On-Surface Synthesis and Characterization of Conjugated Oligomers Using Low Temperature Scanning Tunneling Microscopy and Spectroscopy

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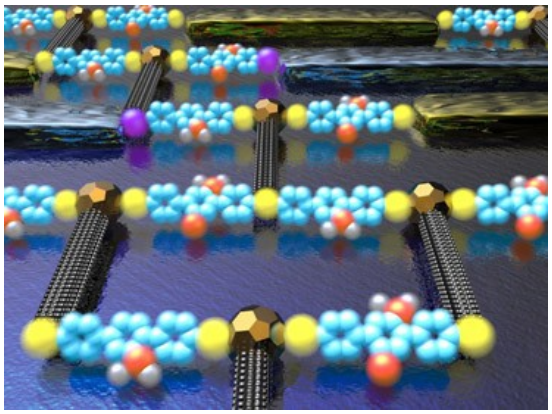
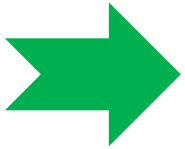
Outline

- **Synthesis of molecular wires**
  - oligomers comprising porphyrins and phenyls
- **Characterization of molecular wires**
  i. resonant charge transport
  ii. negative differential conductance
  iii. spin-spin coupling
  iv. spin crossover
- **Summary**

Introduction: molecular electronics

Molecular electronics is the study and application of ***molecular building blocks*** for the fabrication of electronic components.





Challenges:

[redacted]

Production? → Synthesize molecules with specific functionality

[redacted]

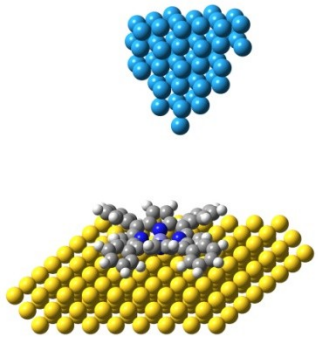
...transport property

[redacted]

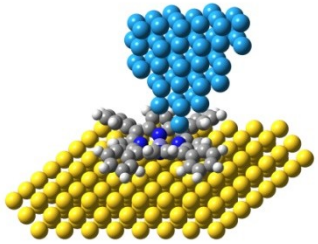
http://www.asdn.net/asdn/electronics/molecular_electronics.shtml

Introduction: STM / STS

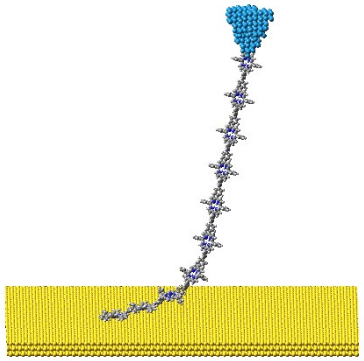
STM



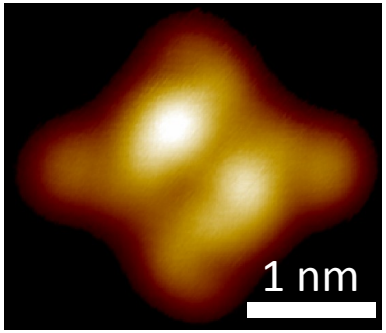
STS



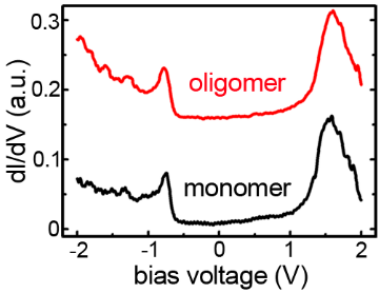
Manipulation + STS



Morphology

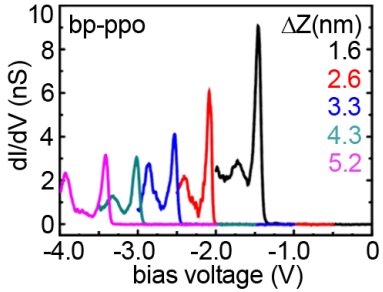


Electronic structure



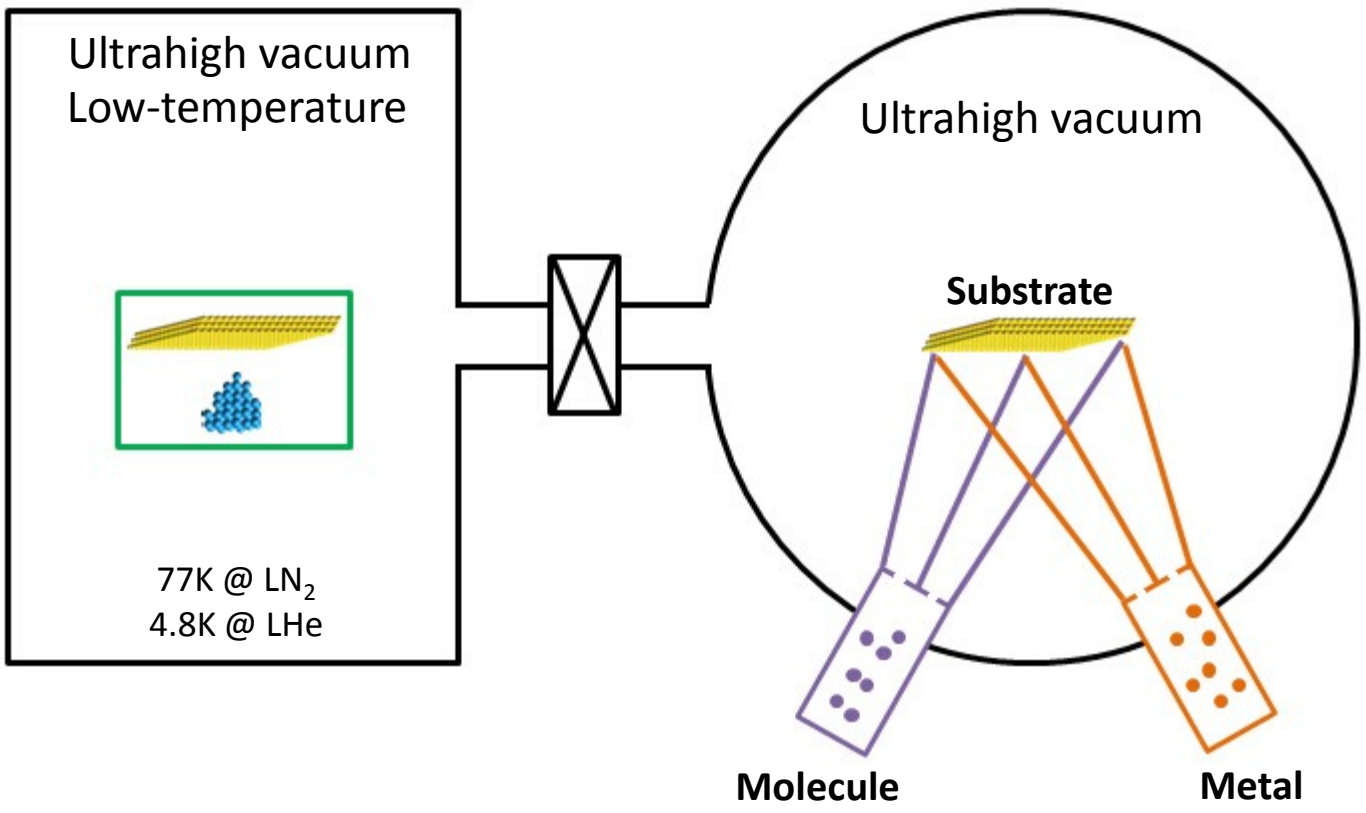
Molecular orbital

Transport property



Conductance

Experimental setup



Characterization:

✓*STM: structural details*
✓*STS: molecular orbital*

Sample preparation:

✓*Organic molecule source*
✓*Metal atom source*

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  - scanning tunneling microscopy and spectroscopy
  - experimental setup

- **Characterization of molecular wires**
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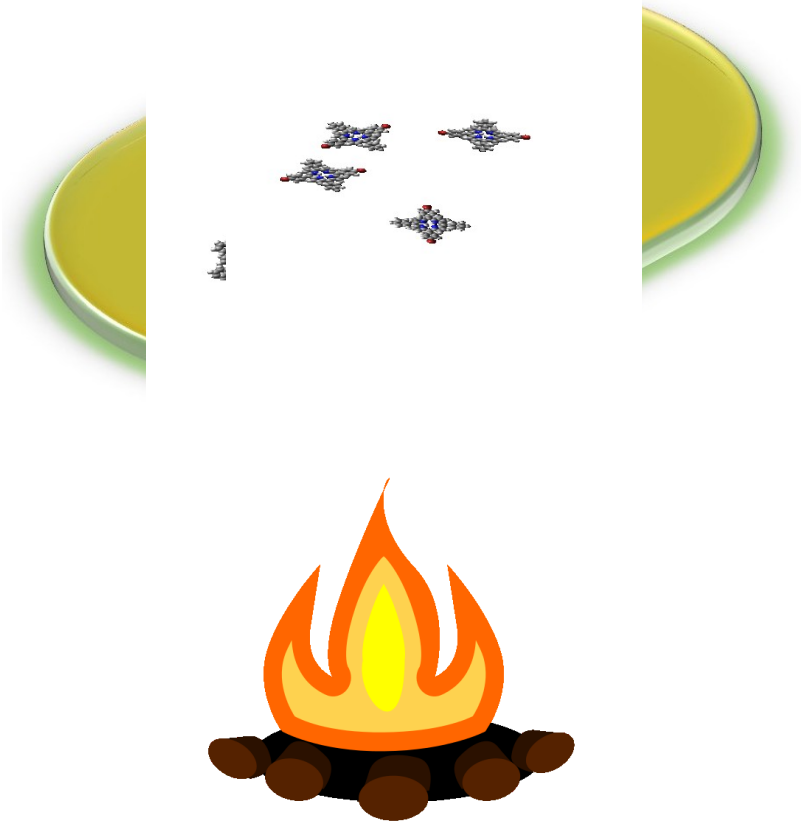
  ii. negative differential conductance
  iii. spin-spin coupling
  iv. spin crossover

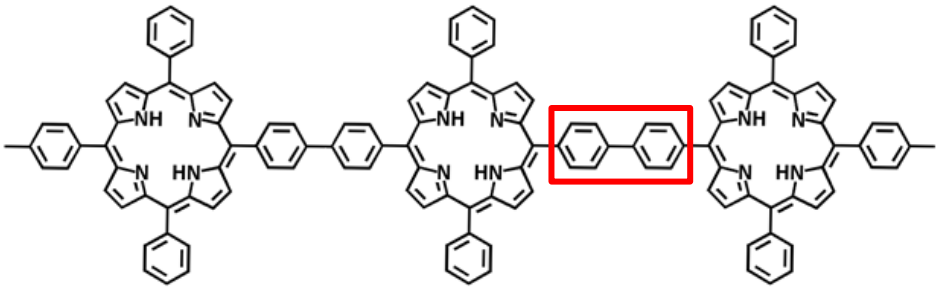
- **Summary**

Synthesis: introduction

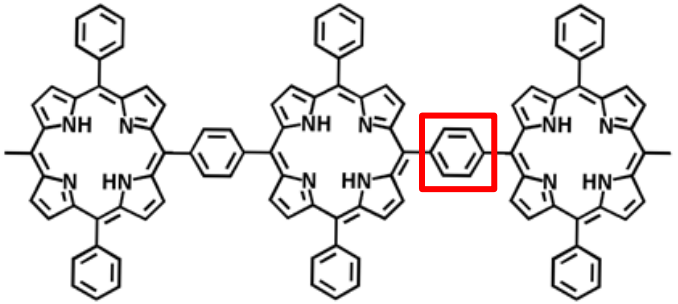
On-surface synthesis



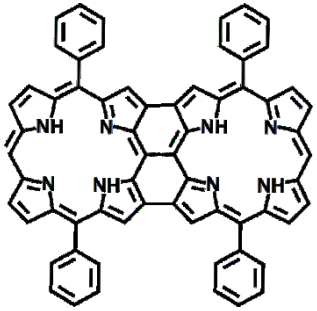
Oligomer 2



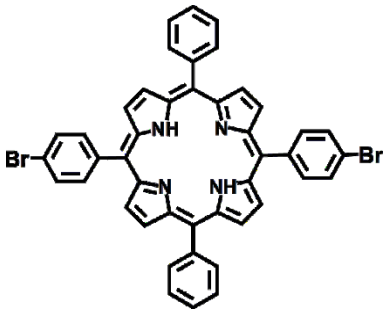
Oligomer 1

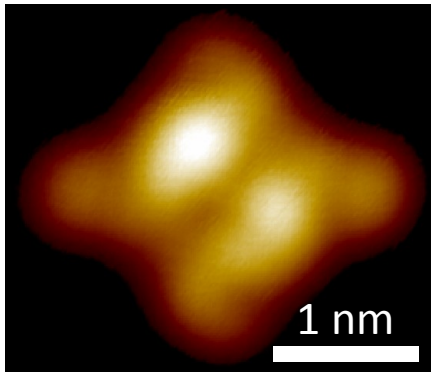


Oligomer 0

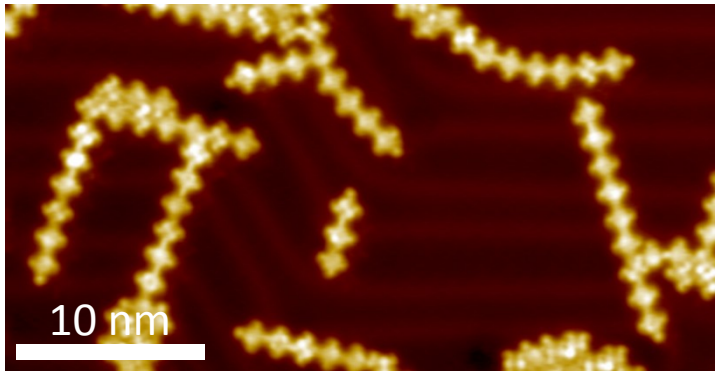


Synthesis: oligomer 2

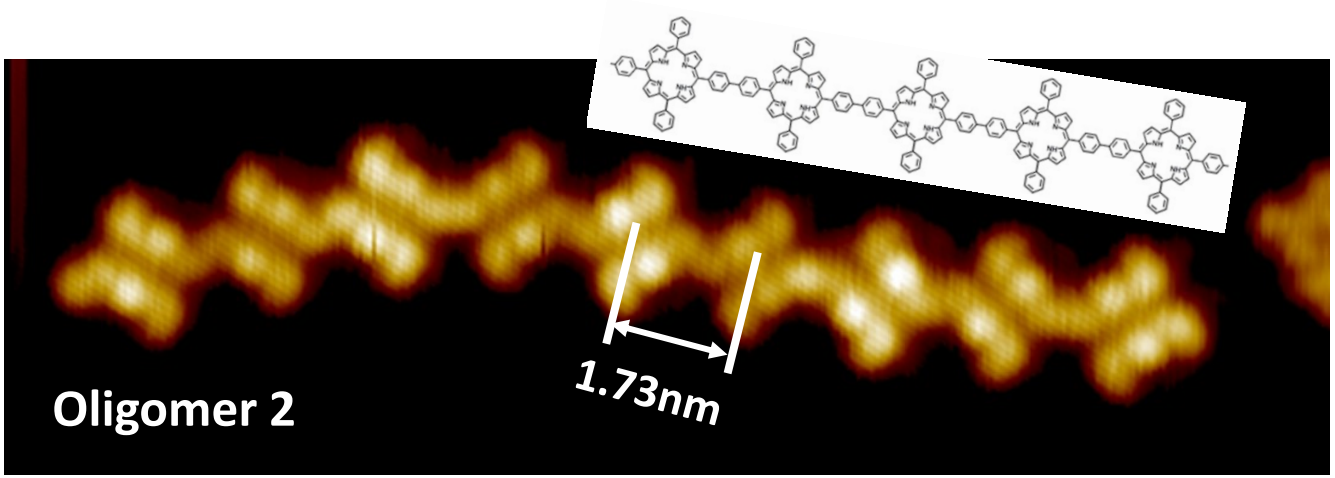




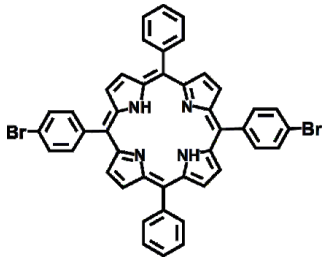
Br_2-TPP @ Au(111)

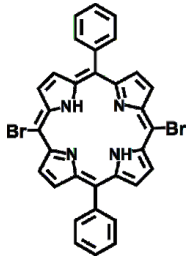


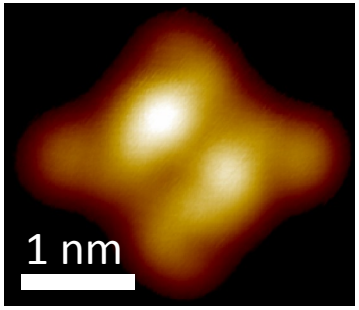
Ullmann coupling reaction
@ 180°C annealing

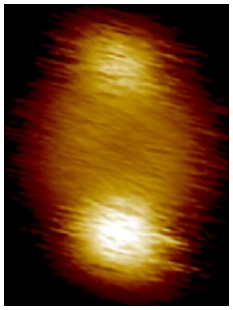


Synthesis: oligomer 1







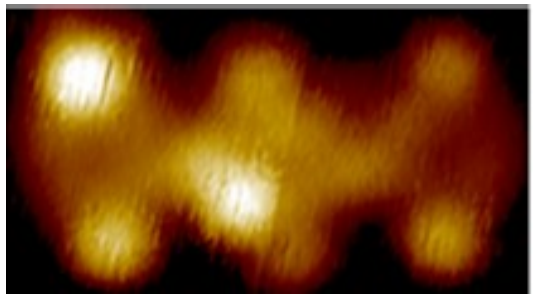


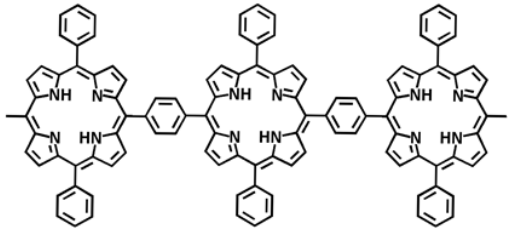
Br_2-TPP

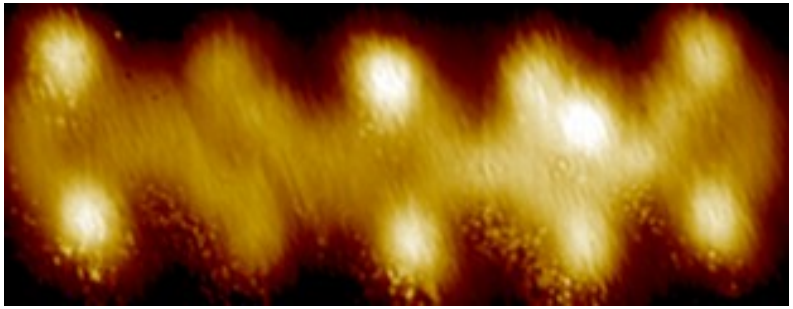
Br_2-DPP

@ Au(111)

Co-deposition and 180°C annealing



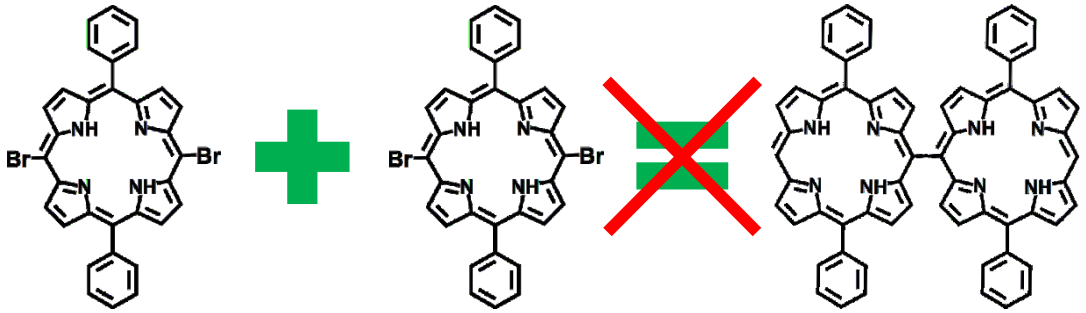




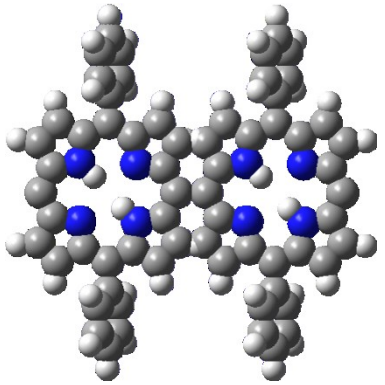
Oligomer 1

Synthesis: oligomer 0

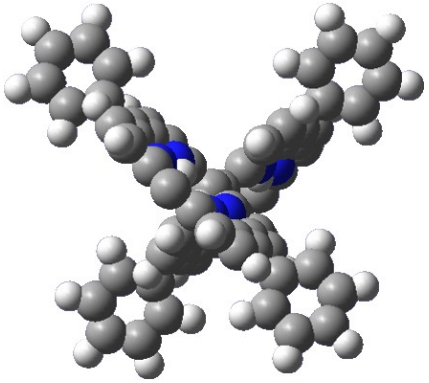
On **surface**:



Steric hindrance



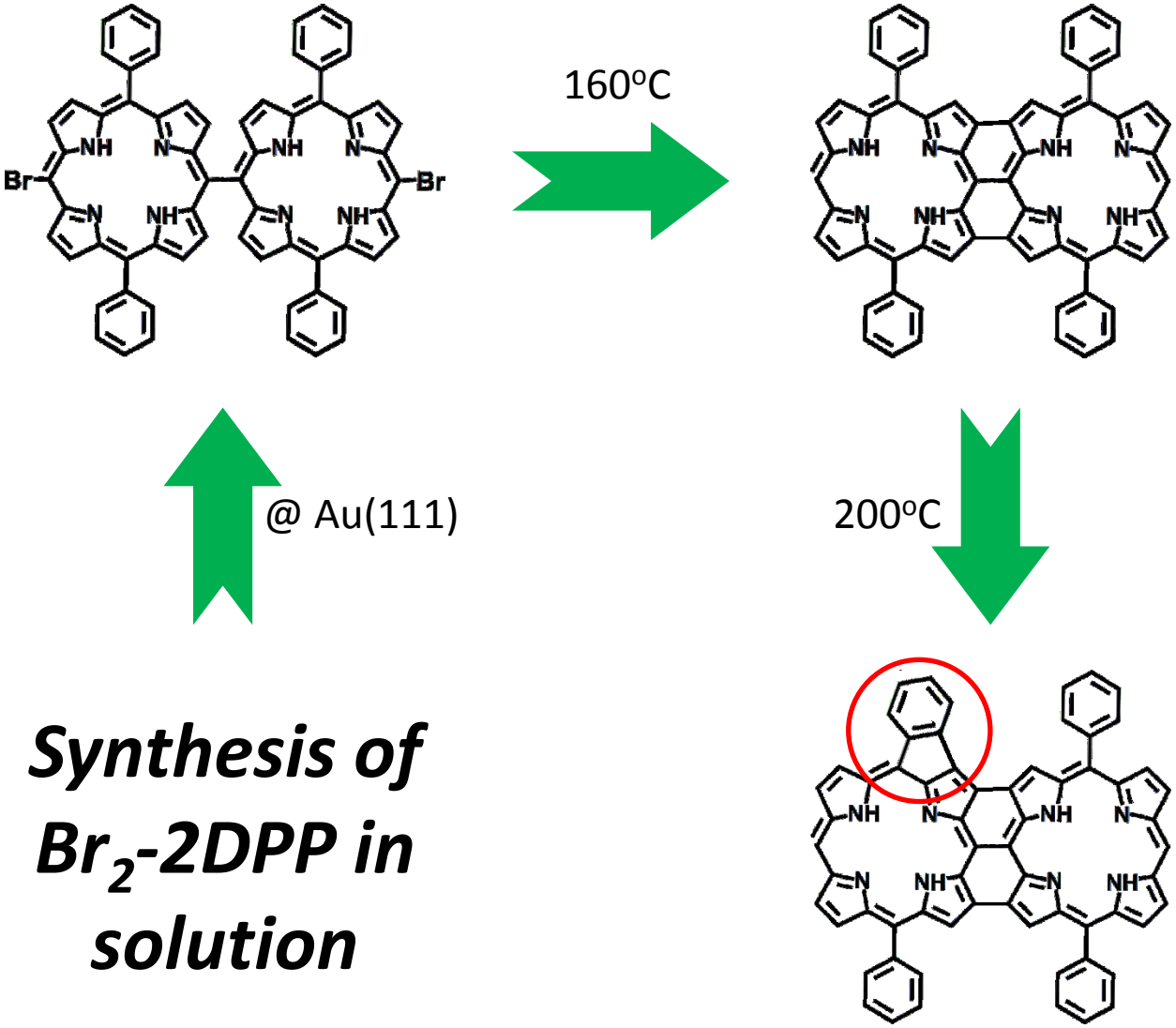
In **solution**:



Br_2-2DPP

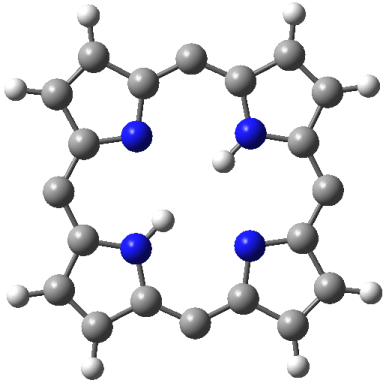
Synthesize in **solution** then deposit on **surface**

Synthesis: oligomer 0

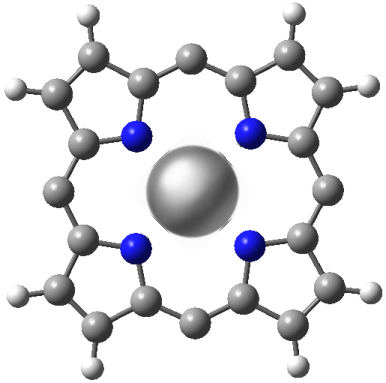


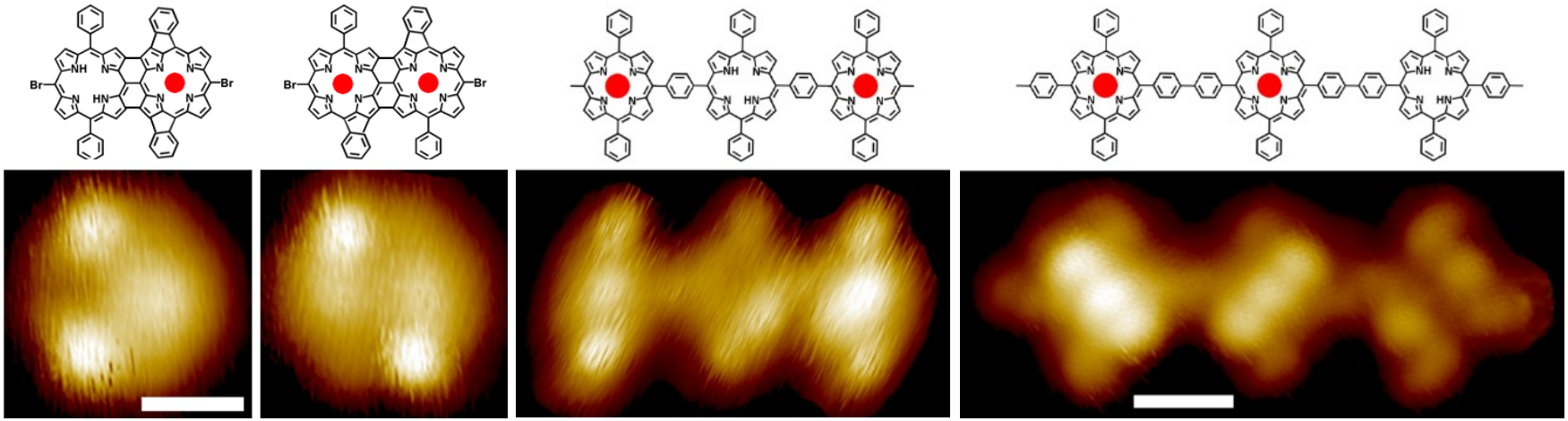
Synthesis of Br_2-2DPP in solution

Synthesis: on-surface metalation



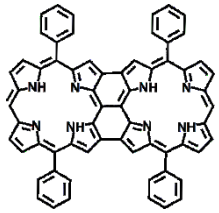
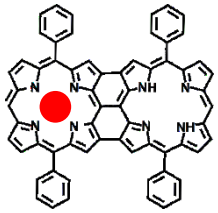
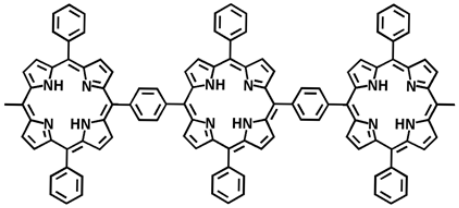
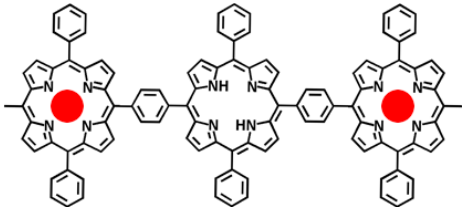
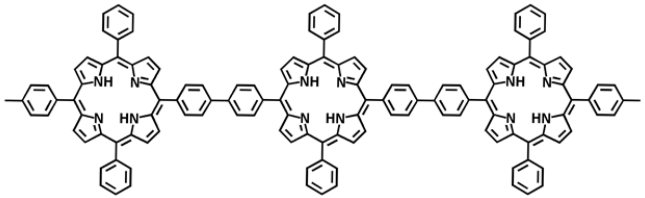
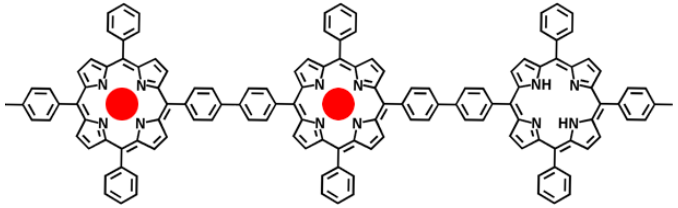
Metalation by
Fe, Ni, Co, Zn,
Mg, Mn, Ce …





Oligomer 0, 1 and 2 can be ***partially*** or ***fully*** metalated by **Fe**

Synthesis: summary

	Molecular wires	Metalation derivatives
Oligomer 0		
Oligomer 1		
Oligomer 2		 Fe

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  - scanning tunneling microscopy and spectroscopy
  - experimental setup
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- **Characterization of molecular wires**

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  iv. spin crossover
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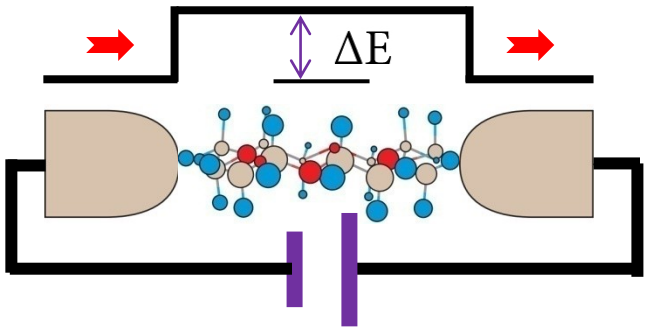
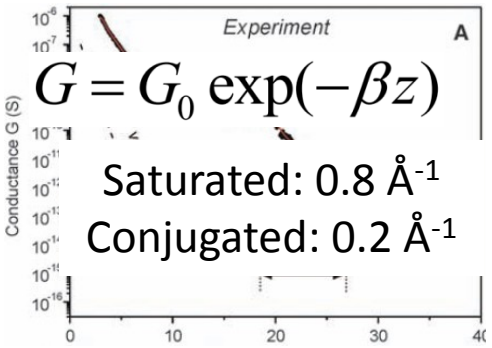
Charge transport: mechanism

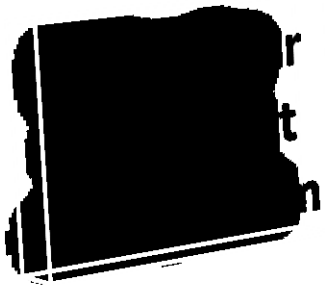
Off-resonance tunneling

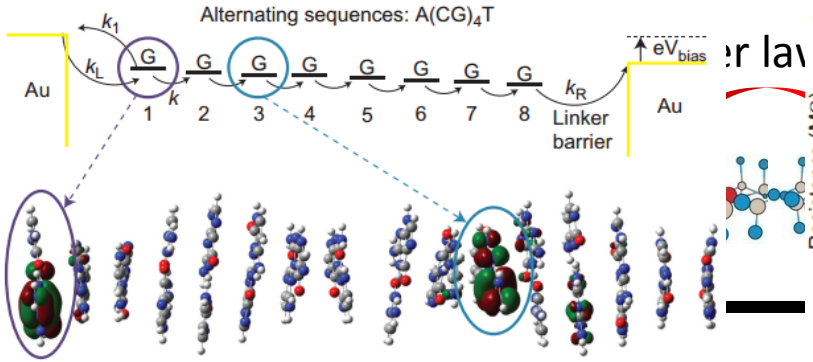


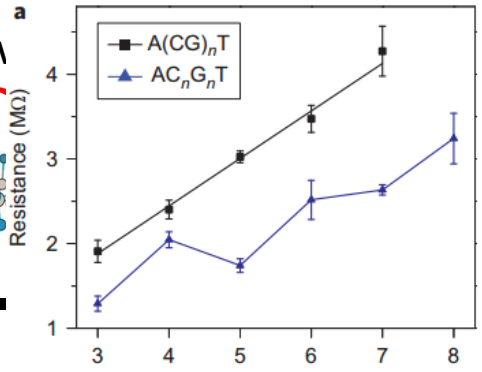


Saturated: 0.8 Å^{-1}

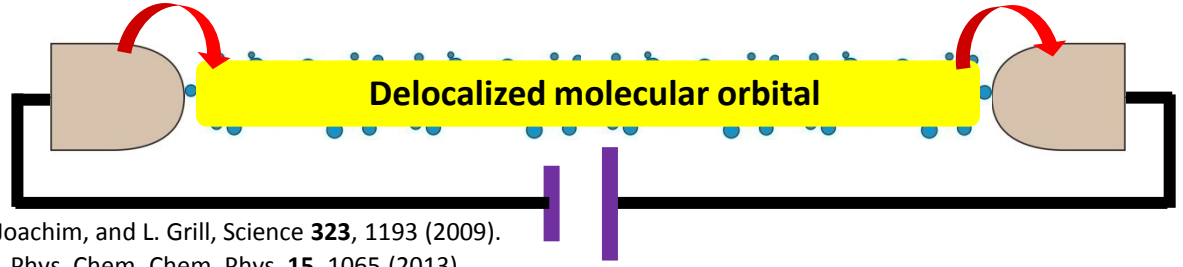
Conjugated: 0.2 Å^{-1}







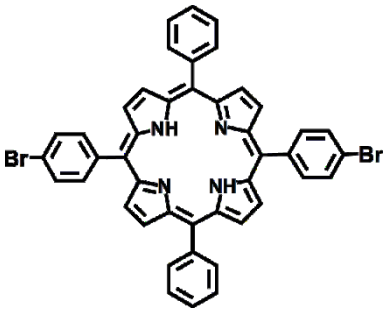
Resonant transport: nearly length-independent

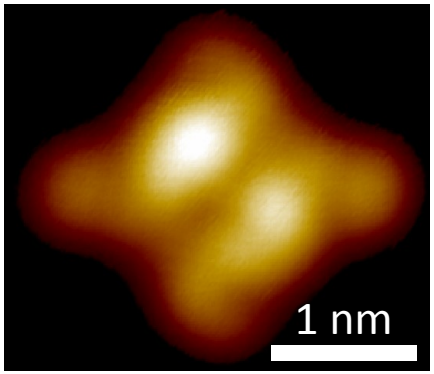


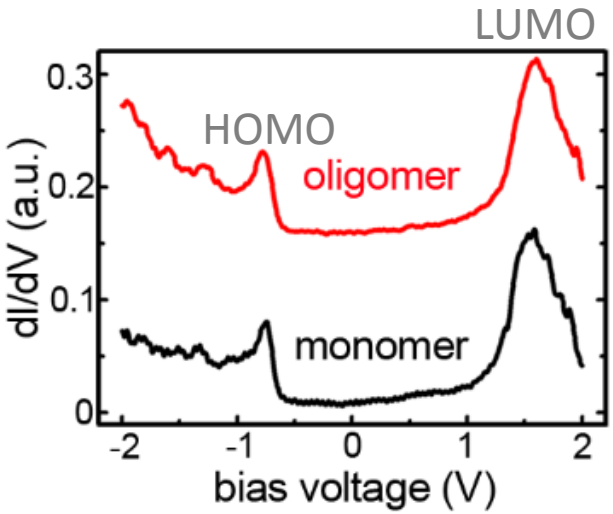
Long distance ?

N. J. Tao, Nature Nanotech. **1**, 173 (2006).
L. Lafferentz, F. Ample, H. Yu, S. Hecht, C. Joachim, and L. Grill, Science **323**, 1193 (2009).
R. L. McCreery, H. J. Yan, and A. J. Bergren, Phys. Chem. Chem. Phys. **15**, 1065 (2013).
L. Xiang, J. L. Palma, C. Bruot, V. Mujica, M. A. Ratner, and N. Tao, Nature Chem. **7**, 221 (2015).
K. H. Khoo, Y. Chen, S. Li, and S. Y. Quek, Phys. Chem. Chem. Phys. **17**, 77 (2015).
G. Sedghi, L. J. Esdaile, H. L. Anderson, S. Martin, D. Bethell, S. J. Higgins, and R. J. Nichols, Adv. Mater. **24**, 653 (2012).

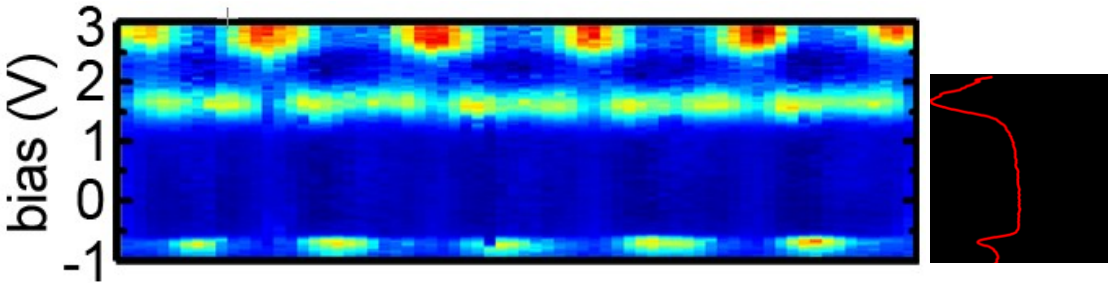
Charge transport: electronic property of oligomer 2

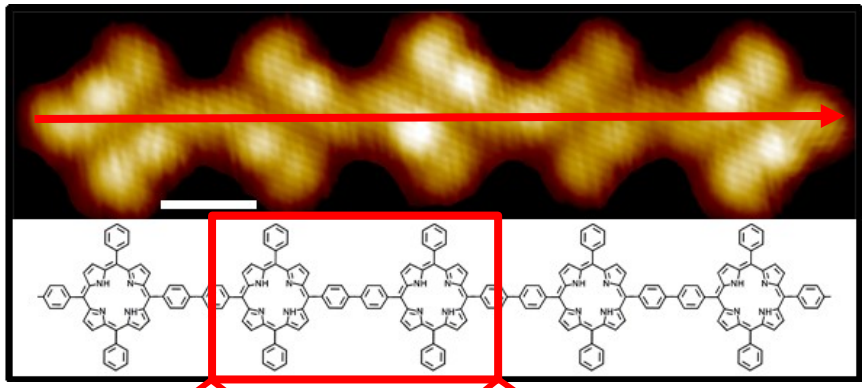


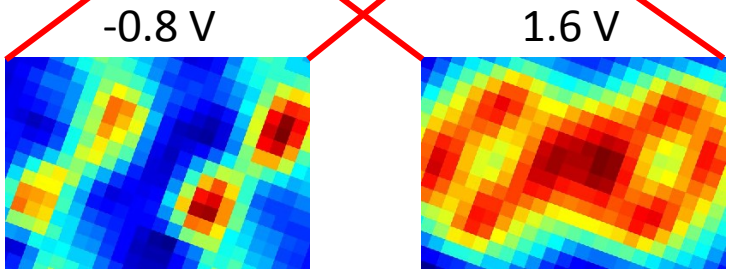




dI/dV along molecular wire

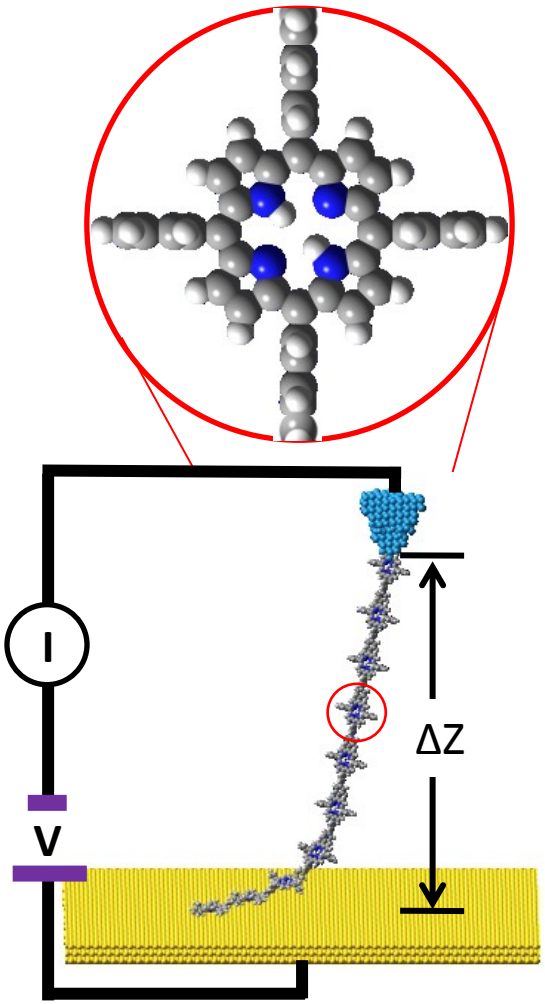




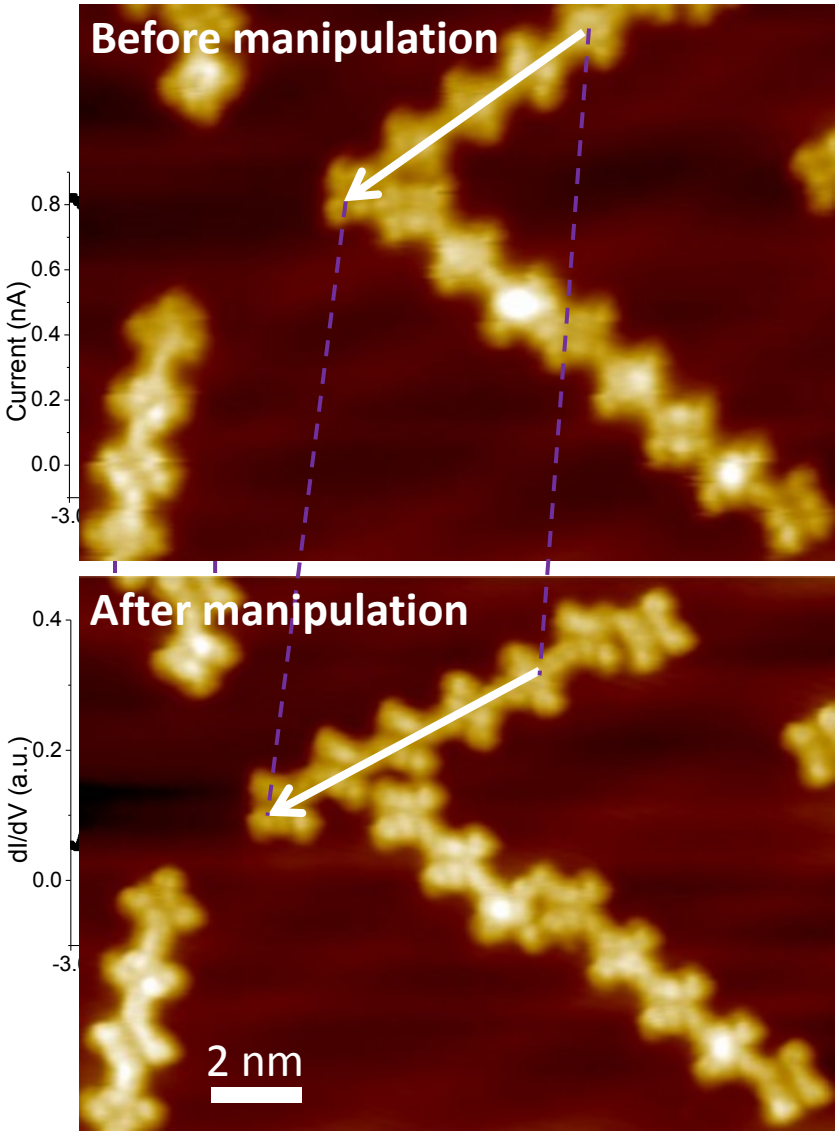


HOMO ➔ **localized** LUMO ➔ **delocalized**

Charge transport: conductance measurement

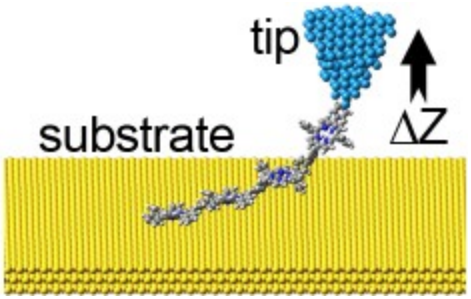


STM vertical manipulation



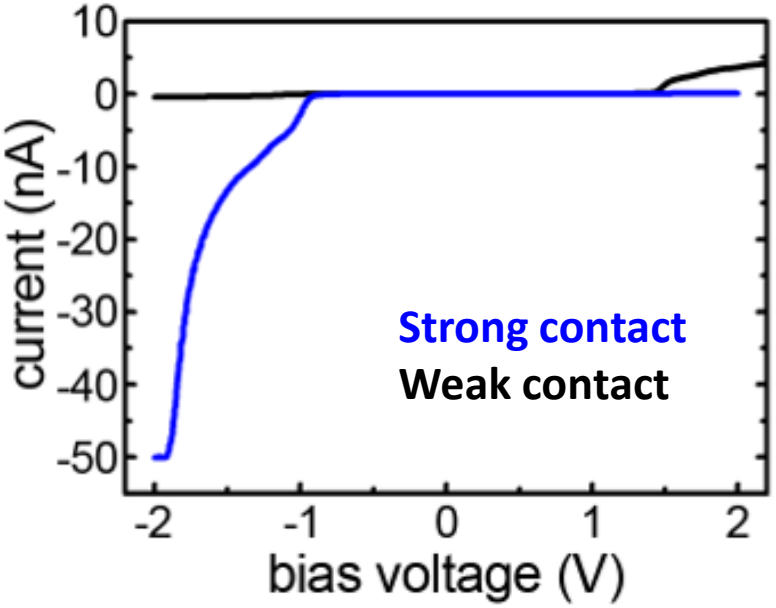
Charge transport: different contacts

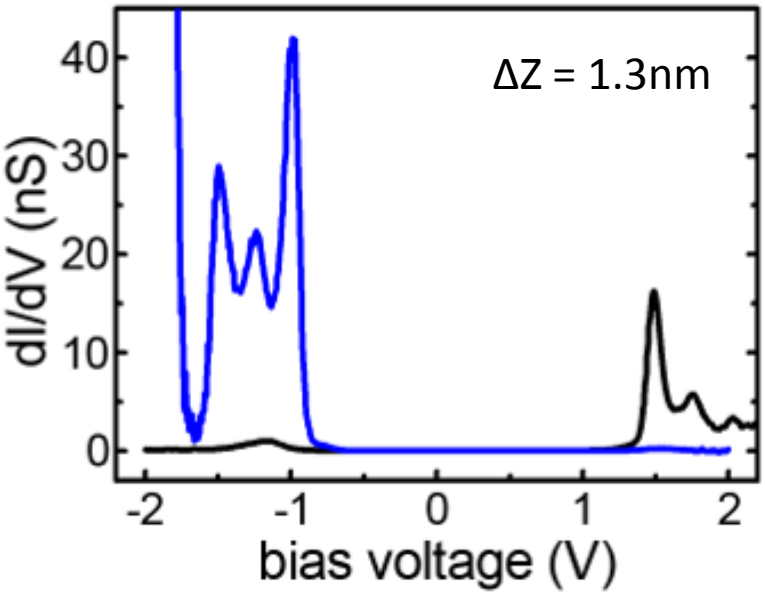
At **lower** tip height:



Z displacement: **> 5nm** (19 %)
< 3nm (81 %)

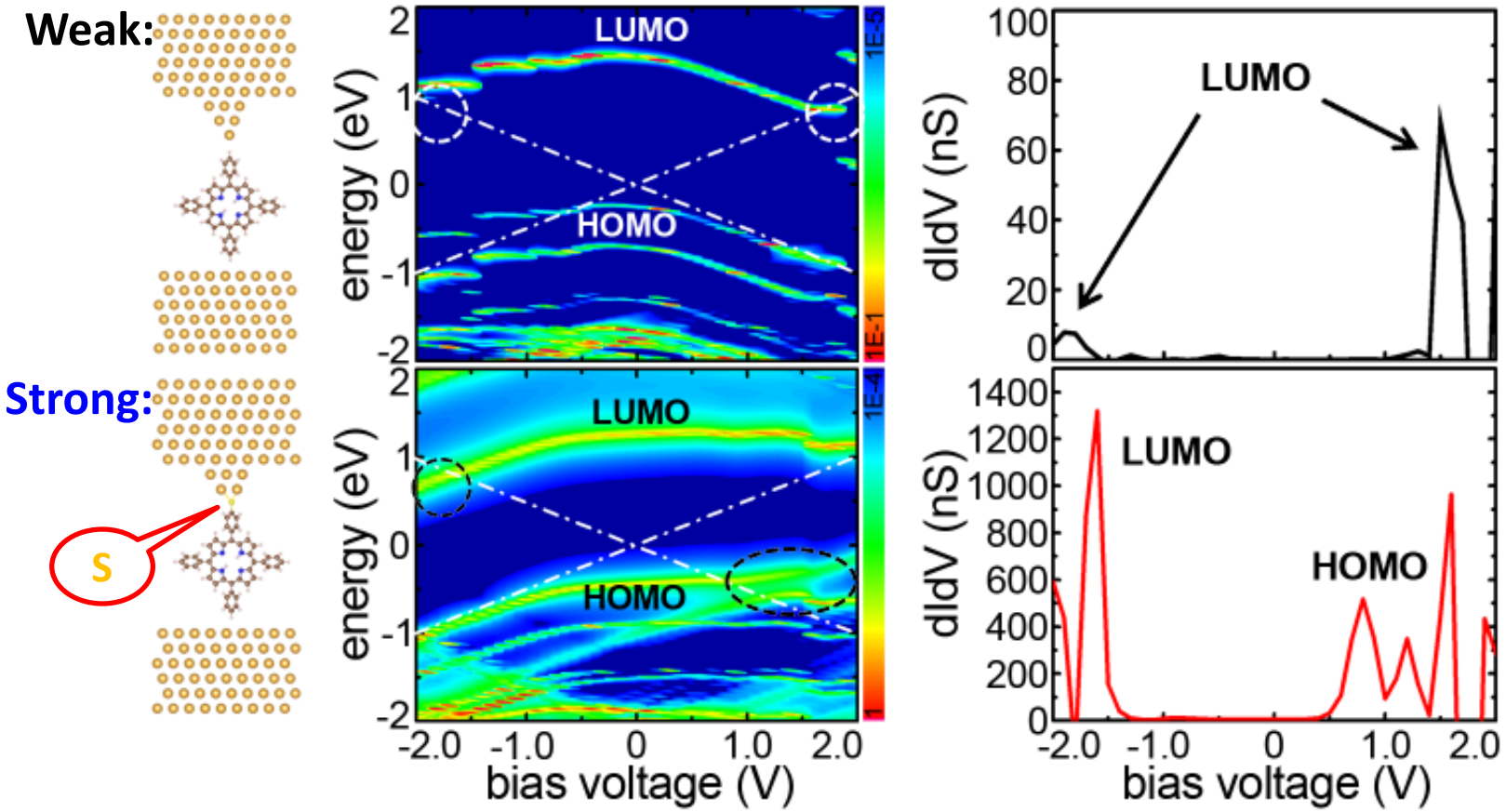
Strong contact vs. **weak** contact





Charge transport: first-principle simulation

NEGF – simulation of transmission:



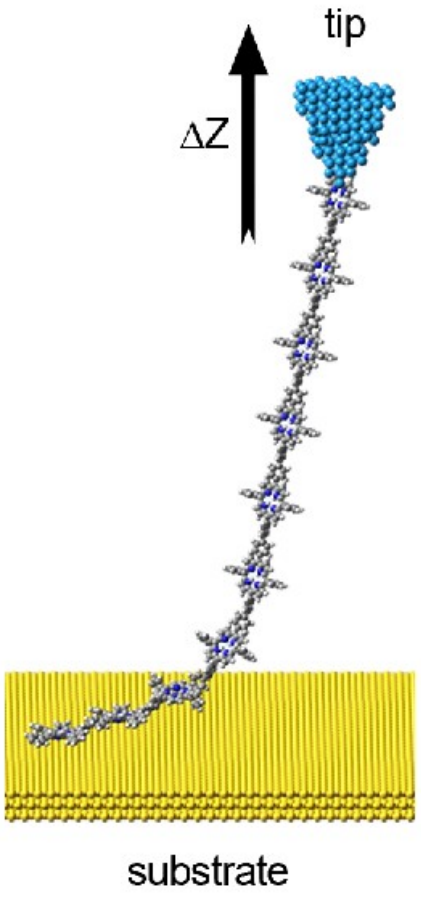
Conclusion : **weak** contact ➔ **physical** adsorption

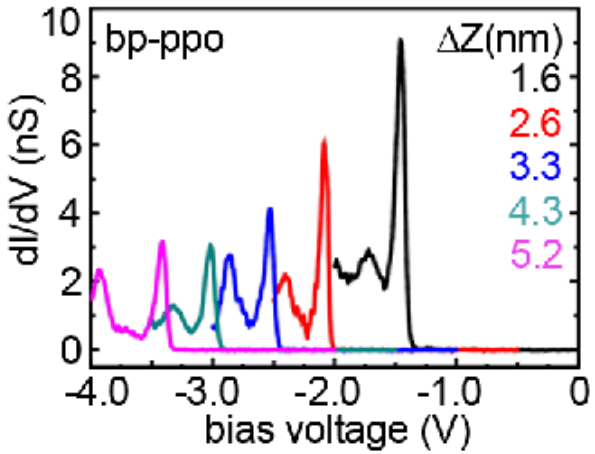
strong contact ➔ **covalent** bonding

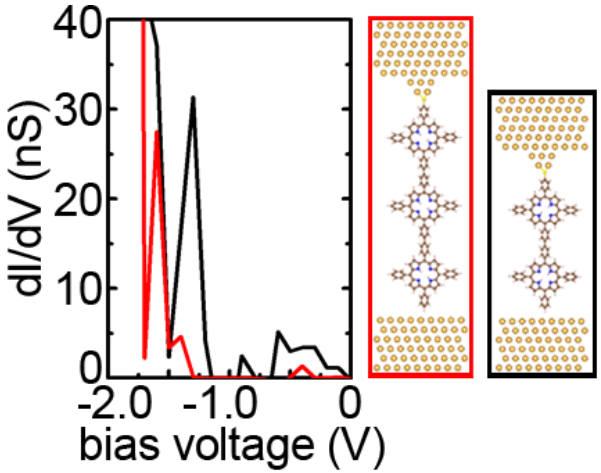
electrons transfer through delocalized LUMO

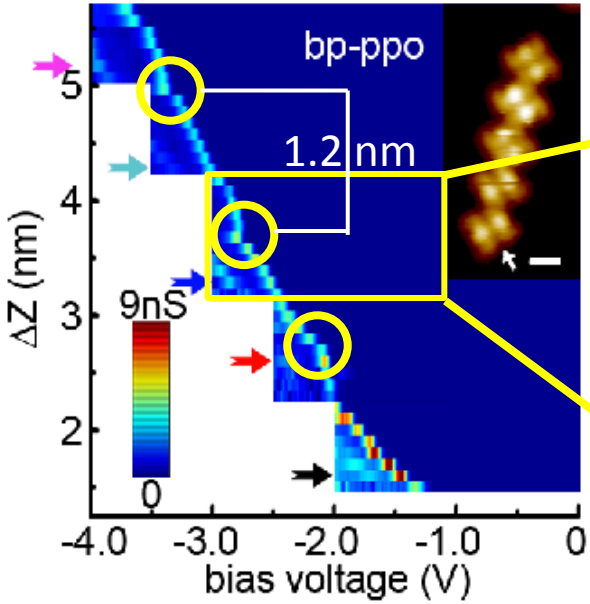
Charge transport: long-range resonant transport

At **higher** tip height:

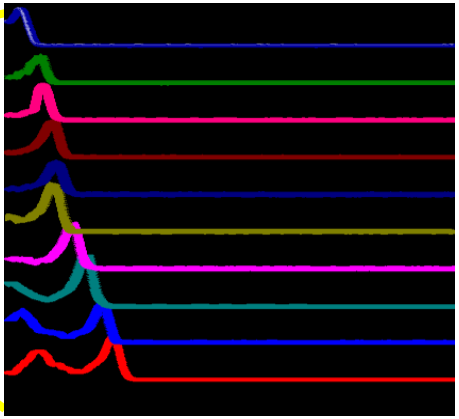






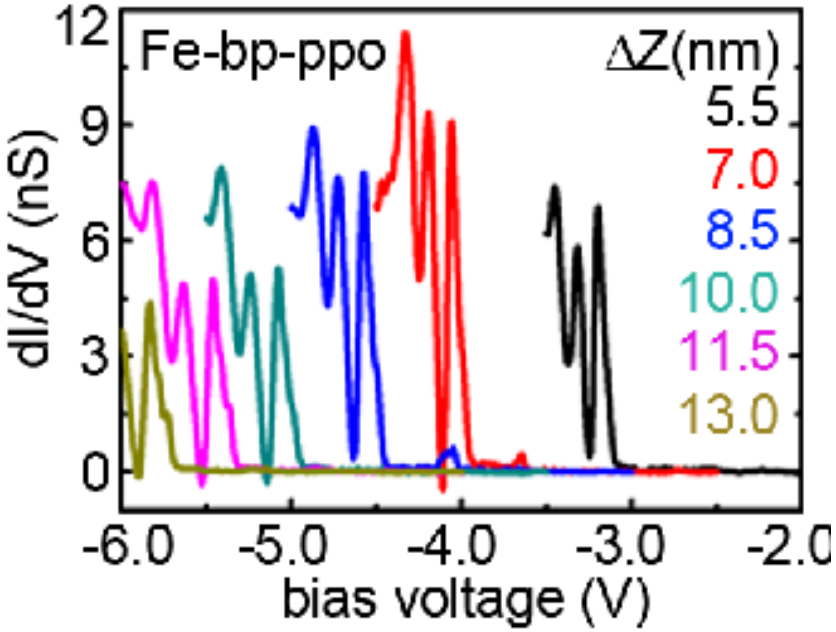


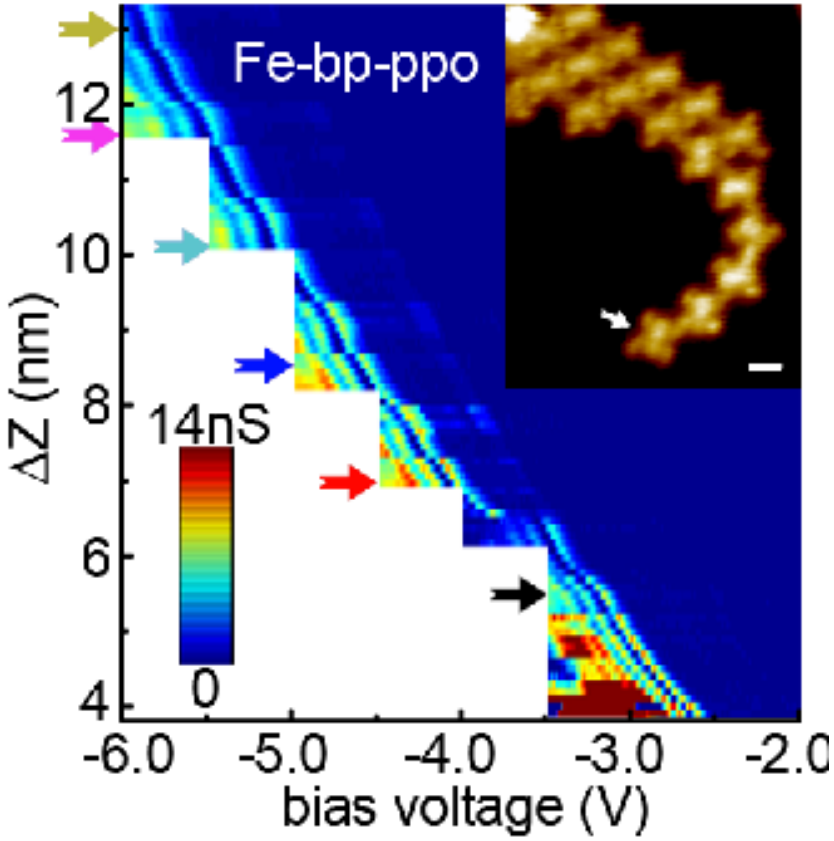
Simulation:



Charge transport: Fe-metalated oligomer 2

At **higher** tip height:





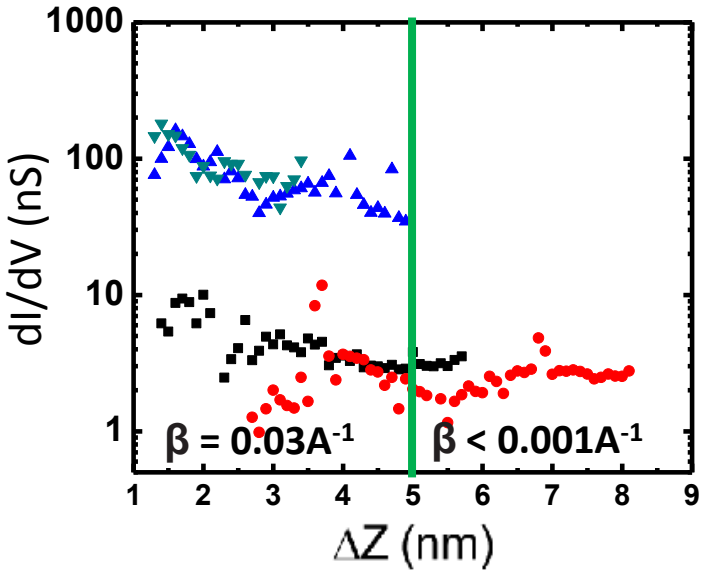
Resonant transport through **delocalized** molecular orbital

magnetic impurities do not affect transport

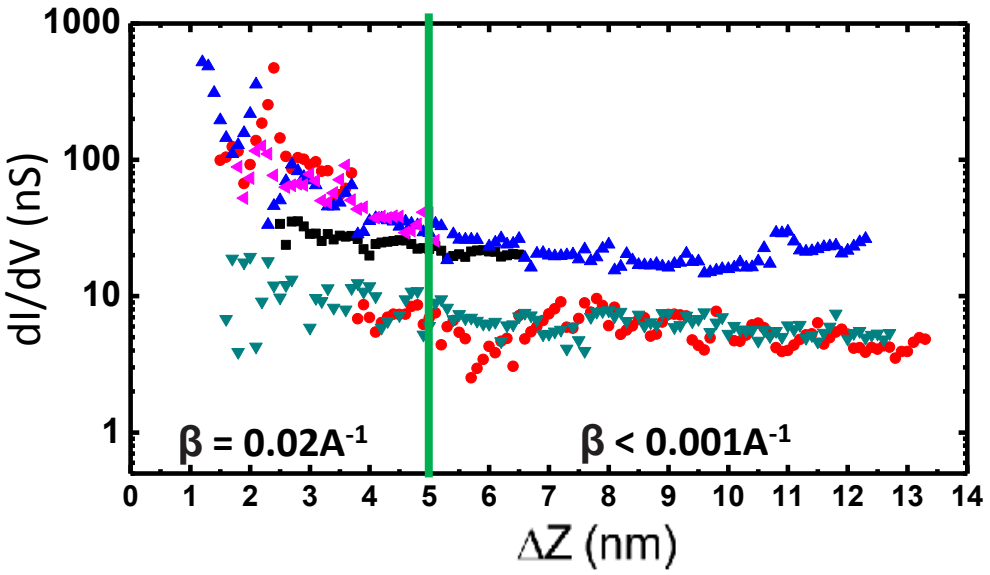
Charge transport: attenuation factor

The magnitude of the first peak

Oligomer 2

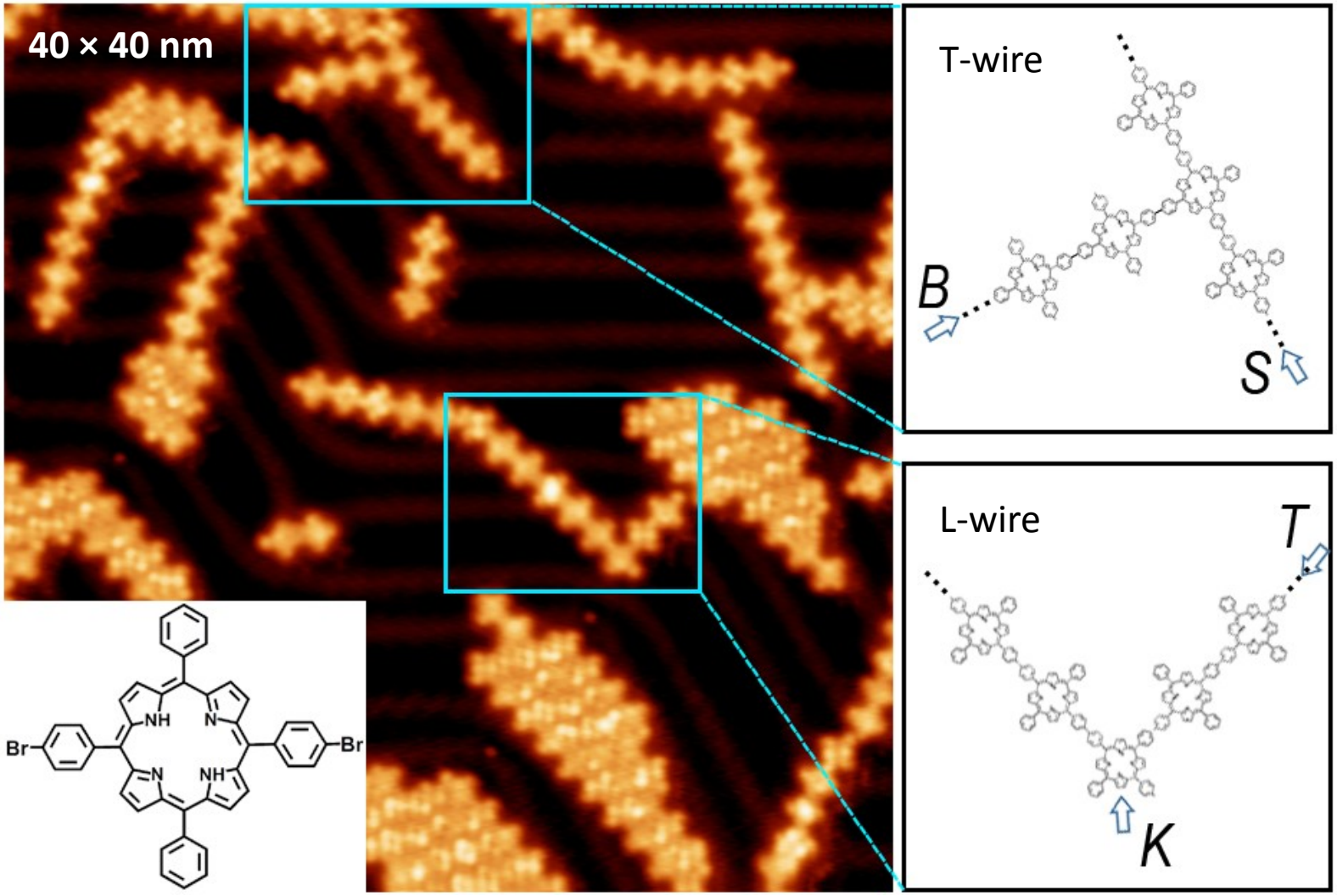


Fe-metalated oligomer 2



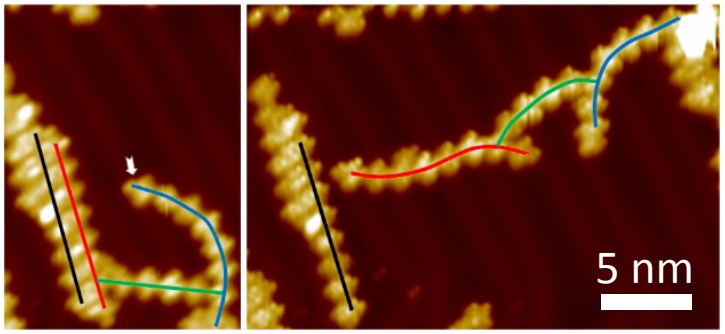
Nearly length-independent

Charge transport: branched molecular wires

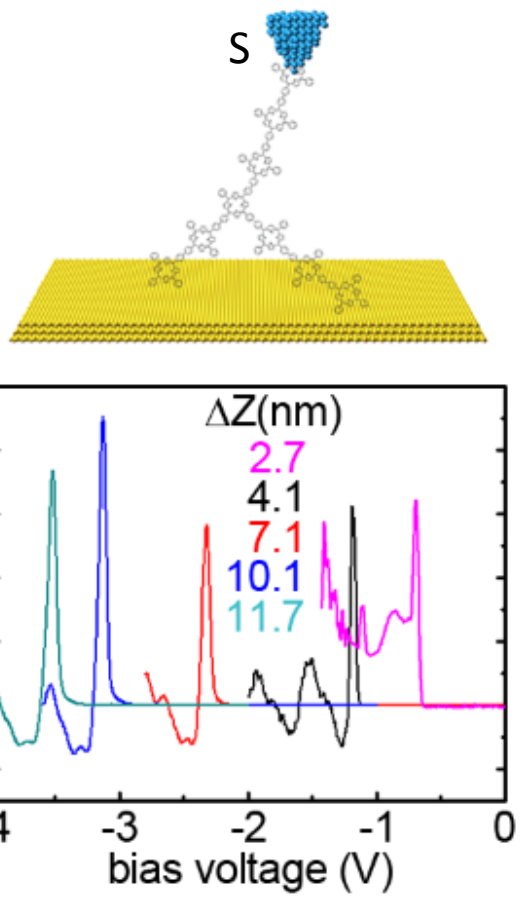


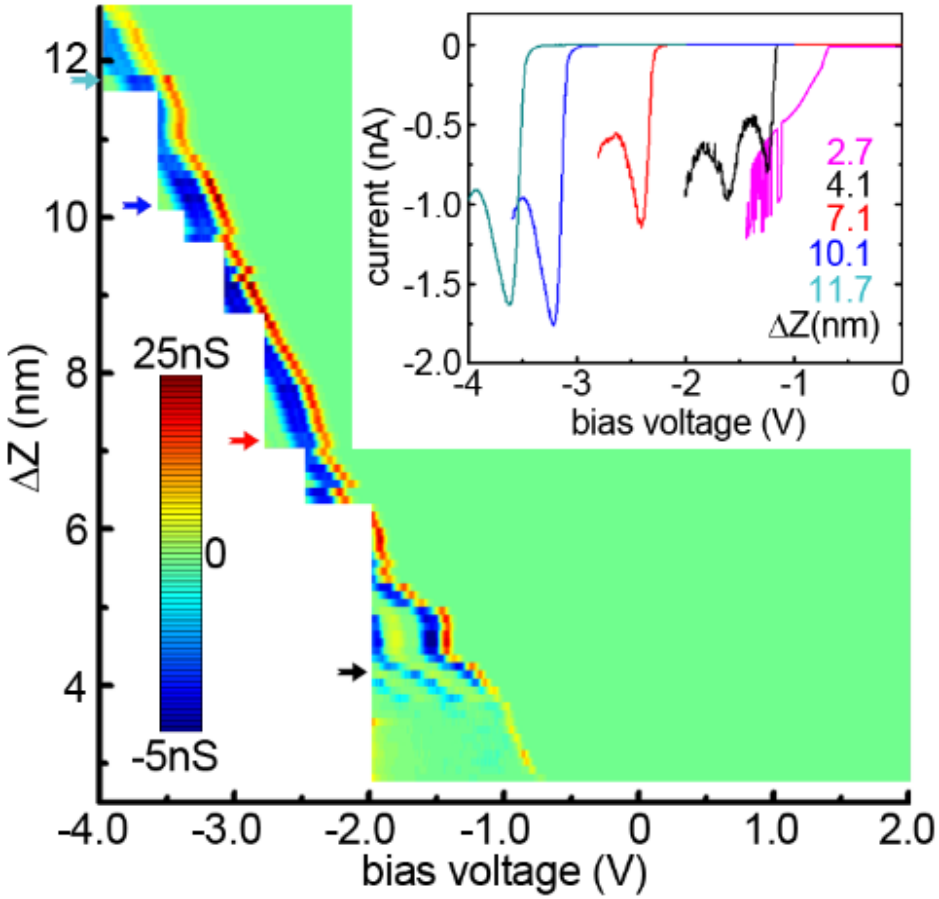
Br_2-TPP molecules @ Au(111) @ 250°C

Charge transport: T-wire exhibiting NDC

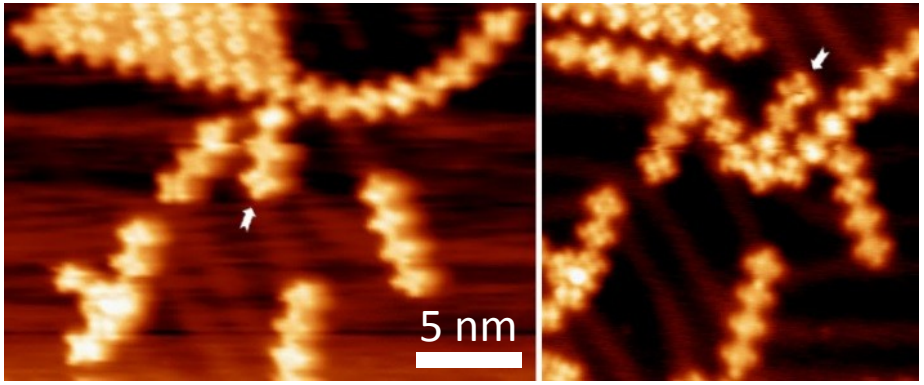


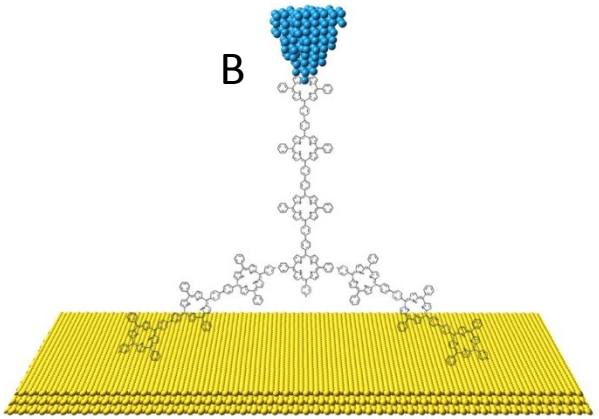
- Lift up T-wire by terminal S
- Stretched after manipulation
- Resonant charge transport
- Negative differential conductance



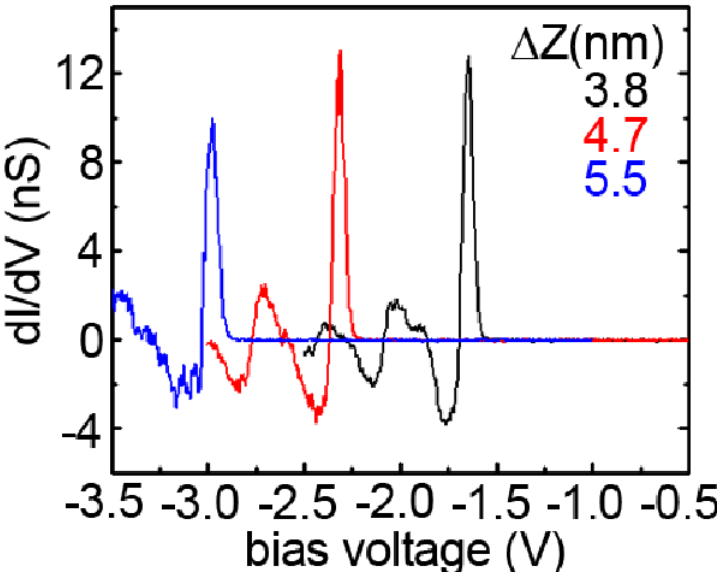


Charge transport: T-wire exhibiting NDC



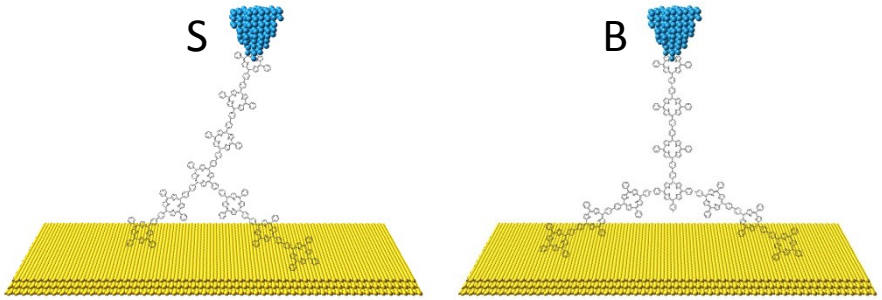


- Lift up T-wire by terminal B
- Flipped after manipulation
- Resonant charge transport
- NDC

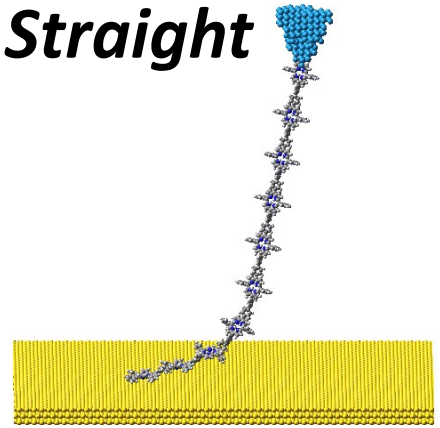


Charge transport: why NDC ?

T-shape

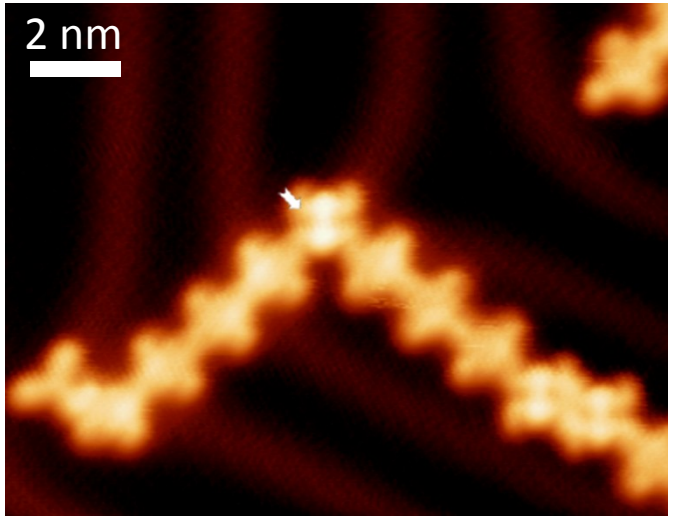


Straight



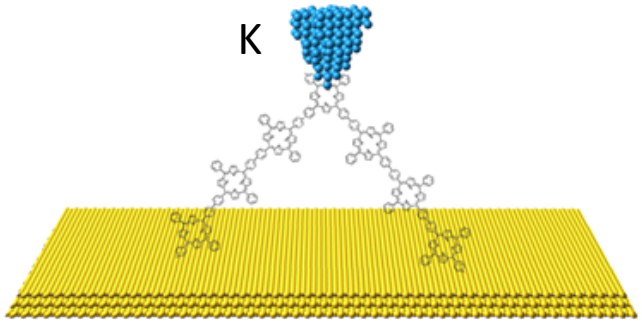
- Multi-pathway for current ?
- Structural kink ?

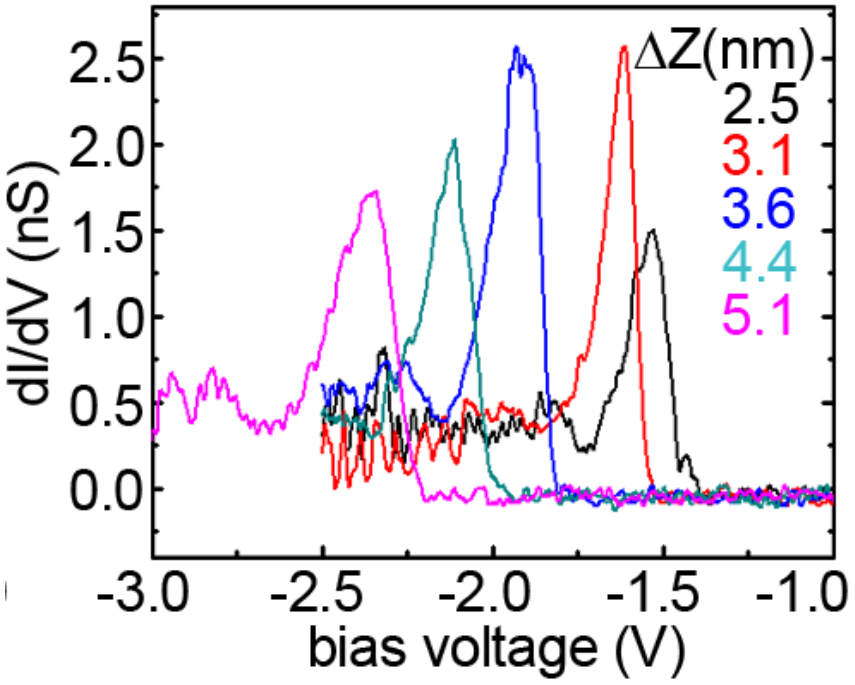
Charge transport: multi-pathway ?



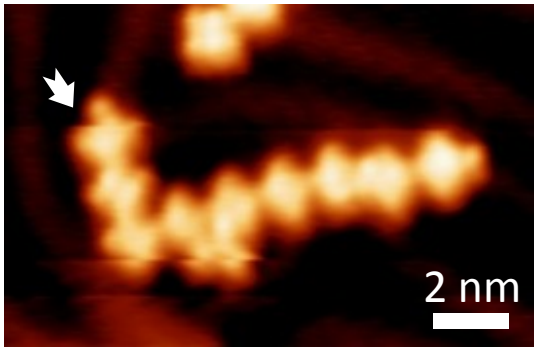
- 90°-kinked L-wire
- Lift up by terminal K
- No NDC

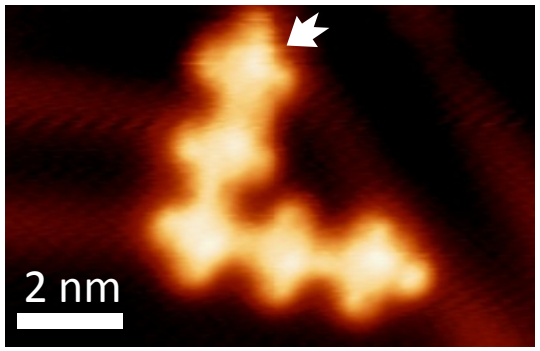
Multi-pathway

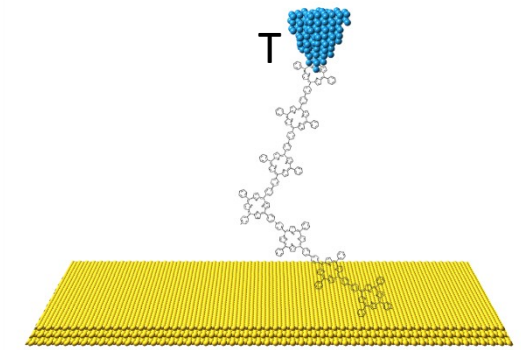


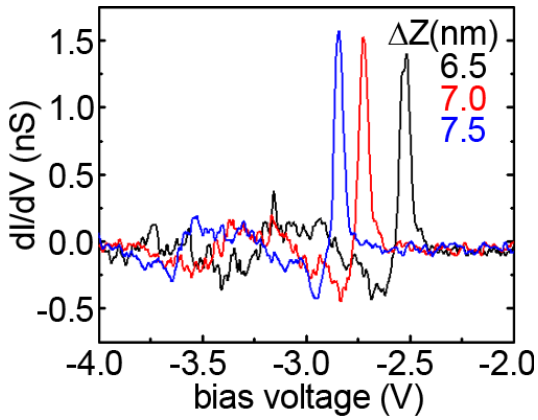


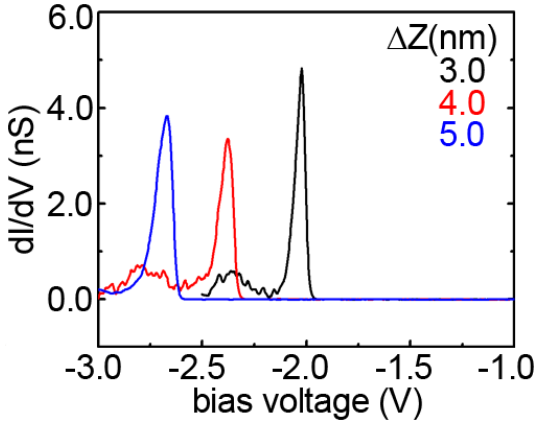
Charge transport: 90° kink ?





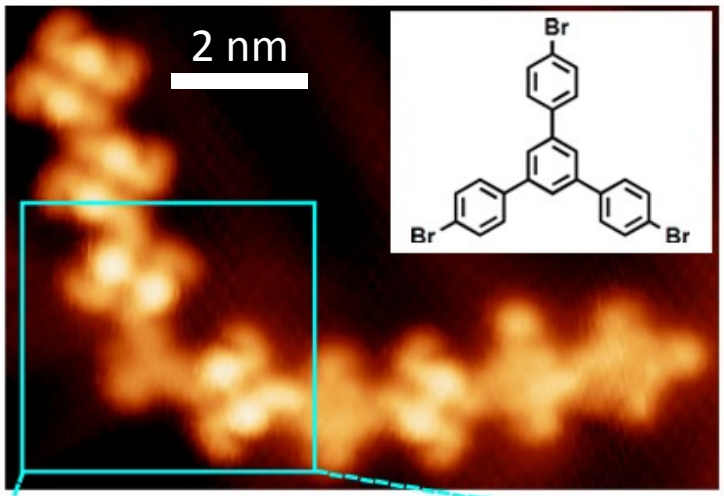


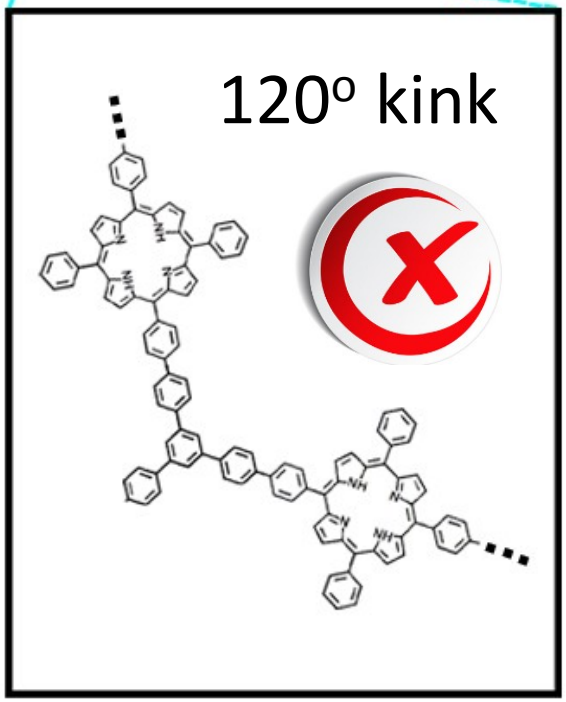


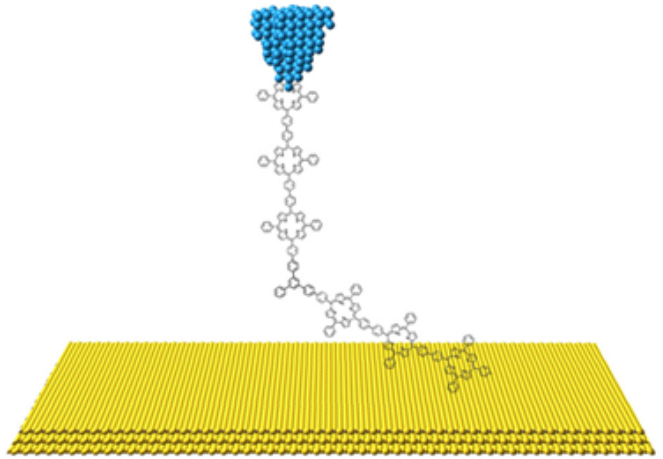


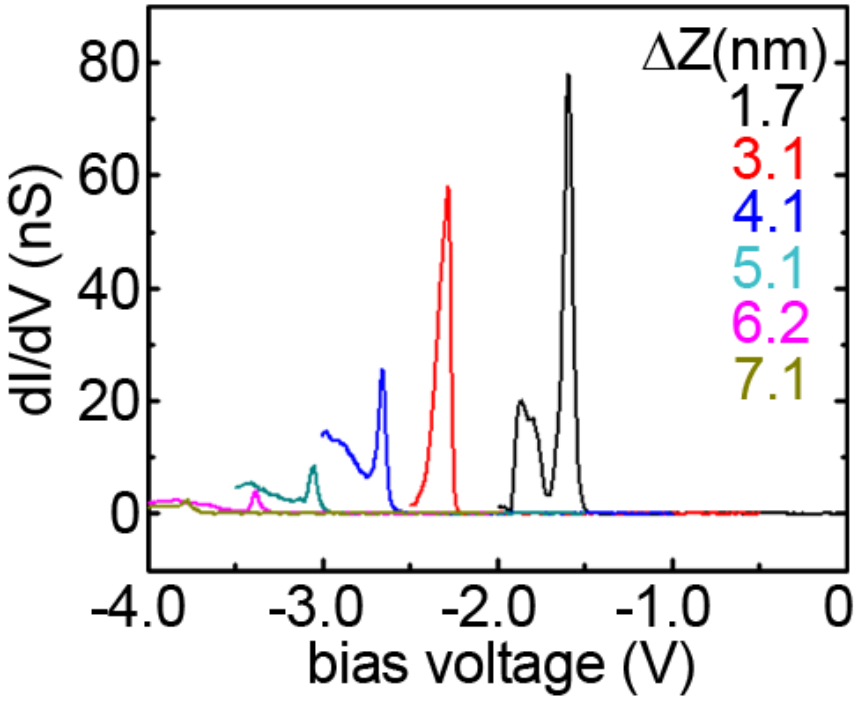
- 90°-kinked L-wire
- Lift up by terminal T
- 67 % with NDC

Charge transport: 120° kink ?

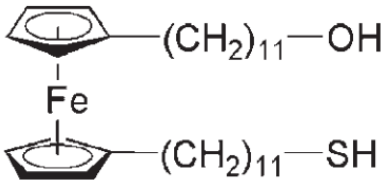




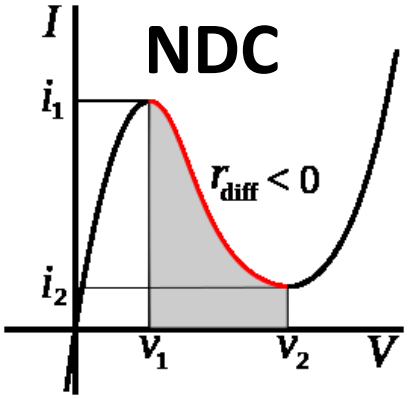


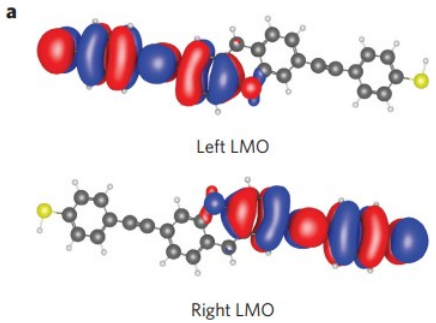


Charge transport: mechanism

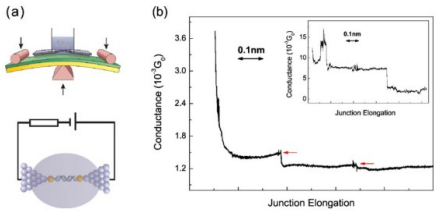


Redox reaction and resonance transport

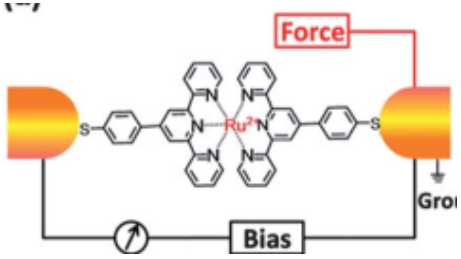




Alignment and **misalignment** of delocalized molecular orbital



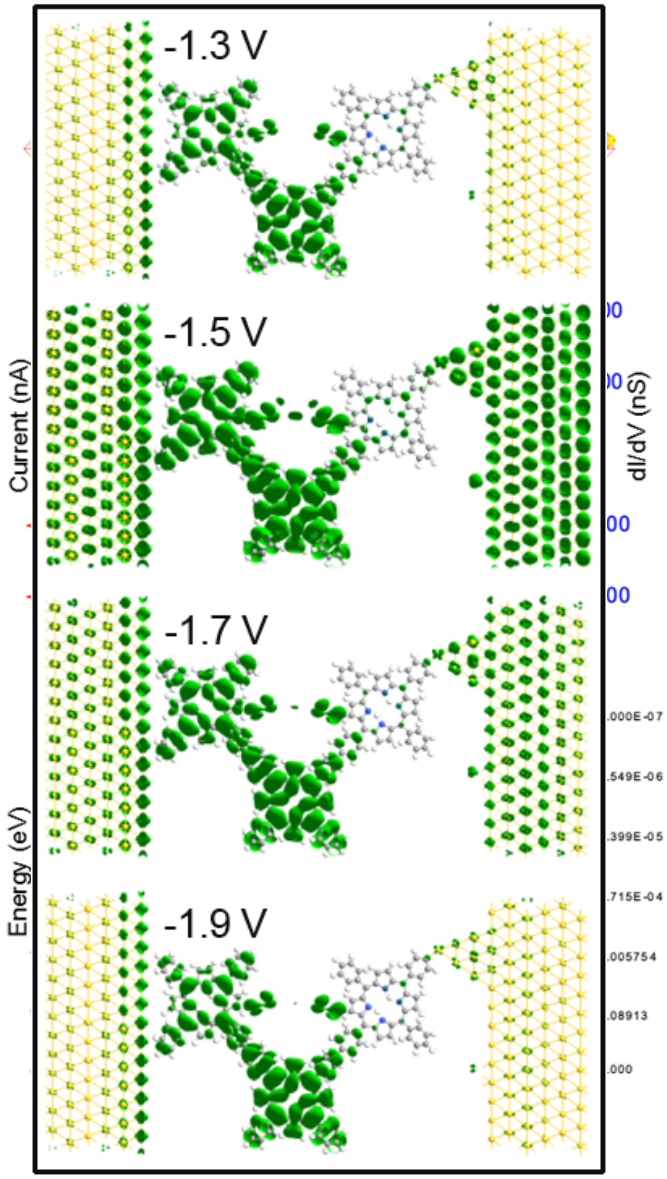
Polaron induced charge **storage**

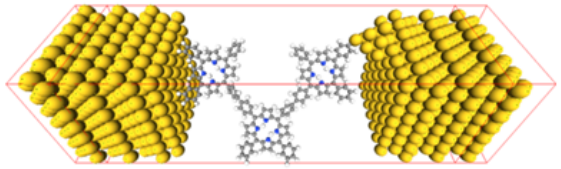


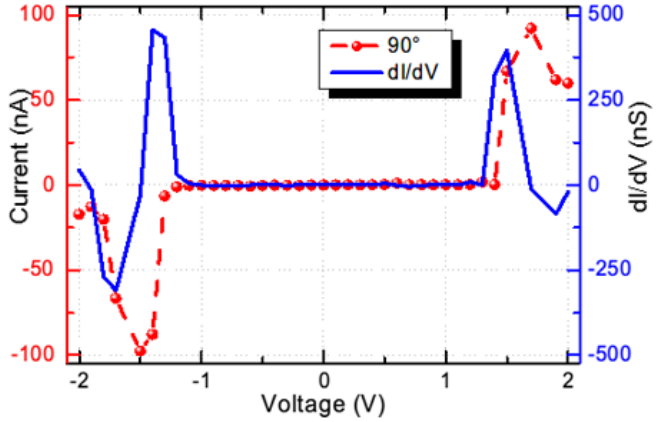
Changes in molecule-electrode **coupling**

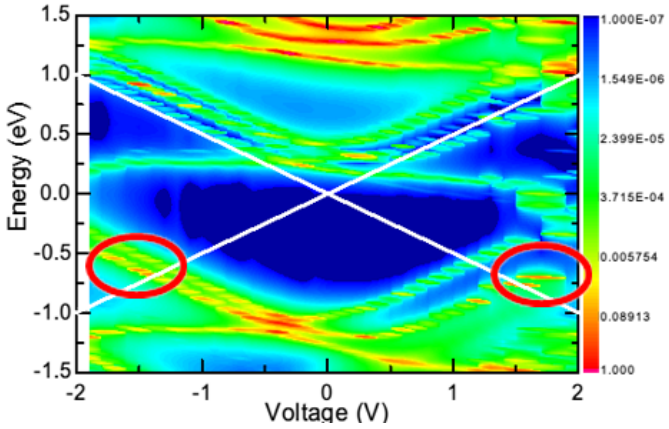
N. Kang, A. Erbe, and E. Scheer, Appl. Phys. Lett. **96**, 023701 (2010)
J. Zhou, S. Samanta, C. Guo, J. Locklin, and B. Xu, Nanoscale **5**, 5715 (2013)
M. L. Perrin *et al.*, Nat. Nanotechnol. **9**, 830 (2014)
E. D. Mentovich, I. Kalifa, A. Tsukernik, A. Caster, N. Rosenberg-Shraga, H. Marom, M. Gozin, and S. Richter, Small **4**, 55 (2008)

Charge transport: first-principle simulation







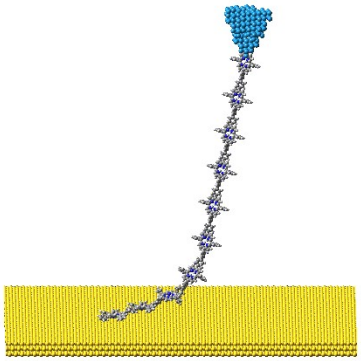


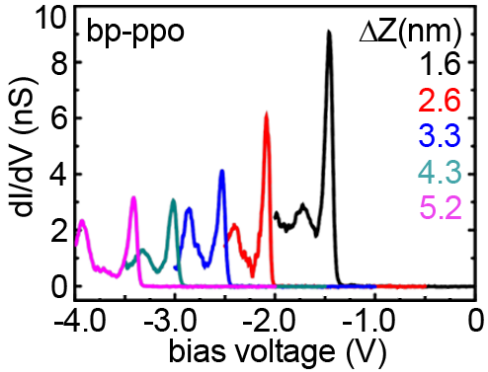
HOMO-1 becomes ***less delocalized*** at high bias

Charge transport: summary

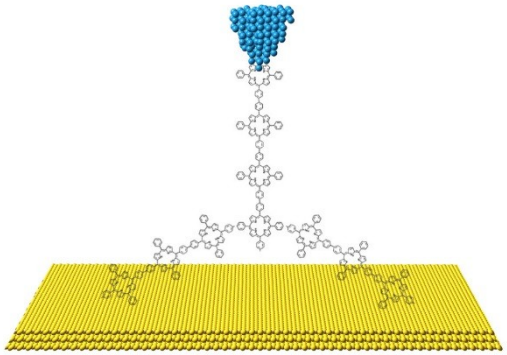
Oligomer 2

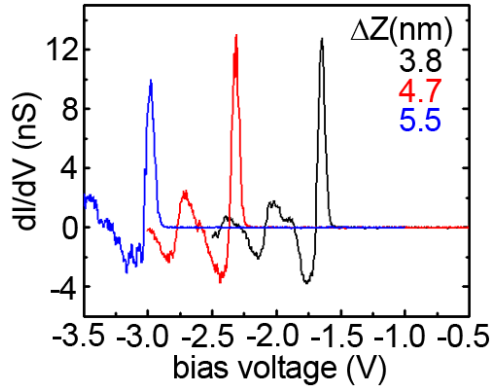
- Resonant charge transport





- Negative differential conductance





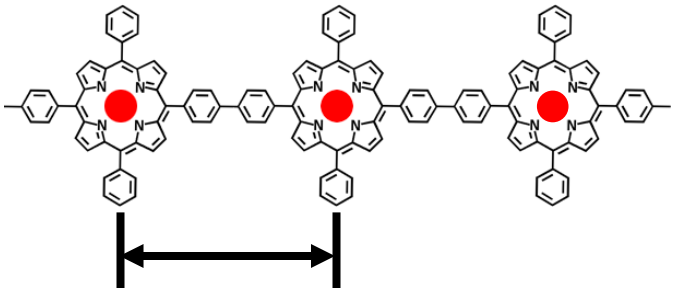
Outline

- **Introduction**
  - molecular electronics
  - scanning tunneling microscopy and spectroscopy
  - experimental setup
- **Synthesis of molecular wires**
  - oligomers comprising porphyrins and phenyls
- **Characterization of molecular wires**
  i. resonant charge transport
  ii. negative differential conductance

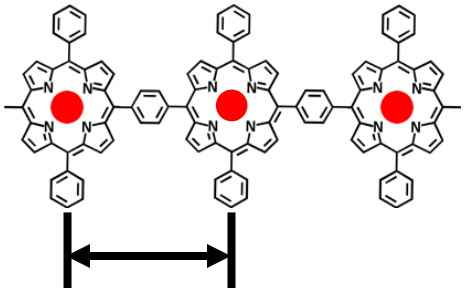
  iv. spin crossover
- **Summary**

Interaction between spins

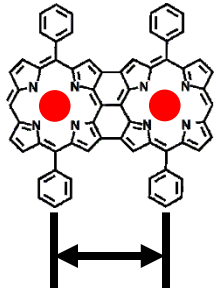
- **Direct** coupling
  - overlap of orbitals with non-zero magnetic moment
  - dipole-dipole coupling
- **Indirect** coupling
  - interacting through a certain medium
  - RKKY – mediated by conduction electrons
  - exchange – mediated by organic molecule



1.73 nm



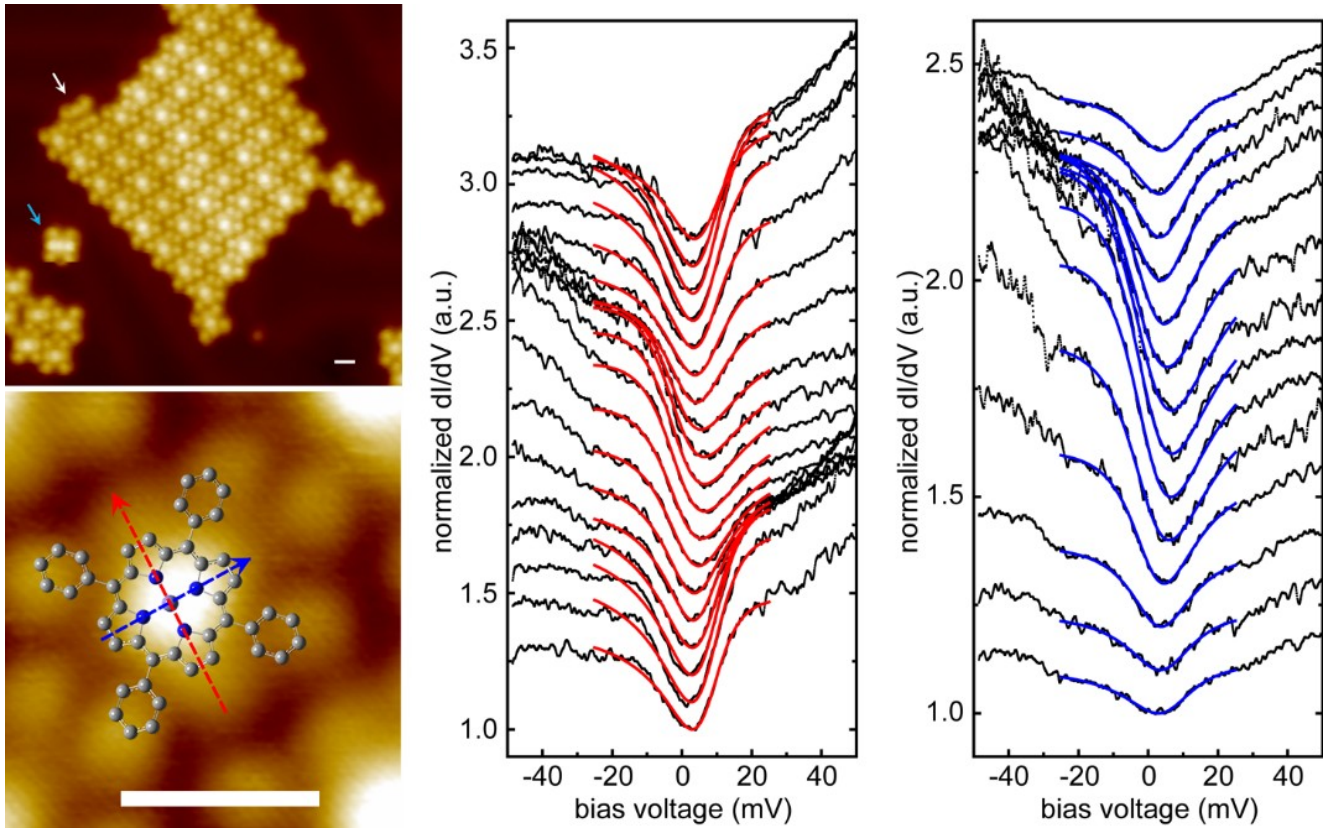
1.31 nm



0.89 nm

Spin-spin coupling: Fe-TPP

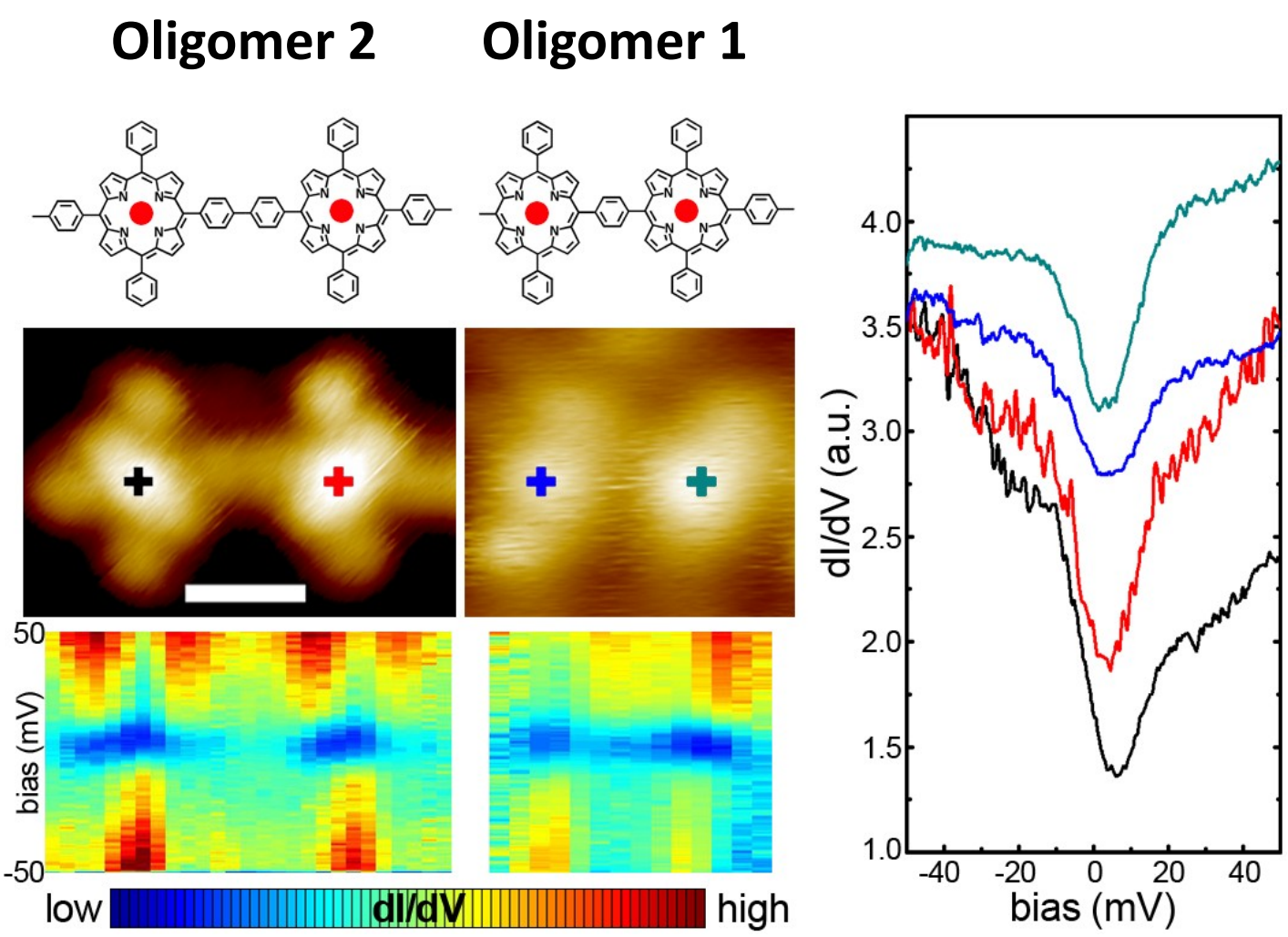
Fe-TPP monomer



Spin-excitation spectroscopy @ 4.8K

Spin signature of individual atoms

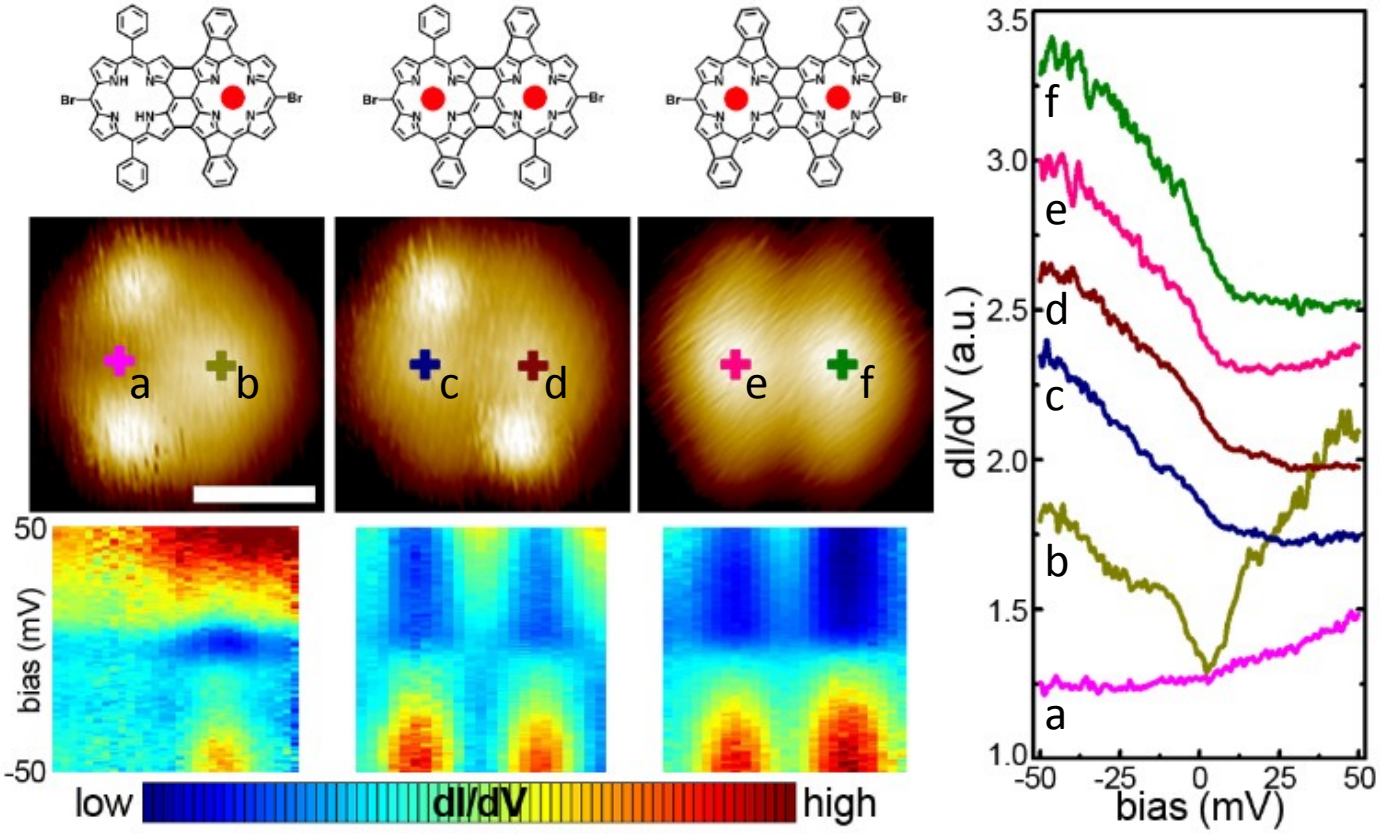
Spin-spin coupling: Fe-metalated oligomer 2 and 1



Spins in the oligomers exhibit the same behavior as isolated spins: neighboring spins are ***decoupled***

Spin-spin coupling: Fe-metalated oligomer 0

Oligomer 0

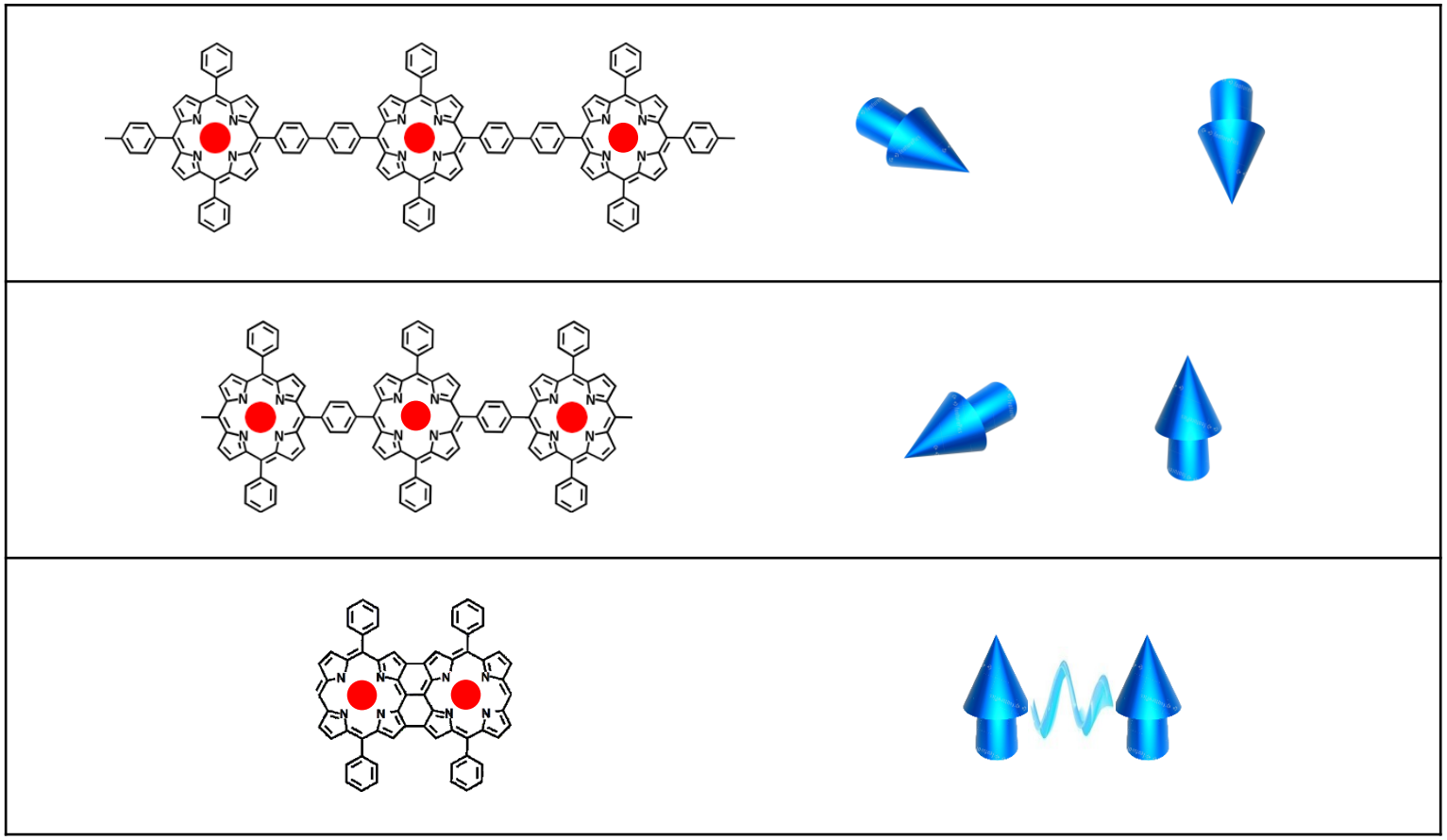


Spin-excitation ***quenched*** → neighboring spins are ***coupled***

Exchange interaction mediated by molecular backbone

Spin-spin coupling: conclusion

Spin-spin **indirect** interaction mediated by molecular backbone



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  i. resonant charge transport
  ii. negative differential conductance
  iii. spin-spin coupling

- **Summary**

Spin crossover: introduction

Spin crossover

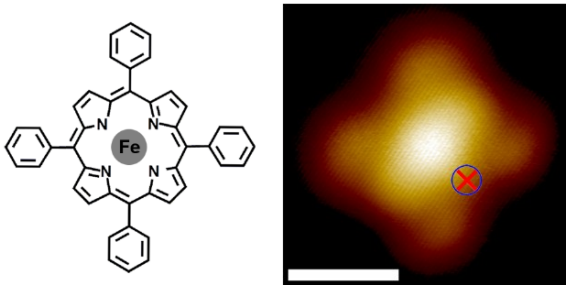
External stimulus:

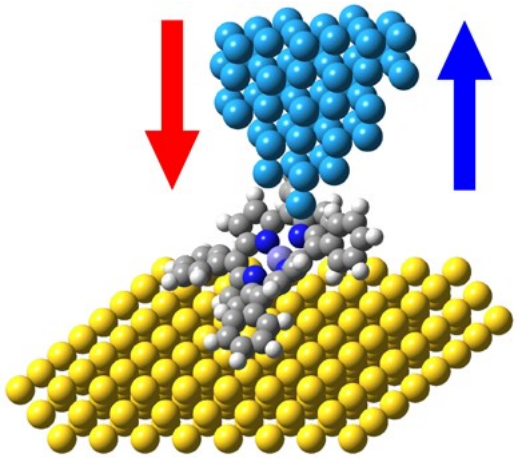
- *Temperature*
- *Light*
- *Charge flow*
- *Pressure*
- *Electric field*
- *… …*

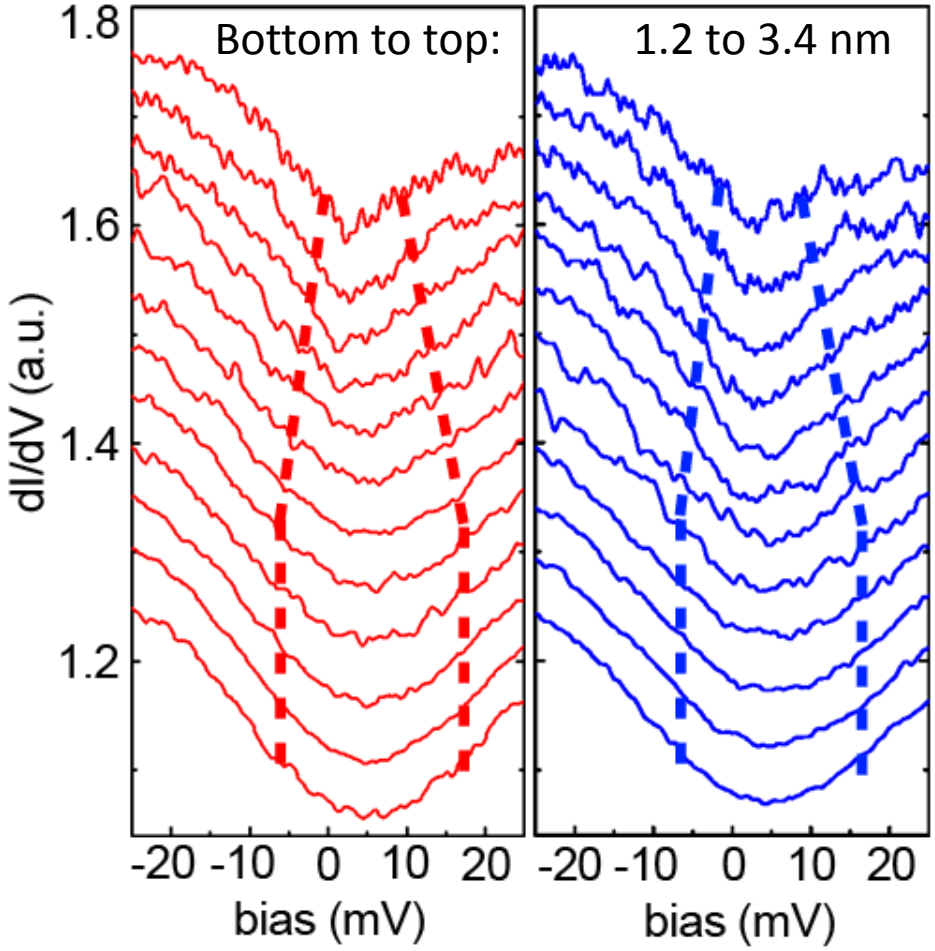
Switches in Molecular electronics

Top Curr Chem (2004) 233:1–47

Spin crossover: vertical manipulation + STS

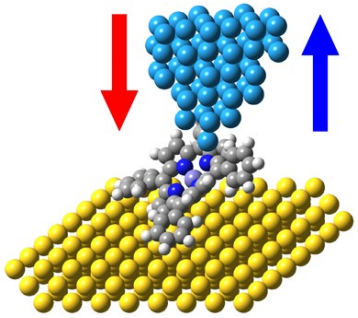


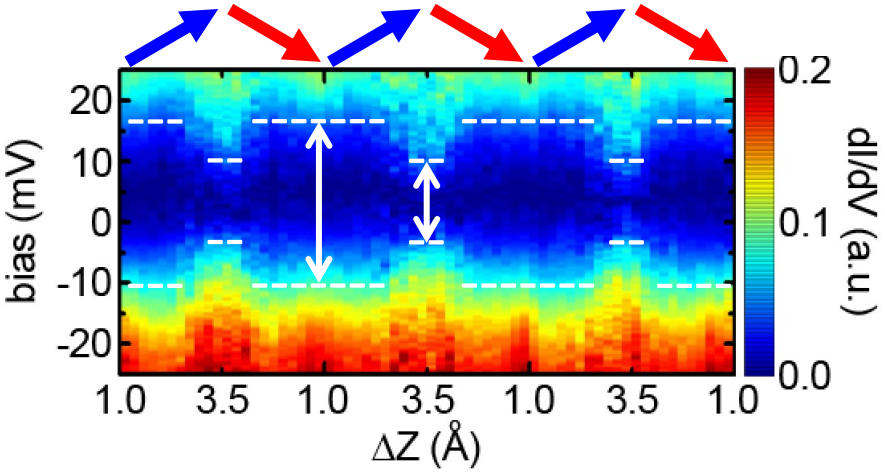


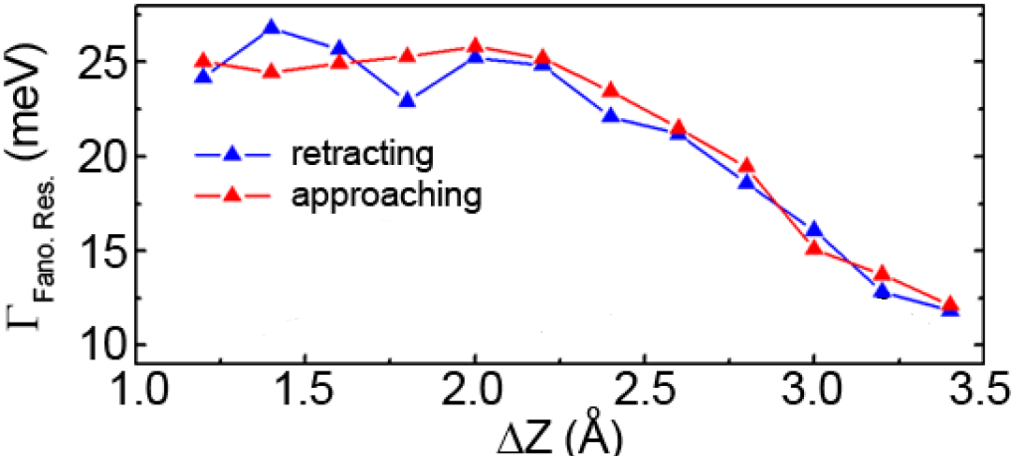


Kondo effect @ 4.8 K

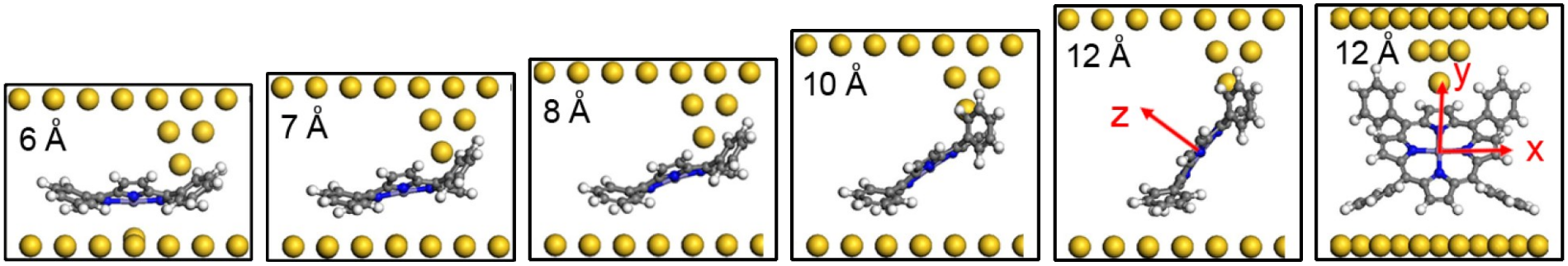
Spin crossover: width of Fano resonance



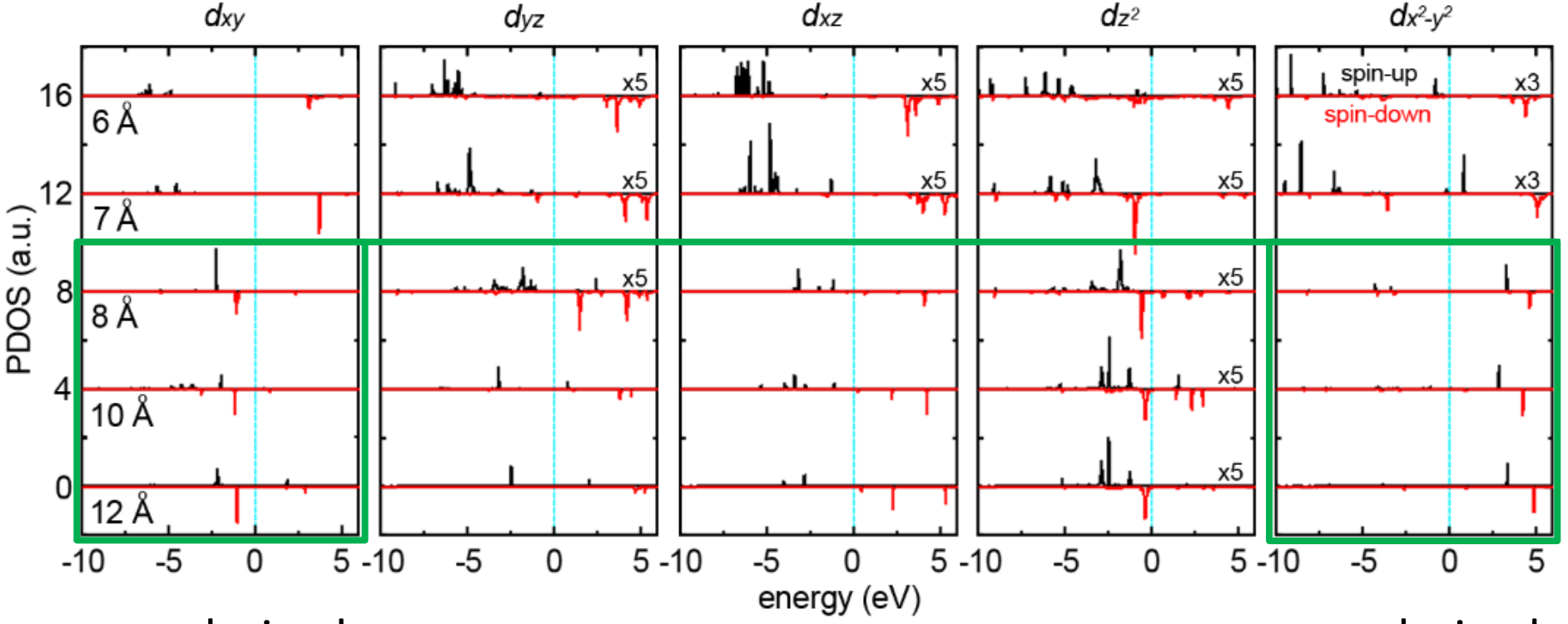




Spin crossover: DFT simulation



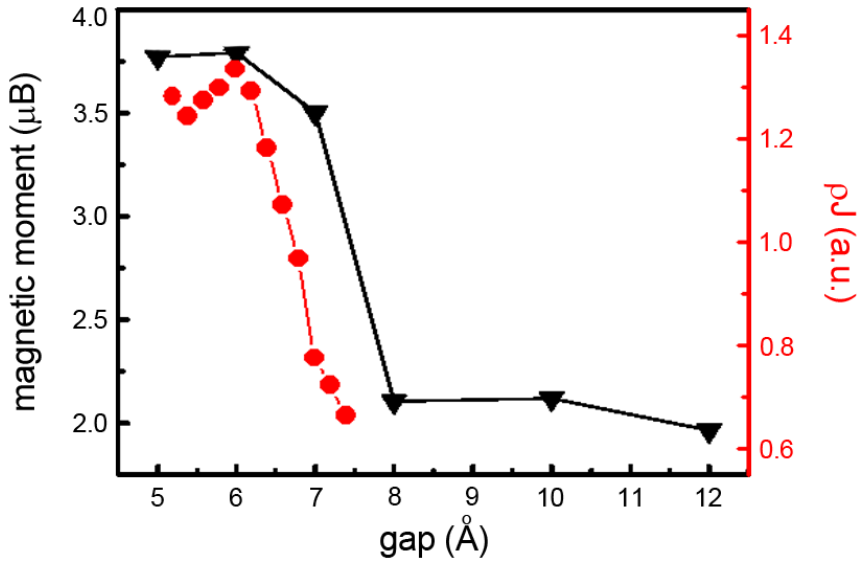
S = 2 **S = 2** **S = 1** **S = 1** **S = 1**



unpolarized

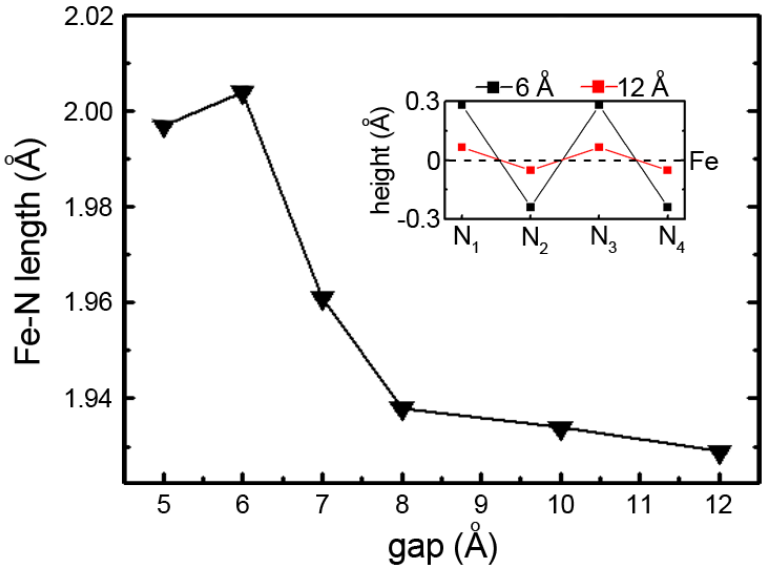
unpolarized

Spin crossover: magnetic moment & Fe-N bond length



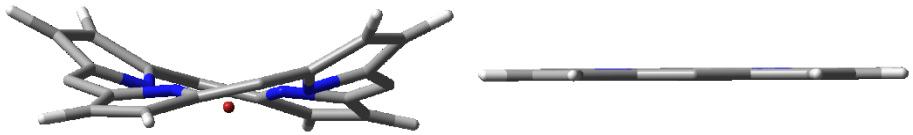
$$T_K \approx \frac{\omega_0}{k_B} \exp\left(\frac{1}{J\rho}\right)$$

ρJ ➔ spin density

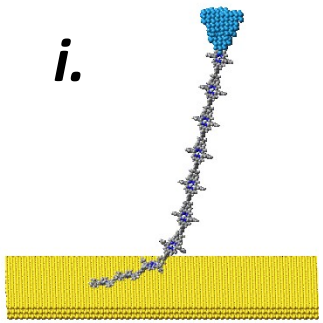


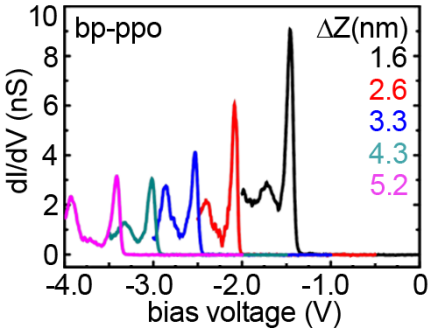
Porphyrin conformation:

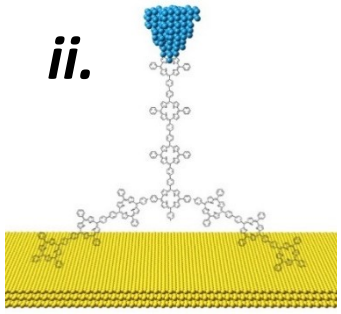
Saddle ⟷ ***planar***

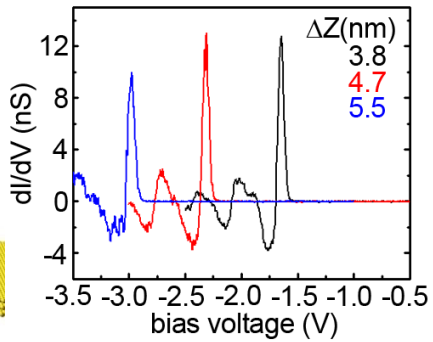


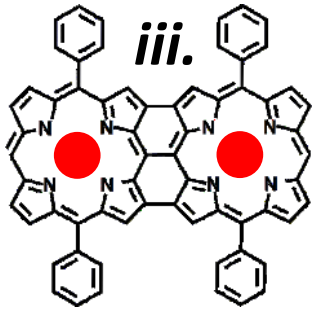
Summary

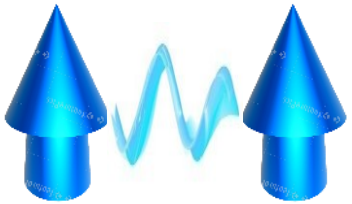

i.

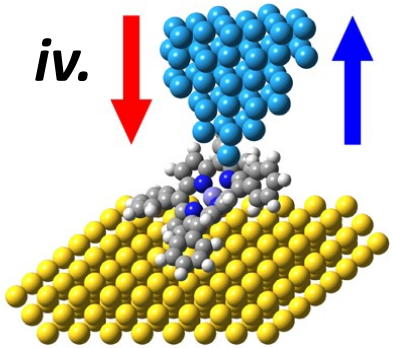

bp-ppo
ΔZ(nm)
1.6
2.6
3.3
4.3
5.2
dI/dV (nS)
bias voltage (V)

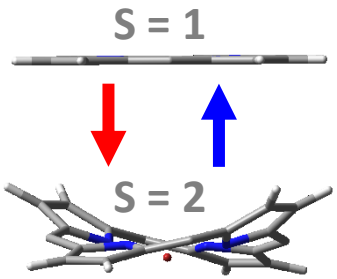

ii.


ΔZ(nm)
3.8
4.7
5.5
dI/dV (nS)
bias voltage (V)


iii.




iv.


S = 1
S = 2

Publications

1. **Kuang G**, Rubio-Verdu C, *et al.* Indirect Spin-Spin Coupling through Molecular Backbone. *in preparation.*
2. **Kuang G**, Yan L, *et al.* Negative Differential Conductance Observed in Poly-Porphyrin Oligomers with Junction Morphology. *in preparation.*
3. **Kuang G**, Zhang Q, Lin T, Pang R, Shi X, Xu H, *et al.* Mechanically-Controlled Reversible Spin Crossover of Single Fe-Porphyrin Molecules. *ACS Nano* 2017, **11**(6)**:** 6295-6300.
4. Zhang Q, Zheng X, **Kuang G**, Wang W, Zhu L, Pang R, *et al.* Single-Molecule Investigations of Conformation Adaptation of Porphyrins on Surfaces. *J Phys Chem Lett* 2017, **8**(6)**:** 1241-1247.
5. Zhao Y-L, Wang W, Qi F, Li J-F, **Kuang G**, Zhang R-Q, *et al.* Donor/Acceptor Properties of Aromatic Molecules in Complex Metal–Molecule Interfaces. *Langmuir* 2017, **33**(2)**:** 451-458.
6. Yan L, **Kuang G**, Zhang Q, Shang XS, Liu PN, Lin N. Self-Assembly of a Binodal Metal-Organic Framework Exhibiting a Demi-Regular Lattice. *Faraday Discuss* 2017.
7. **Kuang G**, Chen S-Z, Wang W, Lin T, Chen K, Shang X, *et al.* Resonant Charge Transport in Conjugated Molecular Wires beyond 10 nm Range. *J Am Chem Soc* 2016, **138**(35)**:** 11140-11143.
8. Lyu G, Zhang Q, Urgel JI, **Kuang G**, Auwarter W, Ecija D, *et al.* Tunable lanthanide-directed metallosupramolecular networks by exploiting coordinative flexibility through ligand stoichiometry. *Chem Commun* 2016, **52**(8)**:** 1618-1621.
9. Zhang Q, **Kuang G**, Pang R, Shi X, Lin N. Switching Molecular Kondo Effect via Supramolecular Interaction. *ACS Nano* 2015, **9**(12)**:** 12521-12528.
10. Wang W, Pang R, **Kuang G**, Shi X, Shang X, Liu PN, *et al.* Intramolecularly resolved Kondo resonance of high-spin Fe(II)-porphyrin adsorbed on Au(111). *Phys Rev B* 2015, **91**(4)**:** 045440.
11. **Kuang G**, Zhang Q, Li DY, Shang XS, Lin T, Liu PN, *et al.* Cross-Coupling of Aryl-Bromide and Porphyrin-Bromide on an Au(111) Surface. *Chem Eur J* 2015, **21**(22)**:** 8028-8032.
12. Lin T, **Kuang G**, Wang W, Lin N. Two-Dimensional Lattice of Out-of-Plane Dinuclear Iron Centers Exhibiting Kondo Resonance. *ACS Nano* 2014, **8**(8)**:** 8310-8316.
13. Lin T, **Kuang G**, Shang XS, Liu PN, Lin N. Self-assembly of metal-organic coordination networks using on-surface synthesized ligands. *Chem Commun* 2014, **50**(97)**:** 15327-15329.
14. Wang S, Wang W, Tan LZ, Li XG, Shi Z, **Kuang G**, *et al.* Tuning Two-Dimensional Band Structure of Cu(111) Surface-State Electrons that Interplay with Artificial Supramolecular Architectures. *Phys Rev B* 2013, **88**(24)**:** 245430.

Acknowledgements

- Prof. Lin Nian (*supervisor*)
- Prof. Jose Ignacio Pascual (*CIC nanoGUNE, San Sebastian, Spain*)
- Prof. Chen Keqiu (*Hunan University*)
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Acknowledgements

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- Prof. Yongli MI
- Prof. Nian LIN (*Supervisor*)

[redacted]