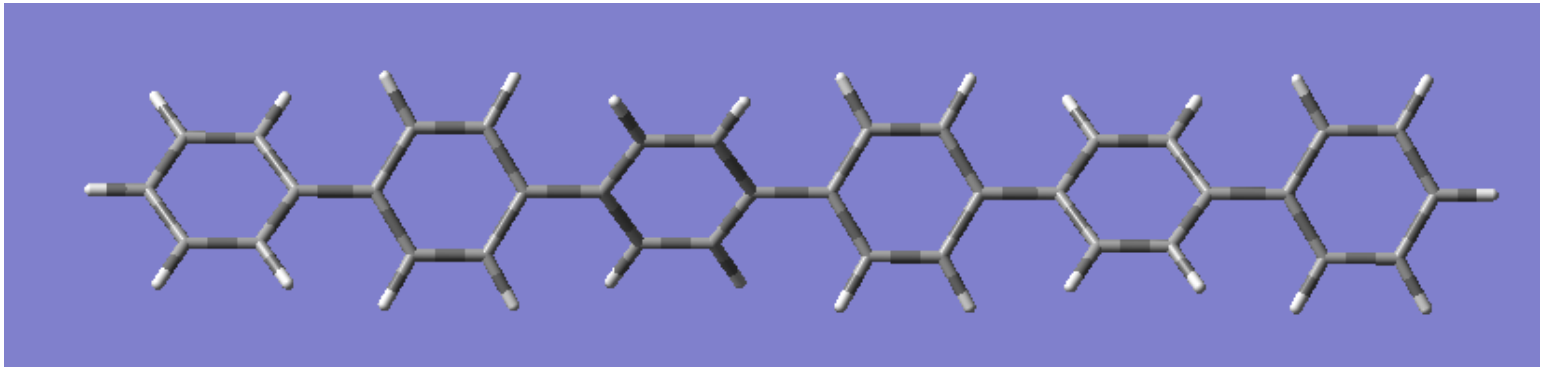
cont

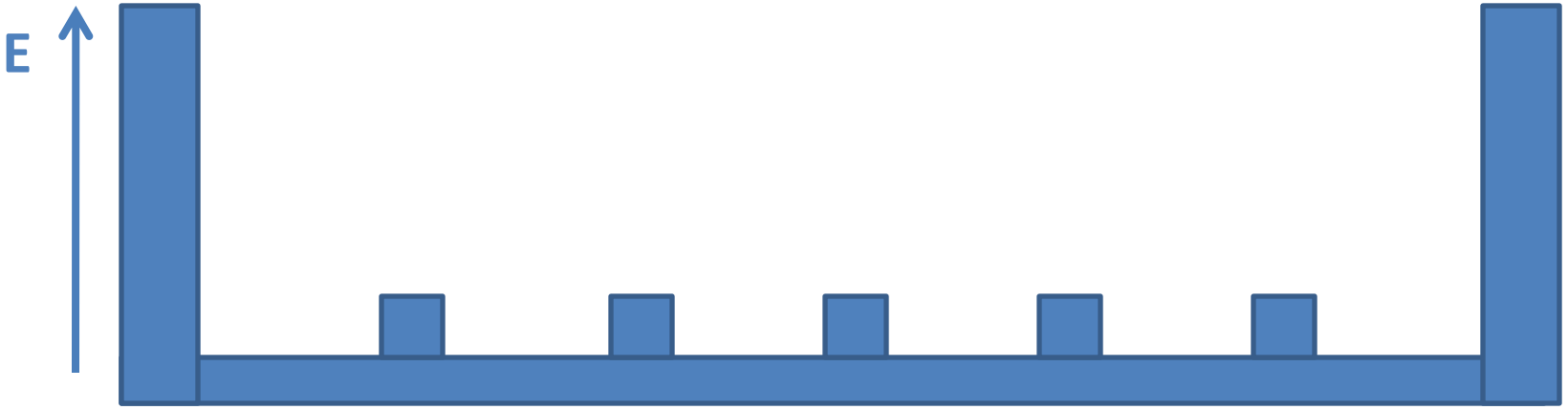
Visua





Model PPP oligomers





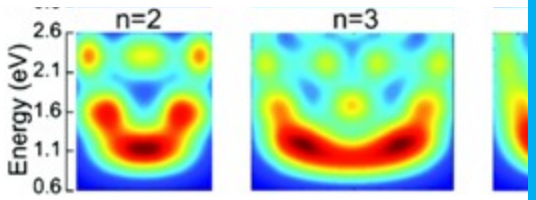
Tight binding approximation

$$H|n\rangle = \varepsilon|n\rangle - t|n+1\rangle - t|n-1\rangle$$

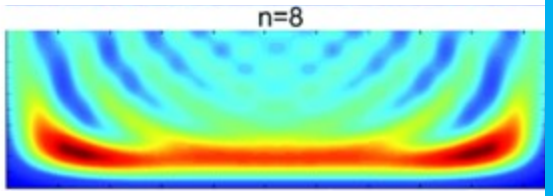
ε : on-site energy,
t : nearest-neighbor hopping integral
$t \propto \cos(\theta)$

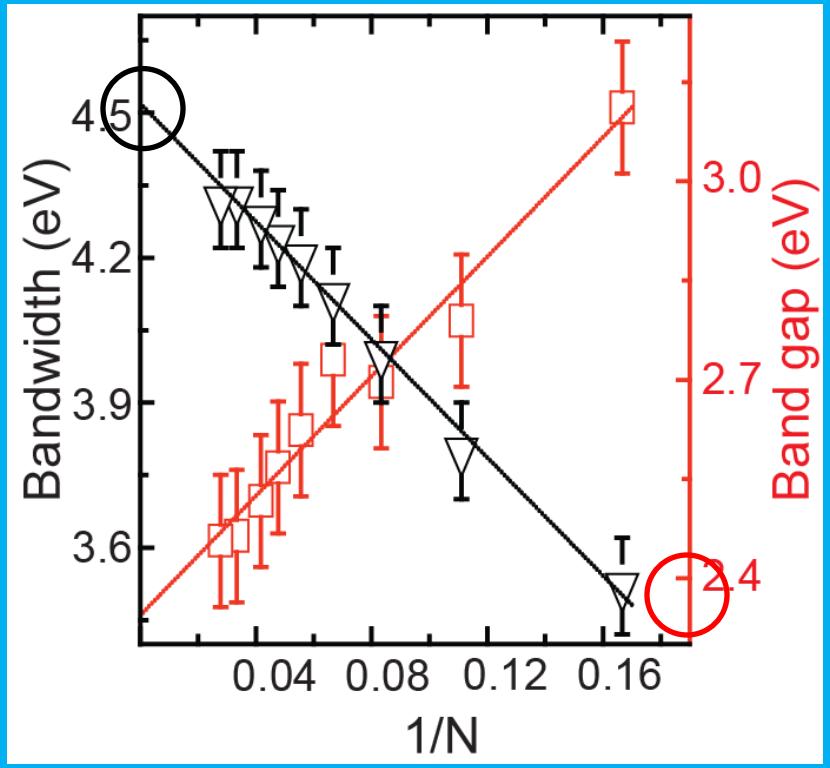
TB simulated LDOS plots

Tight binding



Tight binding





PPP oligomers can be satisfactorily
model

For infinitely long PPP,

Bandwidth: 4.5 ± 0.2 eV

Bandgap: 2.3 ± 0.2 eV

Phys. Rev. Lett. 106, 206803 (2011)

Outline

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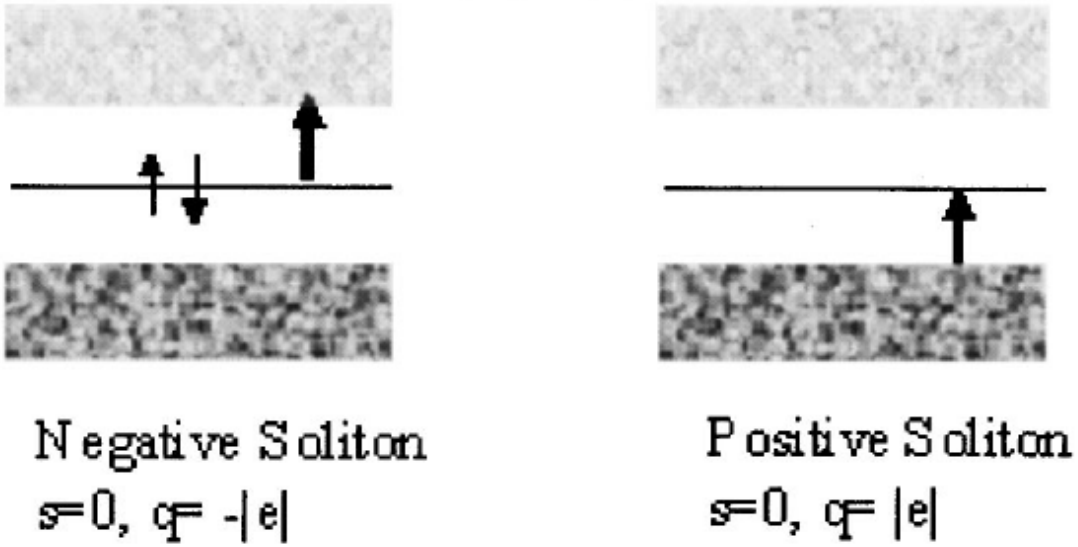
Doping of PPP

- Through doping, the conductance of conjugated polymers can be comparable with metal!
- No direct experimental verification of dopant state at single polymer level!

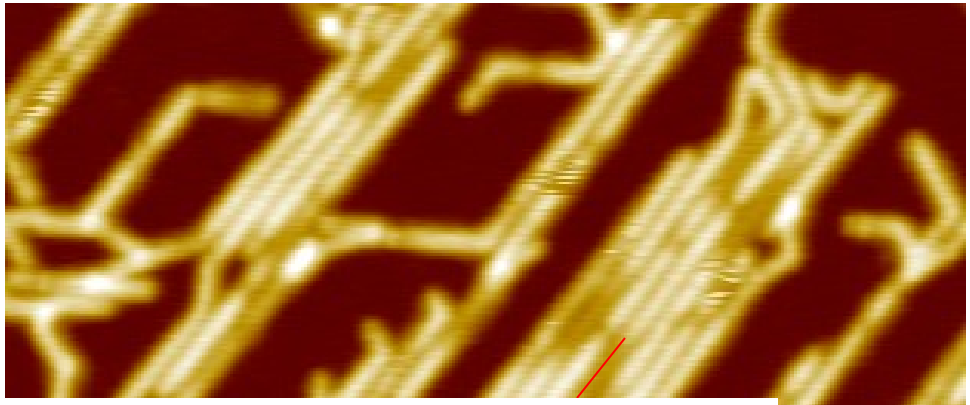


Emerge of in-gap state

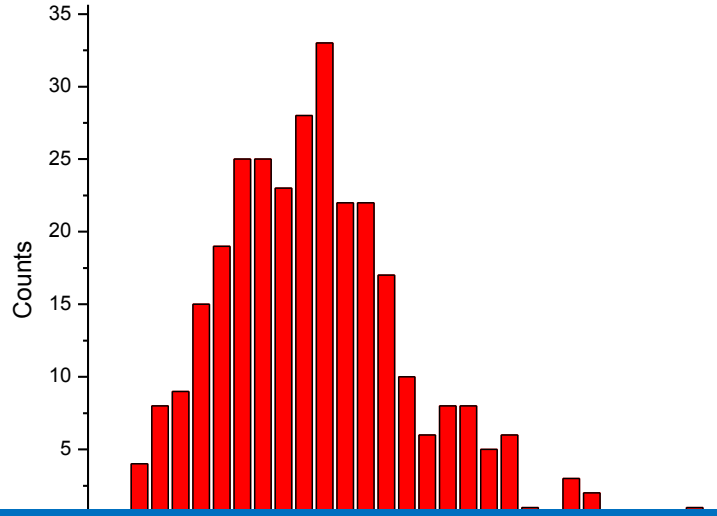
Heeger, A. J., Rev. Mod. Phys. **2001,** 73, 681-700

Chemically doping

40nm by 40nm

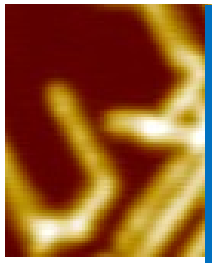


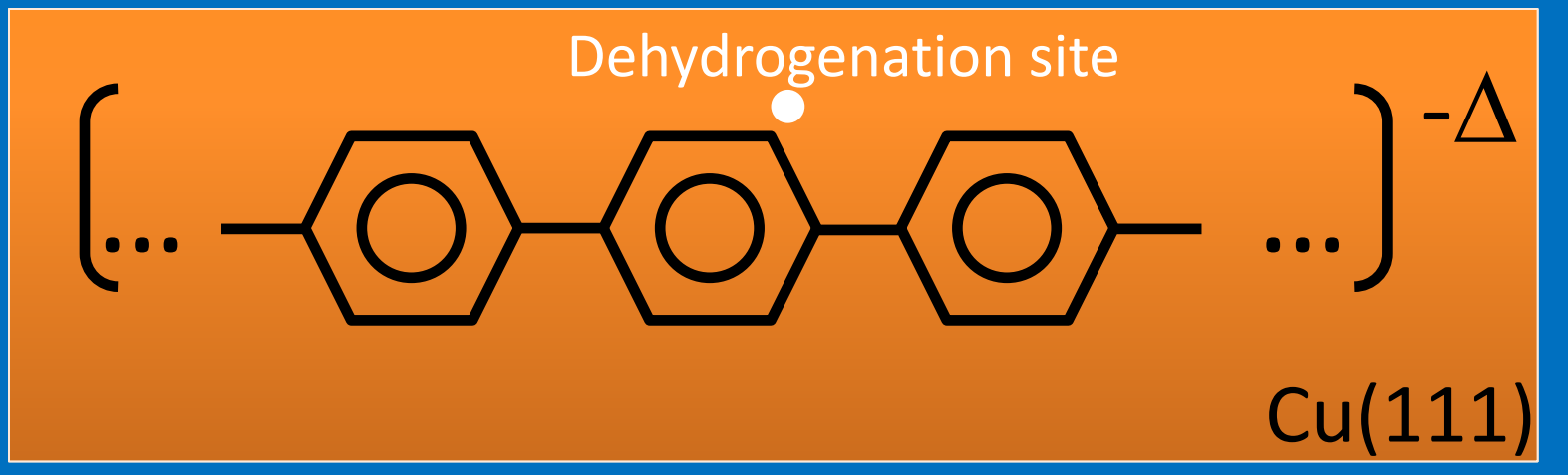
Length distribution of depression section



Two-step doping:

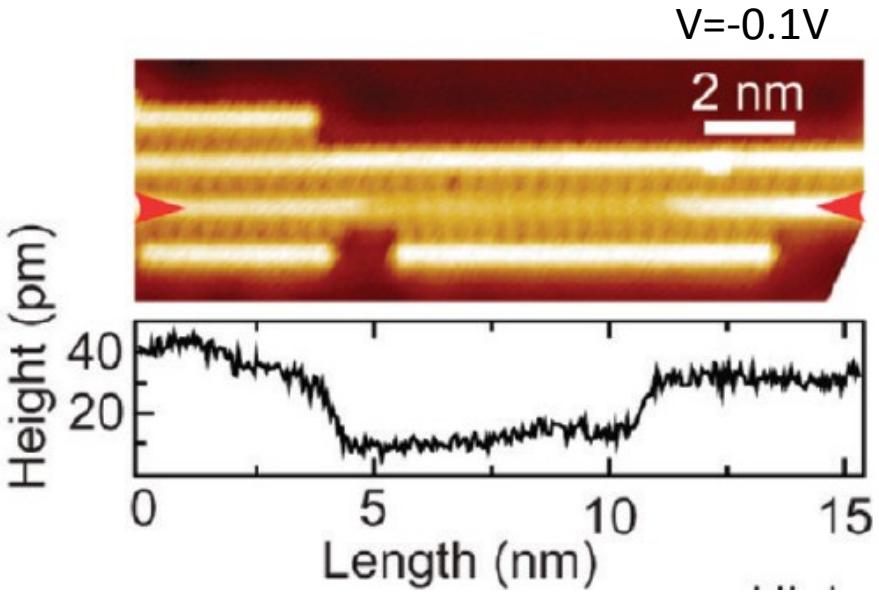
1. Dehydrogenation
2. Negatively charging





Structural deformation of PPP backbone

Lower apparent height

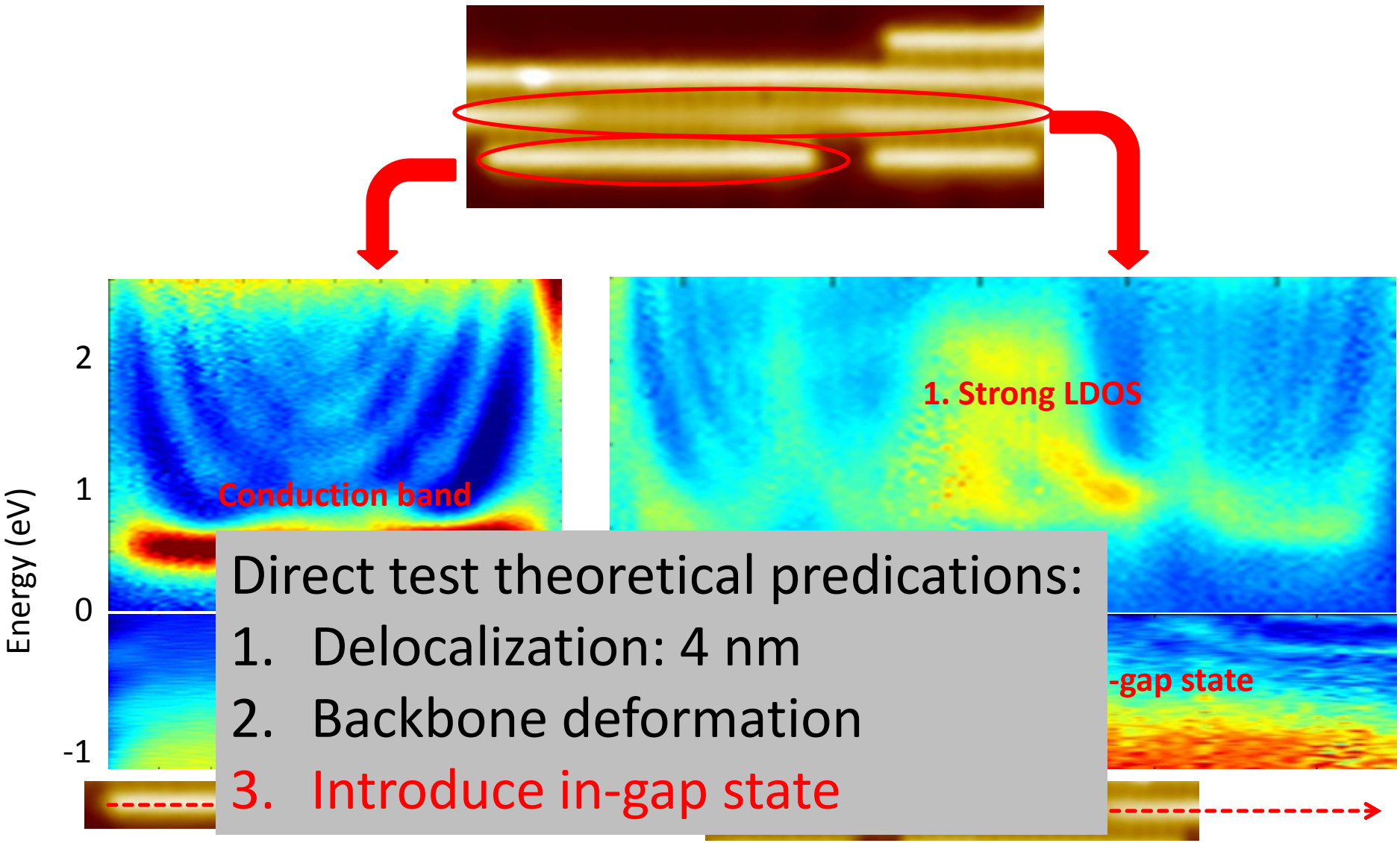


Direct test theoretical predications:

1. Delocalization: ~4 nm (10 phenyl units)
2. Backbone deformation

ACS Nano. 6, 3401 (2012)

Introduce of in-gap states

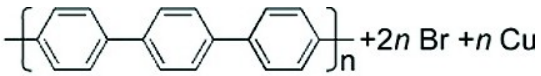


Direct test theoretical predications:

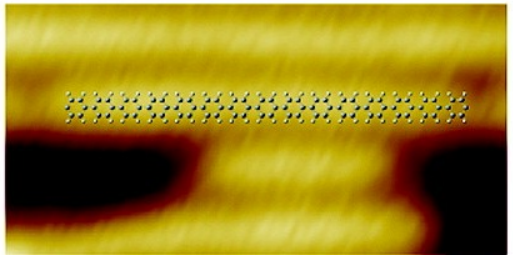
1. Delocalization: 4 nm
2. Backbone deformation
3. Introduce in-gap state

ACS Nano, 6, 3401 (2012)

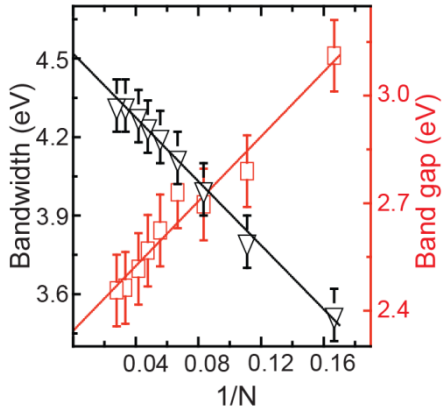
Summary



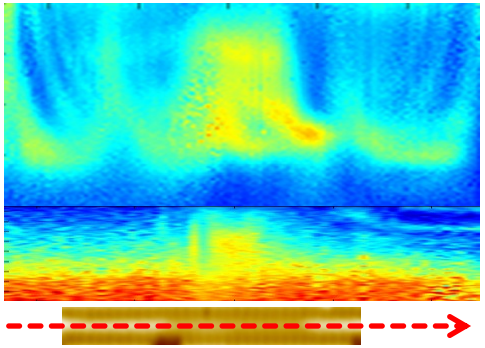
- On-surface Ullmann reaction



- Intrinsic electronic structure for single polymers



- Test theoretical predications of dopant states at sub-nanometer resolution



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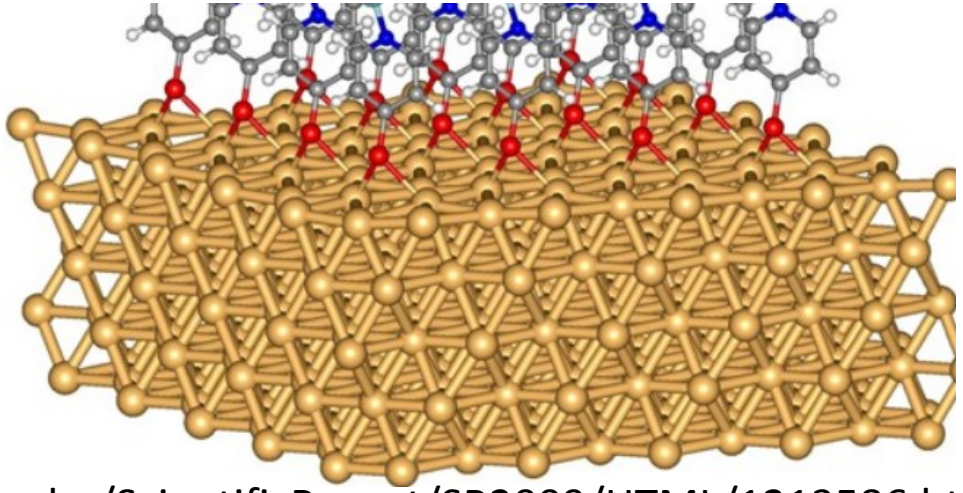
Motivation

- Molecule-metal hybridized systems

1. High carrier mobility
2. Bottom-up fabrication
3. Design new functions

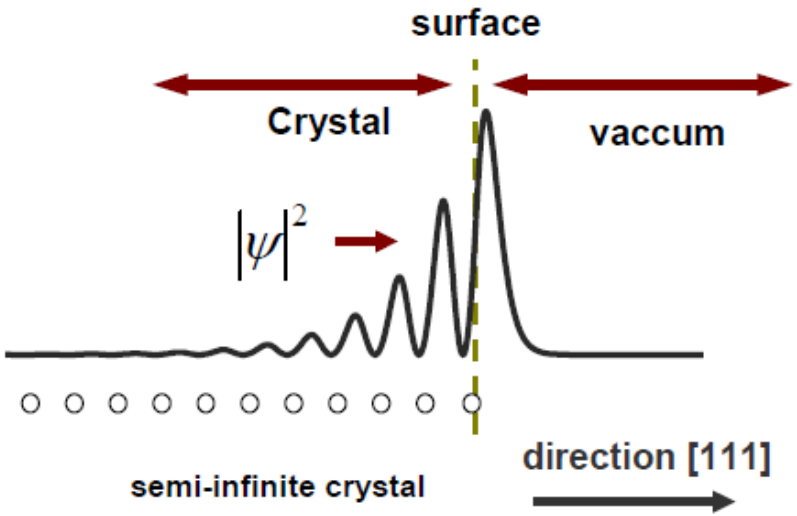


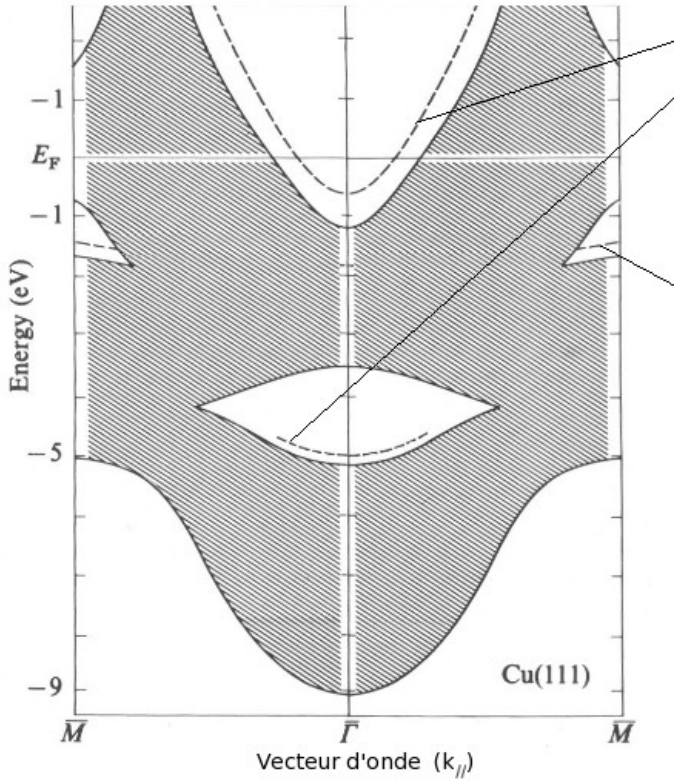
http://www.imec.be/ScientificReport/SR2009/HTML/1213586.html

Shockley surface-state

1. only at the atom layers closest to the surface (Au(111), Cu(111), Ag(111)).
2. Parabolic dispersion (2D free electron gas):

$$E = \frac{\hbar^2 k^2}{2m^*}$$

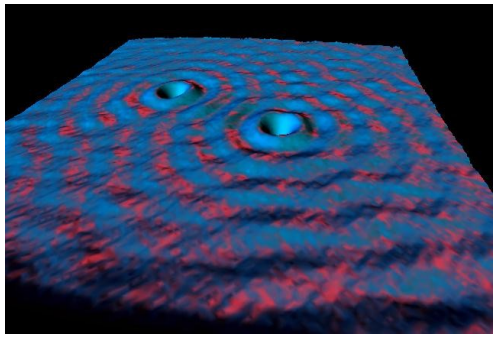




Band structure parallel to surface

Shockley surface-state

1. only at the atom layers closest to the surface (Au(111), Cu(111), Ag(111)).
2. Parabolic dispersion (2D energy gas):
3. STS can visualize the standing waves due to scattering and interference of SS electrons

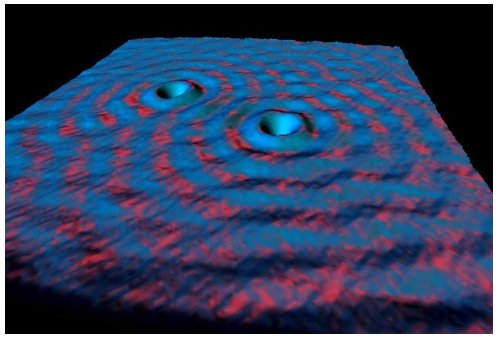


Standing waves in dI/dV mapping

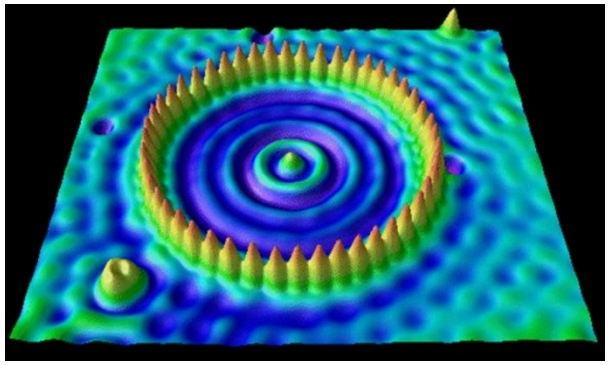
Nature 363, 524-527 (1993).

Shockley surface-state

1. only at the atom layers closest to the surface (Au(111), Cu(111), Ag(111)).
2. Parabolic dispersion (2D energy gas):
3. STS can visualize the standing waves due to scattering and interference of SS electrons
4. Adatoms, molecules can scatter SS electrons



Standing waves in STS mapping



Confined states by quantum corral

Nature 363, 524-527 (1993).

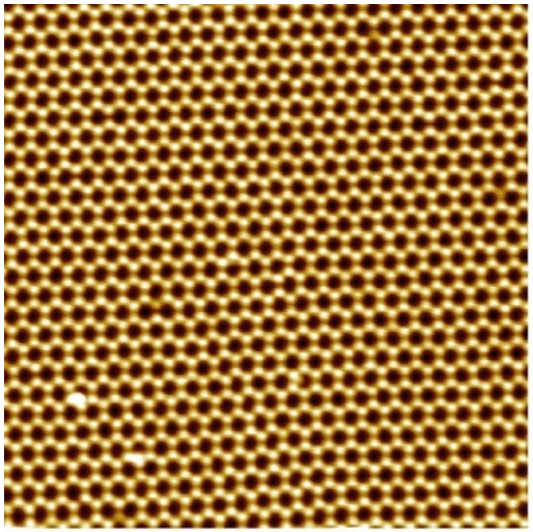
Our Purpose

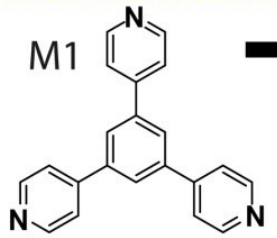
1. Modulate of SS

- Using supramolecule self-assembly to create periodic networks
- Investigate their modulation of SS electrons

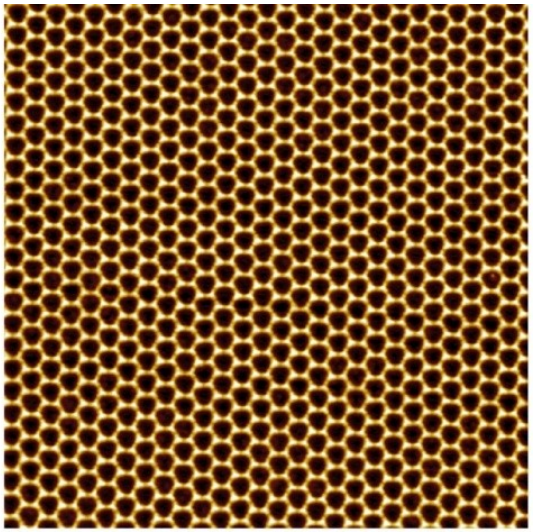
Fabrication of three isostructural molecular self-assemblies

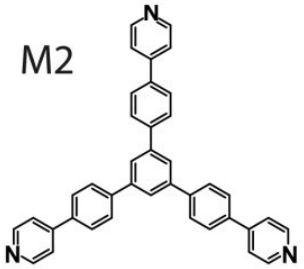
- Supramolecular self-assembly strategy



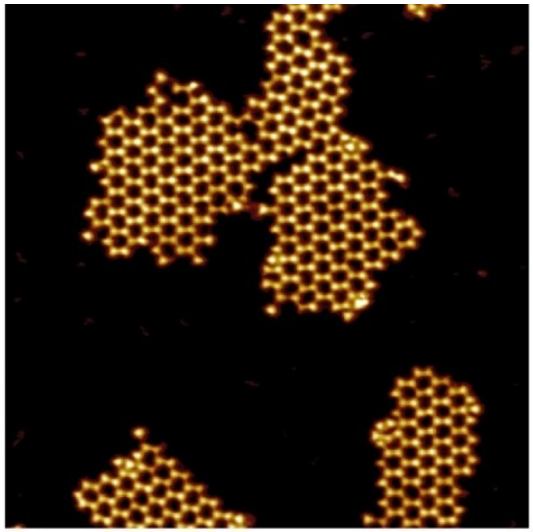


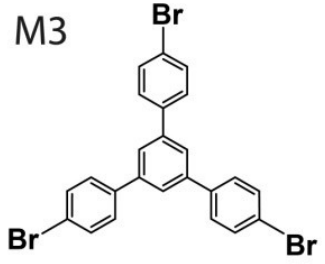
Coordination bond





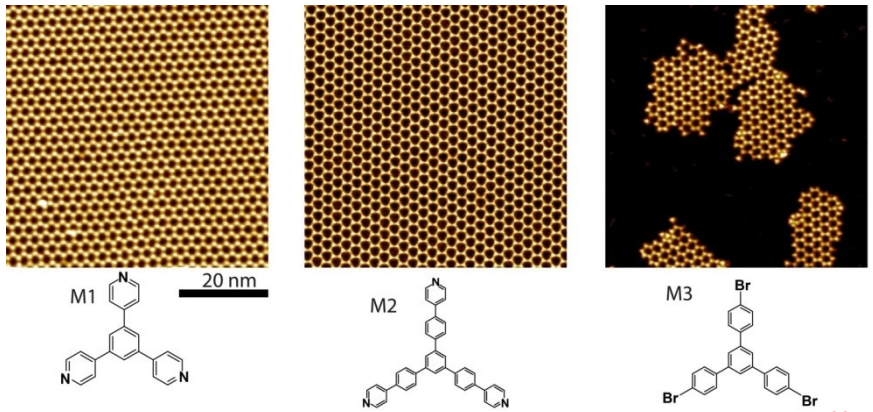
Coordination bond





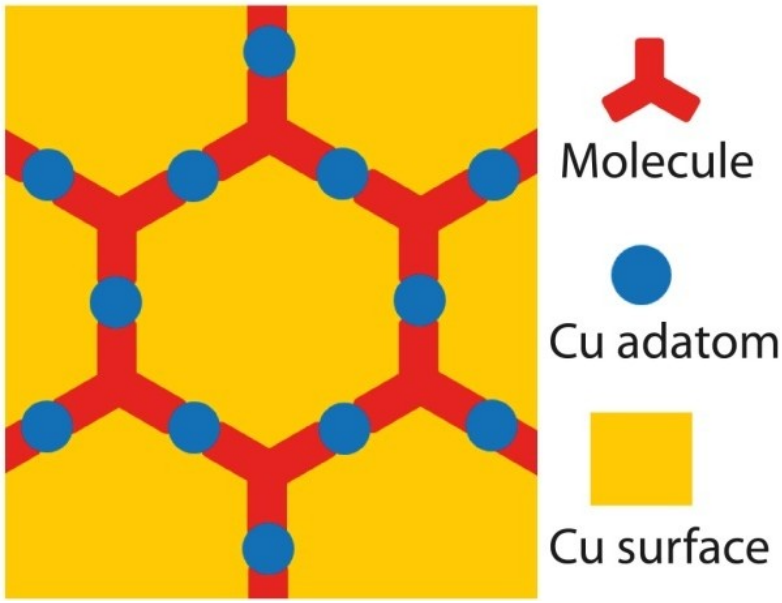
Organometallic bond

S1 S2 S3



Coordination bond
N-Cu-N

Organometallic bond
C-Cu-C



Periodicity: S1=S3 < S2

Bonding strength: S1=S2 < S3

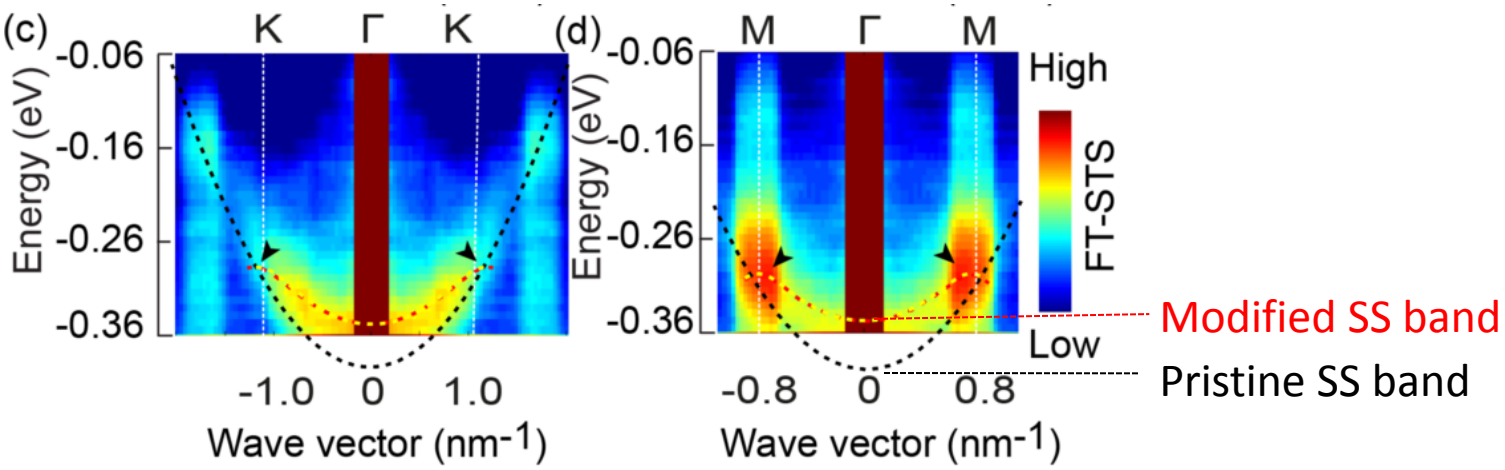
How these three isostructural networks modulate SS ?

Band structure detection

- Fourier-transfromed STS technique

1. Measure STS mapping at different biases
2. Fourier-transform STS mappings into reciprocal space
3. Construct energy dispersions

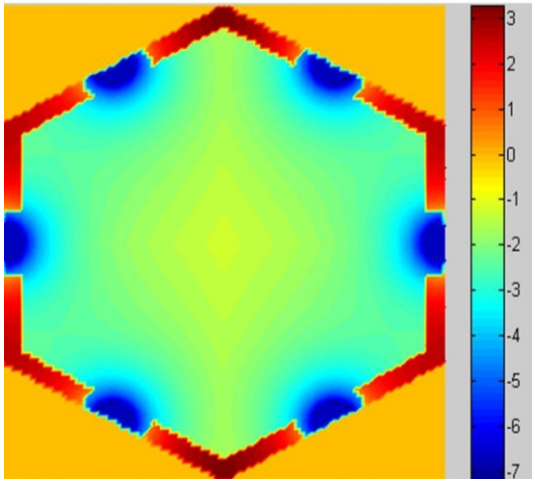
S2



Compare with pristine SS, the band bottom shift 40 mV up!

Plane wave expansion

Solving the Schrödinger equation of free electrons modulated by a periodic potential:

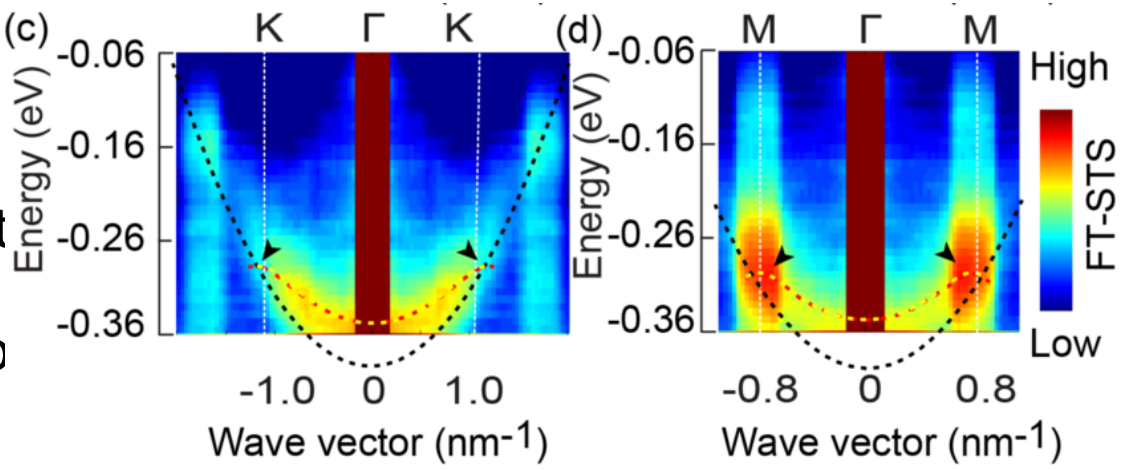


Coordination bond:

Molecule negatively charged
Cu atoms positively charged

Potentials:

1. Set molecules as repul
   Vm=300 mV;
2. Set copper atoms as at
   Vcu=-100 mV;
3. Set Cu surface as zero



S1 vs. S2

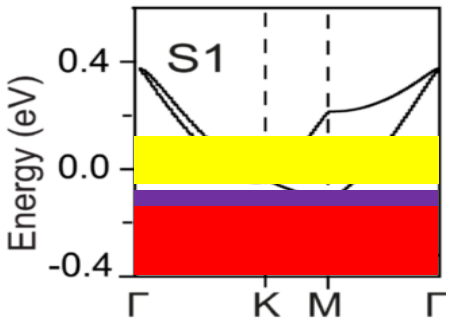
- Density of s

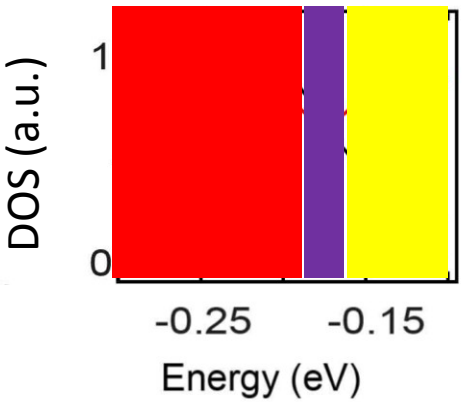
S1 with lattice

S2 with lattice

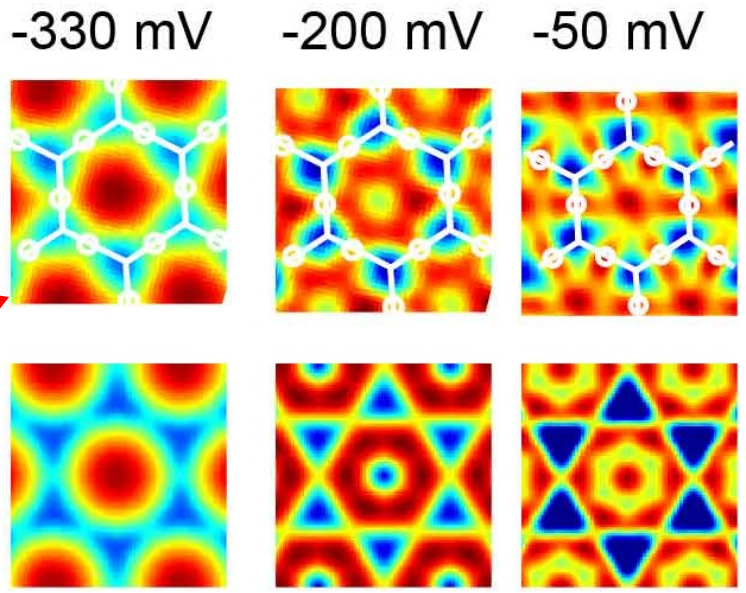
Same stabilized

	S1	S2
Band bottom upshift	74 mV	52 mV
Band gap opening	29 mV	47 mV
Band width	190 mV	56 mV





DOS distribution in a unit cell



S1 vs. S3

- Density of state:

Lattice constant: S1=S3

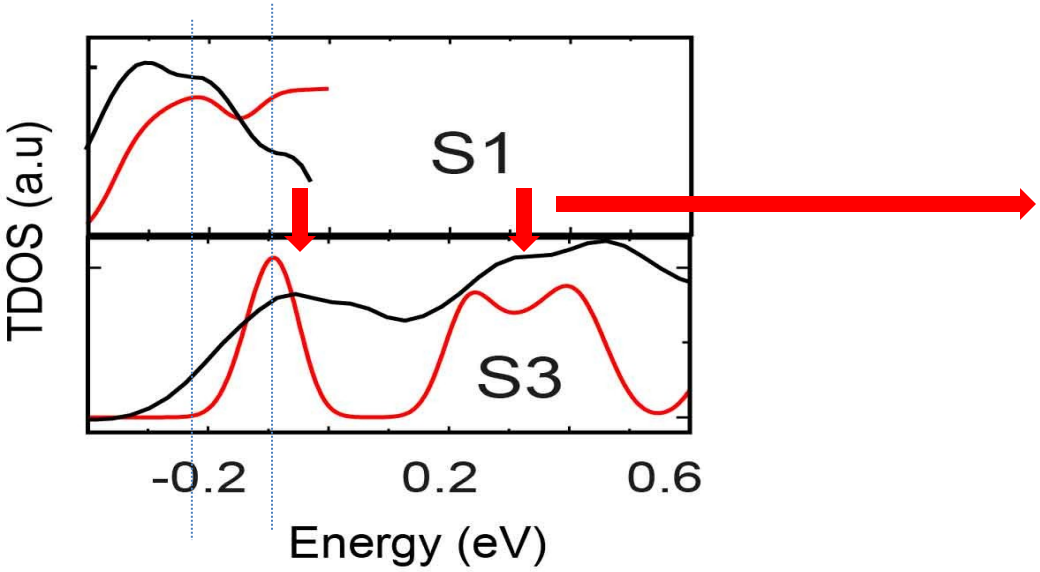
S1: coordination bond.

Vm=300 mV; Vcu=-100 mV;

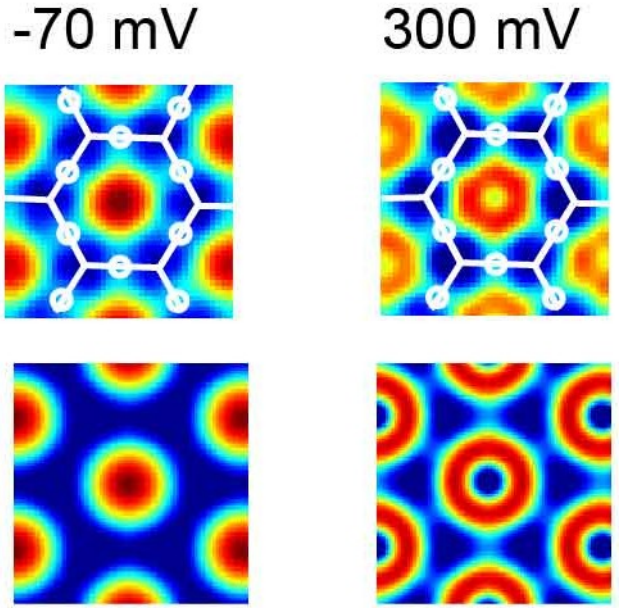
S3: organmetallic bond.

Vm=Vcu= 800 mV

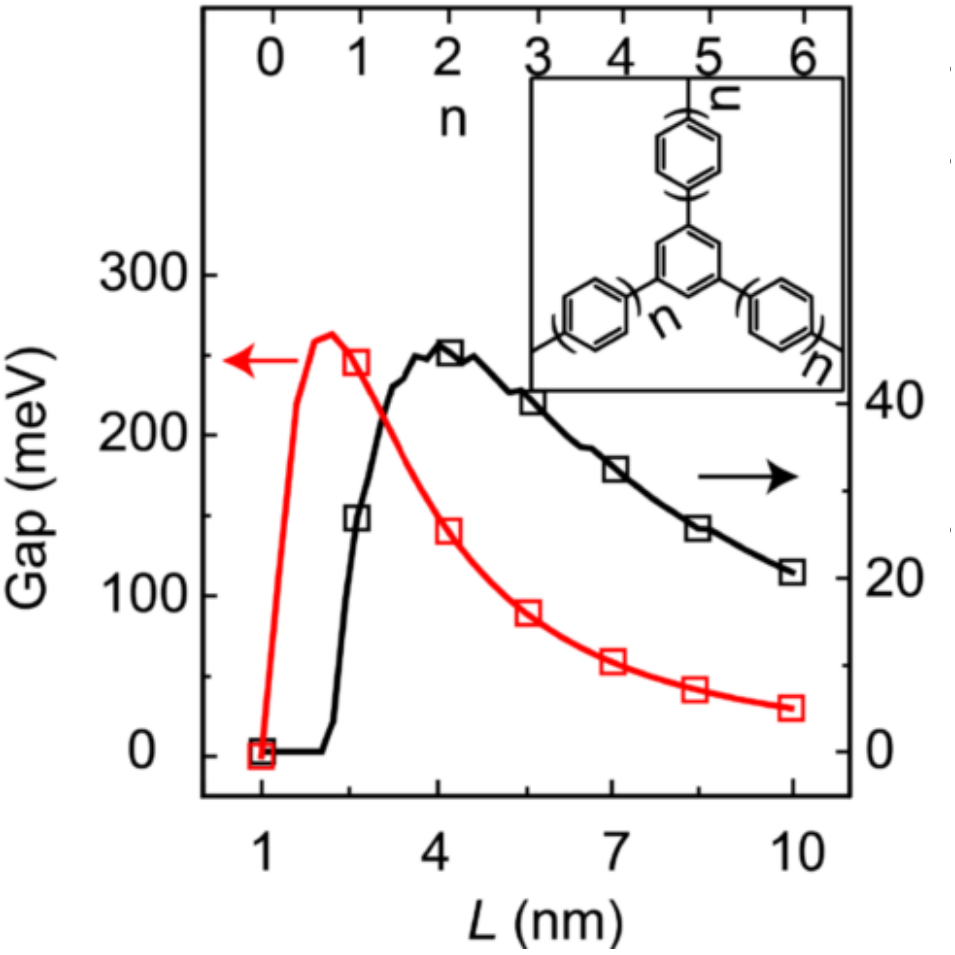
	S1	S3
Band bottom upshift	74 mV	253 mV
Band gap opening	29 mV	247 mV
Band width	190 mV	103 mV



DOS distribution in a unit cell



General trend



Organometallic bond

Coordination bond

Change lattice constant

Change repulsive potential

Result in Tunable band structures

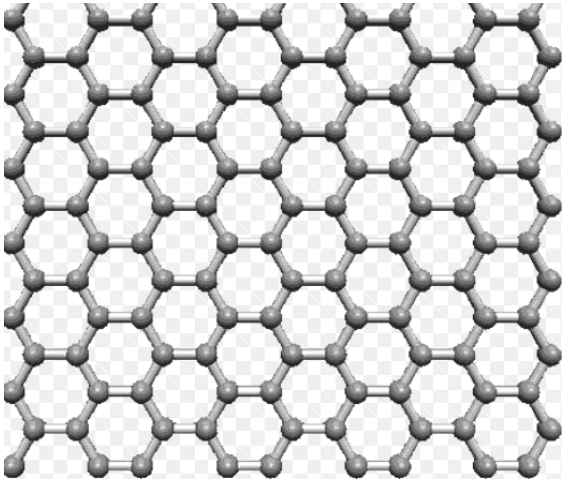
1. Band bottom
2. Band width
3. Band gap

Outline

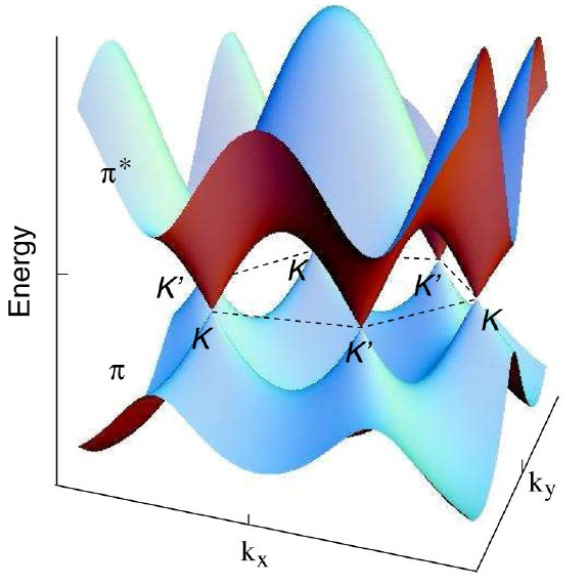
- Single molecular characterization:
  - Superexchange coupling
  - Molecular capacitance and conductance
  - Metal-atom contacts
- Conjugated poly-p-phenylene polymers
  - On-surface Ullmann reactions
  - Intrinsic electronic structures
  - Dopant states
- 2D molecular nanostructures
  - Modulation of Shockley surface-state by supramolecular self-assemblies
  - Fabrication and characterization of molecular graphene

Design molecular graphene

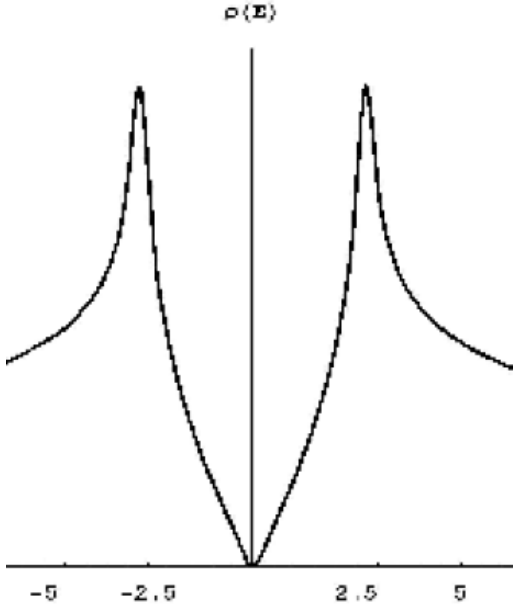
- Molecular graphene: A system shows similar electronic structures as real graphene



Atomic structure



Band structure



Density of state

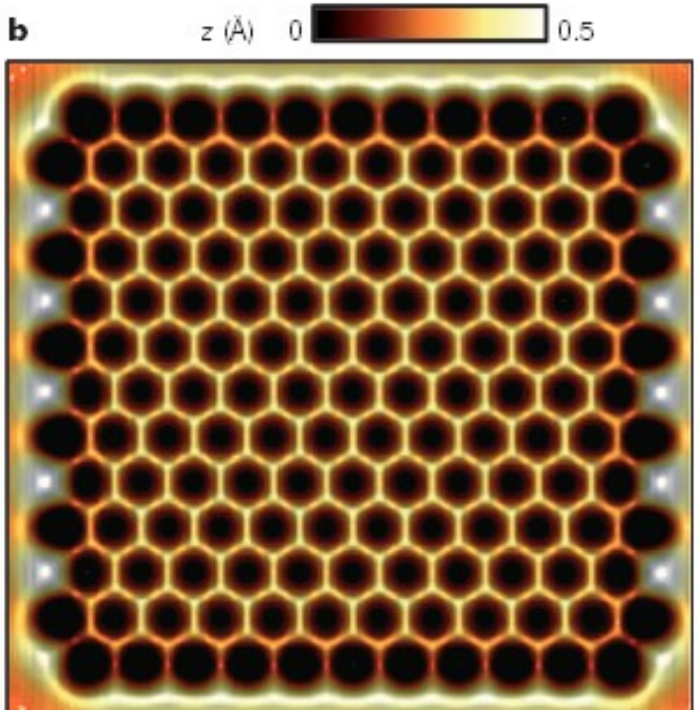
Design molecular graphene

- Molecular graphene: A system shows similar electronic structures as real graphene

- De

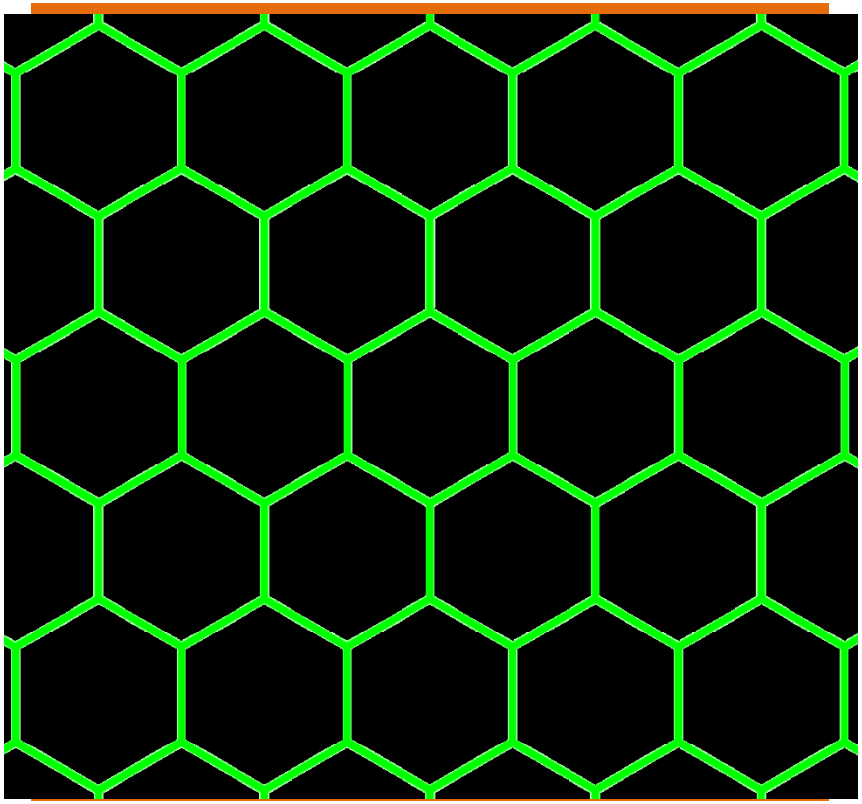
1. D
2. T
3. S
   l

s



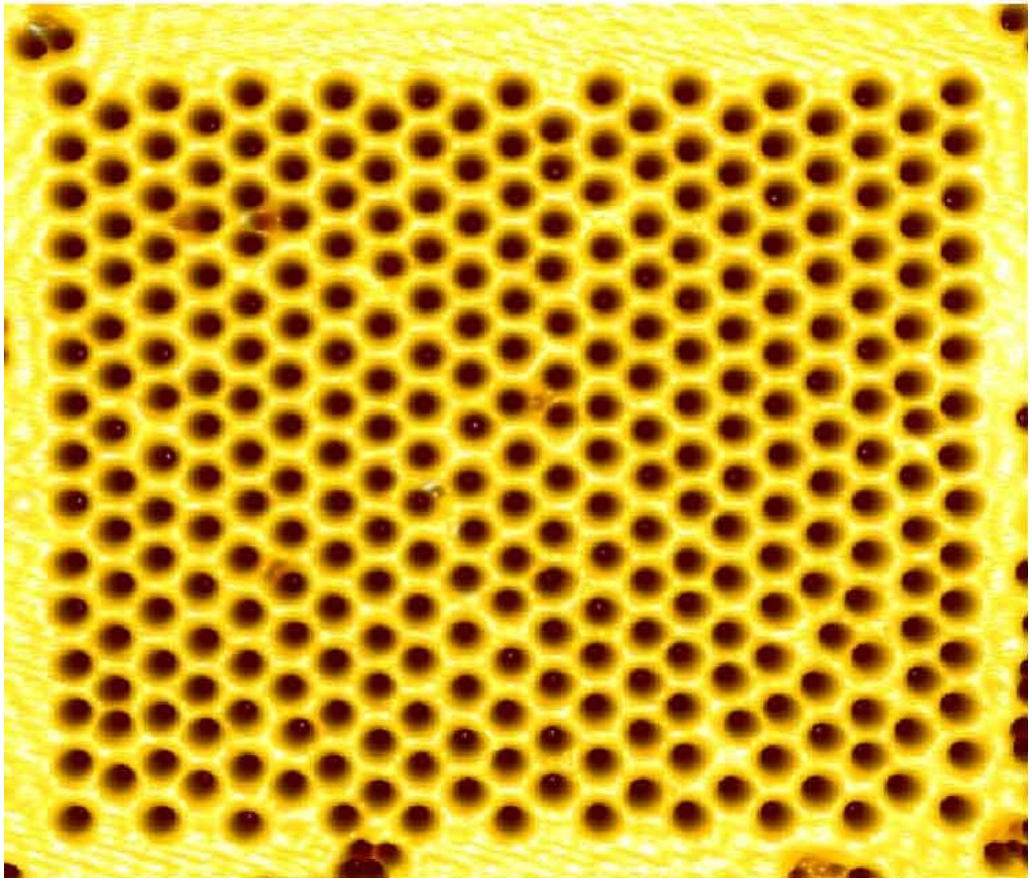
CO on Cu(111)

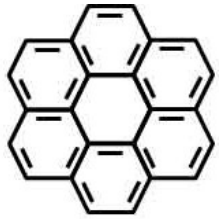
C. Park and S. G. Louise, **Nano Letter**, **7**, 1973 (2009)
K. Gomes et al., **Nature**, **483**, 306 (2012)



Cu(111): SS electrons

STM manipulation

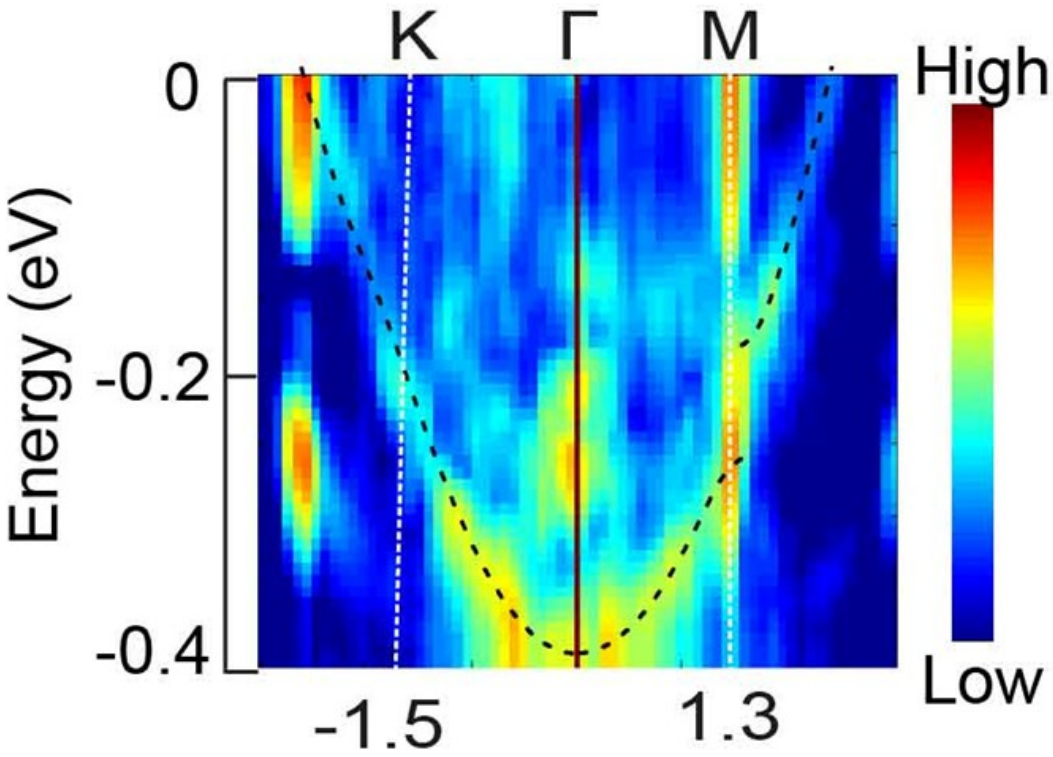


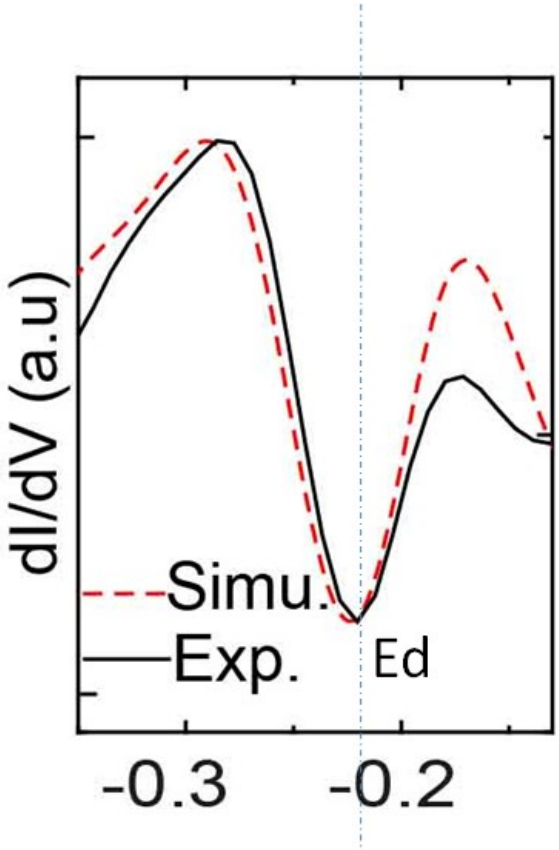


Coronene

1. A small patch of artificial nanostructure composes of ~300 molecules
2. Molecules are triangular patterned

Electronic structure characterization





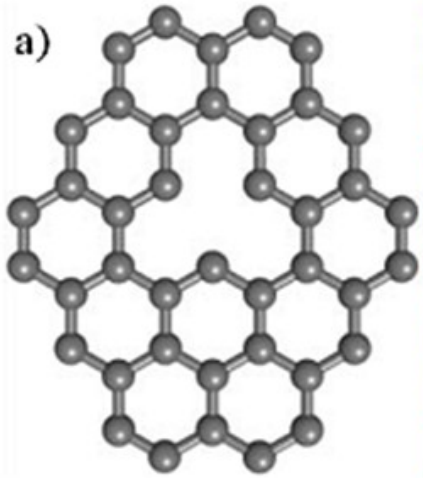
No energy gap at K point
100 mV gap at M point

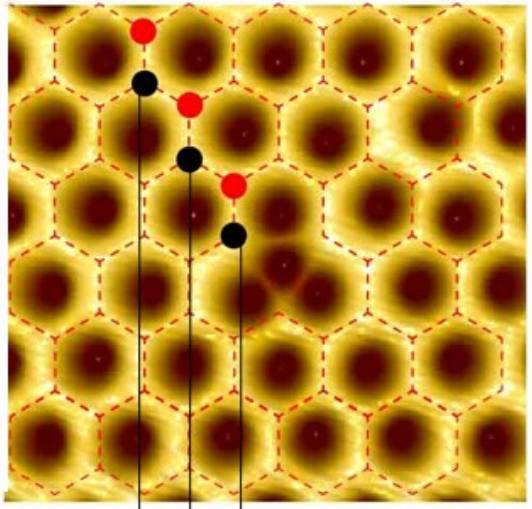
Similar DOS as real graphene

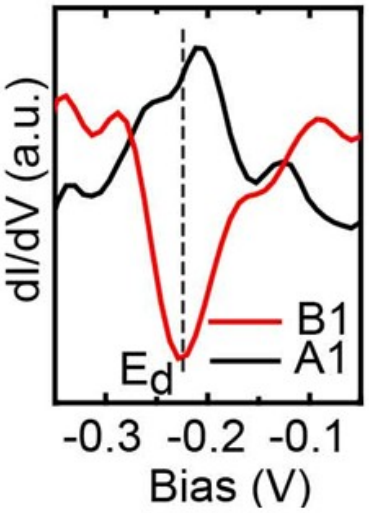
Dirac Fermions are generated !

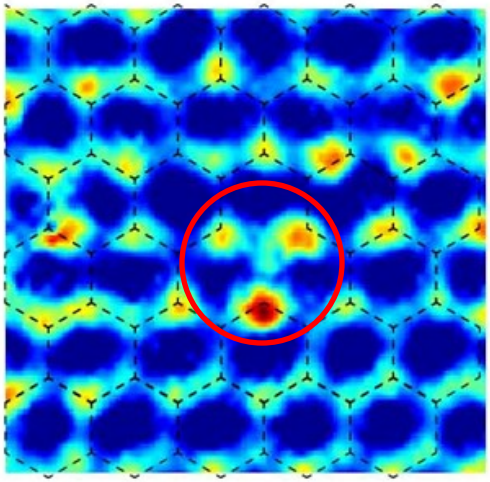
Point defects

- Vacancy: one carbon atom miss
- Molecular graphene: add one more molecule



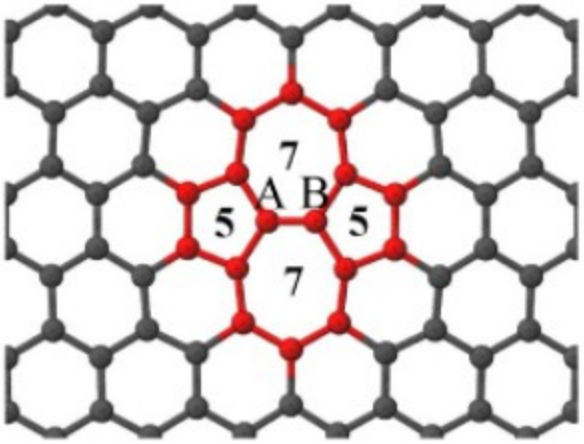






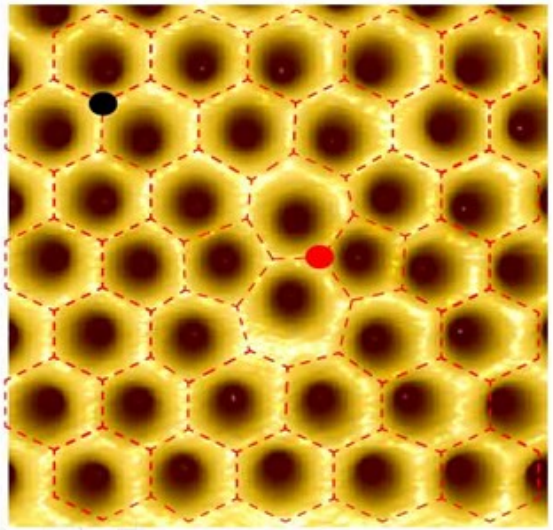
Introduce localized states

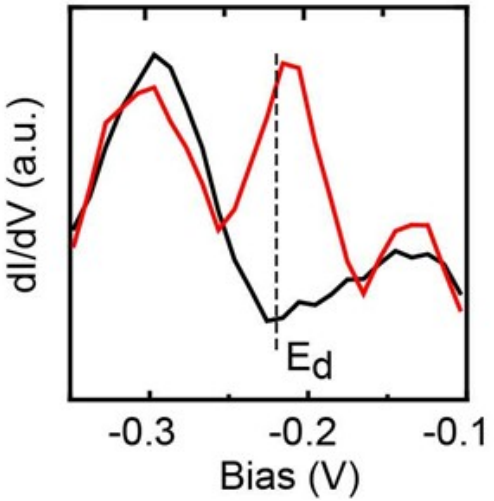
Stone-Wales defect

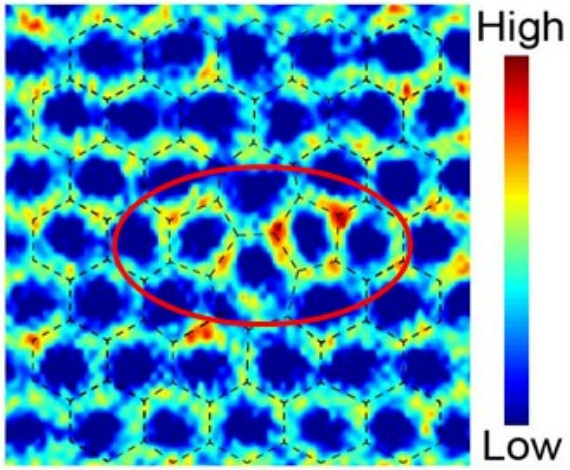


- Stone-Wales defect

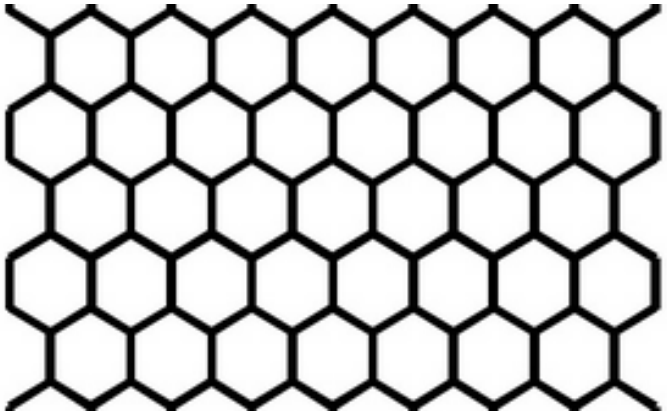
1. Two heptagons and pentagons
2. Localized states

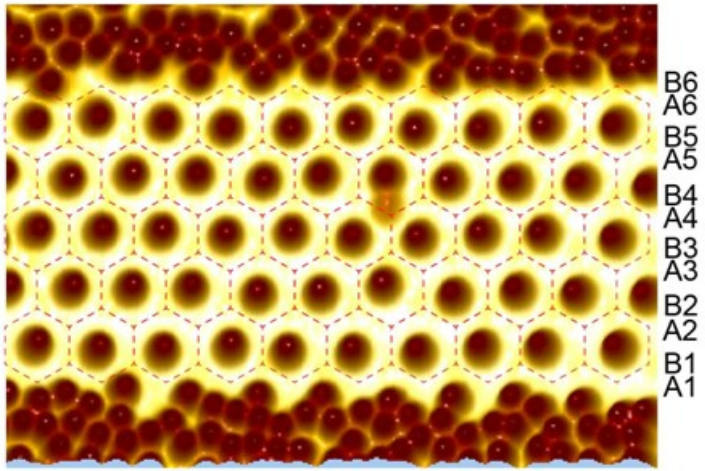


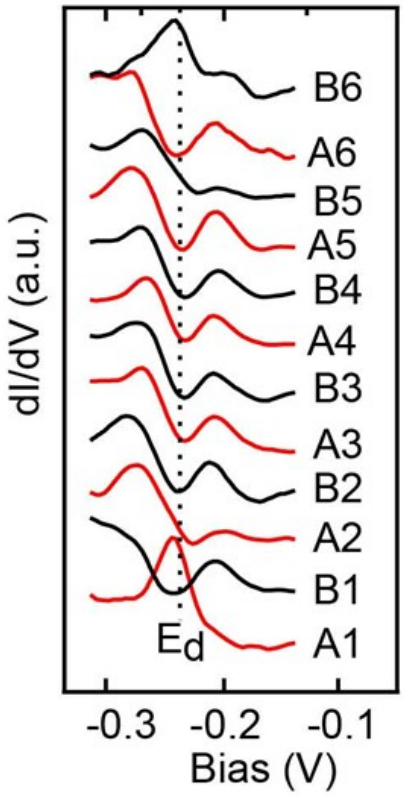


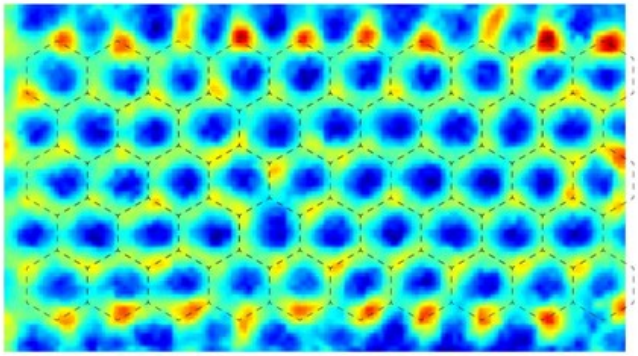


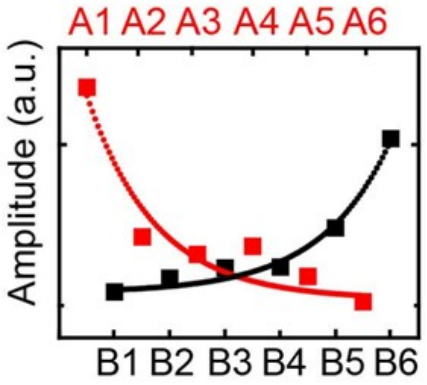
Graphene nanoribbons: zigzag edge





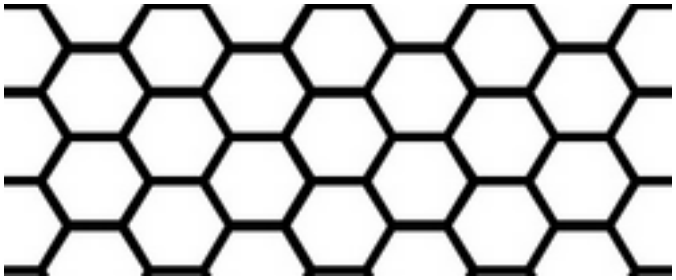


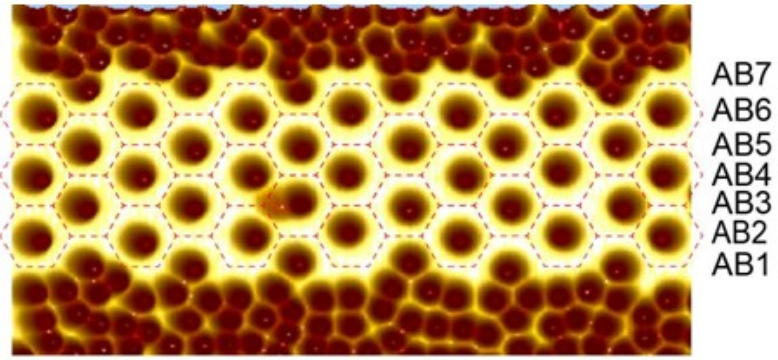


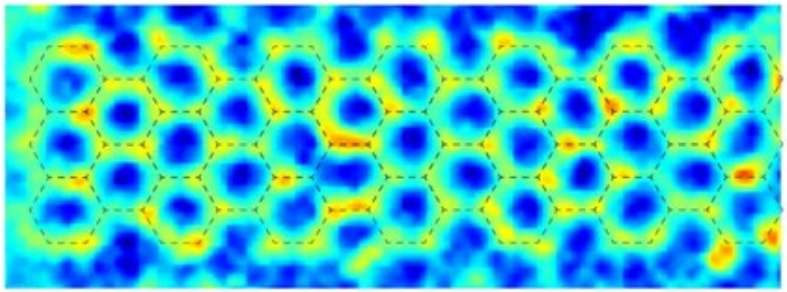


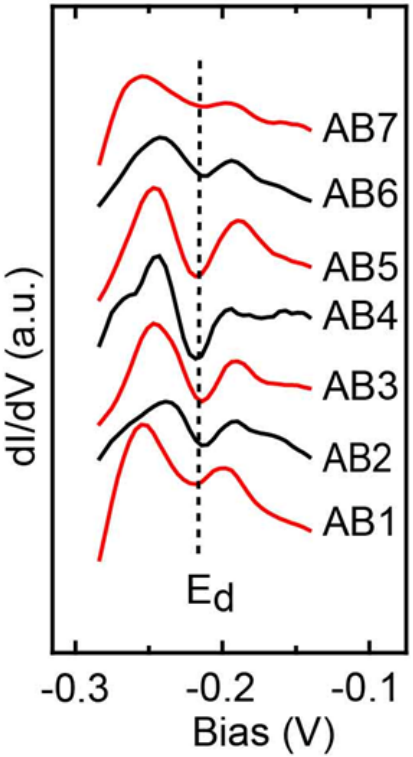
1D edge state!

Graphene nanoribbons: armchair edge









Advantages

1. Atomic resolution
2. Test theoretical predications
3. Predict new properties

Armchair GNR without edge state

Conclusions

- Characterized the charge transport properties of single molecules: superexchange coupling, molecular capacitance and conductance, metal atom contacts

- Studied single conjugated polymers: intrinsic and doped electronic structures

- Fabricated and characterized hybridized systems: modulate of SS; design molecular graphene nanostructures

Publications

[14] **S. Wang**, Y. Zhao, T. Lin, W. Wang, M. Van Hove, N. Lin, Competitive interactions of bromine atoms on Cu(111): a realization of 2D porous liquid phase, ***in preparation*** (2013).

[13] **S. Wang**, L. Tan, W. Wang, T. Lin, S. G. Louise, N. Lin, A combined theoretical and experimental study on the electronic structure of 2D amorphous artificial graphene, ***in preparation*** (2013).

[12] **S. Wang**, W. Wang, N. Lin, Creation, manipulation and characterization of massless Dirac fermions in two-dimensional electron gas, ***in preparation*** (2013).

[11] **S. Wang**, W. Wang, N. Lin, Visualization of the second order Jahn-teller effects in super phenyl ring, ***in preparation*** (2013).

[10] **S. Wang**, W. Wang, L. Tan, X. Li, P. Liu, S. G. Louise, N. Lin, Modulation of Cu(111) surface-state electrons by self-assembled supramolecular structures, **submitted** (2013).

[9] W. Wang, X. Shi, **S. Wang**, J. Liu, M. A. Van Hove, P. N. Liu, R.-Q Zhang, N. Lin, Cooperative modulation of electronic structures of aromatic molecules coupled to multiple metal contacts, **Phys. Rev. Lett.** 110, 046802, (2012)

[8] **S. Wang**, W. Wang, N. Lin, Emerging of localized in-gap states in conjugated polymers of branched topology, ***Phys. Rev. B.*** 86, 045428 (2012).

[7] **S. Wang**, W. Wang, N. Lin, Visualization and Manipulation of Individual Dopant States in Single Conjugated Oligomers, ***ACS Nano.*** 6, 3401 (2012)

[6] W. Wang, **S. Wang**, Y. Hong, B. Z. Tang, N. Lin, Selective supramolecular assembly of multifunctional ligands on a Cu(111) surface: metallacycles, propeller trimers and linear chains, ***Chem. Commun.*** 47, 10073 (2011)

[5] W. Wang, X. Shi, **S. Wang**, M. Van Hove, N. Lin, Single-molecule resolution of an organometallic intermediate in a surface-supported Ullmann coupling reaction, ***J. Am. Chem. Soc***. 133, 13264 (2011)

[4] X.Q Shi, W.H. Wang, **S.Y. Wang**, N. Lin, M.A. Van Hove, Thermally Activated Transformation of the Adsorption Configurations of a Complex Molecule on a Cu(111) Surface, ***Catalysis Today***, 177, 50 (2011)

[3] **S. Wang**, W. Wang, N. Lin, Resolving band structure evolution and defect-induced states of single conjugated oligomers by scanning tunneling microscopy and tight-binding calculations, ***Phys. Rev. Lett***. 106, 206803 (2011)

[2] **S. Wang**, W. Wang, Y. Hong, B. Z. Tang, N. Lin, Vibronic state assisted resonant transport in molecules strongly anchored at an electrode, ***Phys. Rev. B*** 83, 115431 (2011).

[1] W. Wang, **S. Wang**, X. Li, J.-P. Collin, J. Liu, P. N. Liu, N. Lin, Probing Electronic Superexchange Coupling at Isolated Poly-p-phenylene Molecules, **J. Am. Chem. Soc.** 132, 8774 (2010)

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  Dong Lei

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  Kuang Guowen
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  Li Yang

  THAKUR Ram-Krishna

  Shi Ziliang

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  Department of Physics, Hong Kong Baptist University)

- Steven G. Louie' s group
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  Materials Science Division, Lawrence Berkeley National Laboratory)

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Prof. WEN Weijia

Prof. WONG Kam Sing

- Chairman

Prof. K R Jogesh MUPPALA

Thank you!