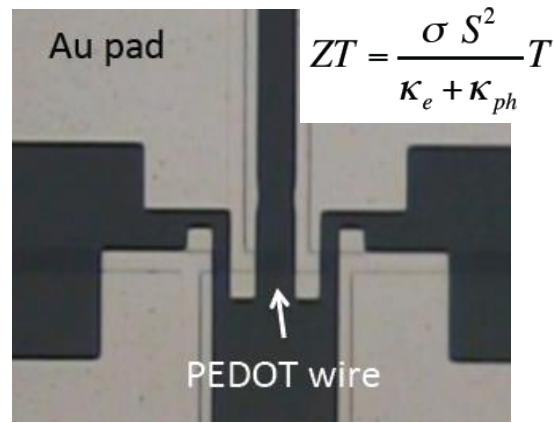
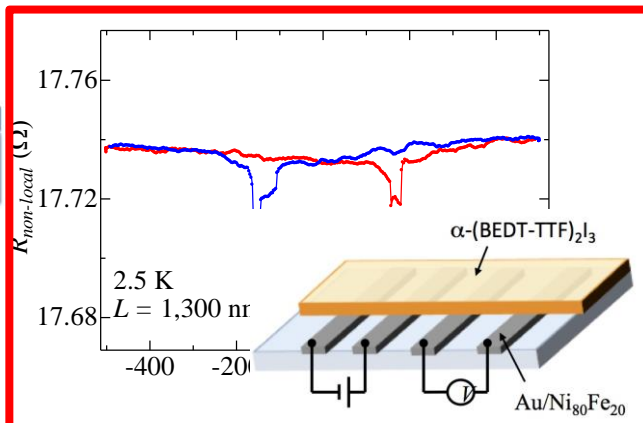
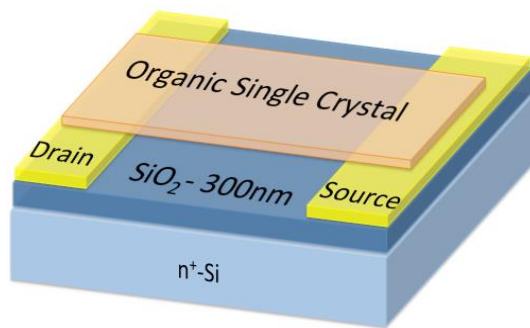


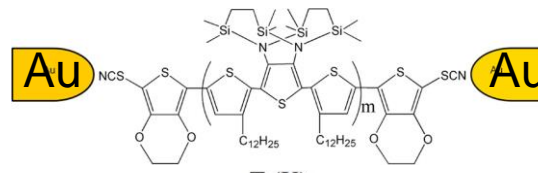
有機スピントロニクス Organic Spintronics

大阪大学院基礎工学研究科
Graduate School of Engineering Science
大戸達彦
Tatsuhiko Ohto

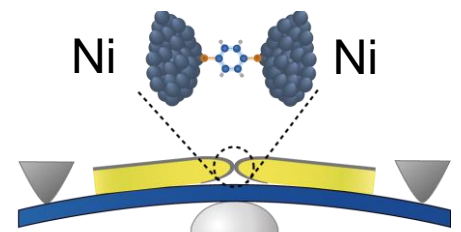
Thin Film



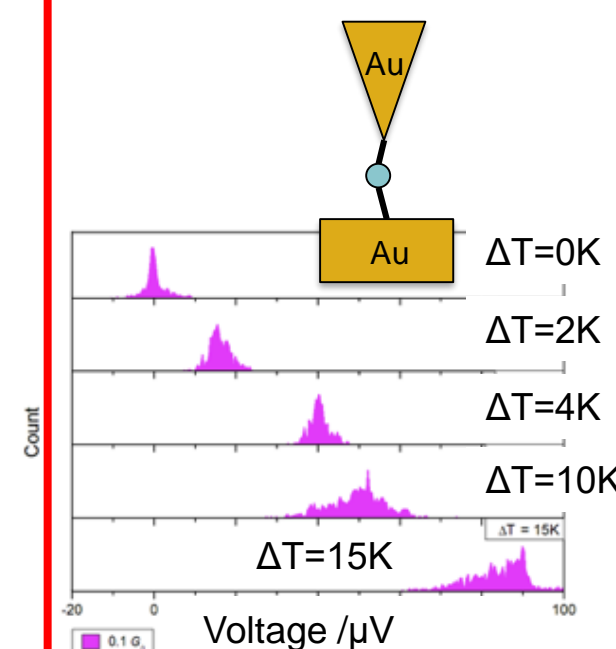
Electronics



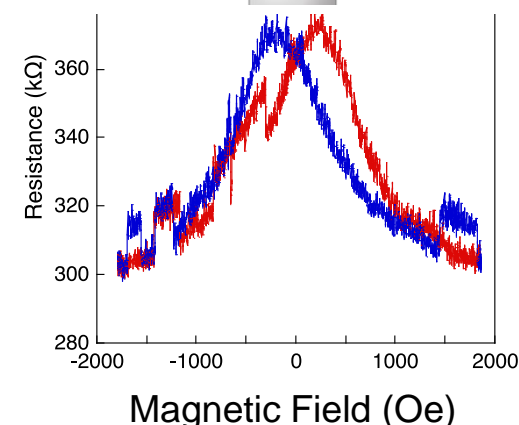
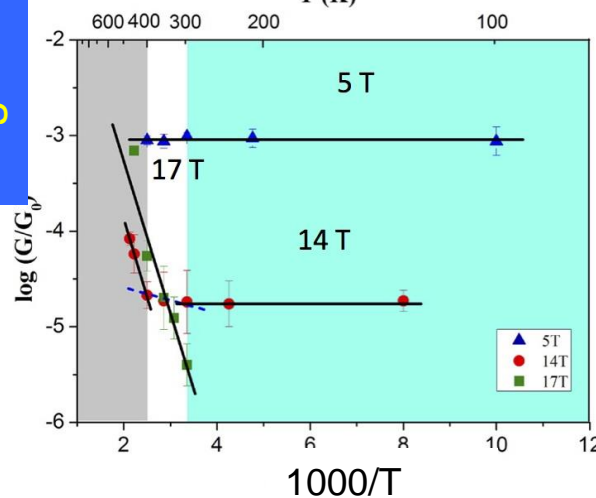
Spintronics



Thermoelectronics



Single Molecule



Spintronics

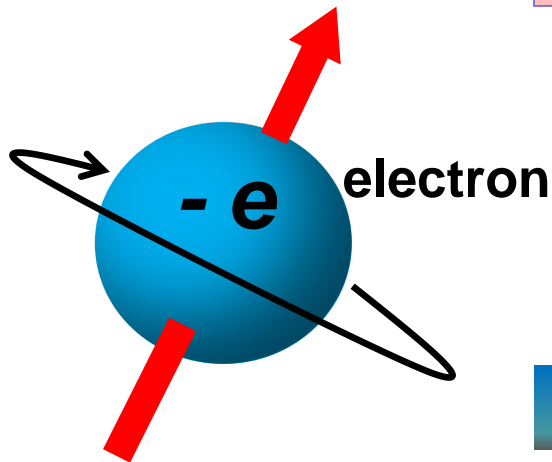
Spin

Magnetics

Spintronics

- Hard disk
- Magnet
- Sensor
- etc...

- TMR head
- ReRAM
- Spin Seebeck
- Spin Transistor
- etc...

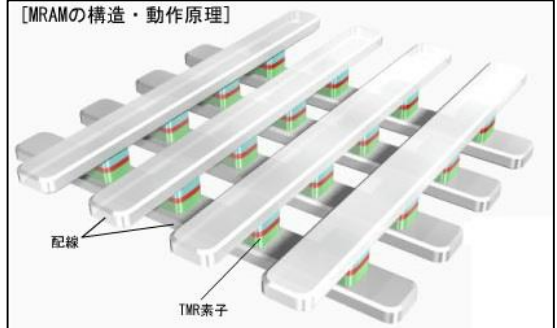


Electronics

- Transistor
- Laser
- LSI
- etc...

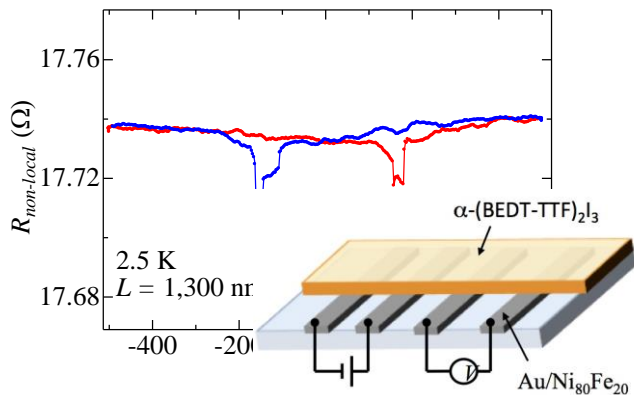


[MRAMの構造・動作原理]

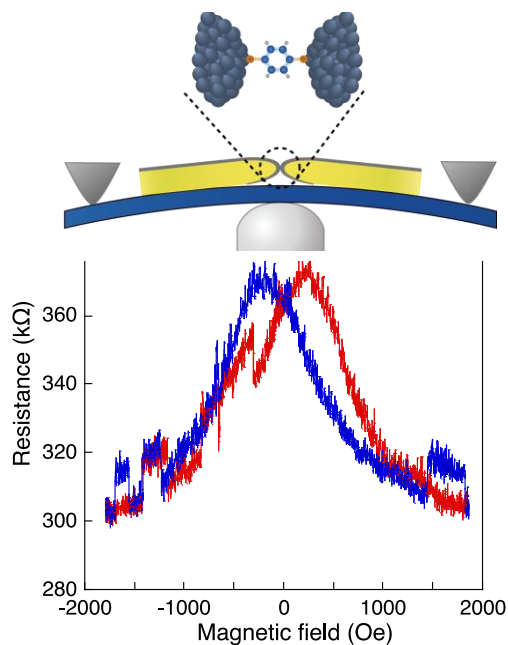


Electron

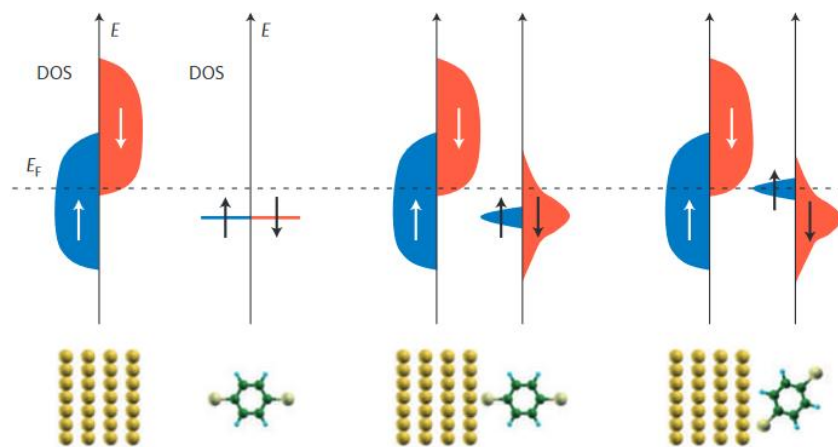
Why organic?



- Weak spin-orbit interaction
- Molecular design
- Abundant
- Frexible, light weight



Possibility of highly efficient spin valve device



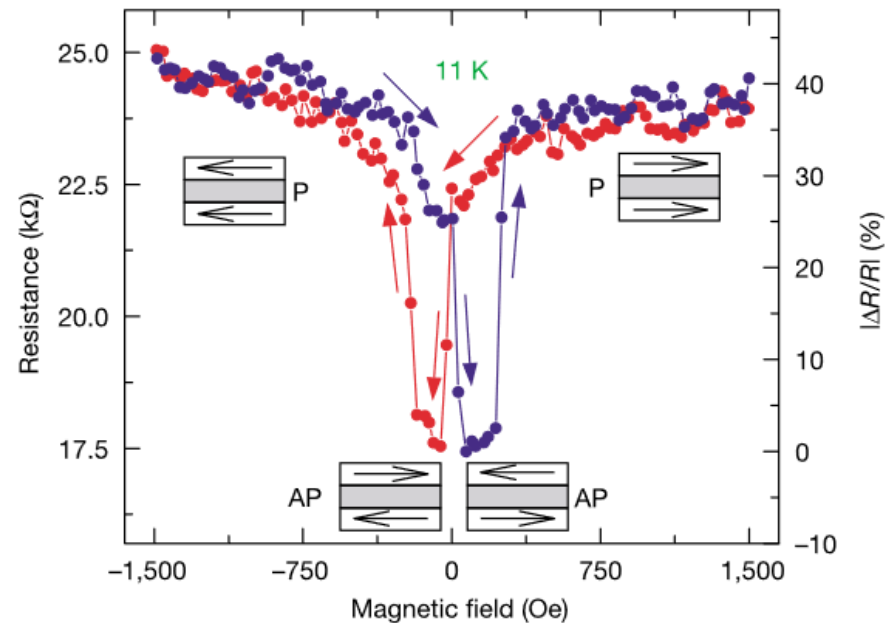
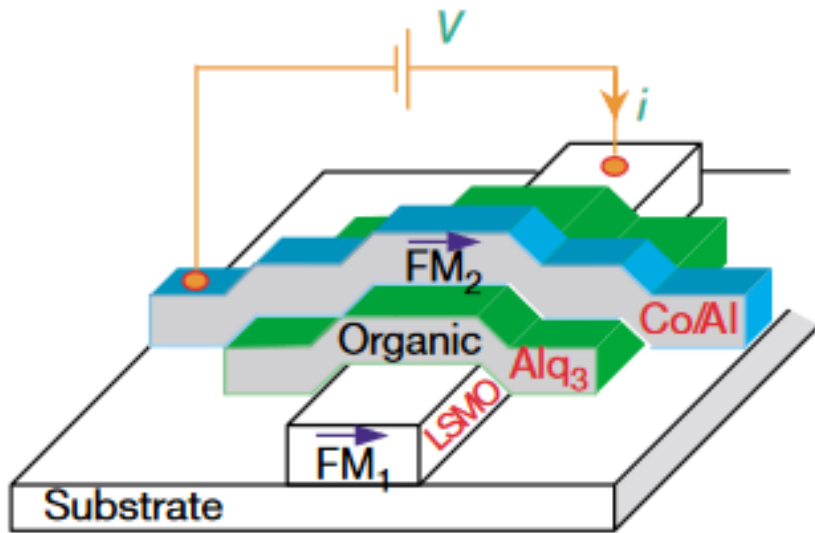
Outline

1. Organic Thin Film Spin Valve
2. Single Molecular Spin Valve
3. Introduction of Non-equilibrium Green's Function (NEGF) method
4. NEGF-DFT and its applications
5. Organic Magnetoresistance, OMAR

1. Organic Thin Film Spin Valve

Organic Spin Valve

2004 Vardeny
Organic Spin Valve

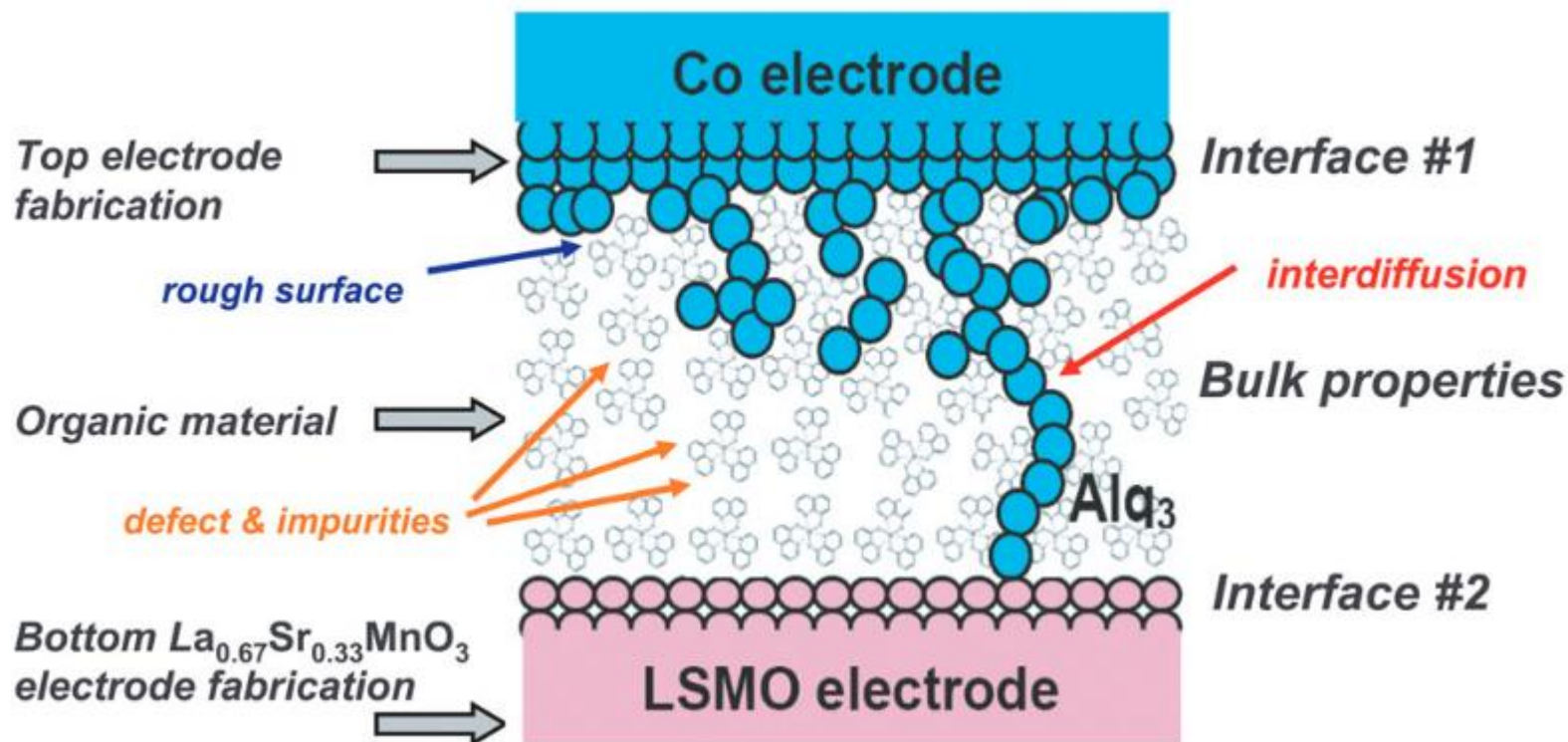


Xiong *et al.* Nature **427** (2004) 821

Weak spin-orbit interaction

Molecular design, light weight

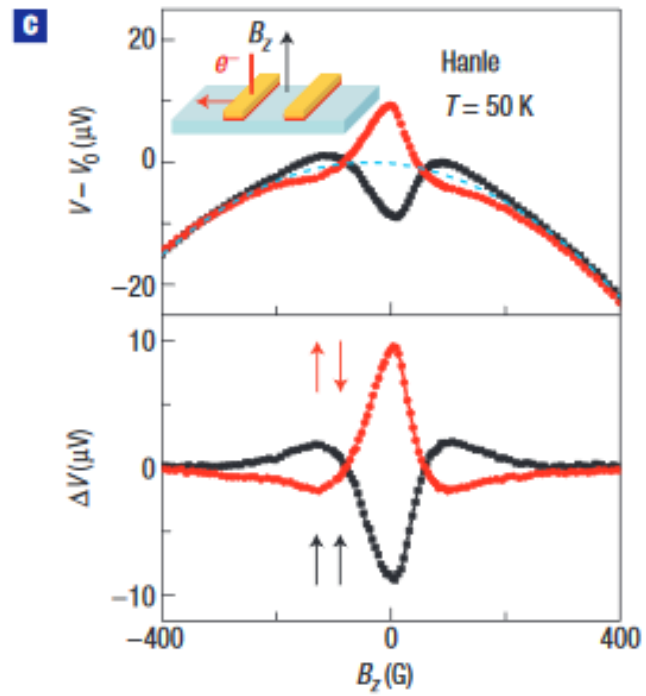
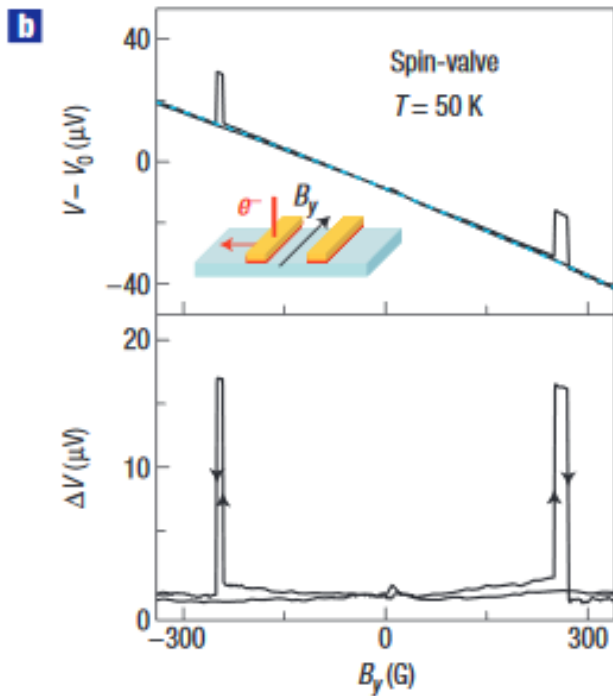
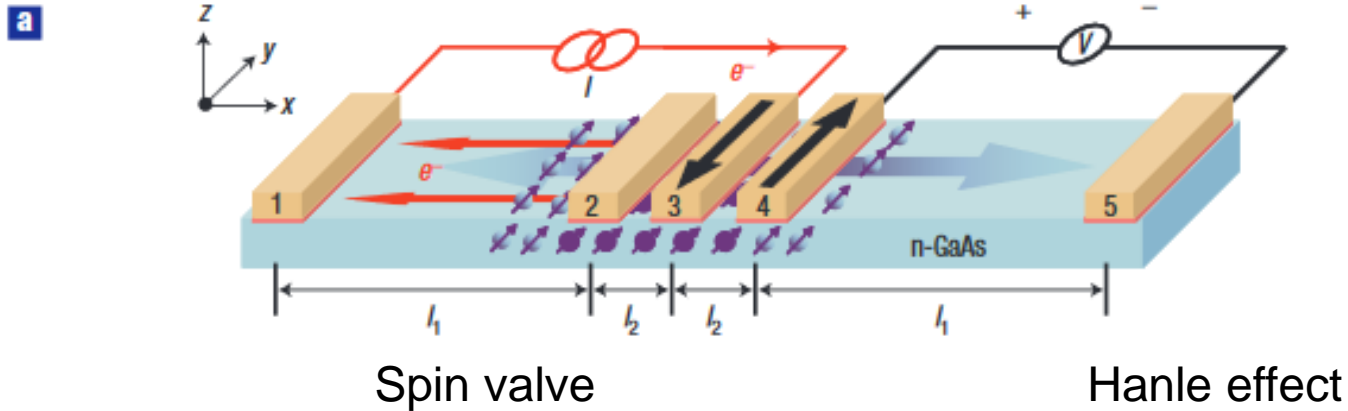
Problems of vertical devices?



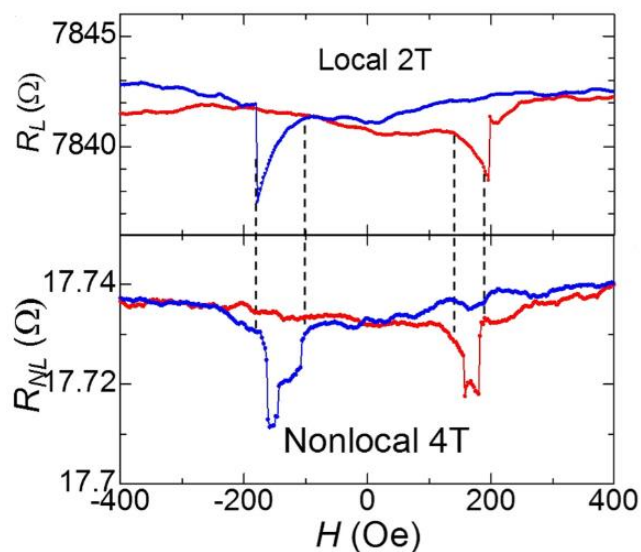
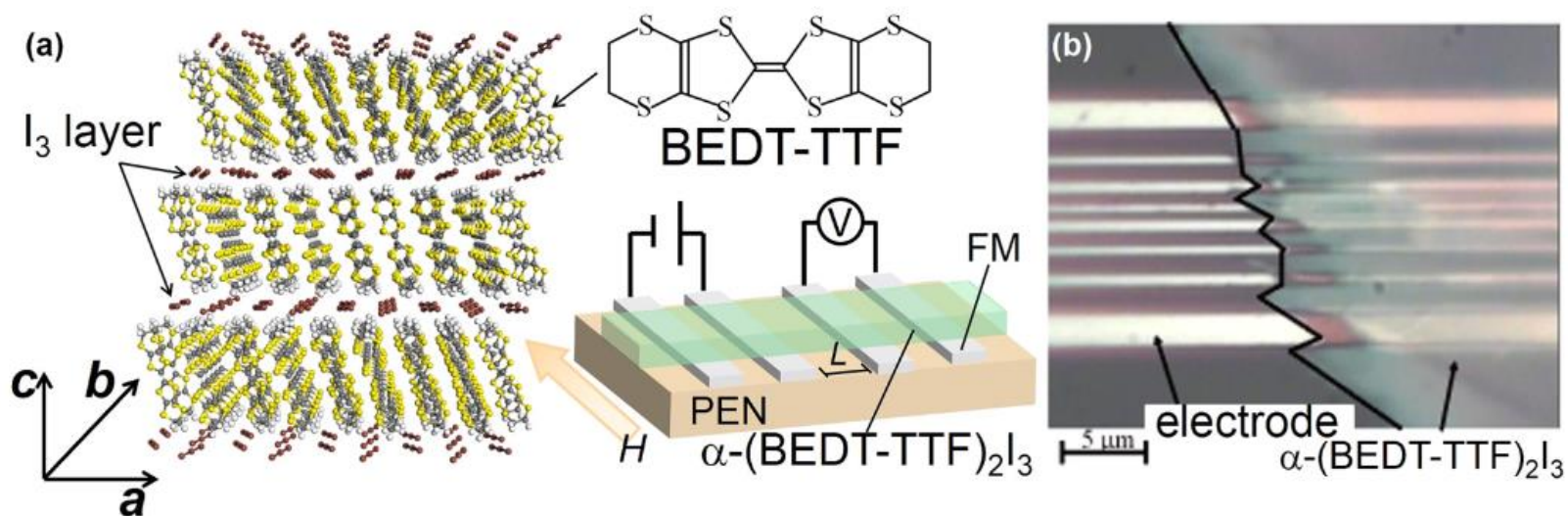
D. Sun et al., *Chem. Commun.*, **50**, 1781 (2014).

Can we inject spin into organic materials?

Lateral Device

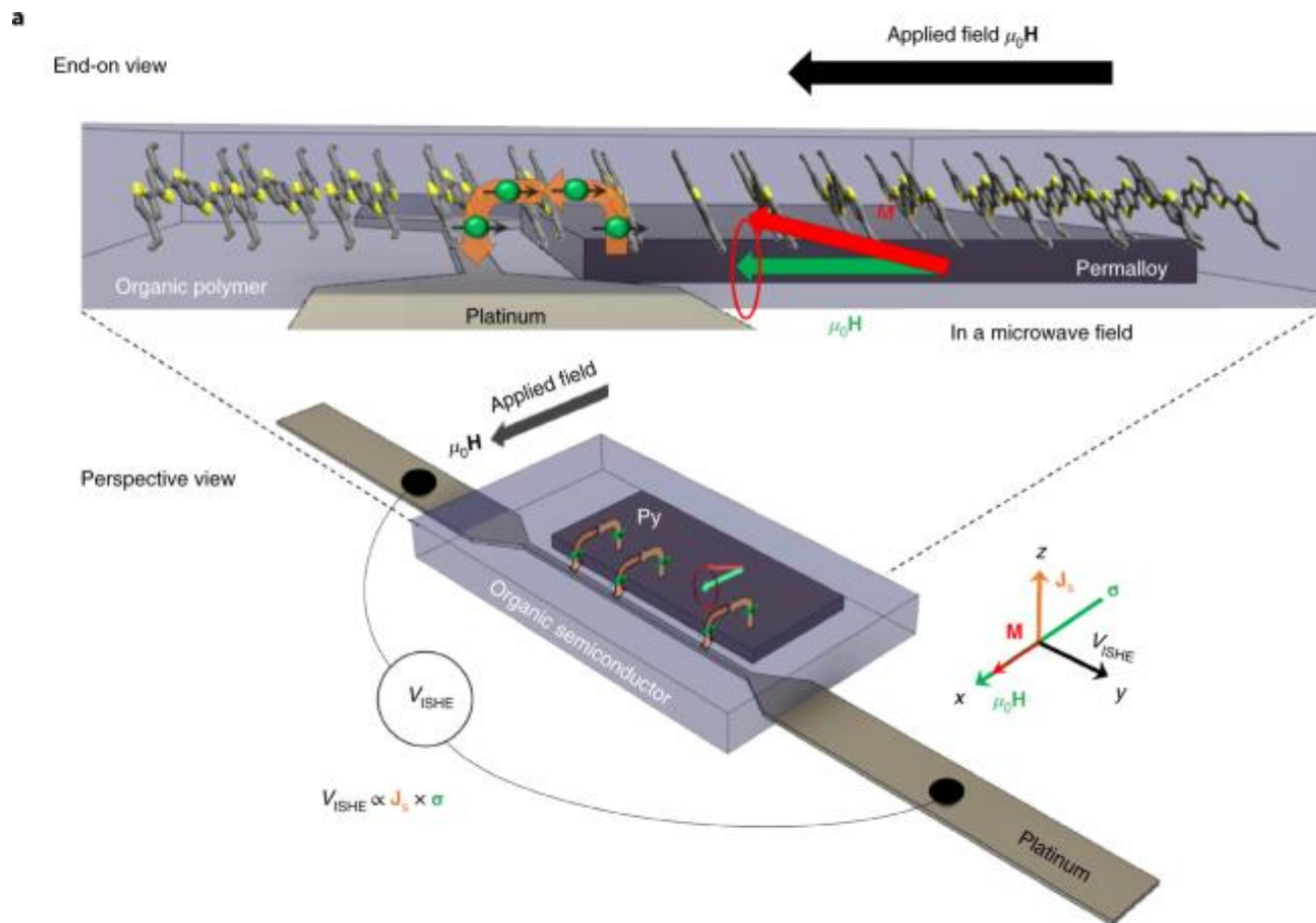


Lateral Organic Spin Valve



Pressured $\alpha-(BEDT-TTF)_2I_3$ Crystal

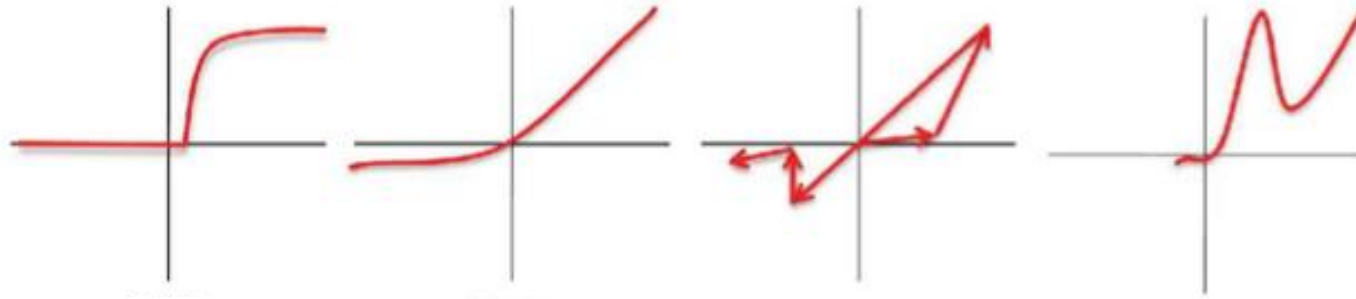
Spin-pumping



The spin diffusion length is more than 1 μm

2. Single Molecular Spin Valve

Single Molecular Electronics

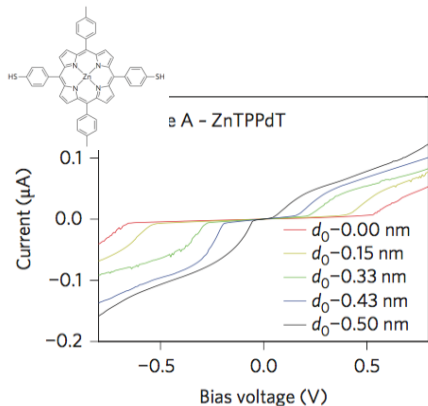


Threshold
*Coulomb blockade

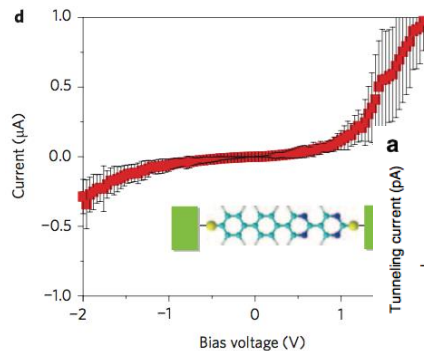
Rectification
(Diode)

Hysteresis
(Memory/Switch)

Negative differential
resistance (NDR)

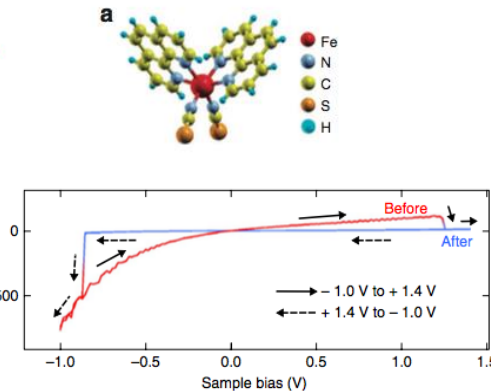


ML Perrin et al., Nature Nanotech. 8, 282 (2013).

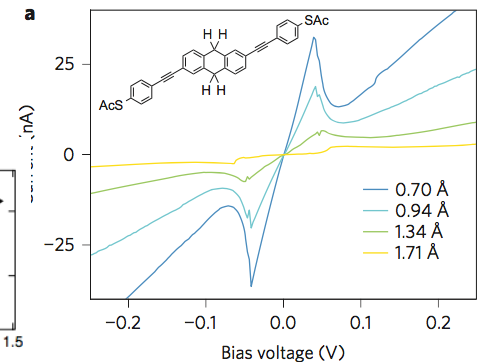


I. Diez-Perez et al., Nature Chem. 1, 635 (2009).

B. Capozzi et al., Nature Nanotech. 10, 522 (2015).
(Asymmetric electrode)

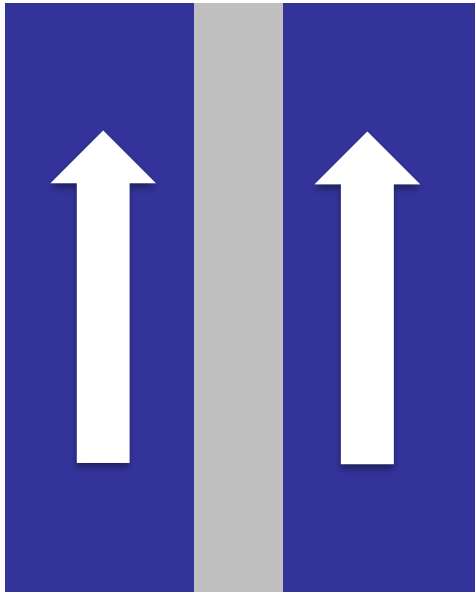


Spin-cross over; T. Miyamachi et al., Nature Comm. 3, 938 (2012)
Mg-Porphine; S. Saha et al., Apl. Mater&Inter., 7, 10085 (2015).

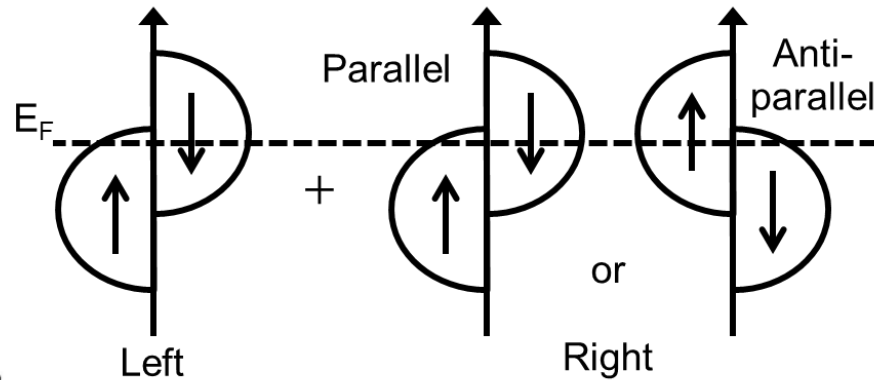


ML Perrin et al., Nature Nanotech. 9, 830 (2014).
(Double barrier resonant tunneling)

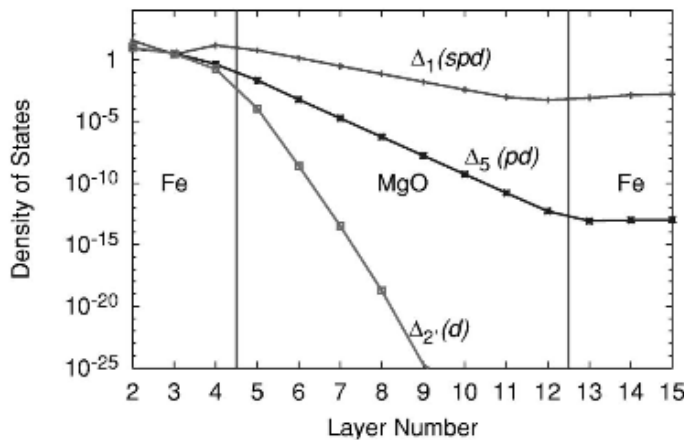
Tunneling Magnetoresistance (TMR)



- Tunneling electron through an insulator
- Spin polarization of electrodes determines the MR ratio

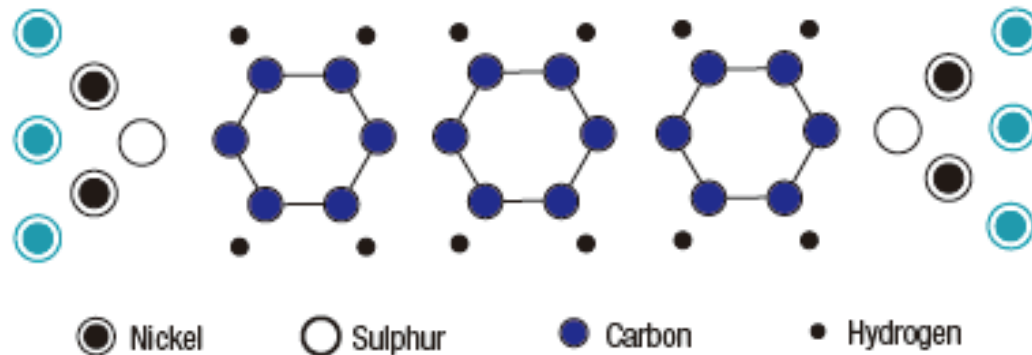


Majority Density of States for Fe|MgO|Fe

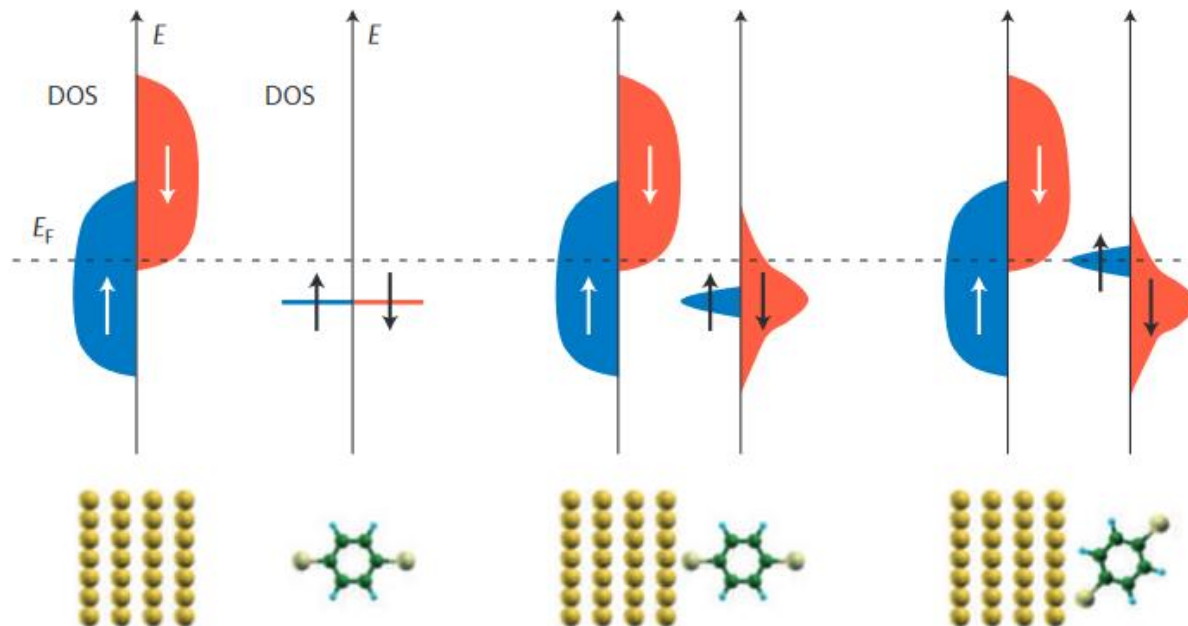


MgO crystal blocks d electron of majority spin

Single Molecular TMR Devices

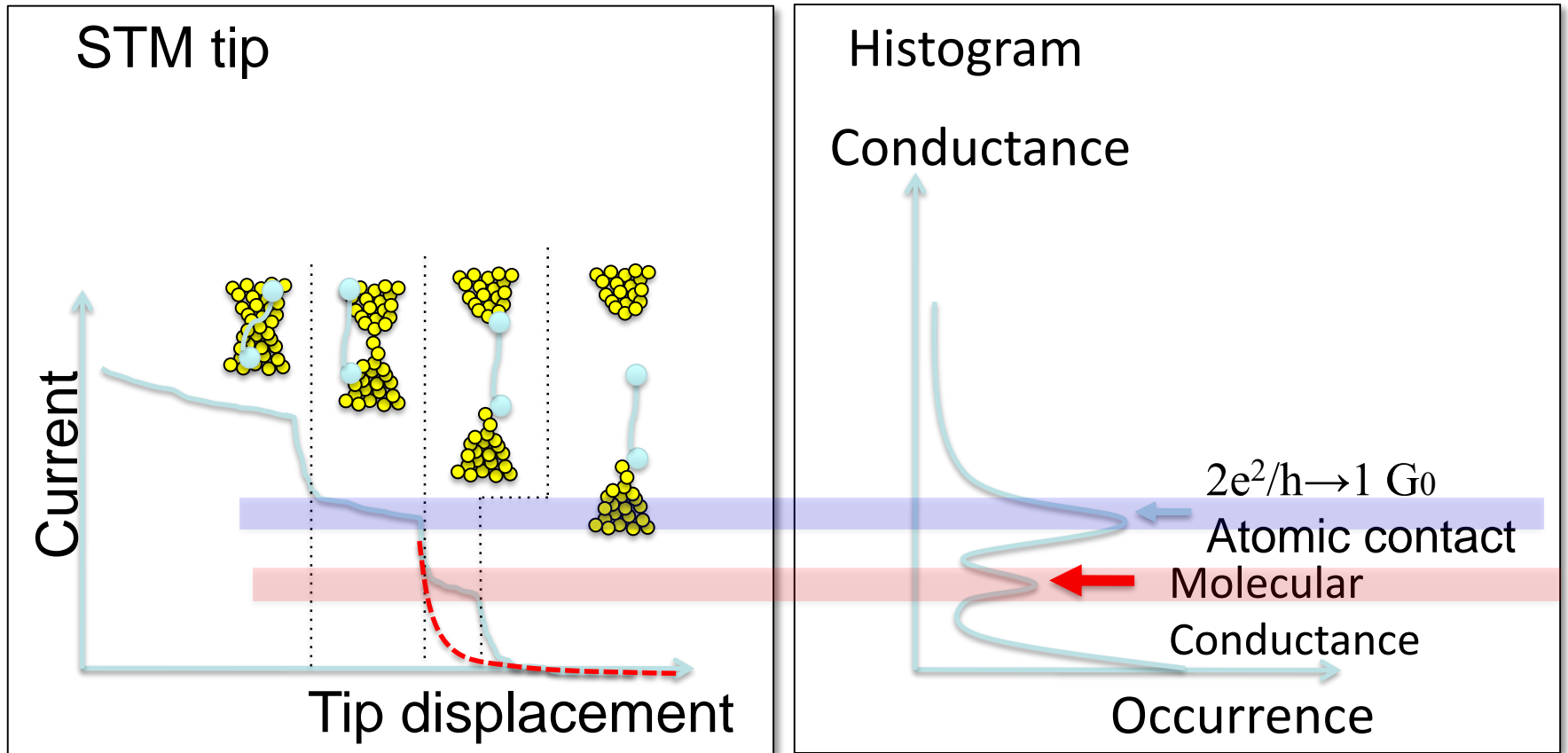


Rocha *et al.* Nat. Mater. **4** (2005) 335



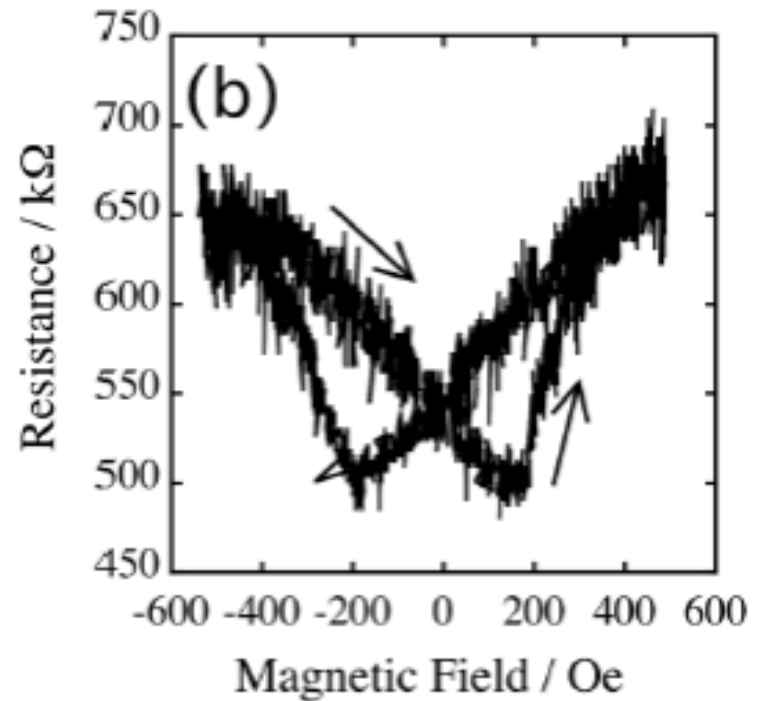
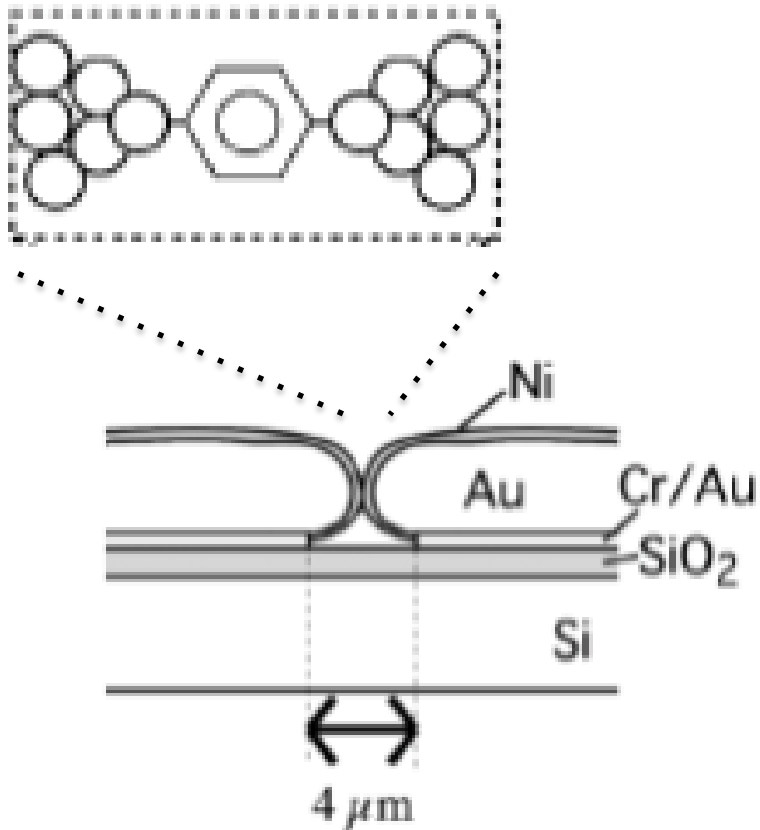
S. Sanvito Nat. Phys. **6** (2010) 562

Experimental Methods



Break Junction (BJ) Method

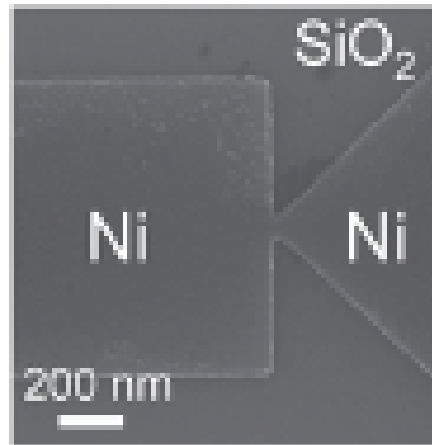
Experimental Methods



MCBJ with magnetic electrodes

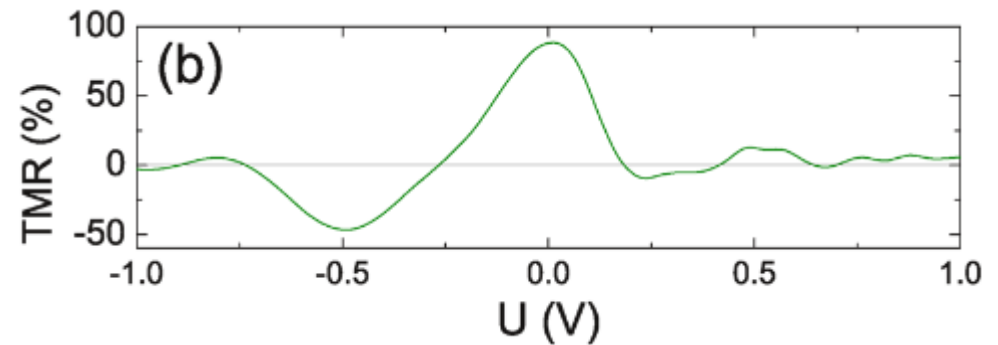
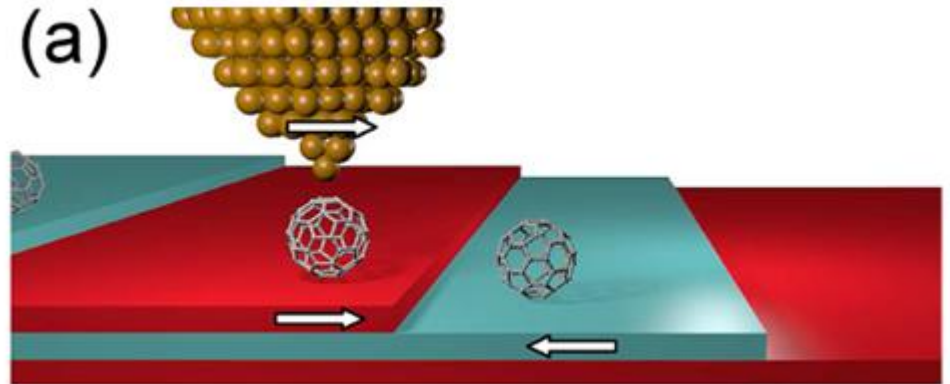
Yamada *et al.* APL **98** (2011) 053110

Experimental Methods



Electrical break junction method,
C₆₀/Ni

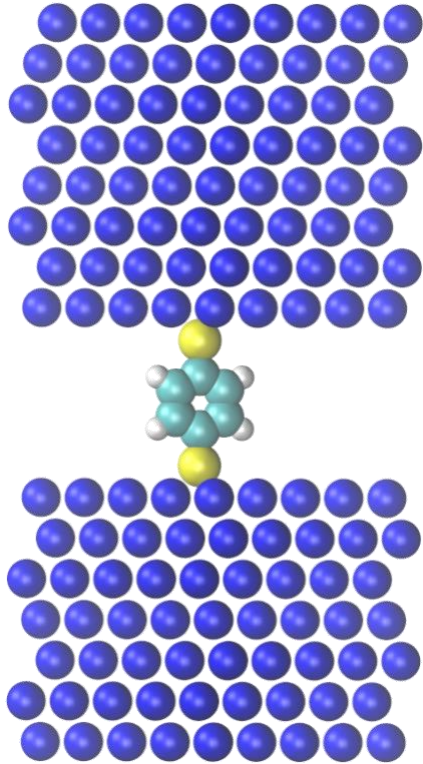
K. Yoshida *et al.* Nano Lett. **13** (2013) 481



Scanning tunneling microscopy
(STM), C₆₀/Cr(001)

S. L. Kawahara *et al.* Nano Lett. **12** (2012) 4558

Theoretical Design of Molecular Spin Valve



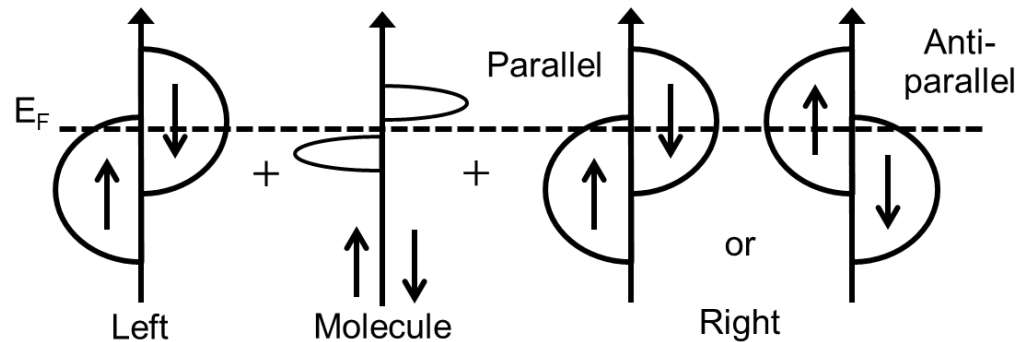
- Origin of magnetoresistance

 - TMR

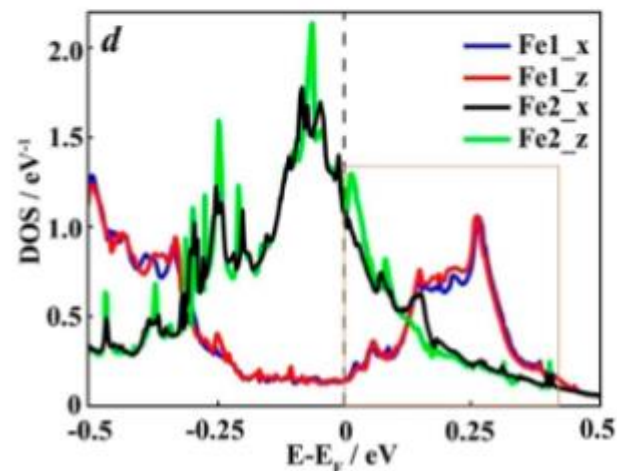
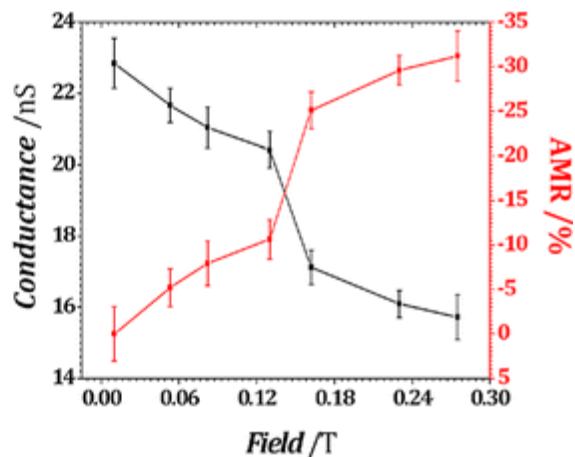
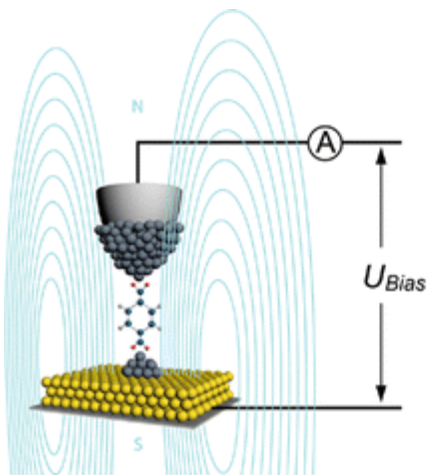
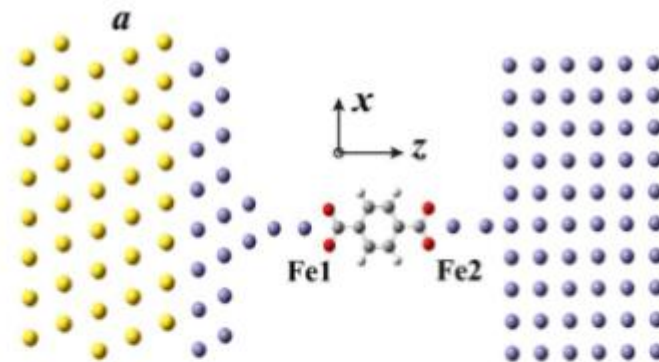
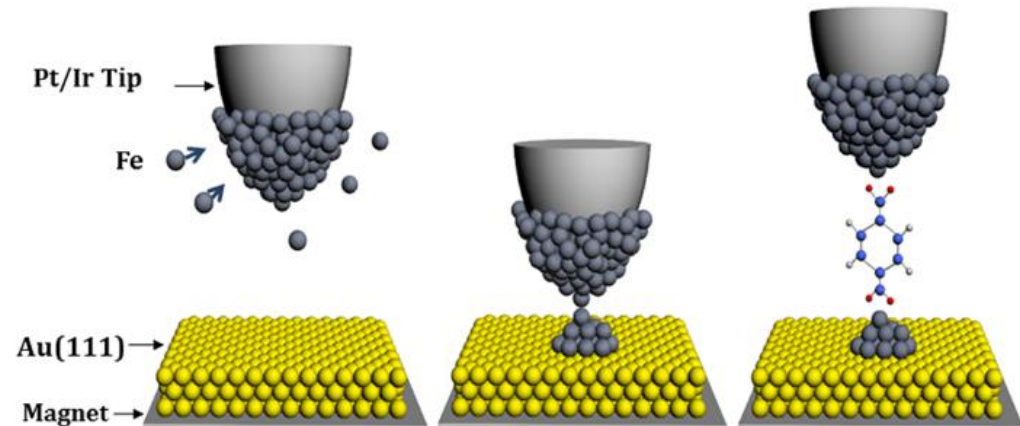
 - TAMR

- Molecular structure

- Spin filter effect



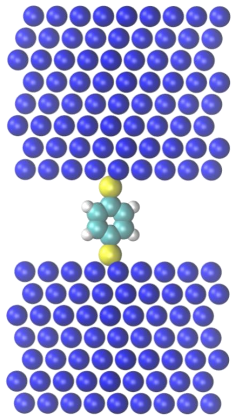
Tunneling Anisotropic MR (TAMR)



3. Non-Equilibrium Green's Function (NEGF) method

Programs

Atomic Orbital (SIESTA)



molecule
10~100 atoms

electrodes
8x8x6x2
=768 atoms(!)

TranSIESTA (Spain, Denmark)
with SIESTA

ATK (Quantum Wise)

Commercial TranSIESTA

SMEAGOL (Ireland, UK)

Spin Transport

HiRUNE (Japan, AIST)

Electron-phonon

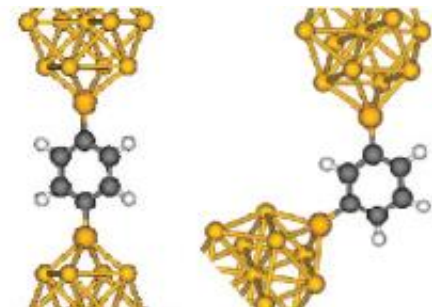
OpenMX (Japan)

Plane Wave

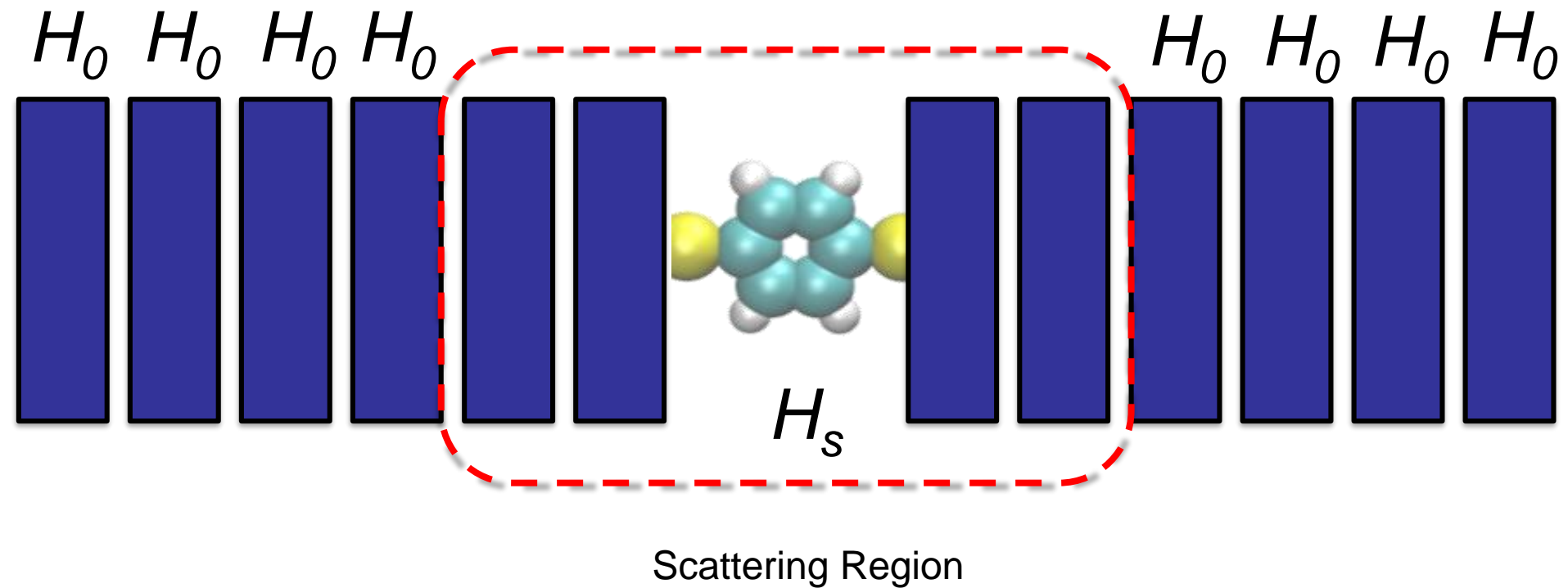
Quantum Espresso

Gaussian Basis

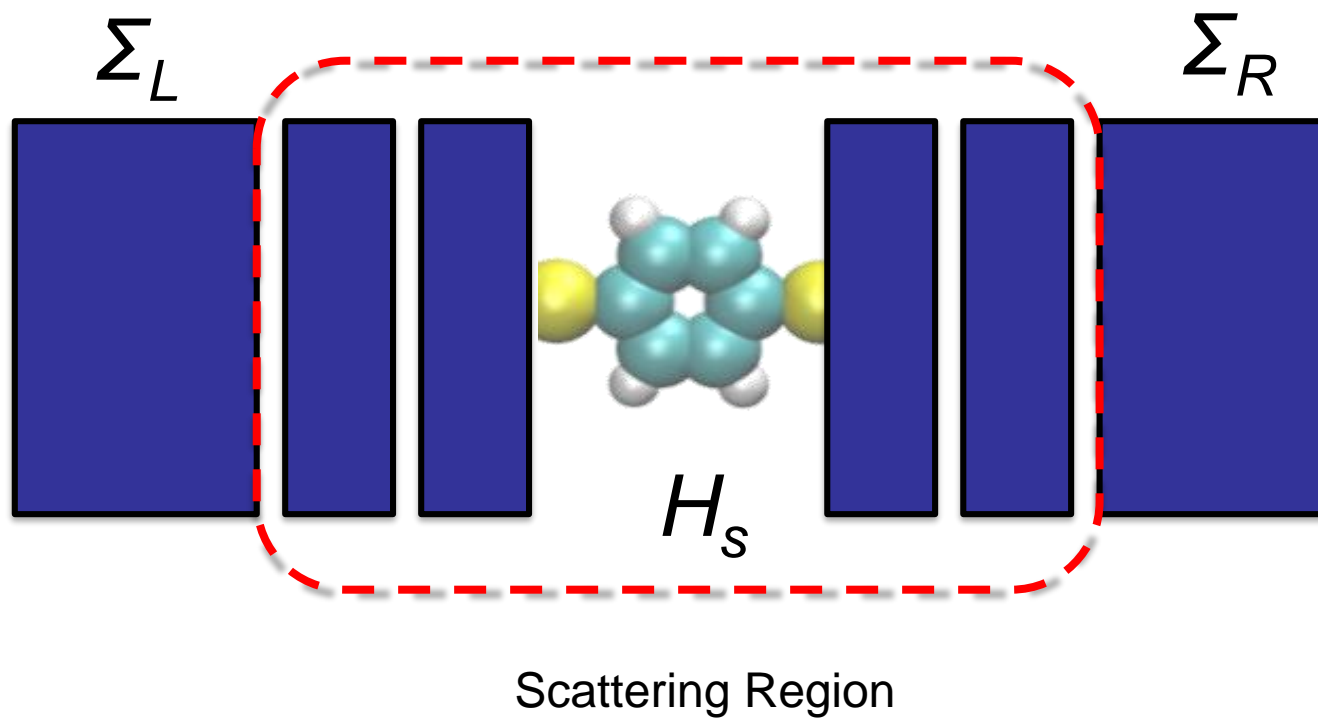
Turbomole



NEGF



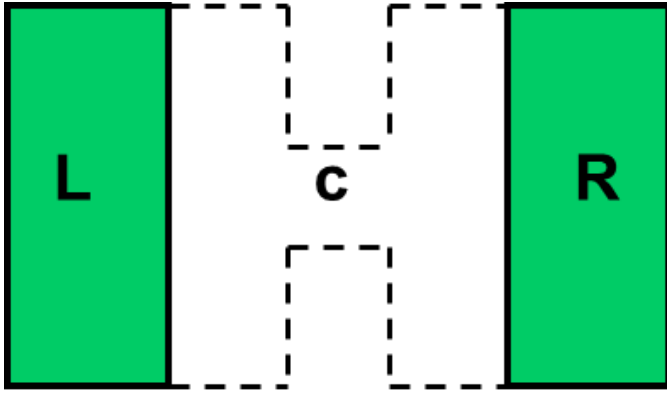
NEGF



$$\mu_L = E_F + 1/2 \text{ eV}$$

$$\mu_R = E_F - 1/2 \text{ eV}$$

NEGF



Hermitian problem for an open infinite system

$$H = H_S + H_0 + H_0 + H_0 + \dots$$

Non-Hermitian problem for a finite system

$$H = H_S + \Sigma_L + \Sigma_R$$

$$\mathbf{G}_{CC}(E) = \left(\begin{array}{ccc} ES_{LL} - \mathbf{H}_{LL} - \Sigma_L(E) & ES_{Lc} - \mathbf{H}_{Lc} & 0 \\ ES_{Lc}^\dagger - \mathbf{H}_{Lc}^\dagger & ES_{cc} - \mathbf{H}_{cc} & ES_{cR} - \mathbf{H}_{cR} \\ 0 & ES_{Rc}^\dagger - \mathbf{H}_{Rc}^\dagger & ES_{RR} - \mathbf{H}_{RR} - \Sigma_R(E) \end{array} \right)^{-1}$$

$$\mathbf{H}_{eff} = \mathbf{H} + \Sigma_L(E) + \Sigma_R(E)$$

$$\Sigma_L(E) = (ES_{LC} - \mathbf{H}_{LC})^\dagger \mathbf{G}_{LL}^0(E) (ES_{LC} - \mathbf{H}_{LC})$$



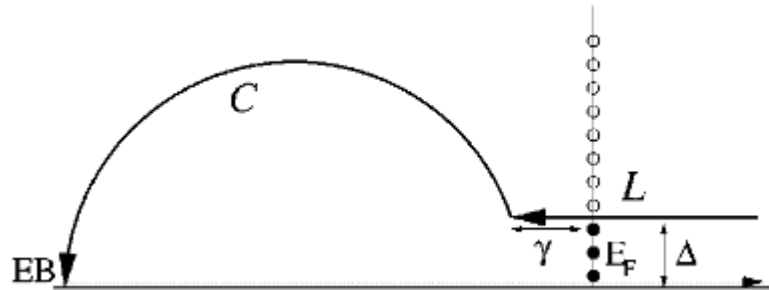
Surface Green's function

NEGF-SCF

“Lesser” Green’s function

$$\mathbf{G}_{cc}^<(E) = \mathbf{G}_{cc}(E)\mathbf{\Sigma}^<\mathbf{G}_{cc}^\dagger(E) \text{ Keldysh-Kadanoff-Baym (KKB) Equation}$$

$$\mathbf{D}_{cc} = \frac{1}{2\pi i} \int dE \mathbf{G}_{cc}^<(E)$$



Integral Contour

M. Brandbyge *et al.* Phys. Rev. B **65**(2002)165401

$$\mathbf{G}_{cc}(E) = \left(\begin{array}{ccc} ES_{LL} - \mathbf{H}_{LL} - \mathbf{\Sigma}_L(E) & ES_{Lc} - \mathbf{H}_{Lc} & 0 \\ ES_{Lc}^\dagger - \mathbf{H}_{Lc}^\dagger & ES_{cc} - \mathbf{H}_{cc} & ES_{cR} - \mathbf{H}_{cR} \\ 0 & ES_{Rc}^\dagger - \mathbf{H}_{Rc}^\dagger & ES_{RR} - \mathbf{H}_{RR} - \mathbf{\Sigma}_R(E) \end{array} \right)^{-1}$$

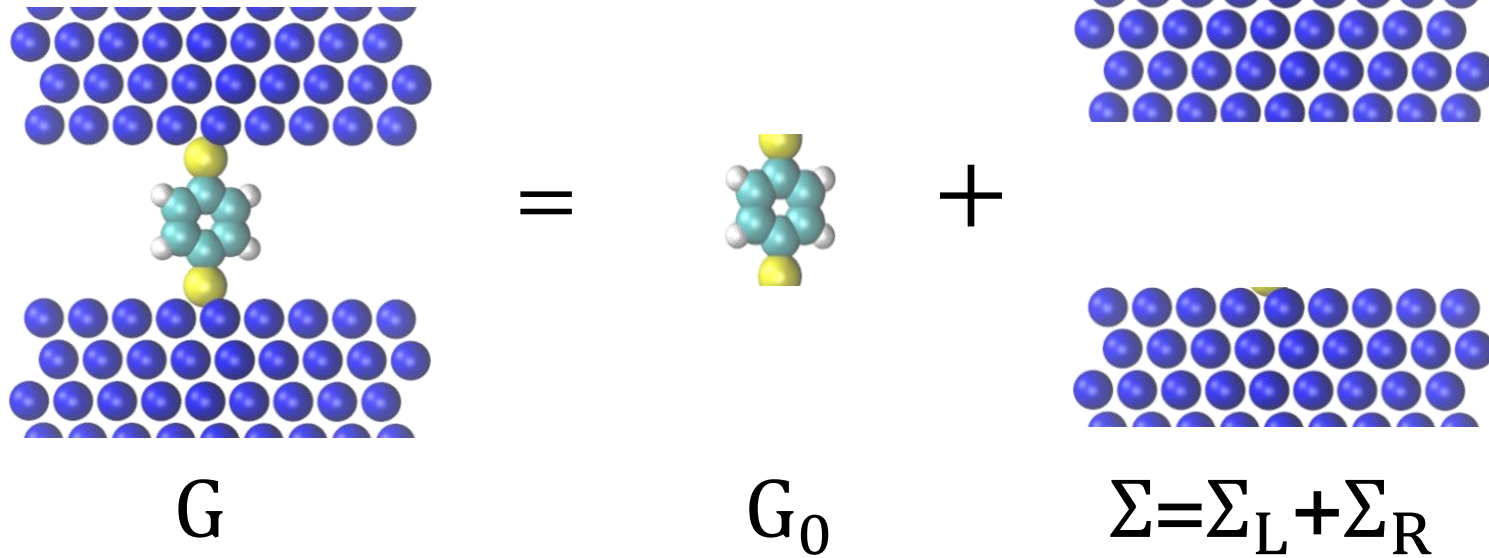
Convergence of density matrix

NEGF

$$G = G_0 + G_0 \Sigma G \quad \text{Dyson Equation}$$

$$\Gamma_L(E) = i(\Sigma_L(E) - \Sigma_L^\dagger(E))$$

$$T = \text{Tr}[G \Gamma_L G^\dagger \Gamma_R]$$



We can add any interactions through Σ

$\Sigma_{L/R}$ ··· left/right electrodes Σ_{e-ph} ··· electron-phonon interaction

$$G^< = G \Sigma^< G^\dagger \quad \text{Keldysh-Kadanoff-Baym (KKB) Equation}$$

↑ lesser self energy

4. NEGF-DFT and its application

What we can obtain...

- Transmission Function

$$T(E, V_b) = \text{Tr} \left[\boldsymbol{\Sigma}_L^<(E) \mathbf{G}_{CC}^>(E) - \boldsymbol{\Sigma}_L^>(E) \mathbf{G}_{CC}^<(E) \right] = \text{Tr} \left[\boldsymbol{\Gamma}_L \left(E + \frac{V_b}{2} \right) \mathbf{G}_{CC}(E) \boldsymbol{\Gamma}_R \left(E - \frac{V_b}{2} \right) \mathbf{G}_{CC}^\dagger(E) \right]$$

- TMR ratio

The ratio of the transmission function with parallel/antiparallel magnetization

- Current voltage characteristics

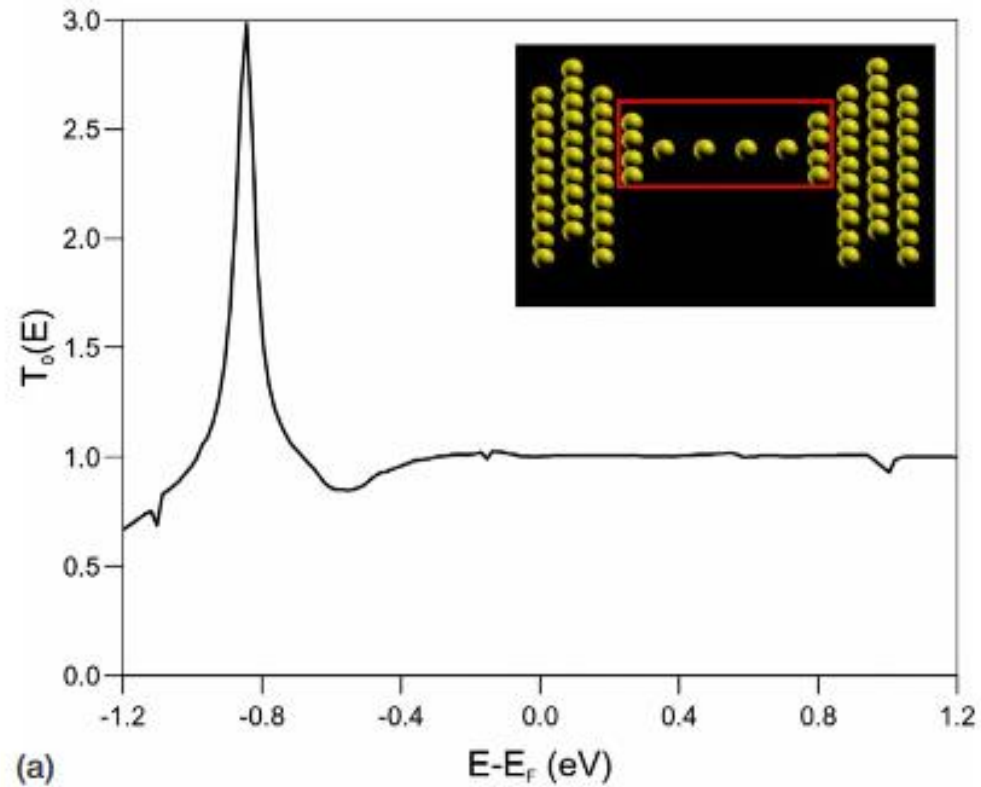
$$I(V_b) = \frac{1}{\pi} \int dE T(E, V_b) \left(f(E - \mu_L) - f(E - \mu_R) \right)$$

- Spin Transfer Torque

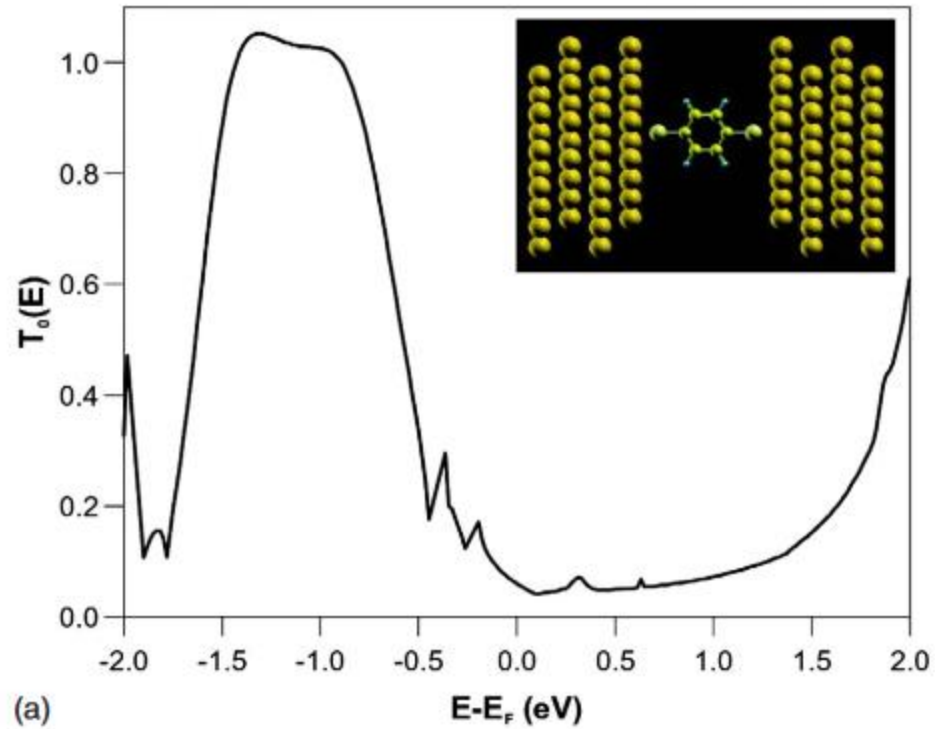
with SMEAGOL

- TAMR

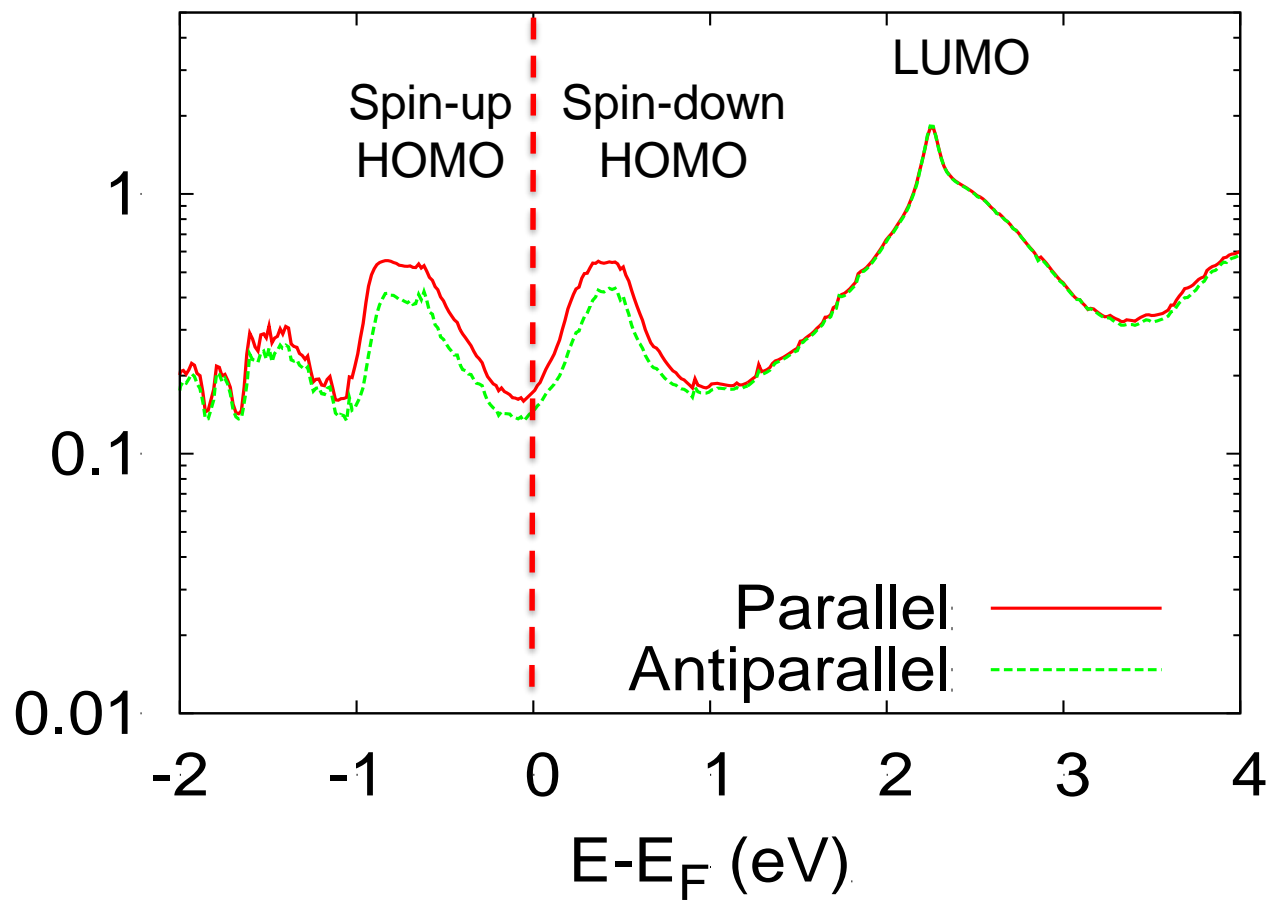
Gold wire



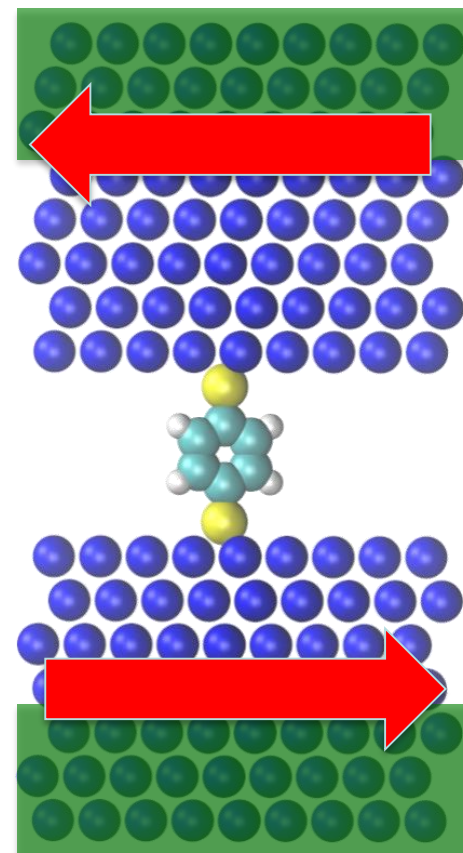
Au-BDT-Au



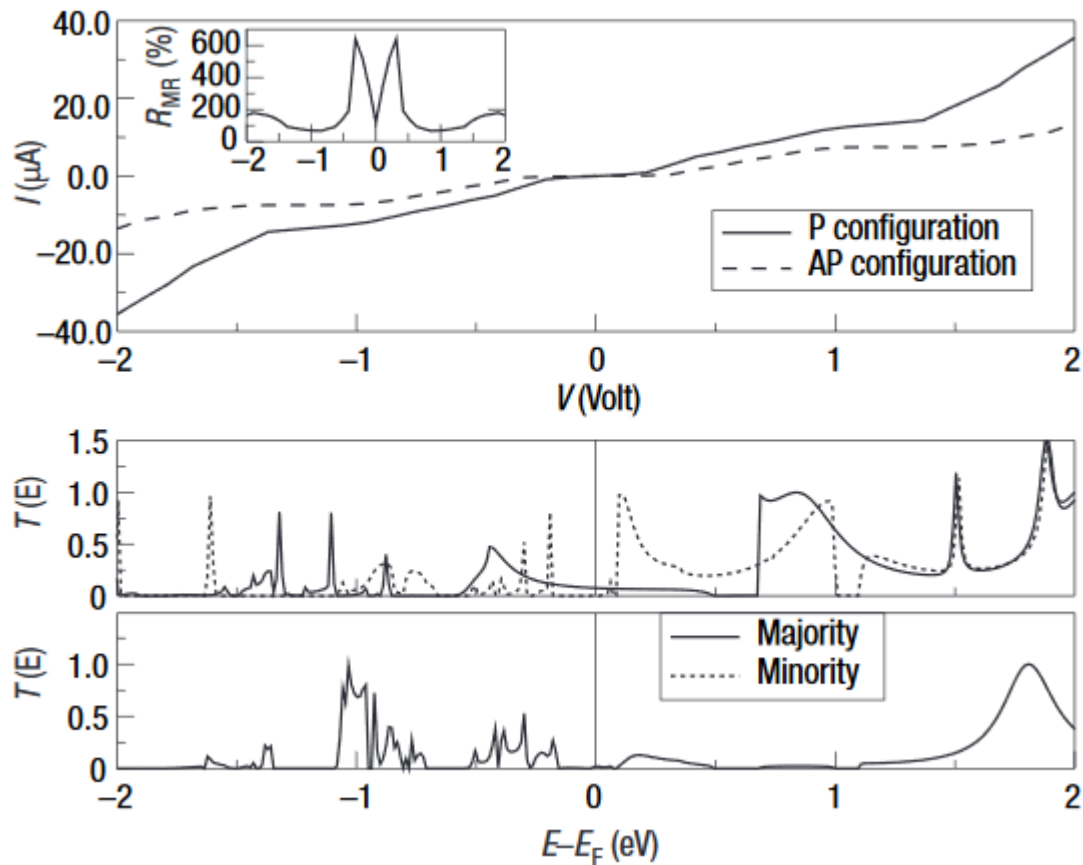
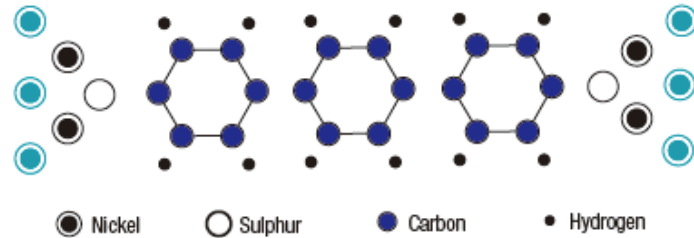
Ni-BDT-Ni



TMR~20%



Possibility of higher TMR



Thermoelectric device



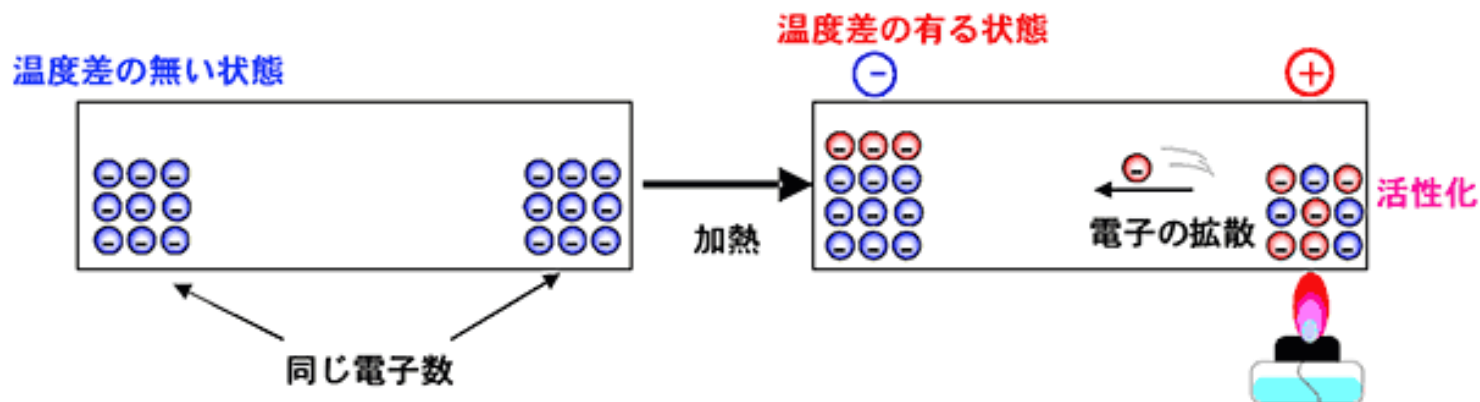
BioLite Inc.

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

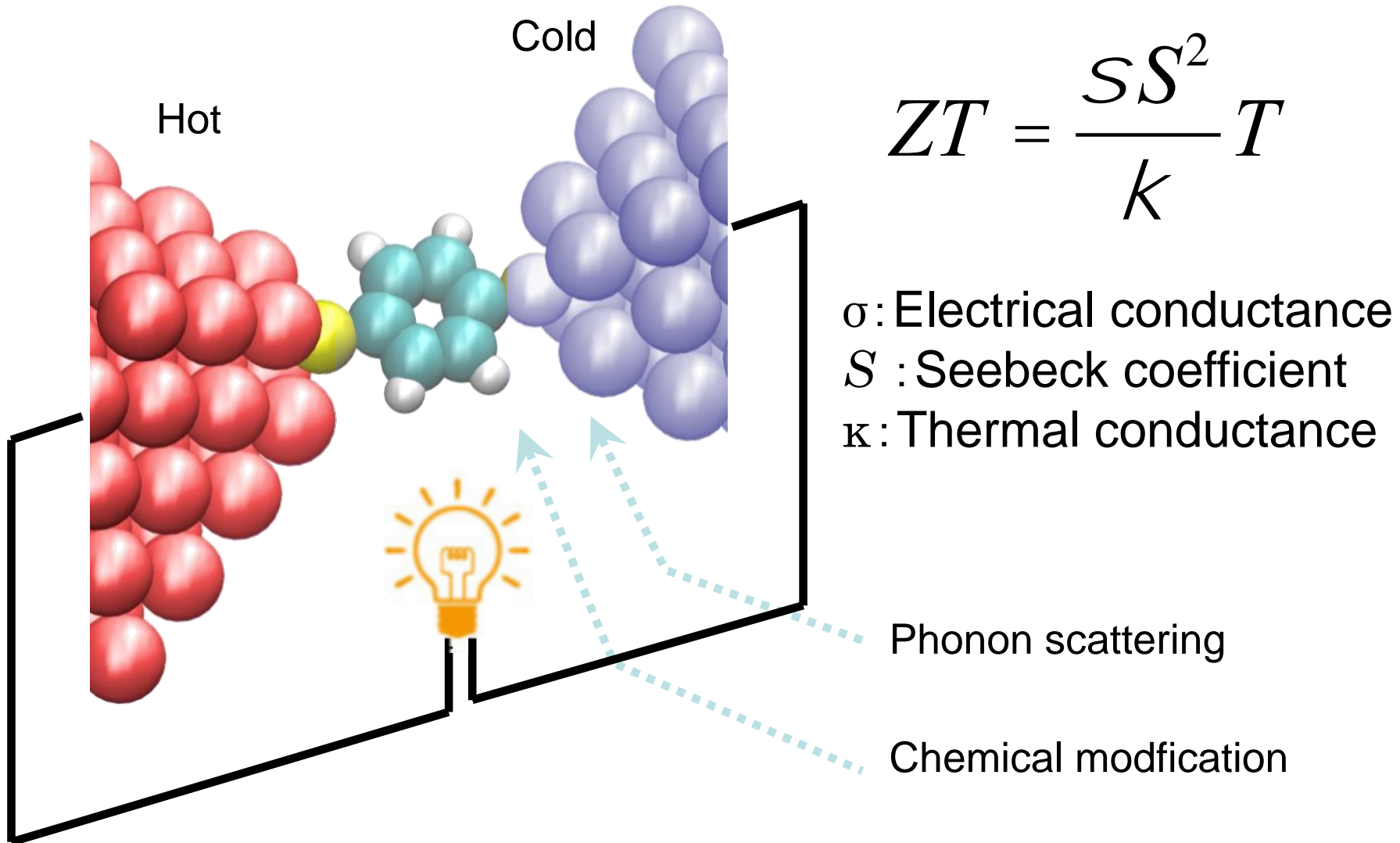
σ : conductivity

S : thermopower

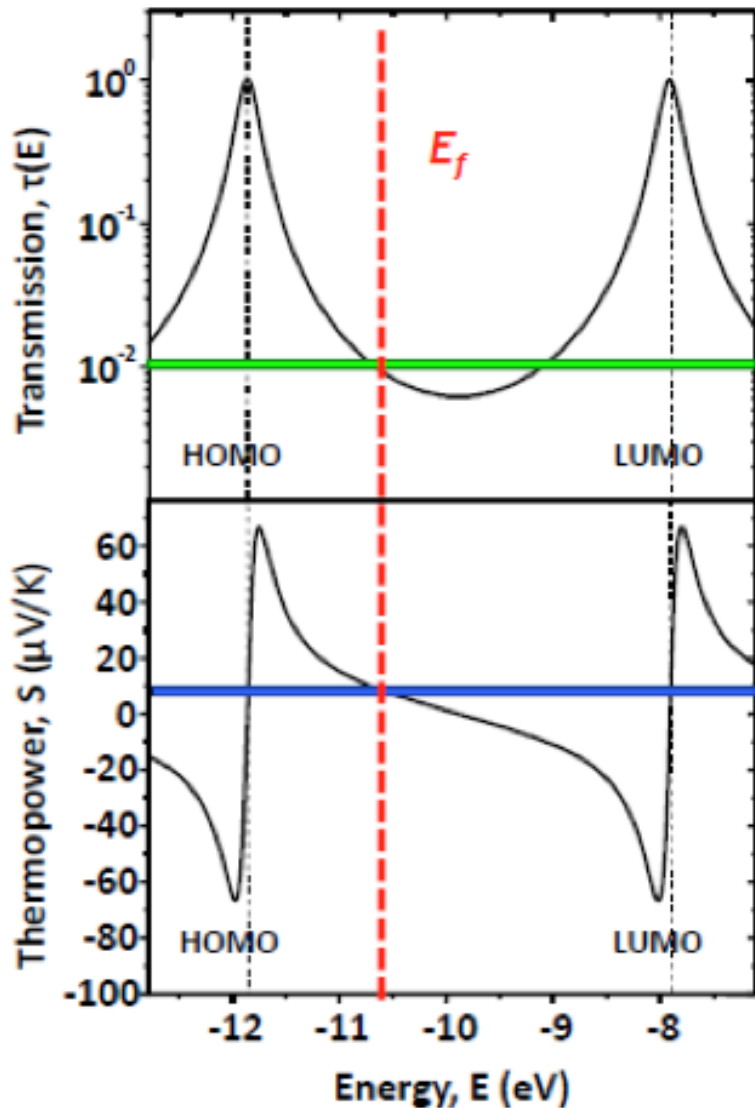
κ : thermal conductivity



Molecular thermoelectric device



Thermopower (Seebeck Coefficient)



$$S = - \frac{\rho^2 k_B^2 T}{3e} \left(\frac{\partial \ln t(E)}{\partial E} \right) \Big|_{E=E_F}$$

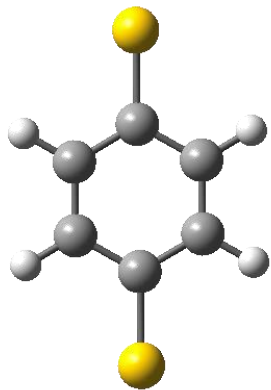
Gradient of the conductance



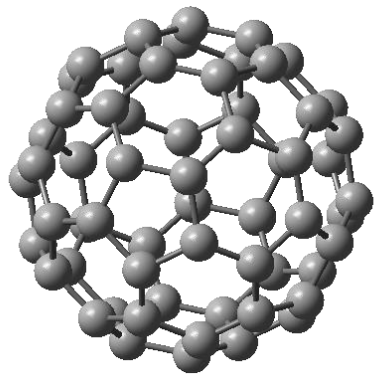
Electron or hole?

Calculation of T(E) from conductance and thermopower

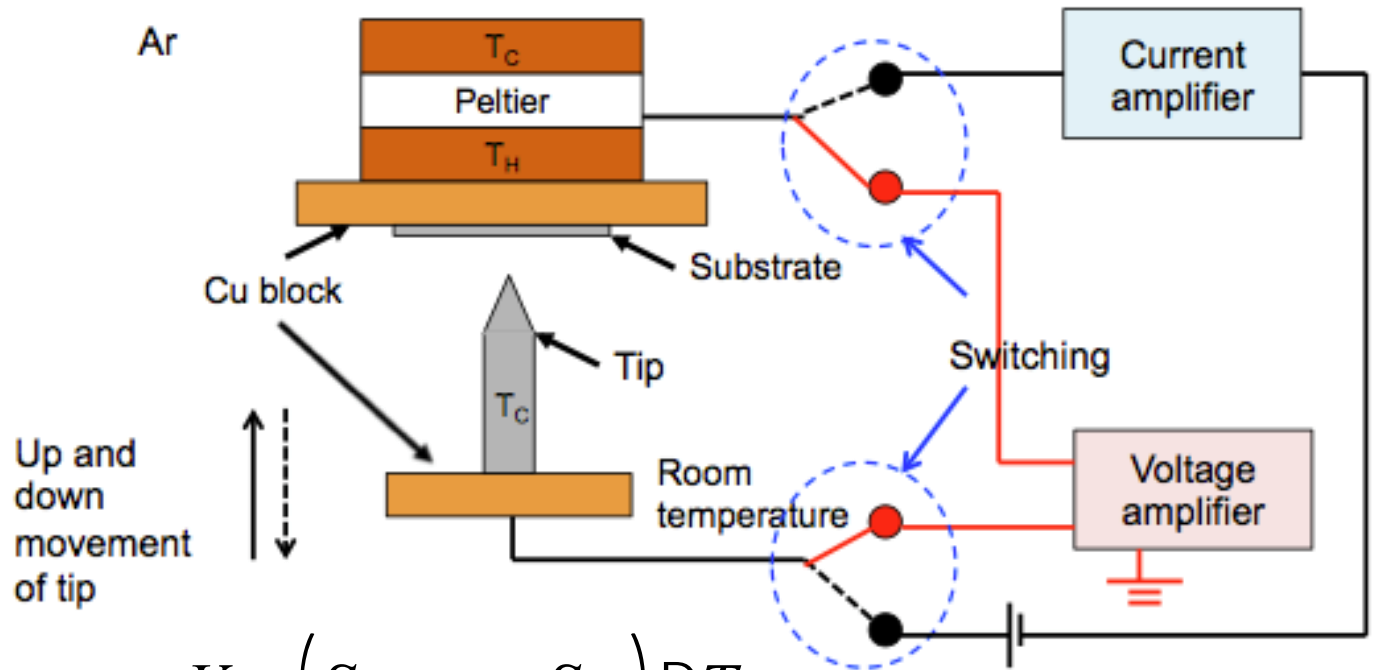
Thermopower measurement



BDT



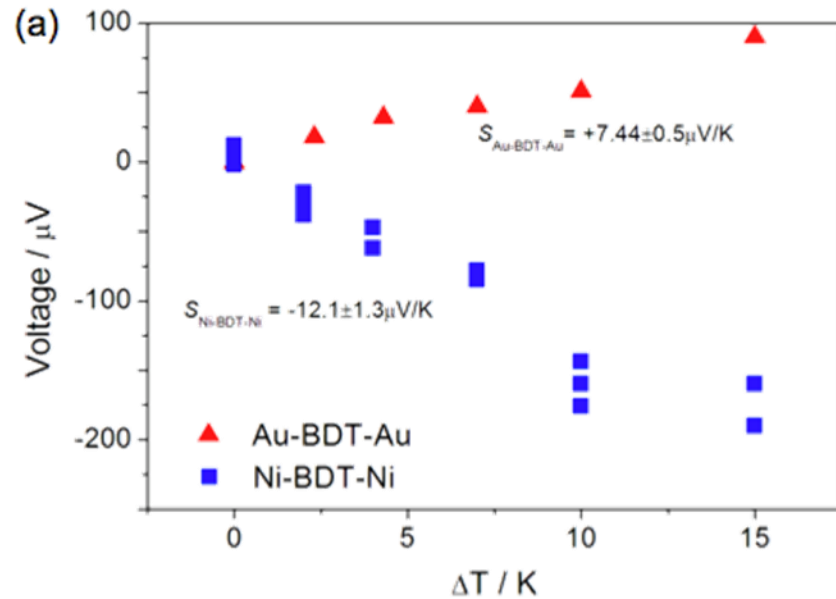
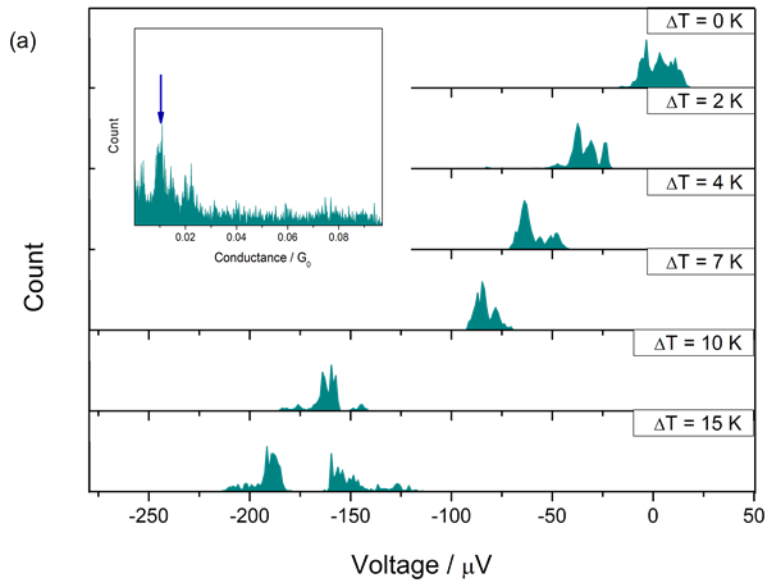
C₆₀



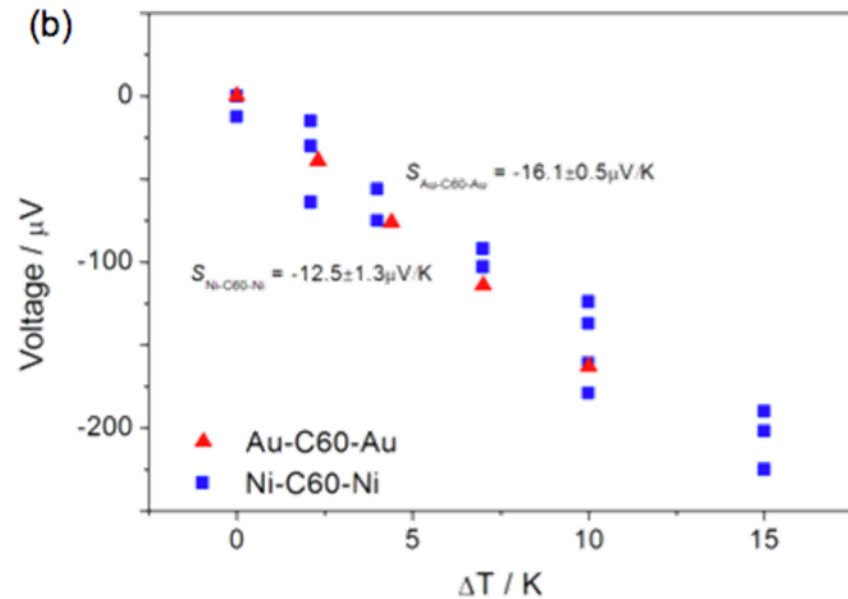
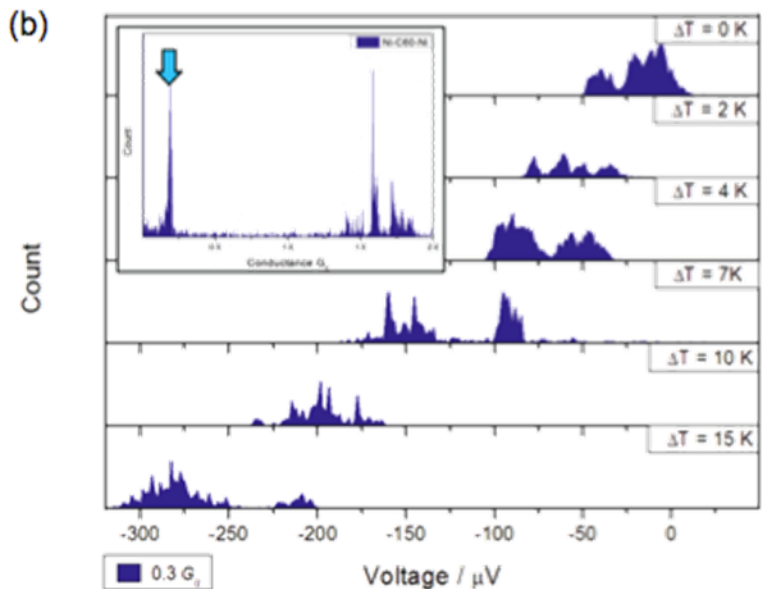
$$V = (S_{\text{junction}} - S_{\text{Cu}}) DT$$

Substrate → Au and Ni

Thermopower measurement



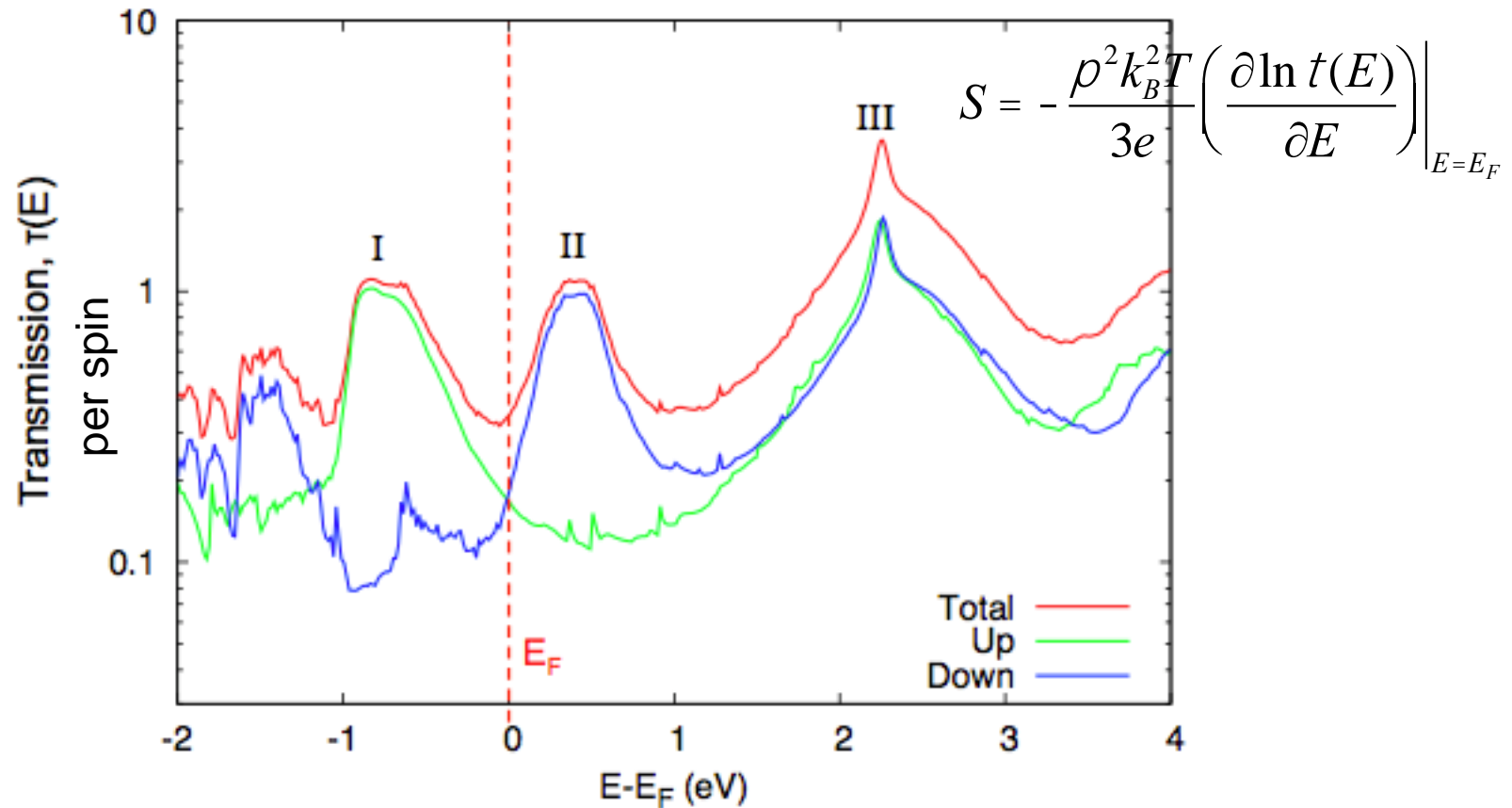
BDT



C_{60}

Ni(111)-BDT-Ni(111)

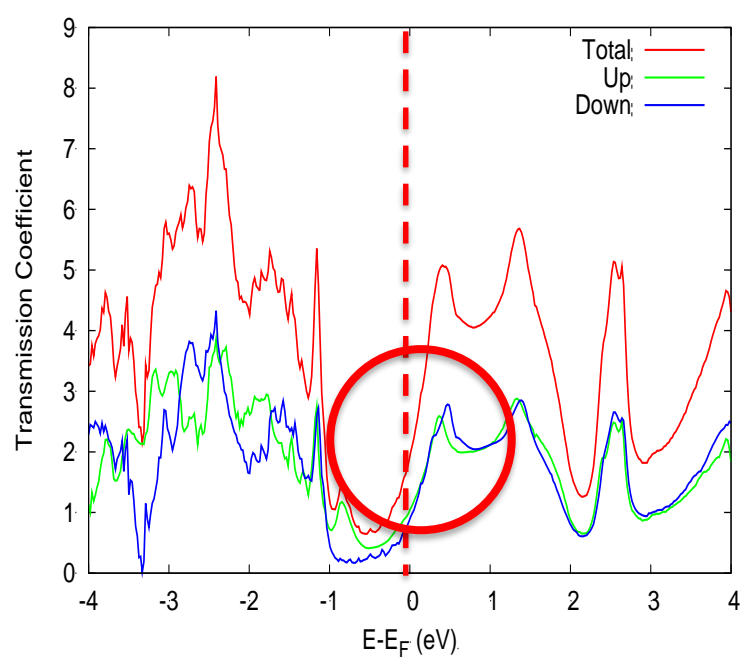
SMEAGOL module (NEGF-DFT), LDA functional



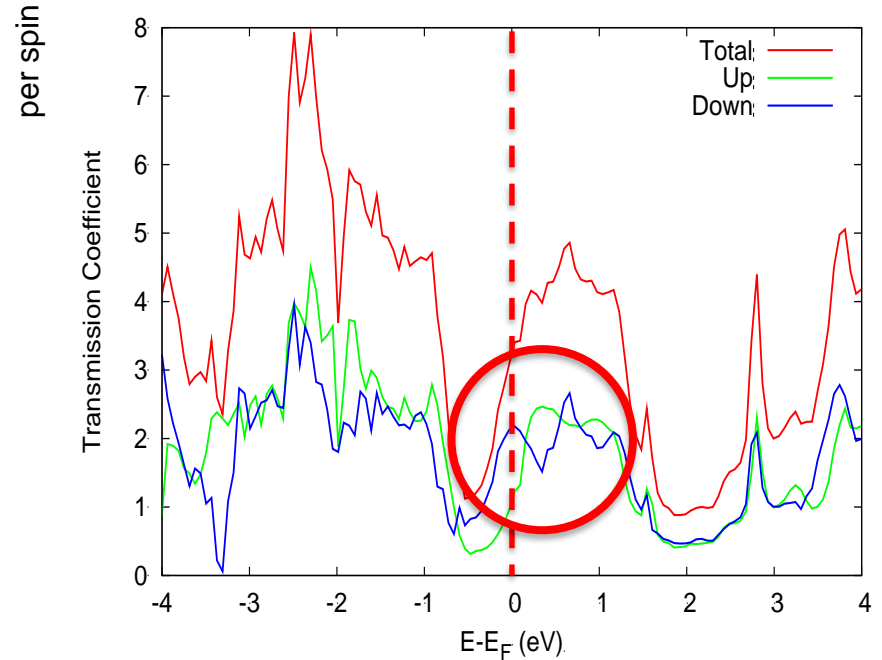
Splitting of HOMO

⇒ Sign change of the Seebeck coefficient

Ni(111)-C₆₀-Ni(111)



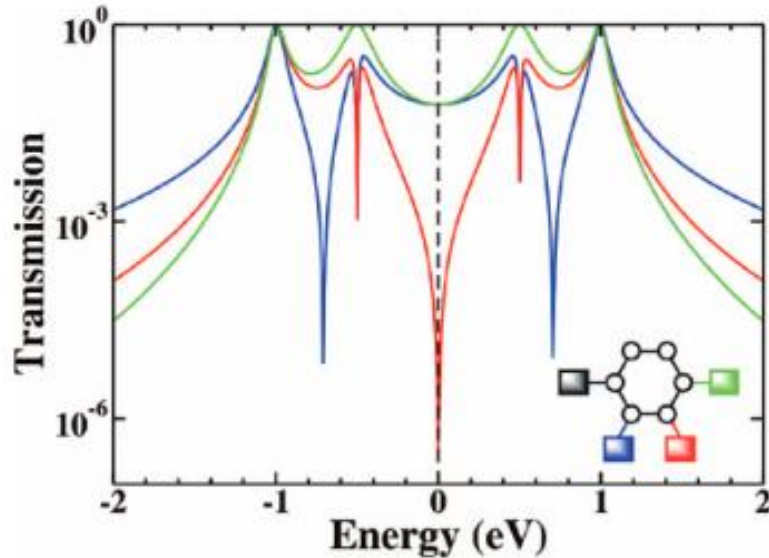
Hexa-faced structure
(most stable)



Penta-faced structure

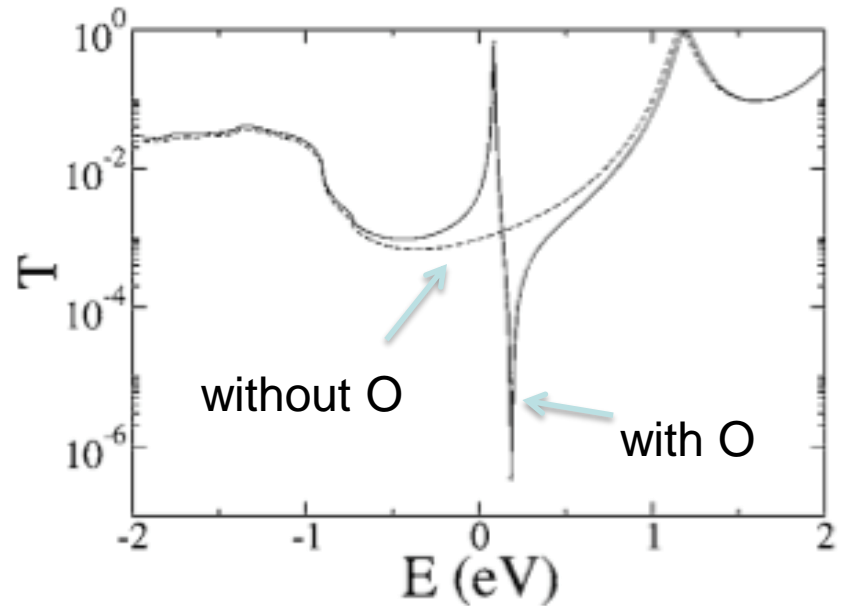
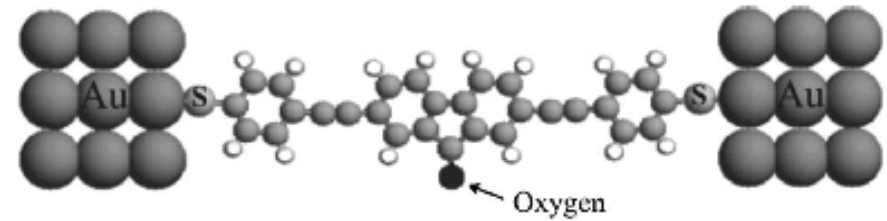
- Transport through LUMO ... negative Seebeck coefficient

How to improve S?



G. C. Solomon *et al.*
J. Chem. Phys. **129** (2008) 054701

Quantum Interference

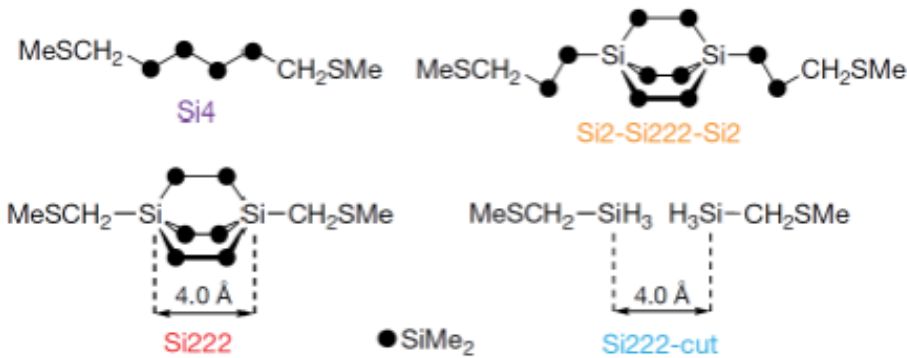


Papadopoulos *et al.* PRB **74**(2006)193306

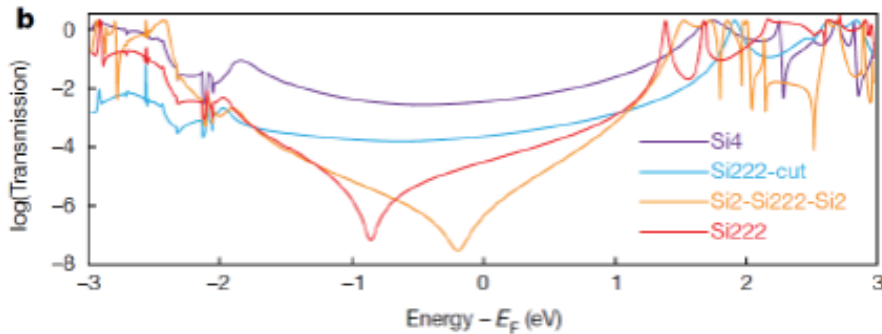
Fano Resonance

Singe Molecular QR

Molecular structures

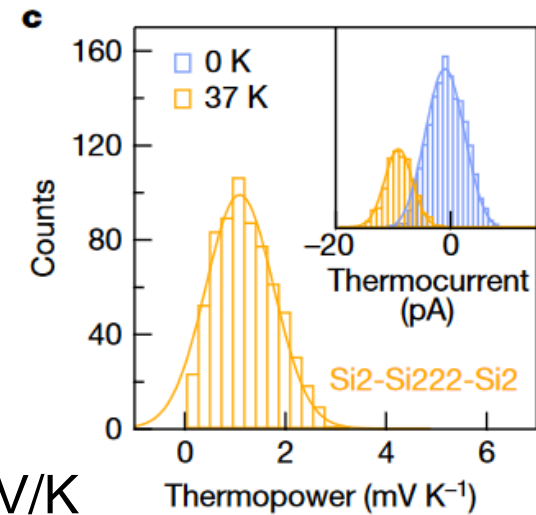
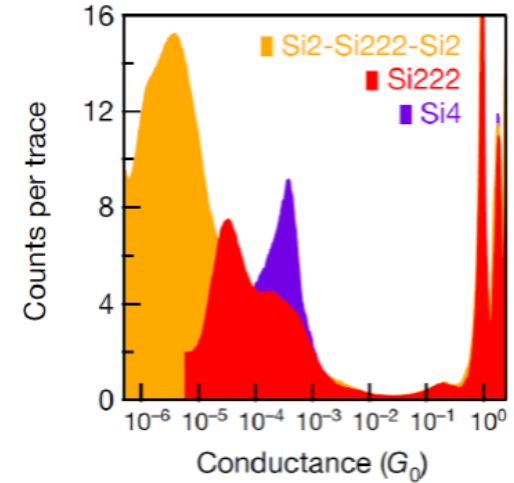


Theoretical transmission function (DFT)



$$S = 970 \mu\text{V/K}$$

Conductance histogram measured using STM BJ



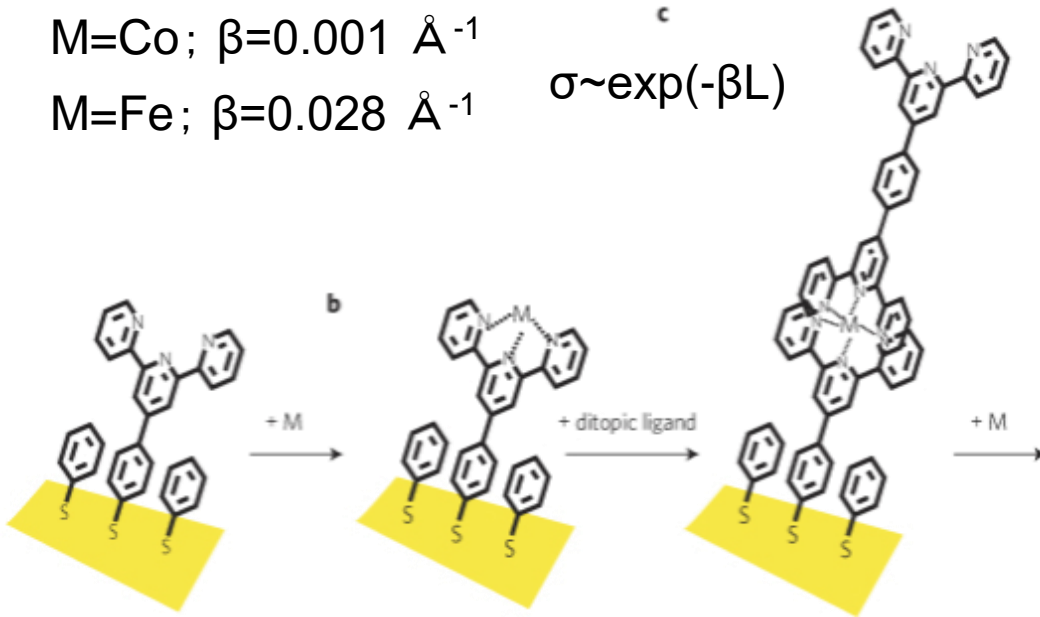
Long range transport wire

Bis(terpyridine)M

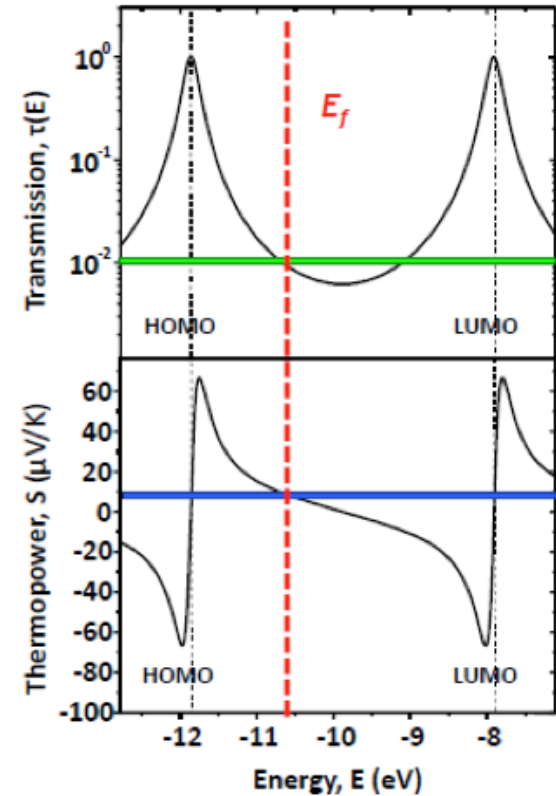
M=Co; $\beta=0.001 \text{ \AA}^{-1}$

M=Fe; $\beta=0.028 \text{ \AA}^{-1}$

c
 $\sigma \sim \exp(-\beta L)$



Tuccitto *et al*, Nat. Mat. **8**(2009) 41



Reddy *et al*, Science **315**(2007) 1568

Resonant tunneling?

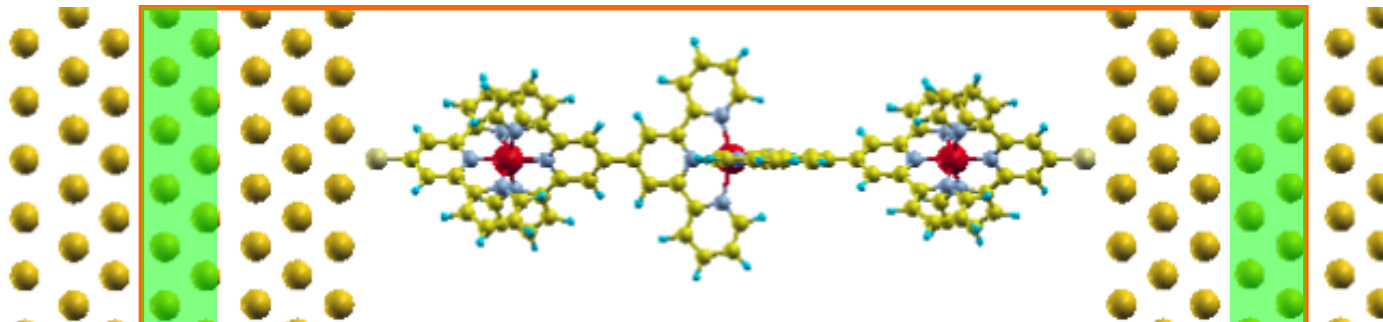


MO level is close to the Fermi level

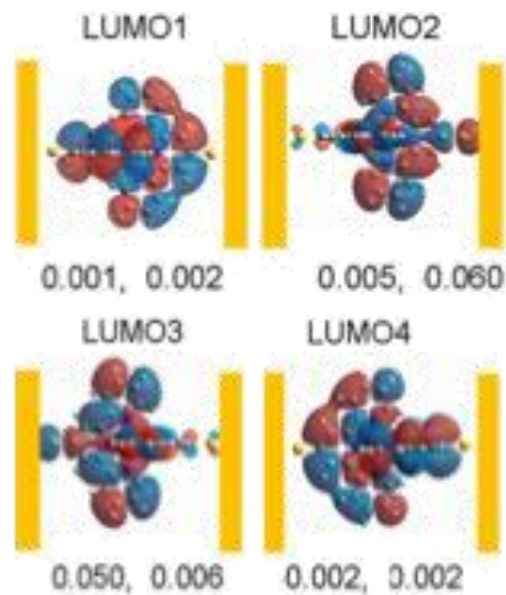
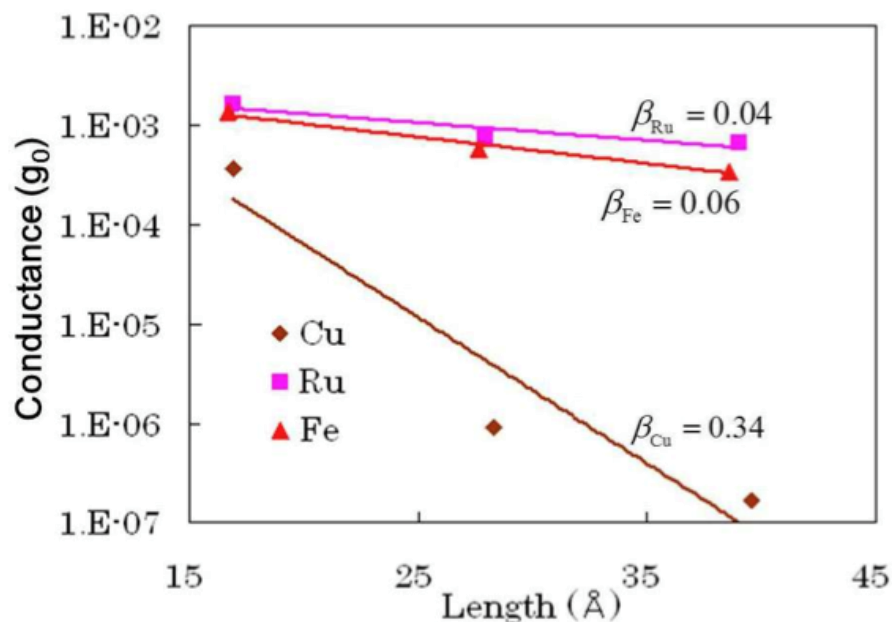
High S is expected

Transport calculations

HiRUNE module (NEGF-DFT), PBE functional

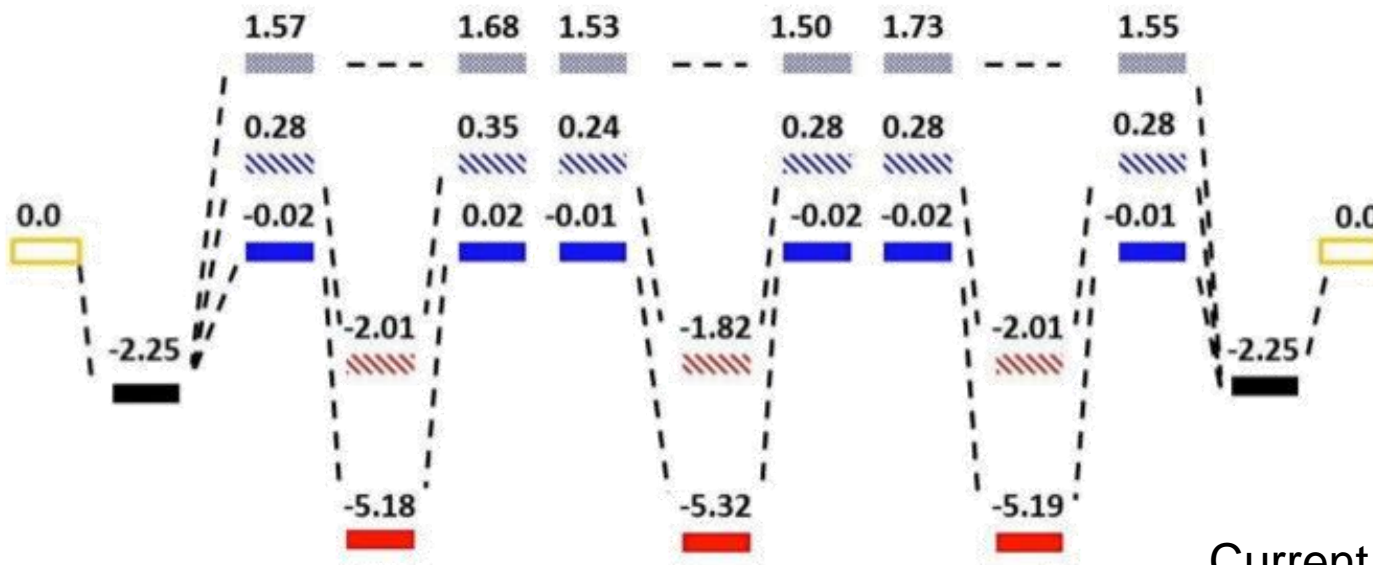


Bridged Bis-terPy(M) M=Cu, Fe, Ru, Vac etc.

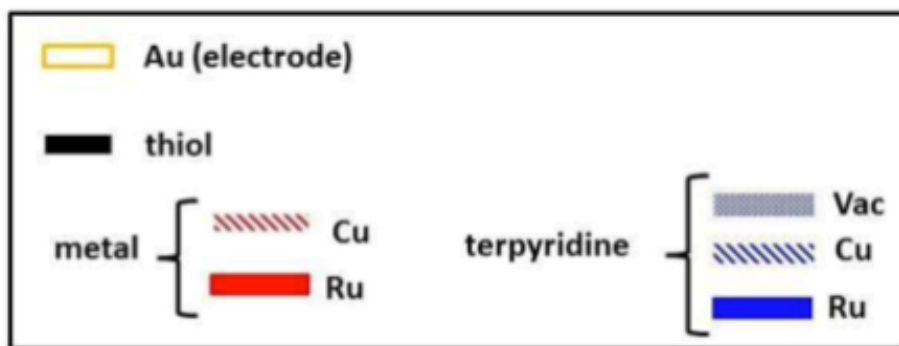
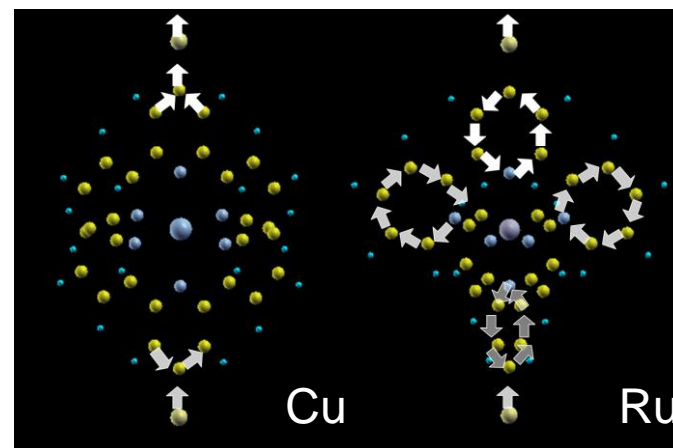


Y_R, Y_L

Energy level diagram

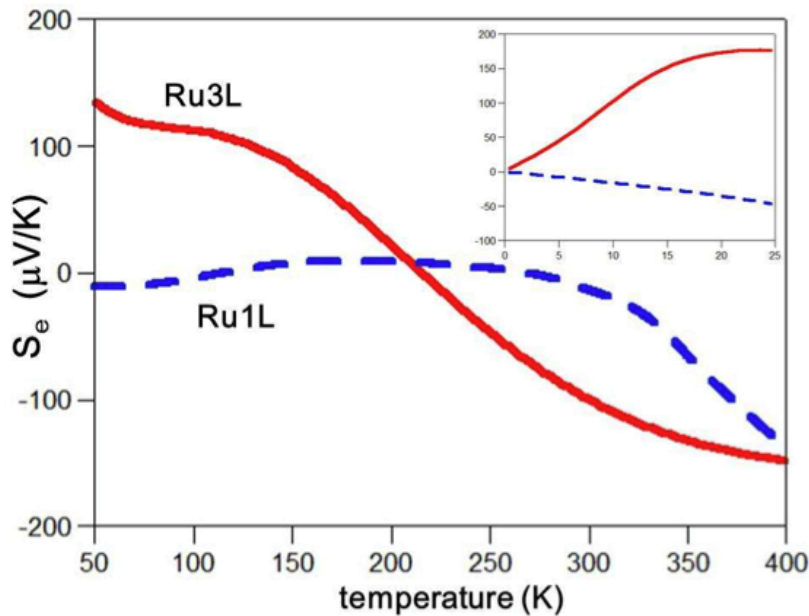
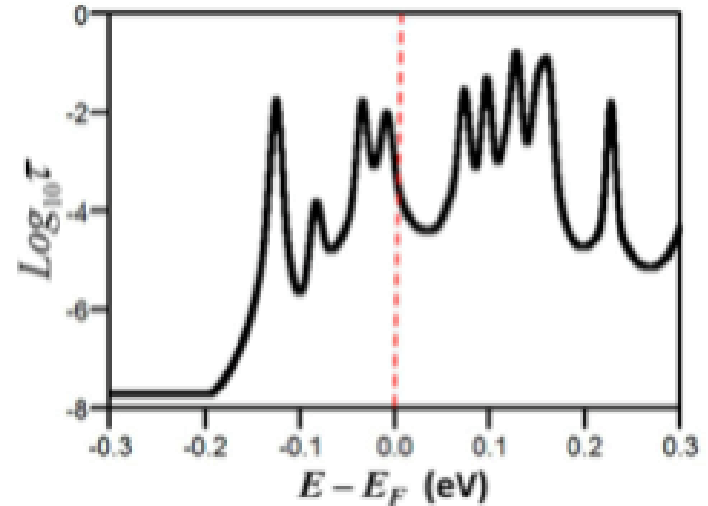
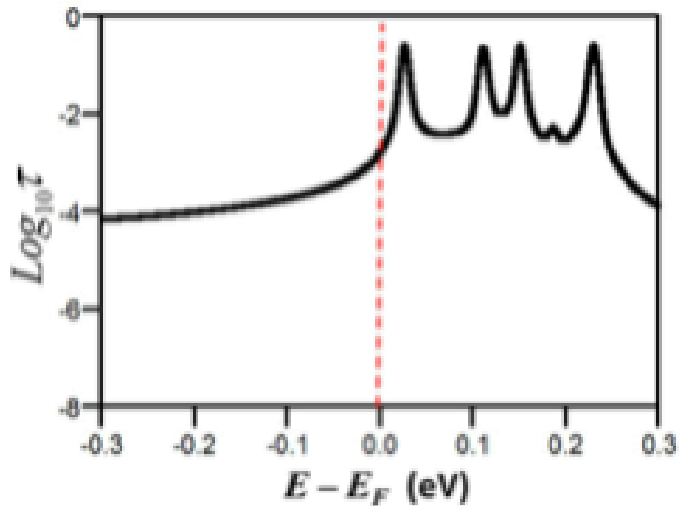


Current Profile



Resonant tunneling through MOs

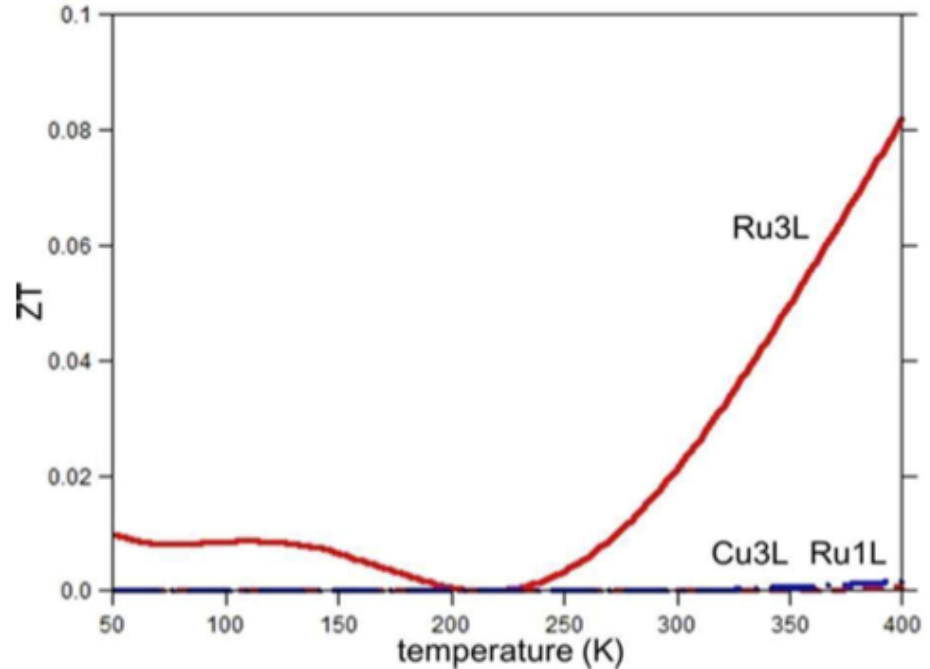
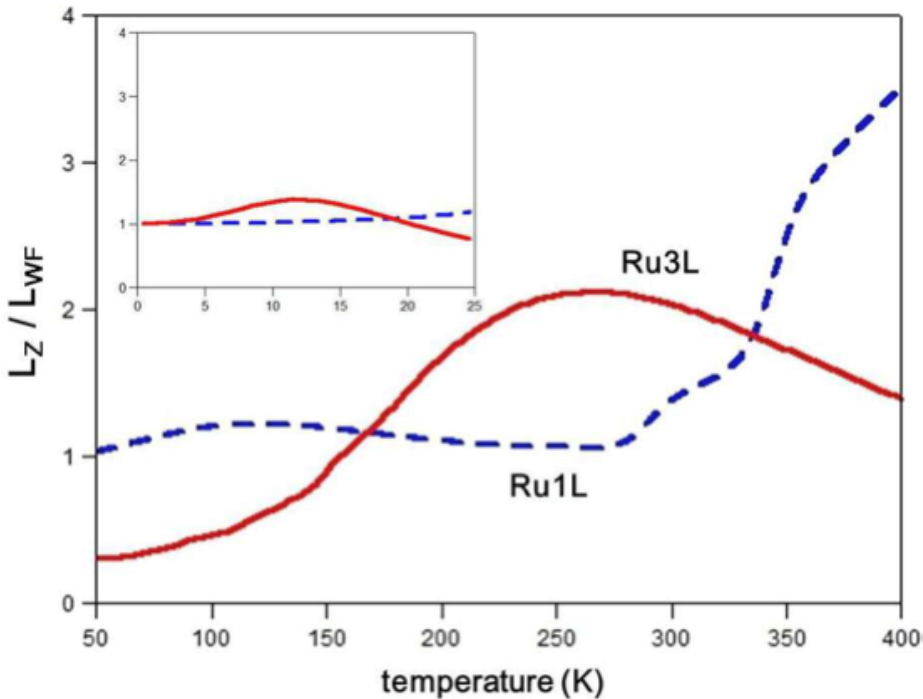
G and S



- Many narrow states
- Sign change of S

$$S = -\frac{1}{T} \frac{\int dE (E - E_F) t(E) \left(-\frac{\partial f}{\partial E} \right)}{\int dE t(E) \left(-\frac{\partial f}{\partial E} \right)}$$

Wiedemann-Franz and ZT



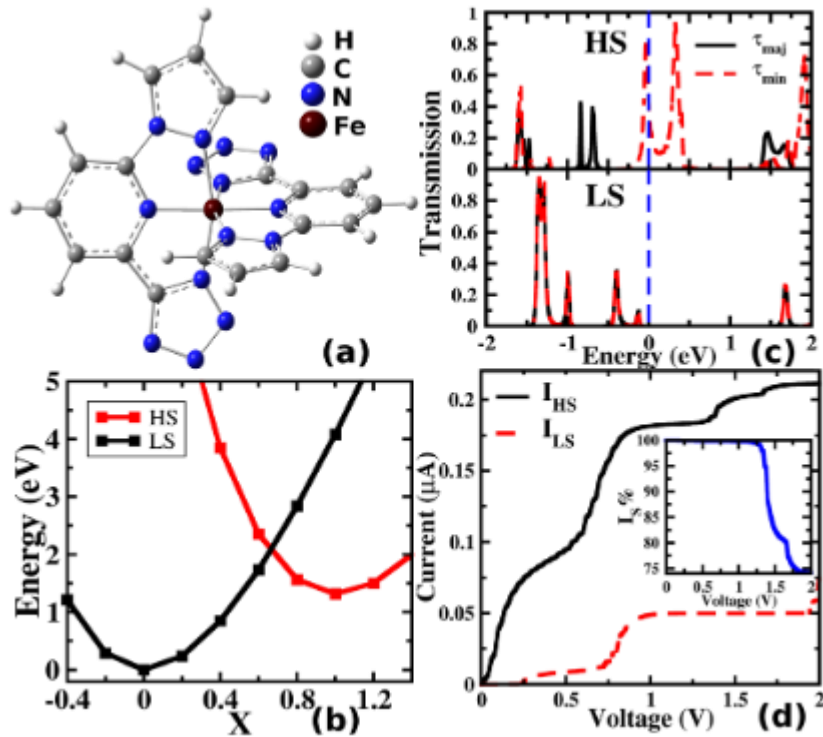
Wiedemann-Franz is broken

Wiedemann-Franz則

$$L_Z = \frac{k}{ST} = \text{const.} \quad L_{WF} = \frac{\rho^2 k_B}{3}$$

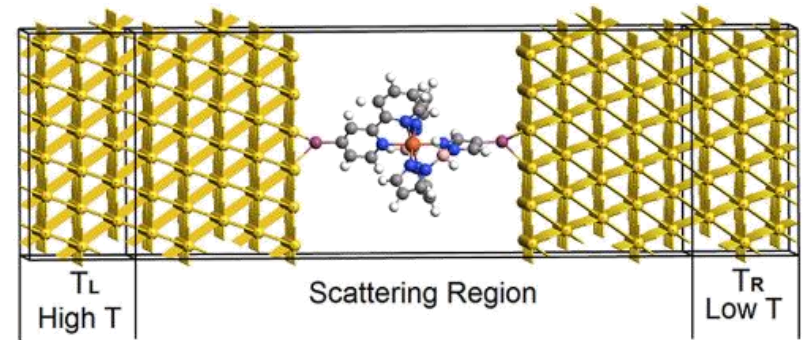
At a temperature, $ZT=0$

Metal-complex-based thermoelectric devices

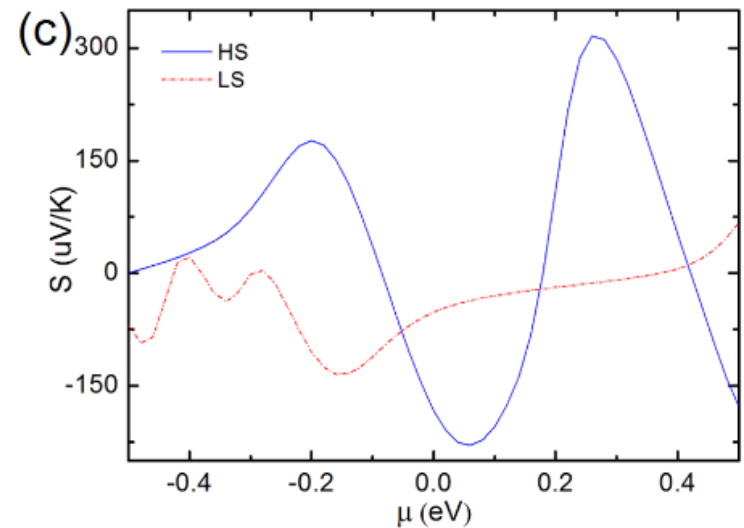


D. Ghosh *et al.*

Appl. Phys. Lett. **106** (2015) 193105



$\text{Fe}[(\text{H}_2\text{Bpz}_2)_2\text{bipy}]$



N. Liu *et al.*

J. Phys. D: Appl. Phys. **51** (2018) 145102

5. Organic Magnetoresistance

Organic magnetoresistance (OMAR)

Usual MR

MAGNETIC

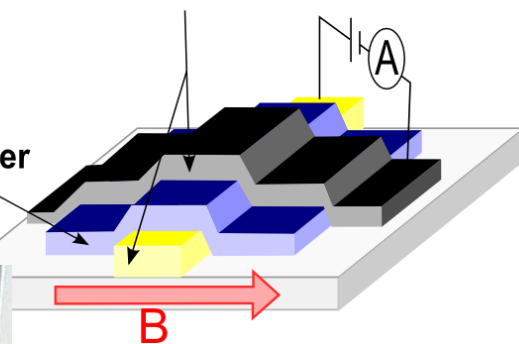
Electrodes

OMAR

**NON
MAGNETIC**

GMR, TMR
Spinvalve.

Organic layer



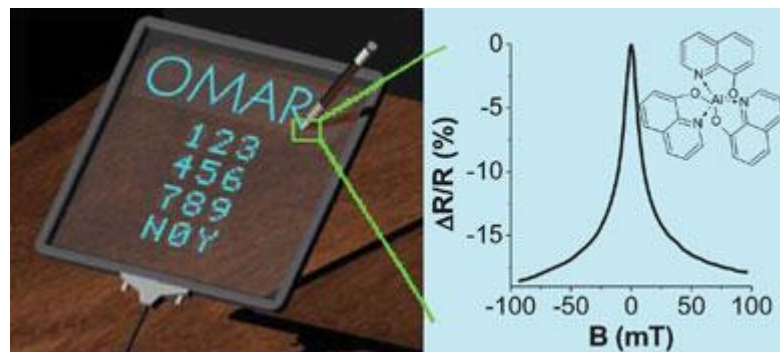
Room temperature.
Low magnetic field (mT)

Up to several 1000%

Y. Wang et al. Phys. Rev. X 6, 011011 (2016)



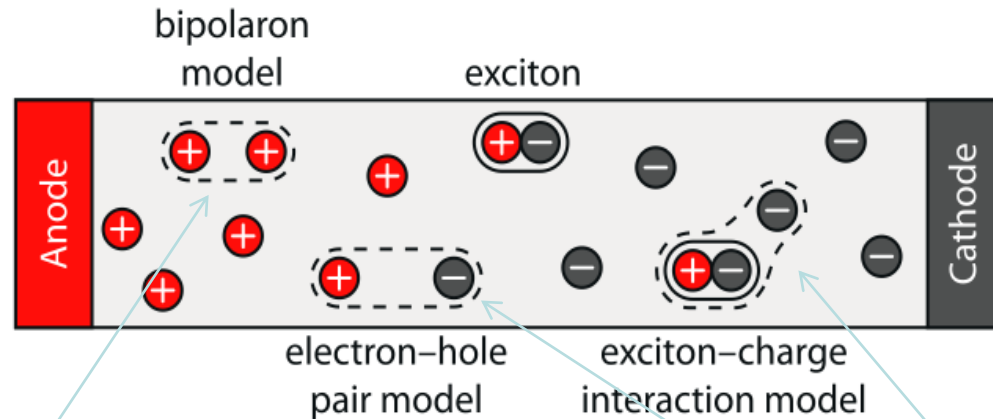
$$MC(\%) = \frac{I(B) - I(0)}{I(0)}$$



Nguyen et al. J. Mater. Chem. 17 (2007) 1995

Theory: Single vs. Double carriers

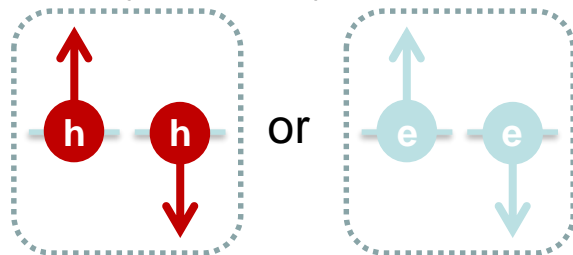
The magnetic field modifies the ratio between SINGLET and TRIPLET



P. Bobbert *et al.*, Phys. Rev. Lett. **99**, 216801 (2007).

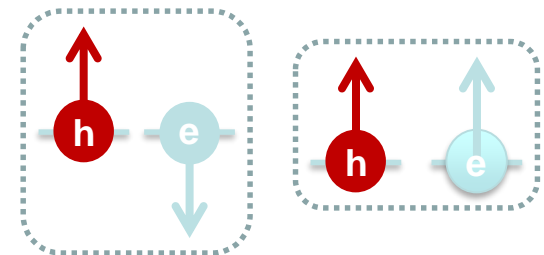
Single carriers

Only **ONE** type of carrier



Double carriers

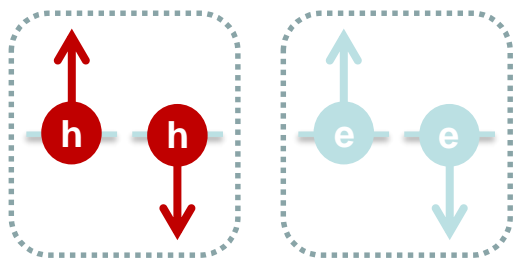
BOTH hole and electron are required



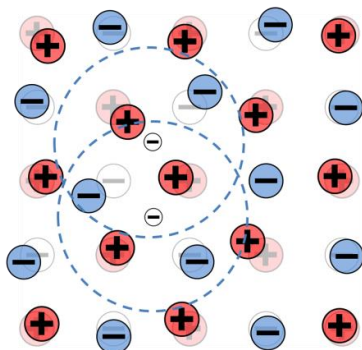
Theory: Single vs. Double carriers

The magnetic field modifies the ratio between SINGLET and TRIPLET

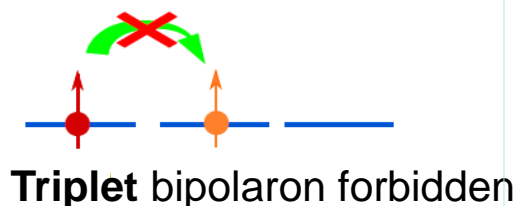
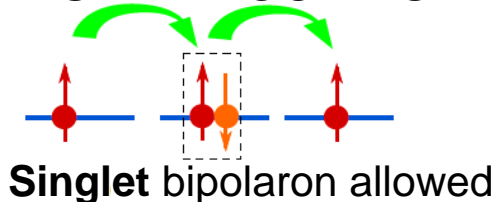
Single carriers



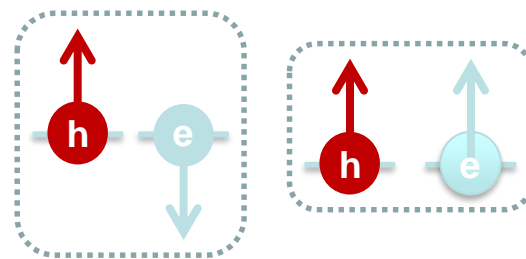
BIPOLARON



SPIN BLOCKING

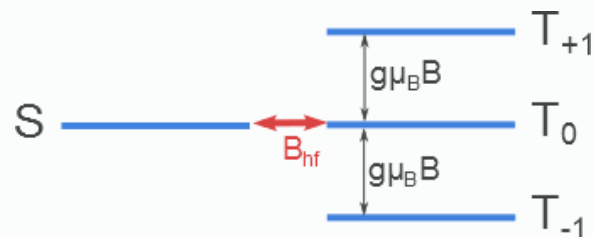


Double carriers



Singlet: Recombination/Dissociation

Triplet: Reaction with charge

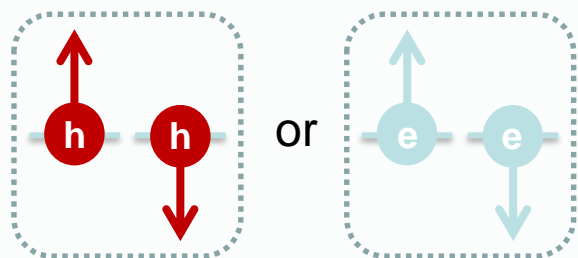


Modified **singlet to triplet ratio**

Theory: Single vs. Double carriers

Single carriers

Bipolarons

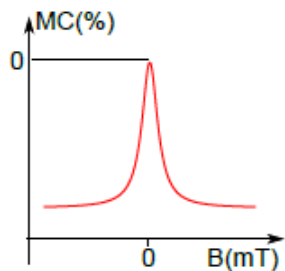


B decreases the number of bipolarons

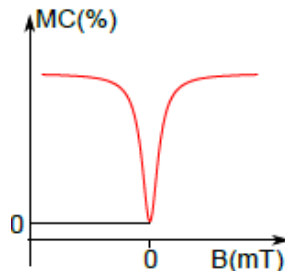
Bipolaron lifetime

short

long



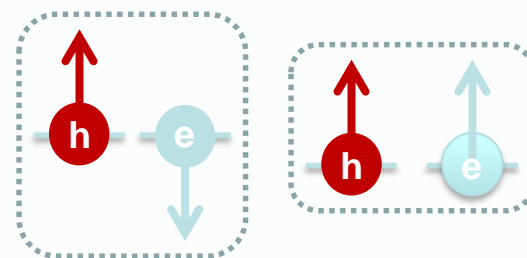
-MC



+MC

Double carriers

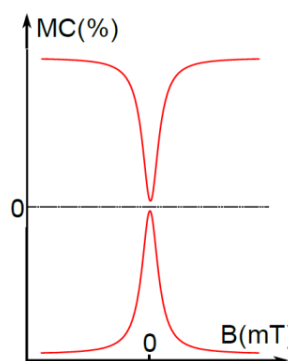
Excitons and e/h pairs



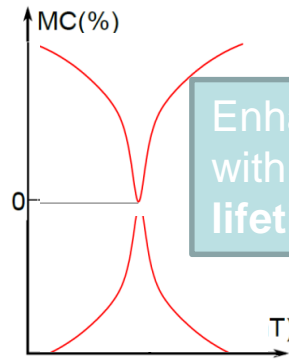
B changes the singlet/triplet ratio

Singlet:
recombination

Triplet:
Reaction with charge



+MC or -MC

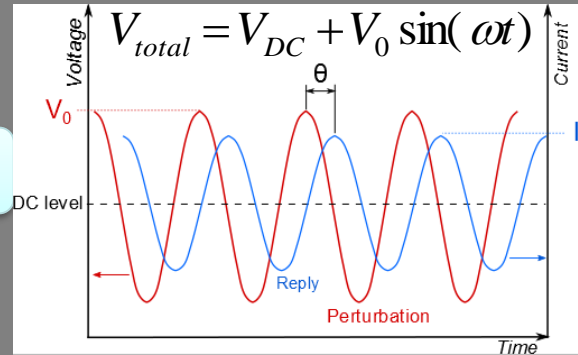


**+MC or -MC
with HFE**

Enhanced
with long
lifetime

Impedance spectroscopy

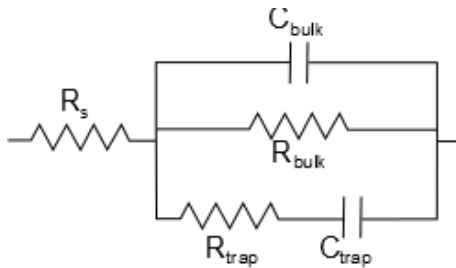
Measurement



$$Z = \frac{V}{I} = \frac{V_0 e^{i(\omega t)}}{I_0 e^{i(\omega t + \theta)}}$$

Equivalent circuit

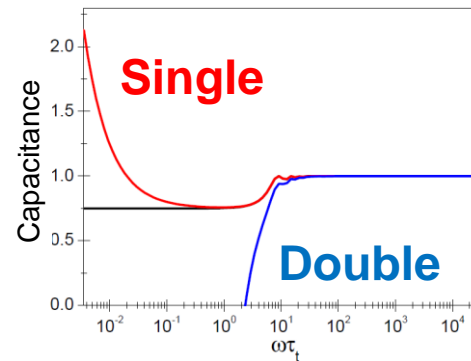
Fitting of the data



Nyquist diagram, Phase.

Give information on electronic processes

Capacitance vs frequency



$$\frac{1}{Z} = G + i\omega C$$

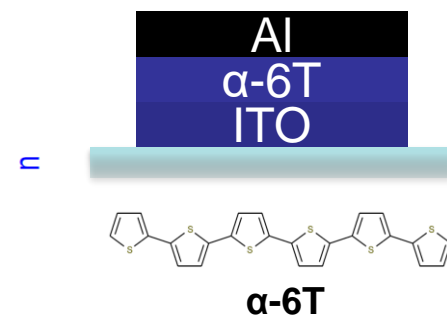
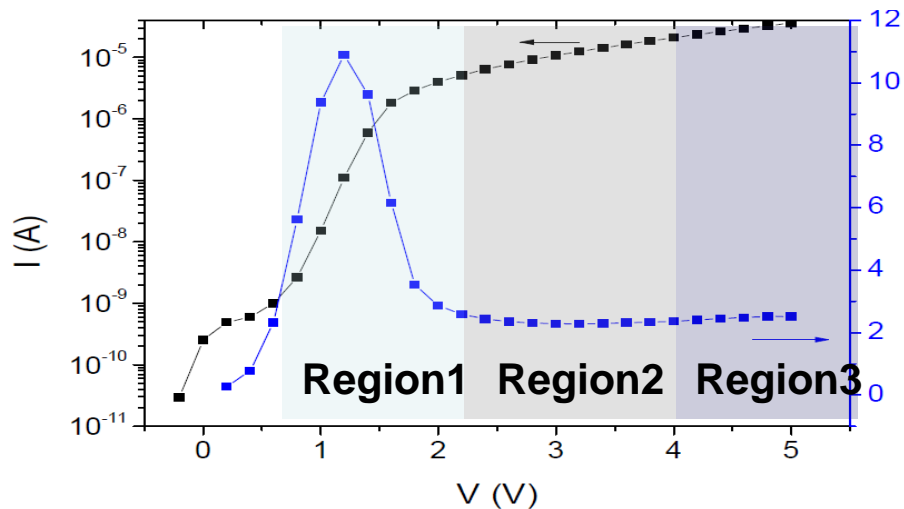
Sign : type of injection
Value : traps characterization

OMAR results

I-V characteristics:

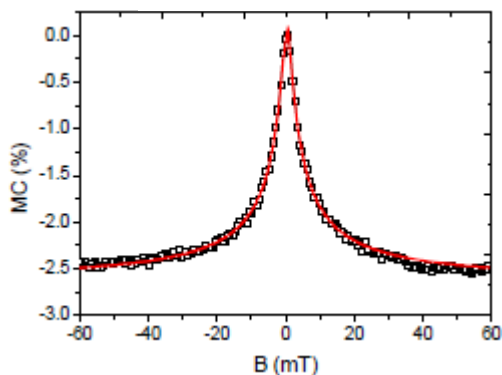
Int. J. Nanotechnol.,
12, 238-247, 2015

$$MC(\%) = \frac{I(B) - I(0)}{I(0)}$$



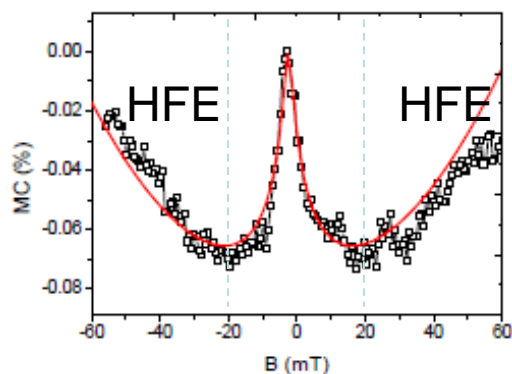
OMAR results:

Region 1



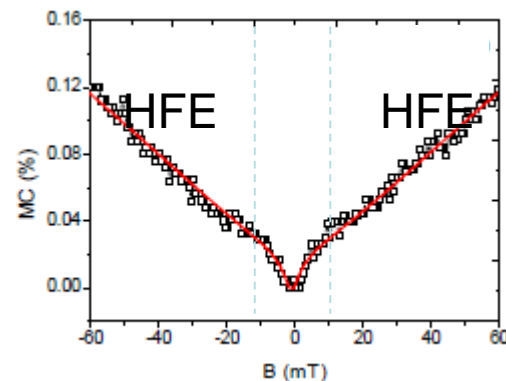
-MC

Region 2



-MC with HFE

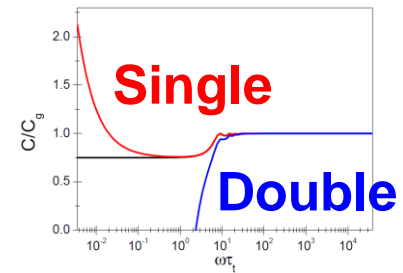
Region 3



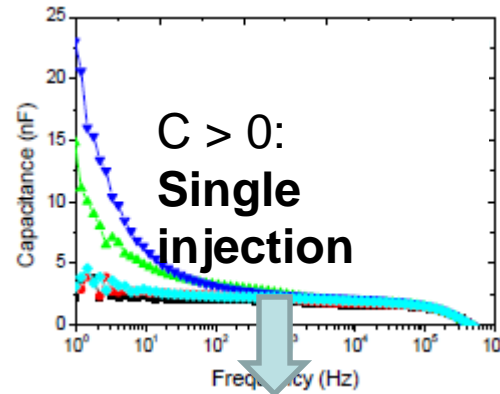
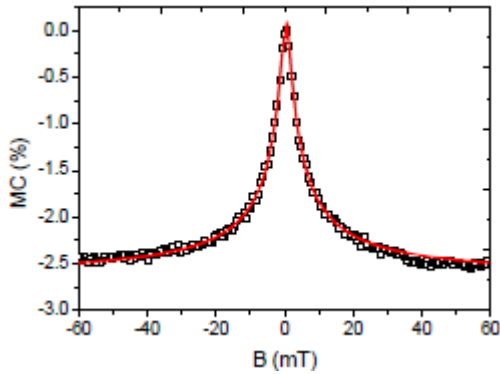
+MC with HFE

How to explain the various OMAR shapes?

Capacitance results

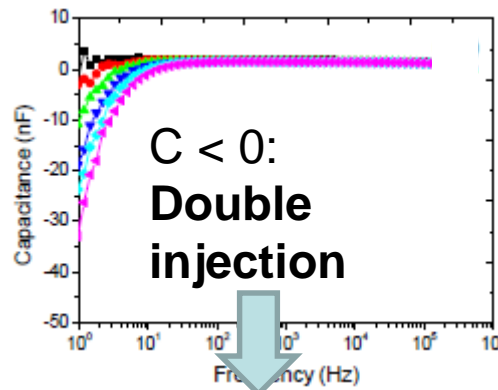
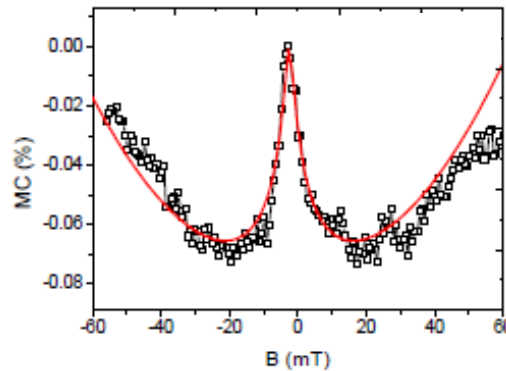


Region 1



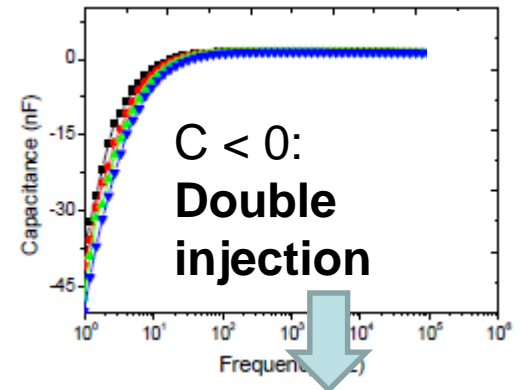
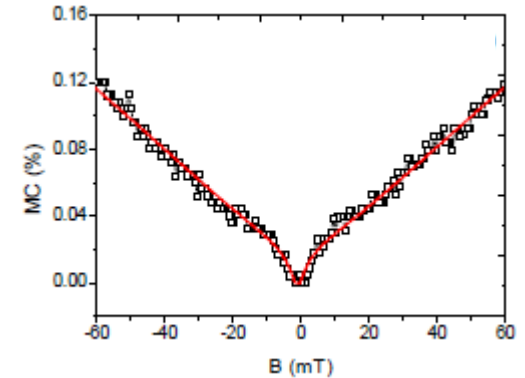
Bipolaron OMAR
Negative OMAR

Region 2



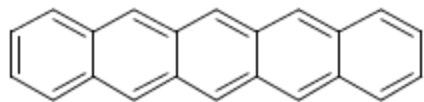
**Transition: double
+ single carriers
OMAR mix**

Region 3



Double carriers OMAR
Positive OMAR

Pentacene (Pen)

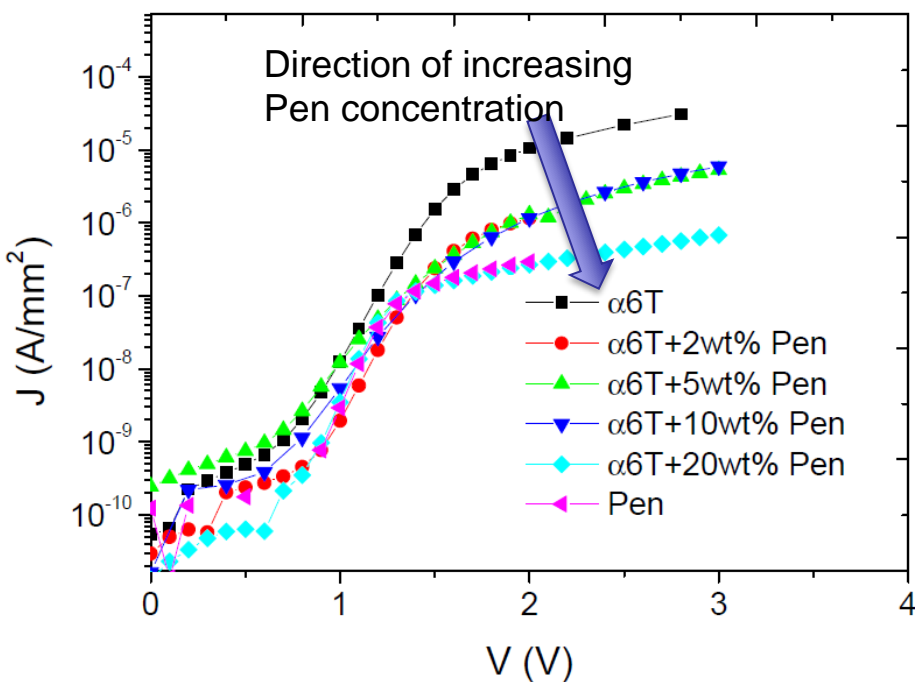


Pentacene doping

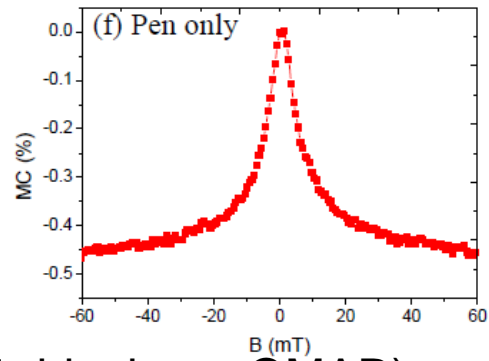
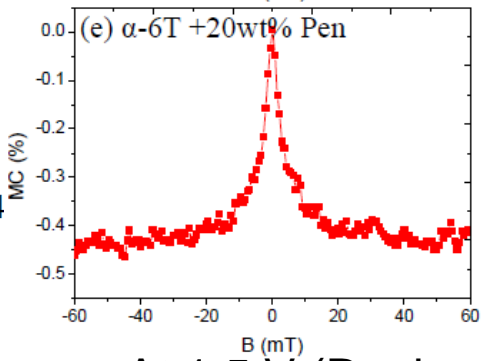
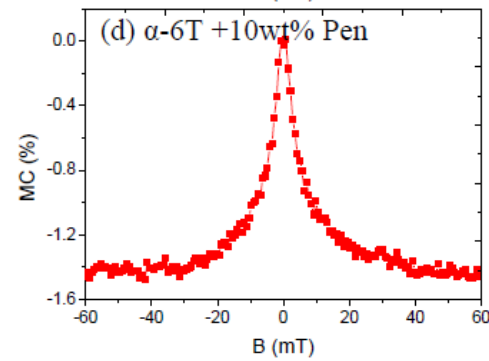
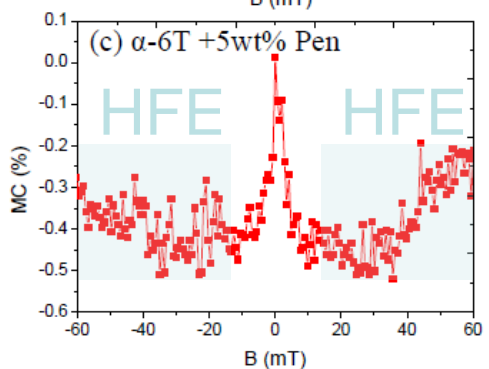
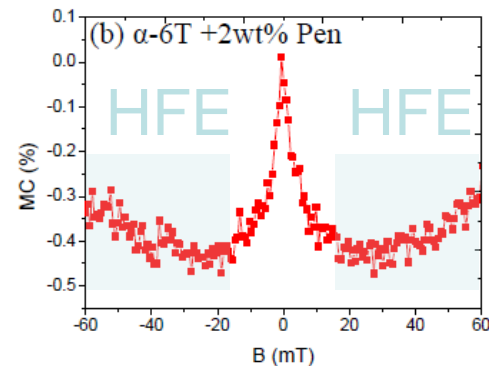
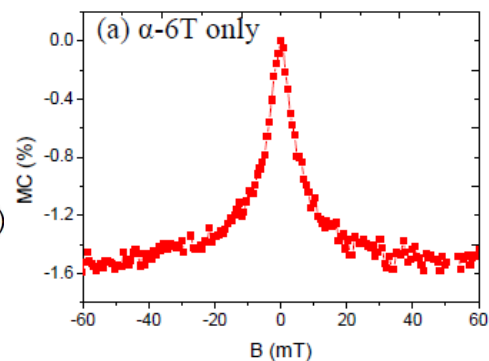
α -6T



0 2 5 10 20 100 [Pen] (wt%)

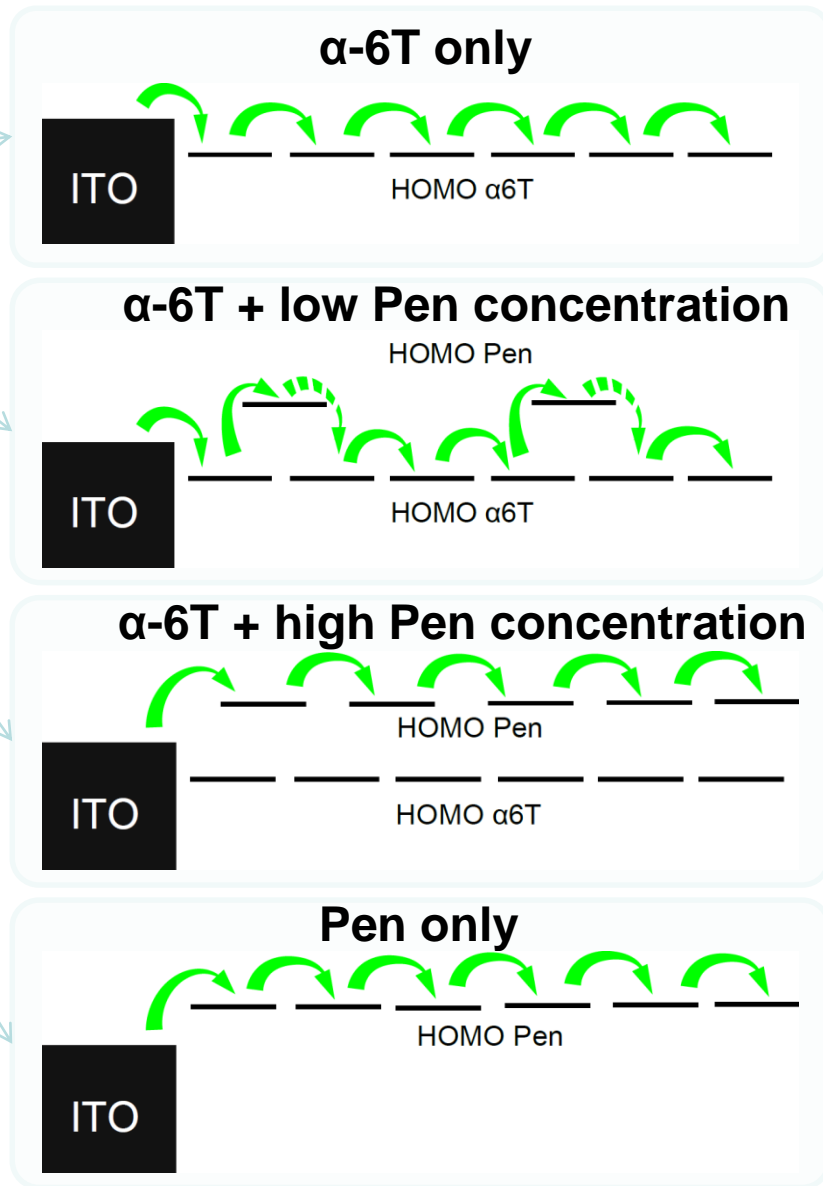
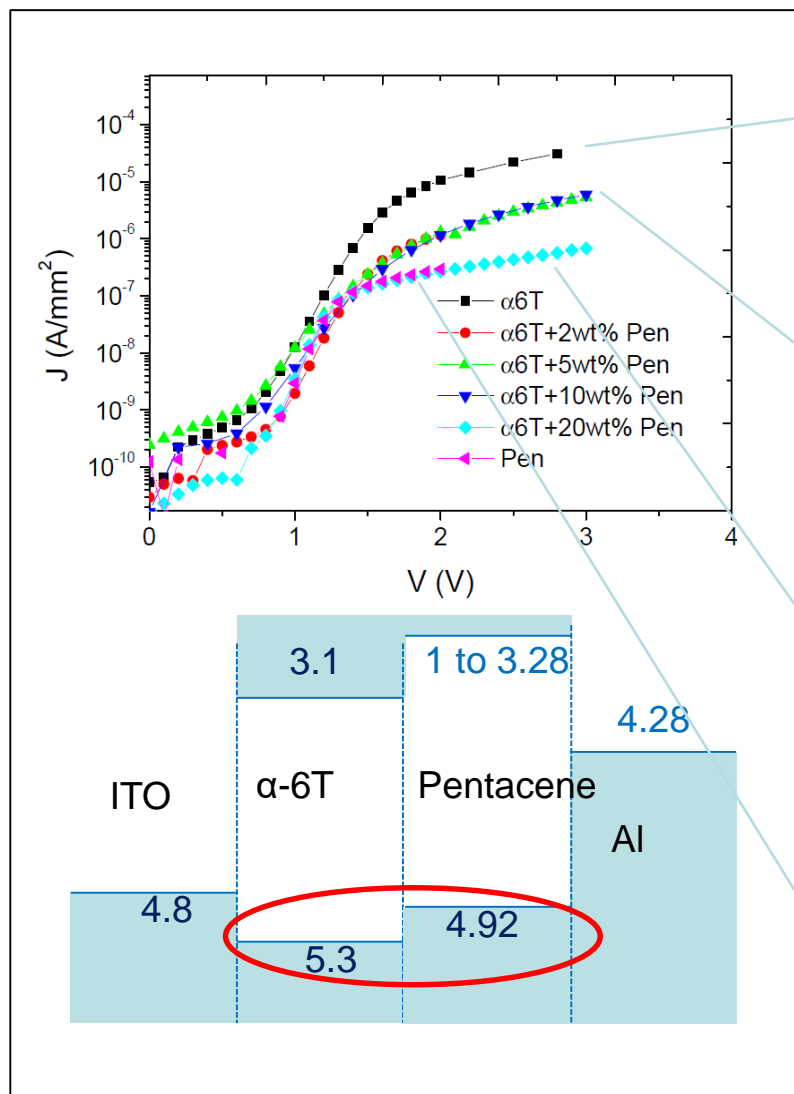


The current decreases with Pen.
At low Pen concentration only, HFE appears.

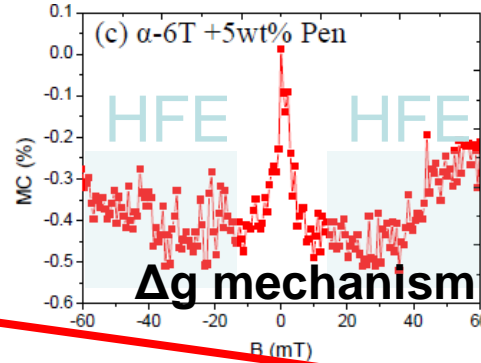
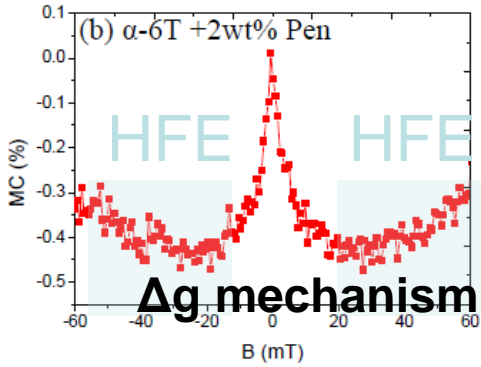


At 1.5 V (Region 1, bipolaron OMAR)

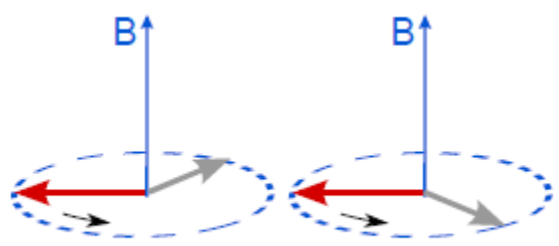
I-V characteristics



OMAR results

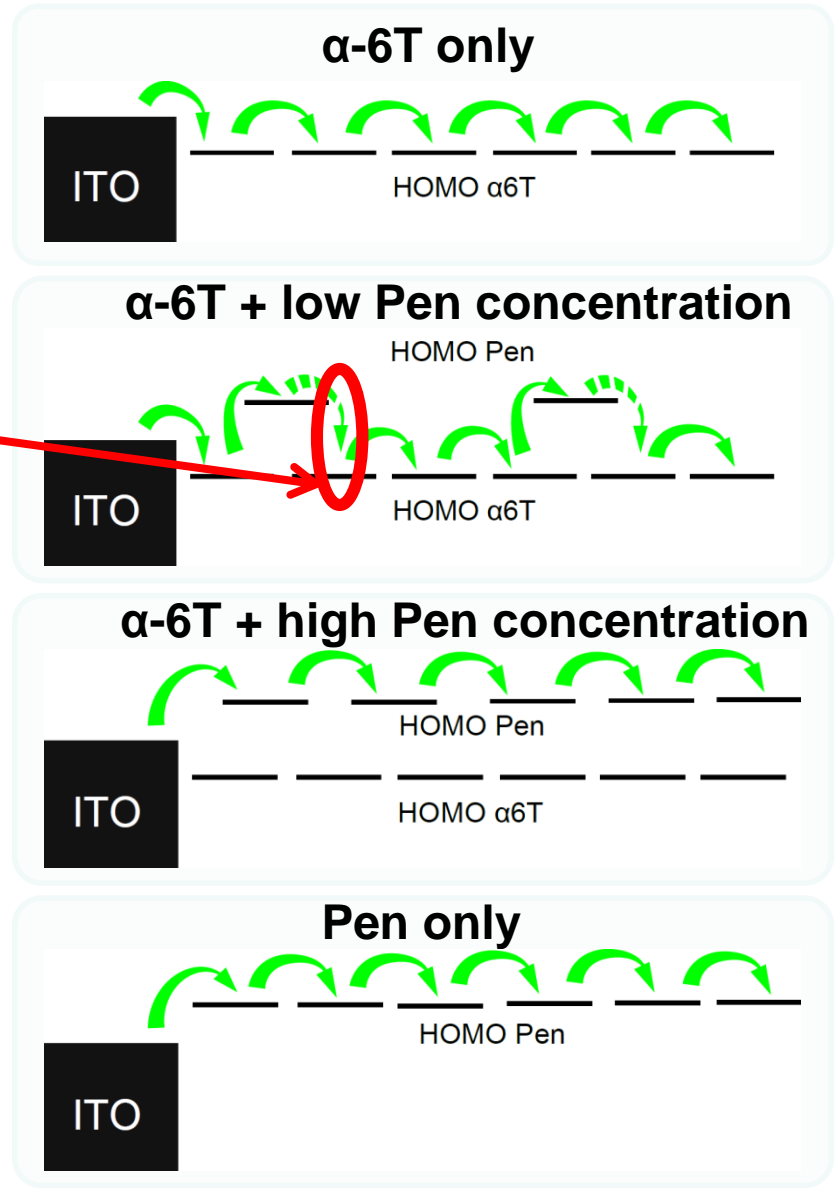


Different environment



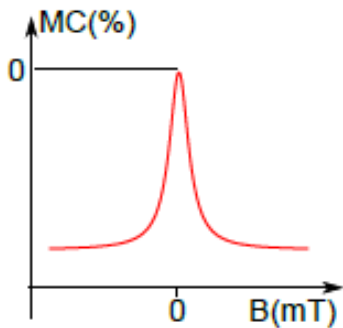
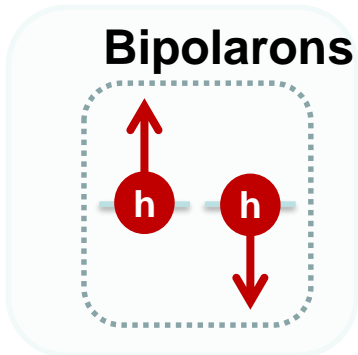
Spin precession out of phase. Cause an effect opposite to the effect at low field.

Bobbert et al., PRB **84** (075204) 2011



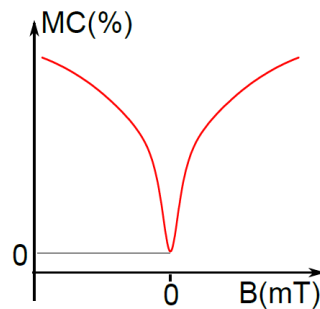
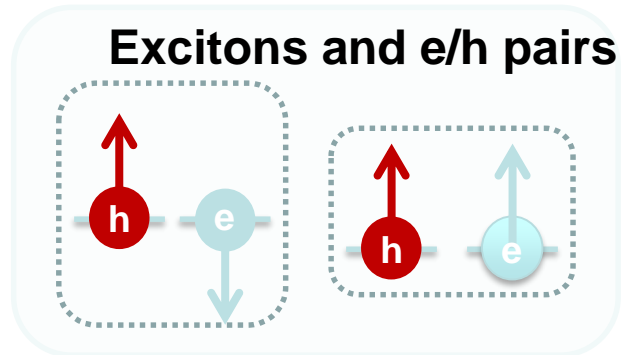
Summary

Single carriers



-MC

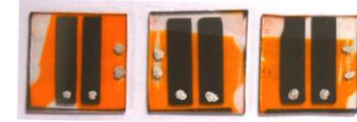
Double carriers



+MC with HFE

Disorder

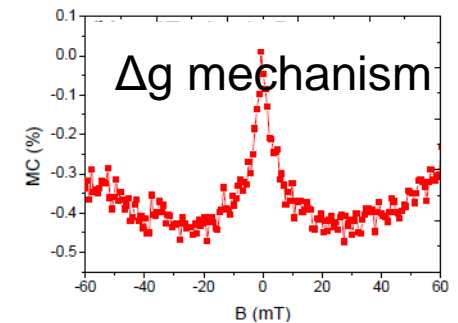
α -6T



0 2 5



10 20 100 [Pen] (wt%)

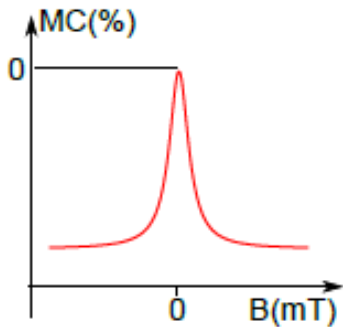
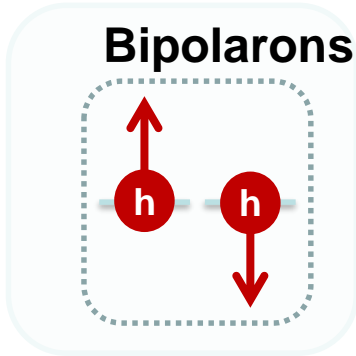


The mechanism is identified.

Magnitude and shape of OMAR is tuned.

Perspective

Single carriers



-MC

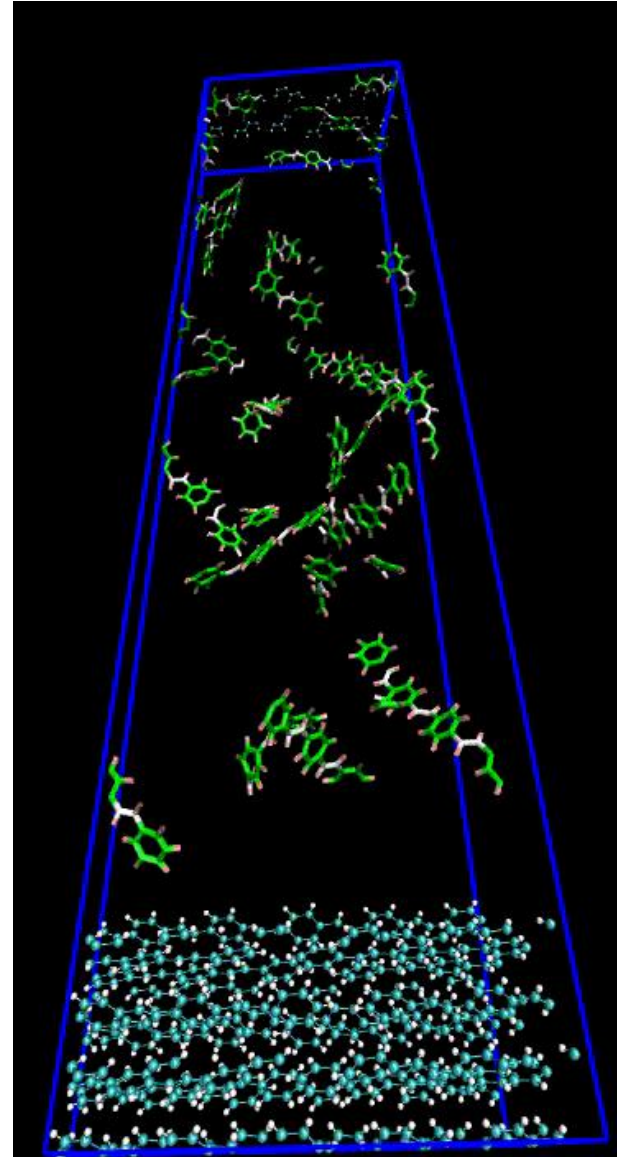
• Bipolaron is a deep mid-gap state

• How much defective are organic semiconductors?

Realistic landscape



Carrier dynamics simulation



Summary

- Theoretical design of molecular spin valve
- NEGF-DFT and its application to spintronics and thermoelectronics

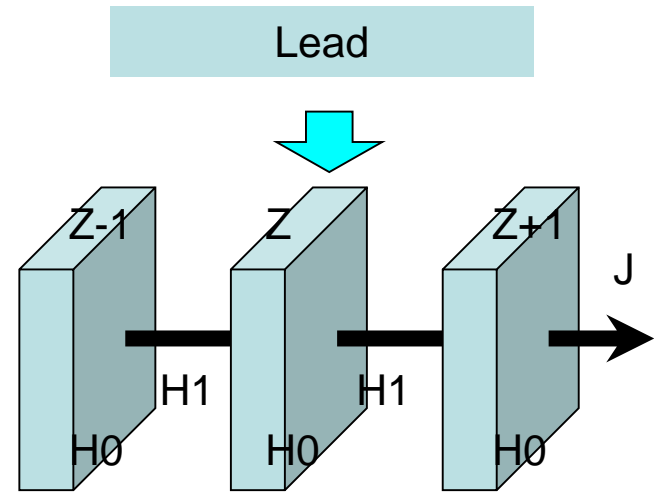
- Single Molecular Magnet
- OMAR and its mechanisms

Surface Green's Function

Recursive Method

M. P. Lopez Sancho *et al.* J. Phys. F **14**(1984)1205

$$H = \begin{pmatrix} \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & H_0 & H_1 & 0 & \dots & \dots & \dots & \dots \\ \dots & H_{-1} & H_0 & H_1 & 0 & \dots & \dots & \dots \\ \dots & 0 & H_{-1} & H_0 & H_1 & 0 & \dots & \dots \\ \dots & 0 & 0 & H_{-1} & H_0 & H_1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$



$$t_0 = (E - H_0)^{-1} H_0^+ \quad t_i = (I - t_{i-1} \widetilde{t}_{i-1} - \widetilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2$$

$$\widetilde{t}_0 = (E - H_0)^{-1} H_0 \quad \widetilde{t}_i = (I - t_{i-1} \widetilde{t}_{i-1} - \widetilde{t}_{i-1} t_{i-1})^{-1} \widetilde{t}_{i-1}^2$$

$$t_n - t_{n-1} < \varepsilon$$

$$T = t_0 + \widetilde{t}_0 t_1 + \widetilde{t}_0 \widetilde{t}_1 t_2 + \dots + \widetilde{t}_0 \dots \widetilde{t}_{n-1} t_n$$

$$G_0 = (E - H_0 - H_1 T)^{-1}$$

Surface Green's Function

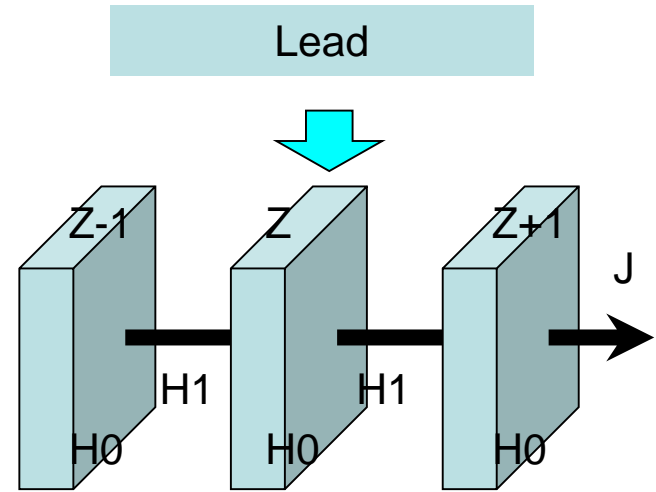
Tight Binding Layer (TBL) Method

S. Sanvito *et al.* Phys. Rev. B **59**(1999)11936

$$g_{z,z'} = \begin{cases} \sum_{l=1}^M \phi_{k_l} e^{ik_l(z-z')} \tilde{\phi}_{k_l}^\dagger \nu^{-1}, & z \geq z' \\ \sum_{l=1}^M \phi_{\bar{k}_l} e^{i\bar{k}_l(z-z')} \tilde{\phi}_{\bar{k}_l}^\dagger \nu^{-1} & z \leq z' \end{cases}$$

$$\nu = \sum_{l=1}^M H_{-1} \left[\phi_{k_l} e^{ik_l(z-z')} \tilde{\phi}_{k_l}^\dagger - \phi_{\bar{k}_l} e^{i\bar{k}_l(z-z')} \tilde{\phi}_{\bar{k}_l}^\dagger \right]$$

Green's function of infinite leads



$$\sum_{l=1}^M \phi_{k_l} \tilde{\phi}_{k_l}^\dagger = \sum_{l=1}^M \phi_{\bar{k}_l} \tilde{\phi}_{\bar{k}_l}^\dagger = \mathbf{I} \quad \tilde{\phi}_{k_l}^\dagger \phi_{k_h} = \tilde{\phi}_{\bar{k}_l}^\dagger \phi_{\bar{k}_l} = \delta_{lh} \quad \text{Solution of H, } \phi \dots$$

→ Dual basis $\tilde{\phi}$

$$\Delta_z(z', z_0) = \Delta_z(z', z_0) = \sum_{l,h=1}^M \phi_{\bar{k}_h} e^{i\bar{k}_h(z-z_0)} \tilde{\phi}_{\bar{k}_h}^\dagger \phi_{k_l} e^{ik_l(z_0-z')} \tilde{\phi}_{k_l}^\dagger \nu^{-1}$$

Boundary condition $Z = Z_0$

$$g_L = \left[\mathbf{I} - \sum_{l,h=1}^M \phi_{\bar{k}_h} e^{i\bar{k}_h} \tilde{\phi}_{\bar{k}_h}^\dagger \phi_{k_l} e^{ik_l} \tilde{\phi}_{k_l}^\dagger \right] \nu^{-1} \quad \rightarrow \text{Semi-infinite (Surface Green's function)}$$