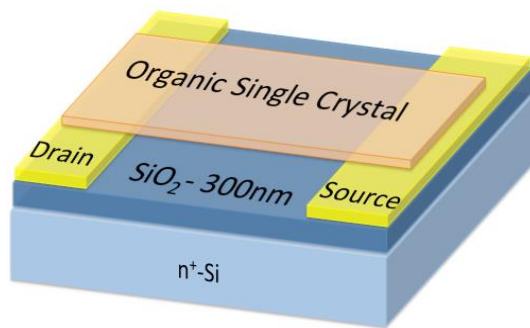


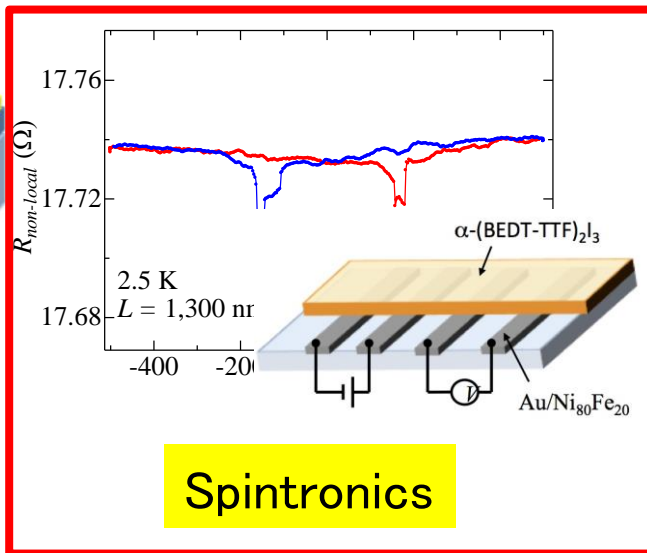
# 有機スピントロニクス

基礎工学研究科  
大戸達彦

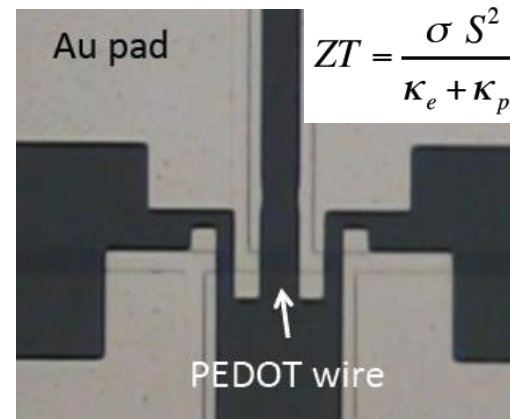
Thin Film



Electronics

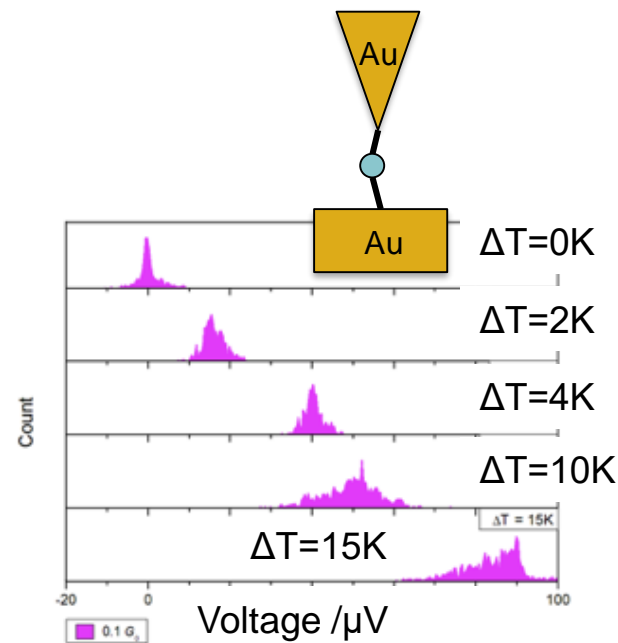
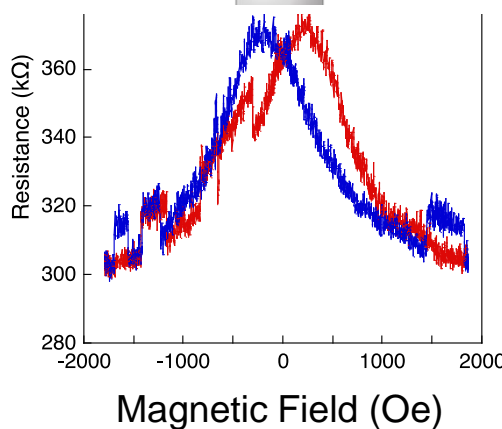
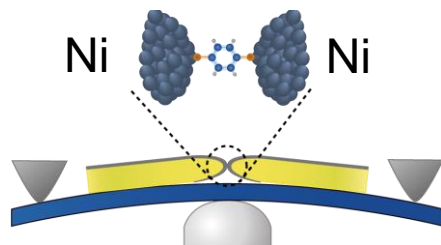
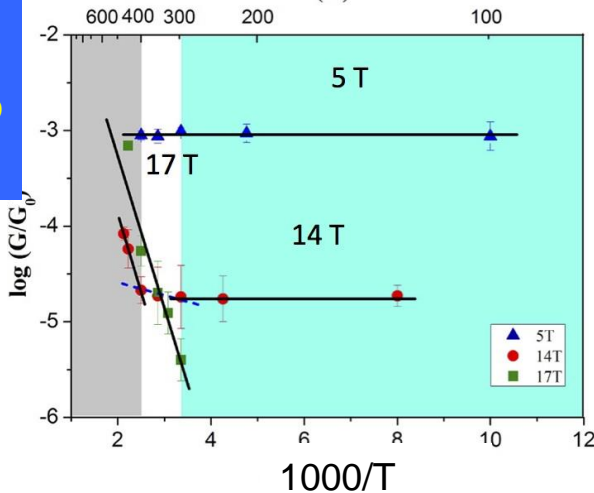
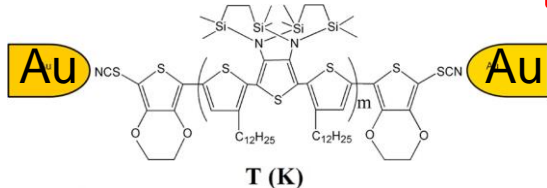


Spintronics



Thermoelectronics

Single Molecule



# Spintronics

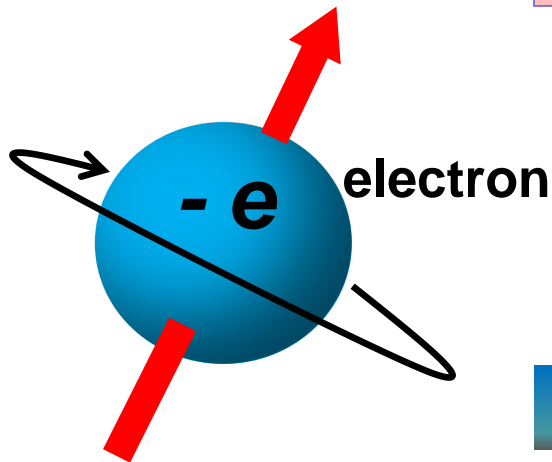
Spin

Magnetics

Spintronics

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

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



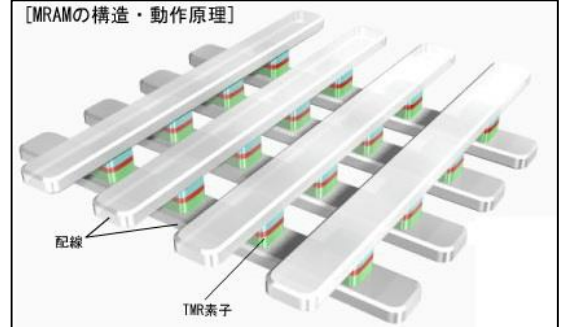
Electronics

- Transistor
- Laser
- LSI
- etc...

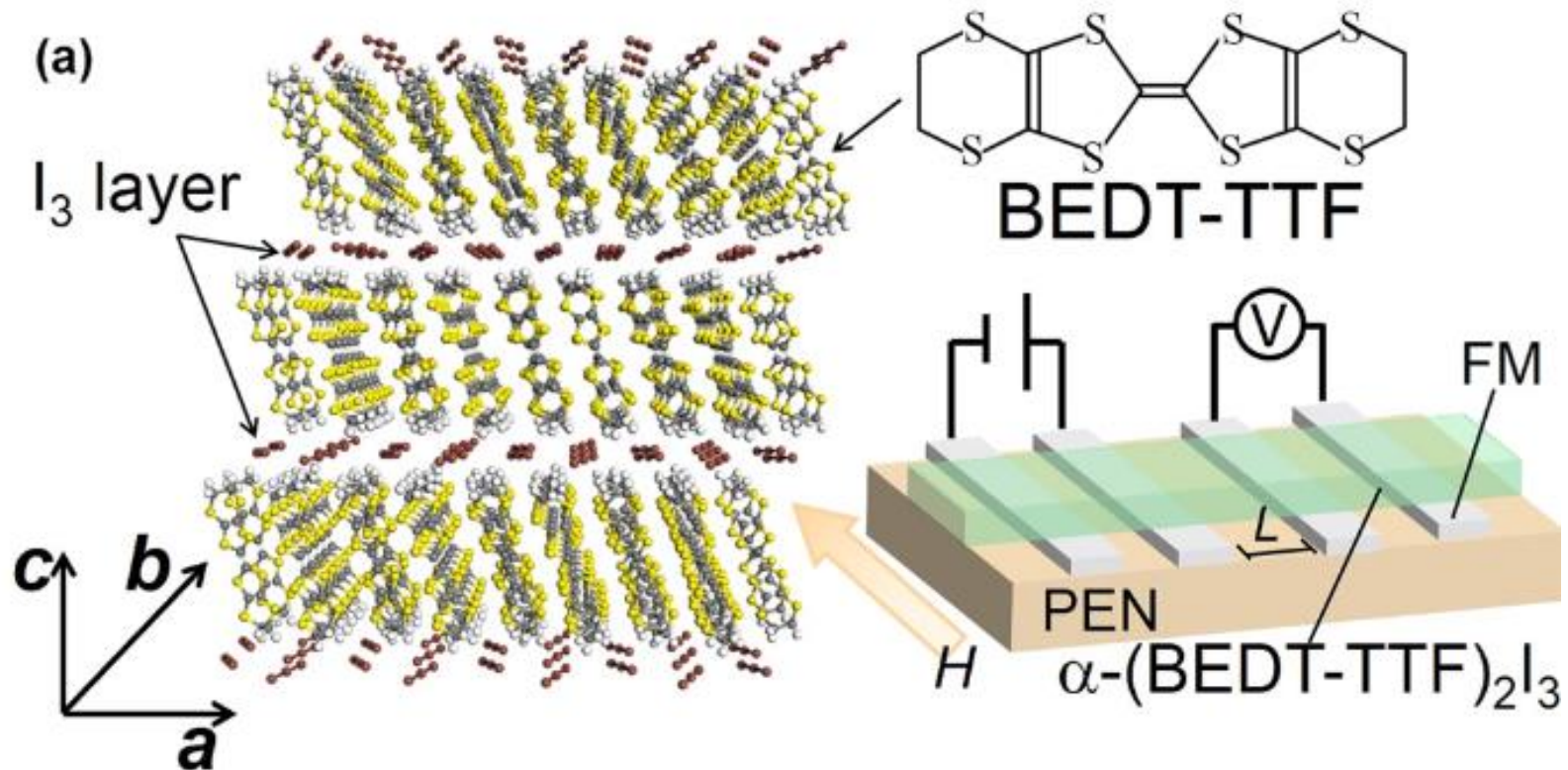
Electron



[MRAMの構造・動作原理]



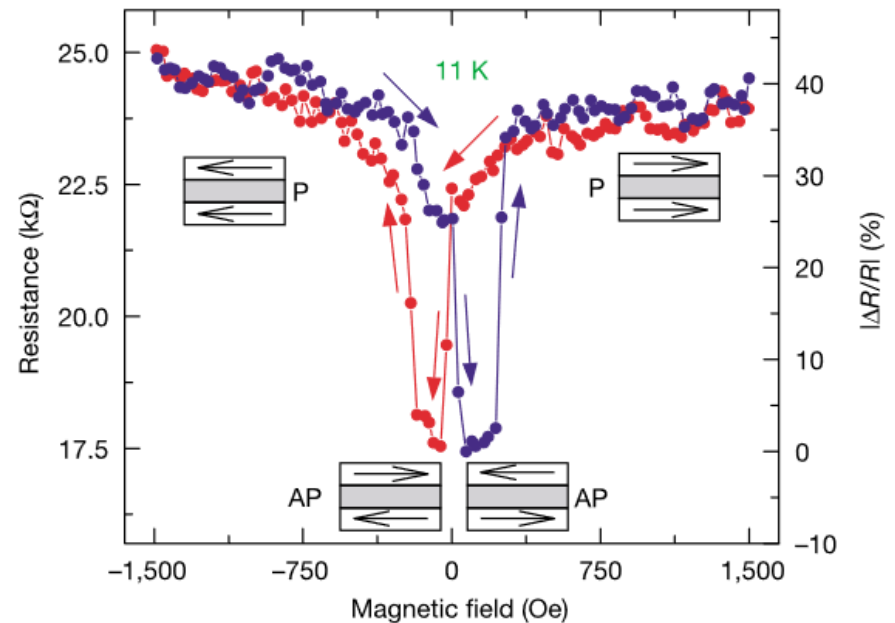
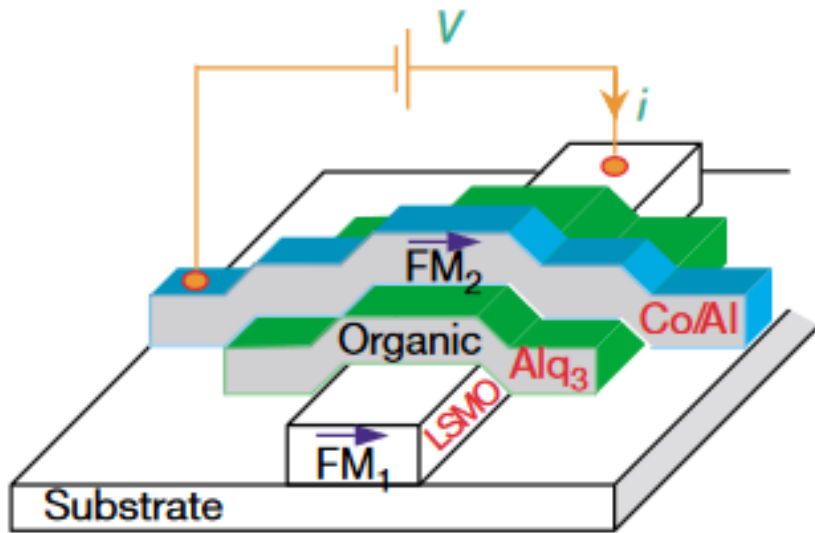
# First report of lateral organic spin valve



T. Kamiya *et al.* Phys. Rev. B **95** (2017) 085307

# Organic Spin Valve

2004 Vardeny  
Organic Spin Valve

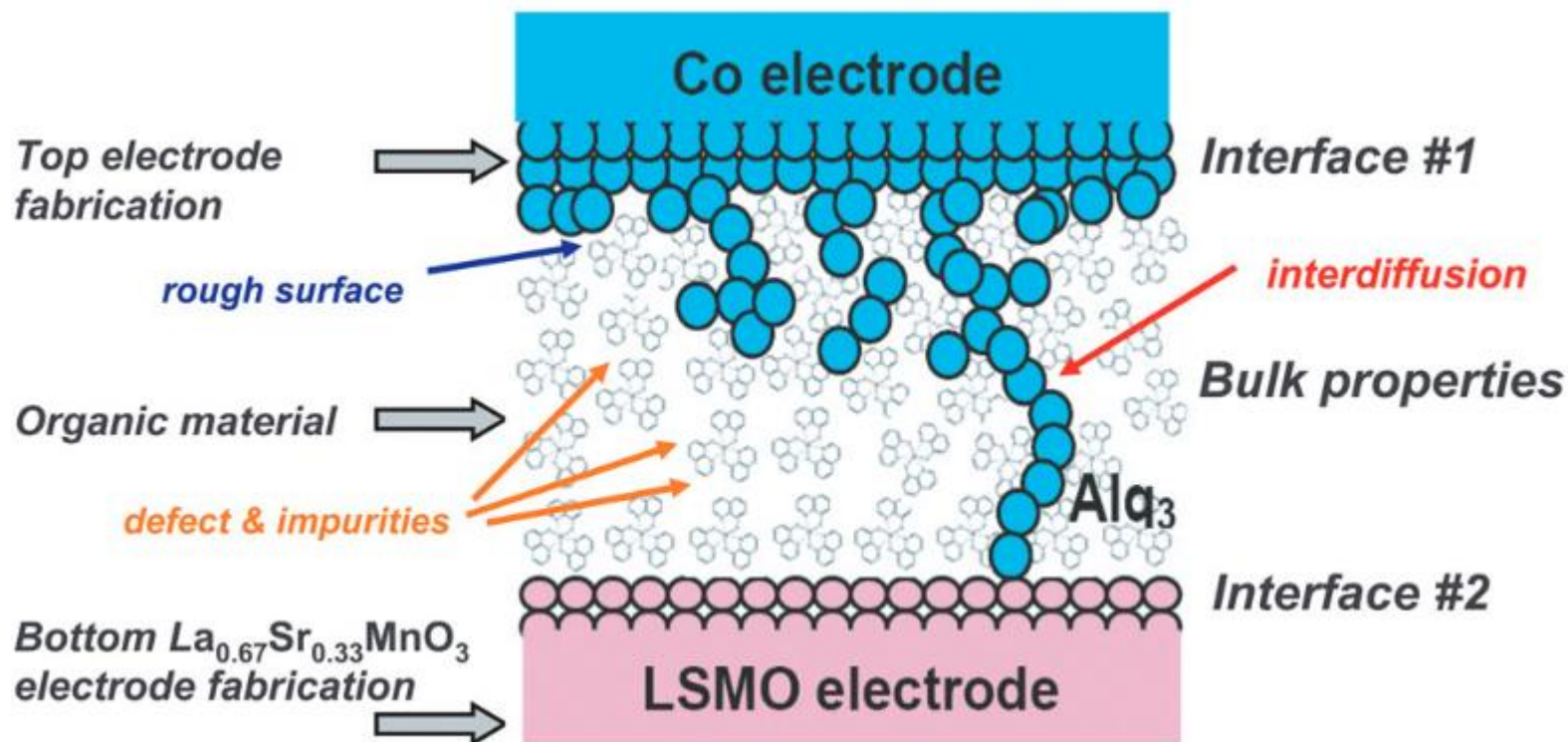


Xiong *et al.* Nature **427** (2004) 821

Weak spin-orbit interaction

Molecular design, light weight

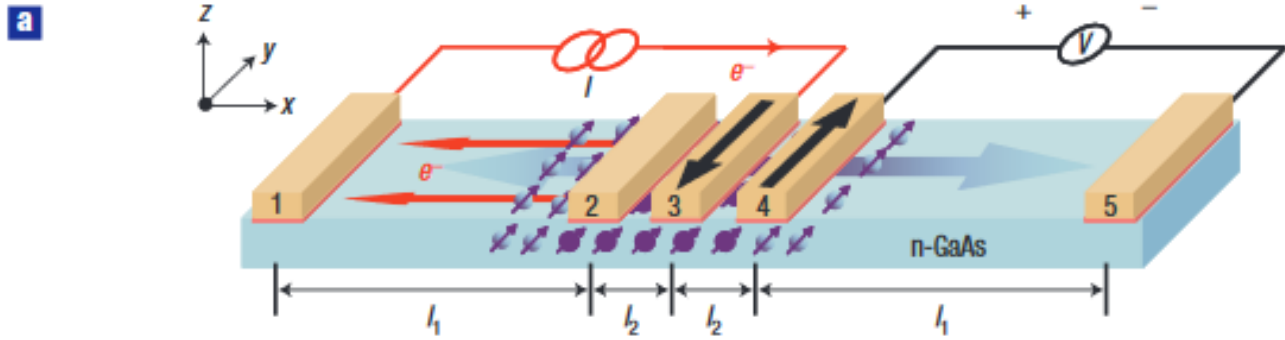
# Problems of vertical devices?



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

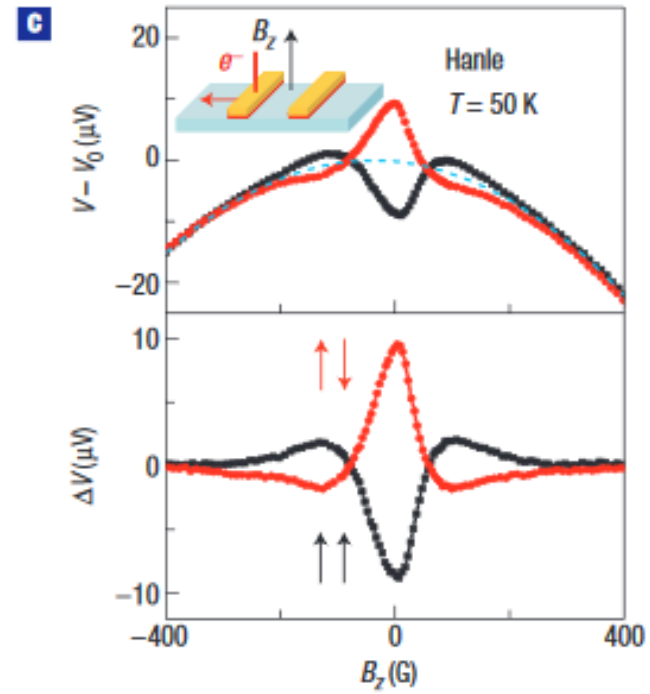
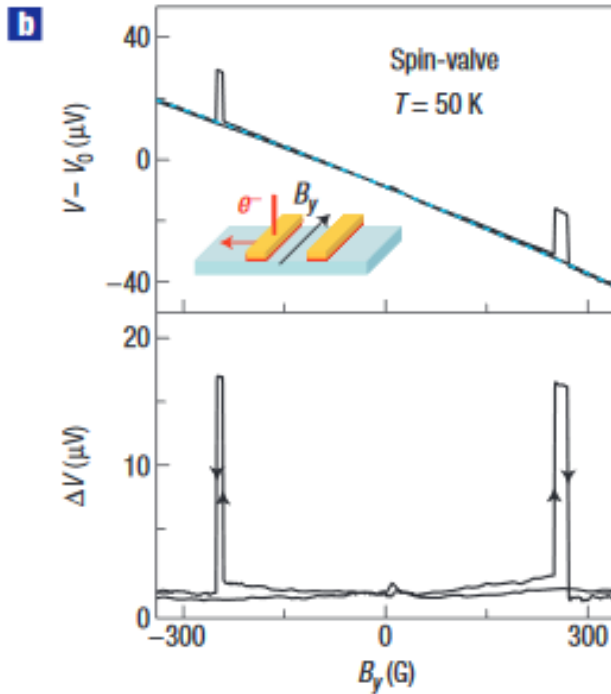
Can we inject spin into organic materials?

# Lateral Device

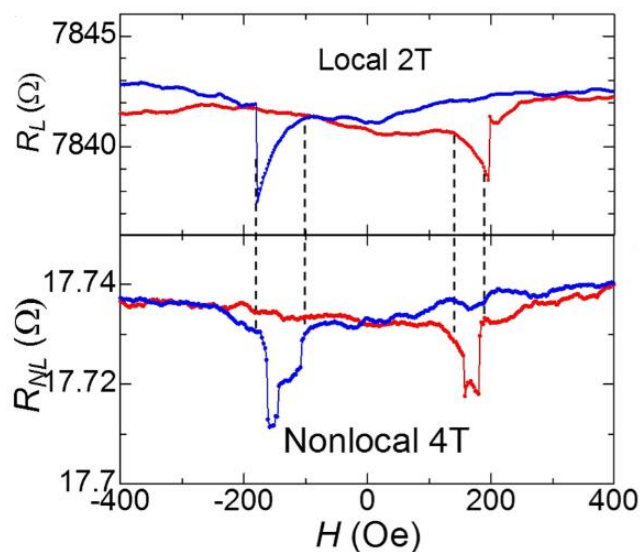
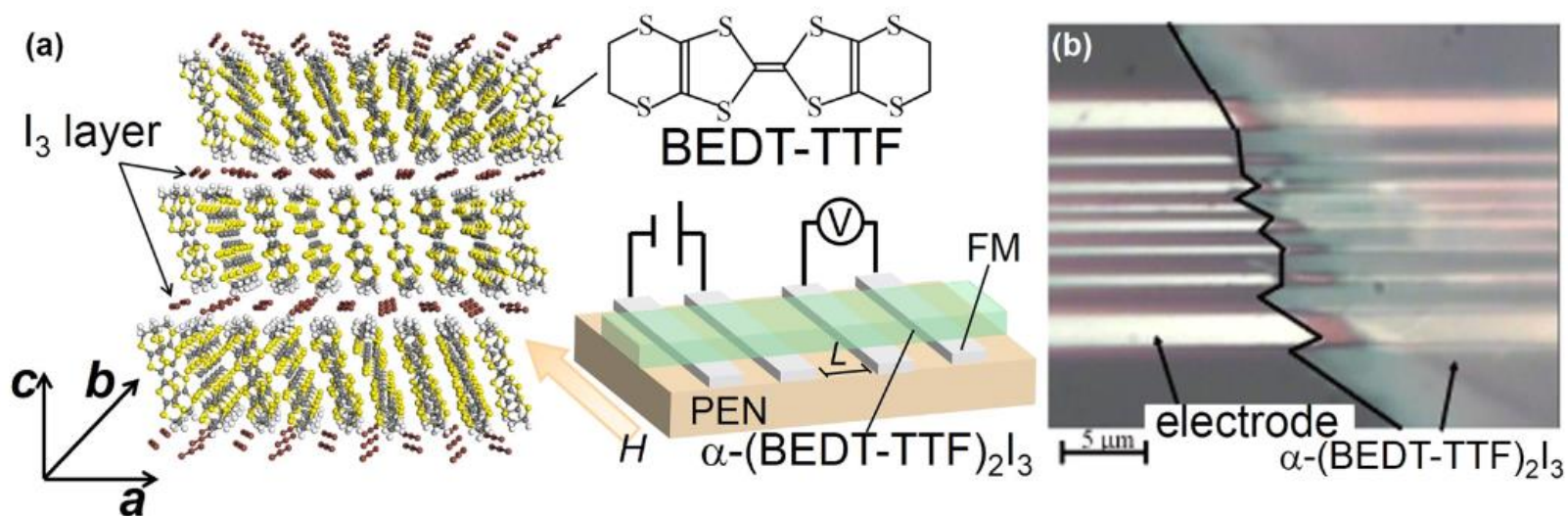


Spin valve

Hanle effect



# Lateral Organic Spin Valve



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

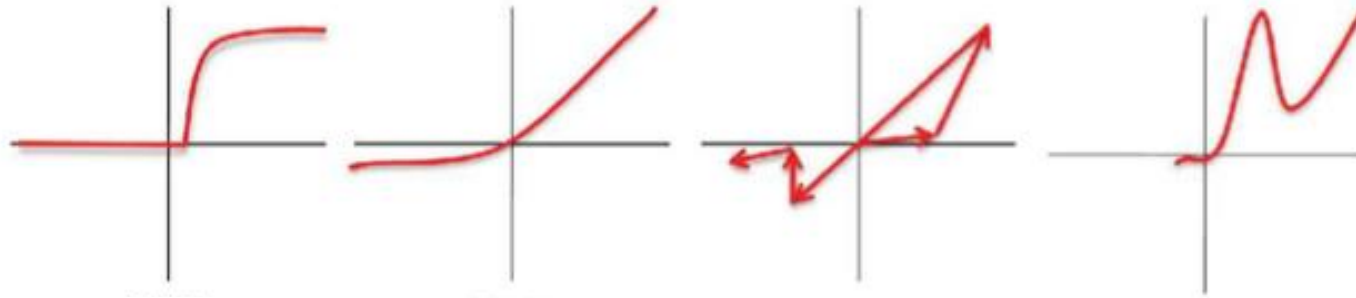


# Outline

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

# **1. Single Molecular Spin Valve**

# Single Molecular Electronics

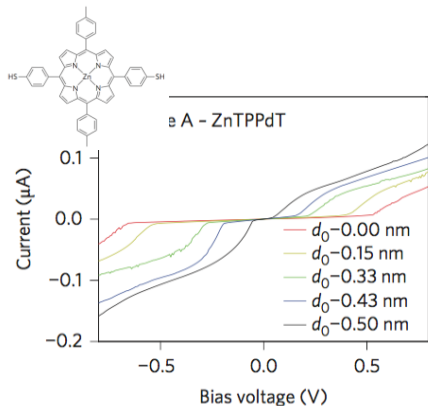


Threshold  
\*Coulomb blockade

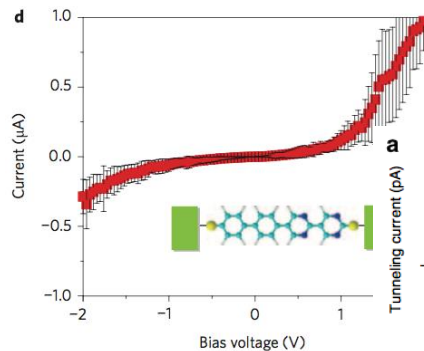
Rectification  
(Diode)

Hysteresis  
(Memory/Switch)

Negative differential  
resistance (NDR)

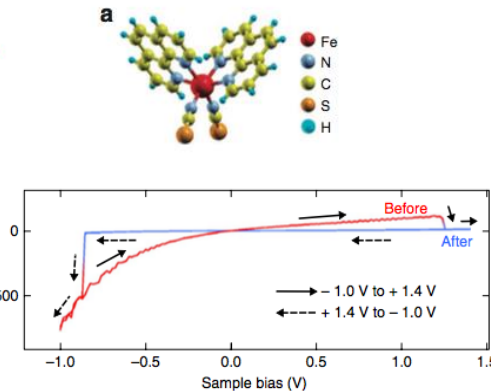


ML Perrin et al., Nature Nanotech. 8, 282 (2013).

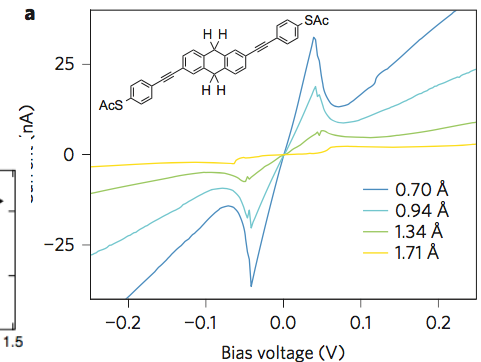


I. Diez-Perez et al., Nature Chem. 1, 635 (2009).

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

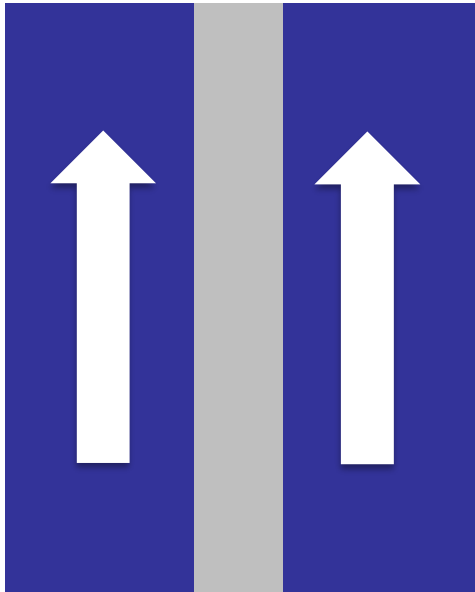


Spin-cross over; T. Miyamachi et al., Nature Comm. 3, 938 (2012)  
Mg-Porphine; S. Saha et al., Apl. Mater&Inter., 7, 10085 (2015).

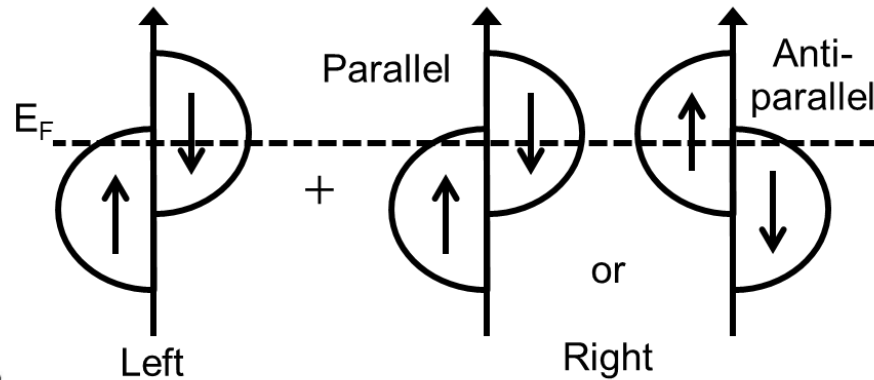


ML Perrin et al., Nature Nanotech. 9, 830 (2014).  
(Double barrier resonant tunneling)

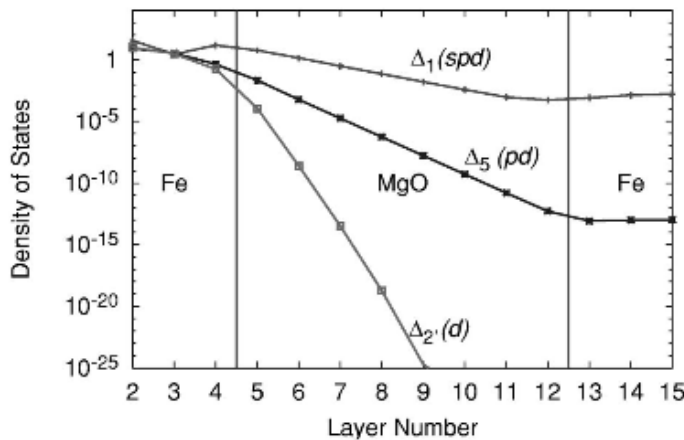
# Tunneling Magnetoresistance (TMR)



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

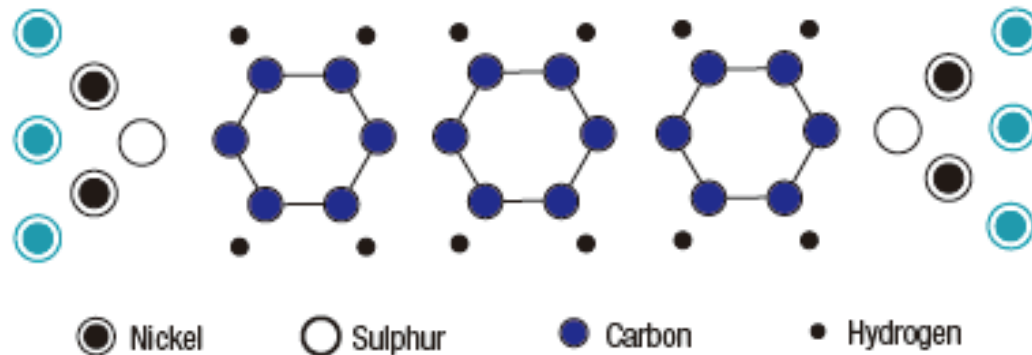


Majority Density of States for Fe|MgO|Fe

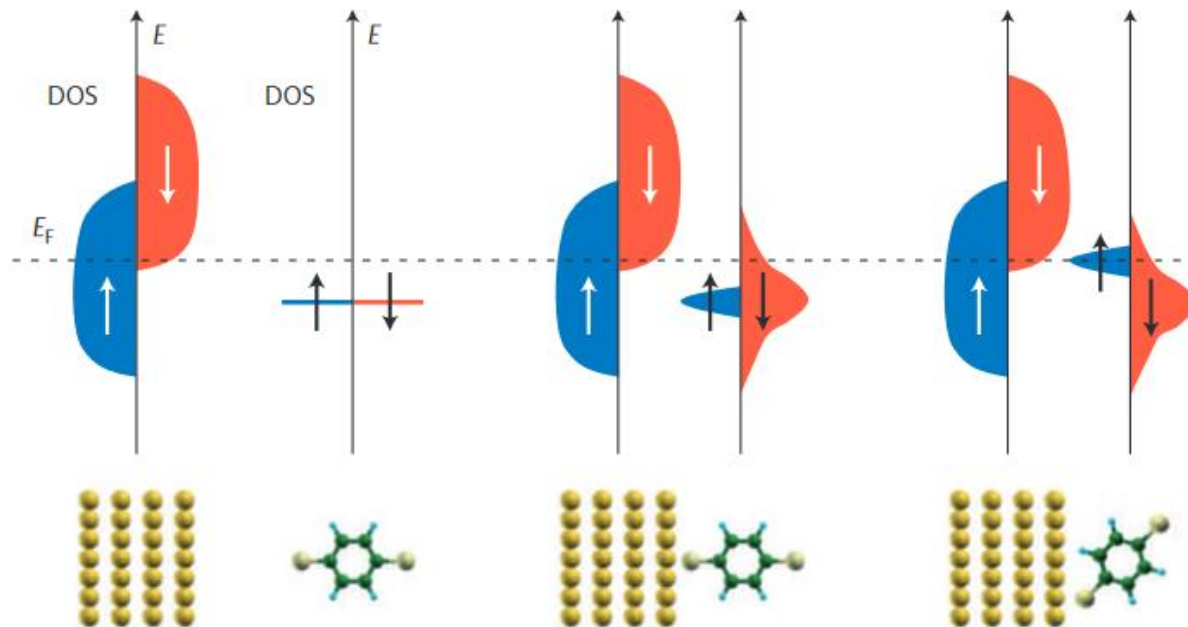


MgO crystal blocks d electron of majority spin

# Single Molecular TMR Devices

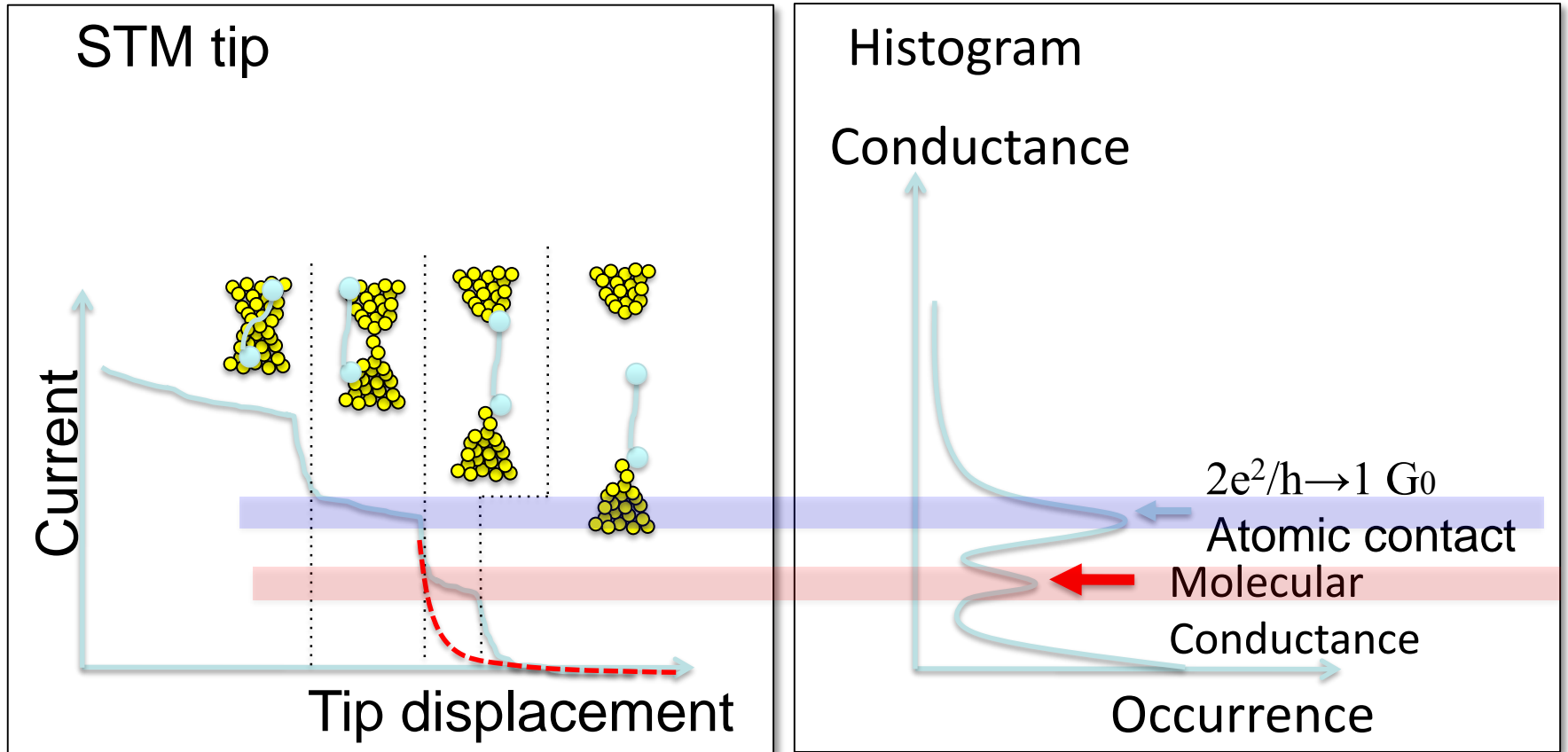


Rocha *et al.* Nat. Mater. **4** (2005) 335



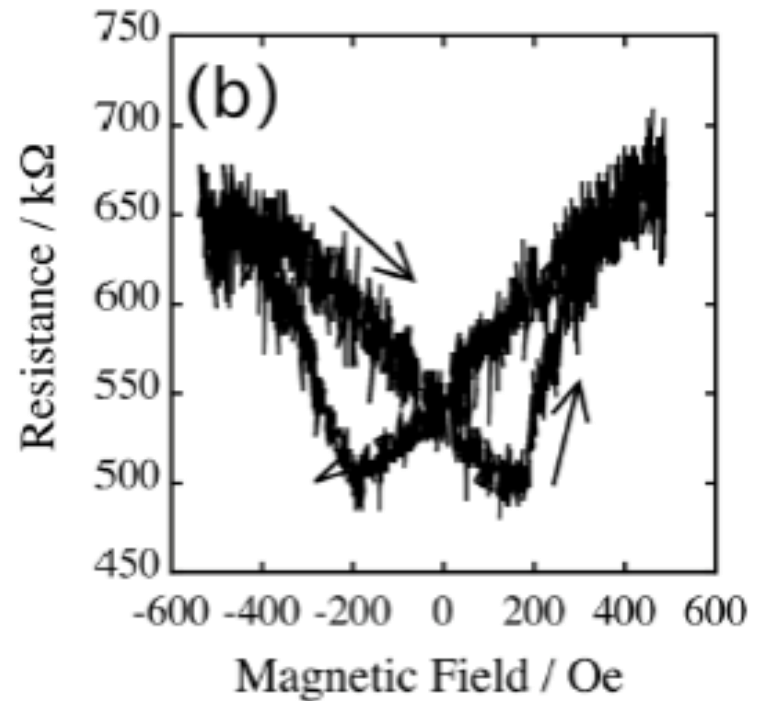
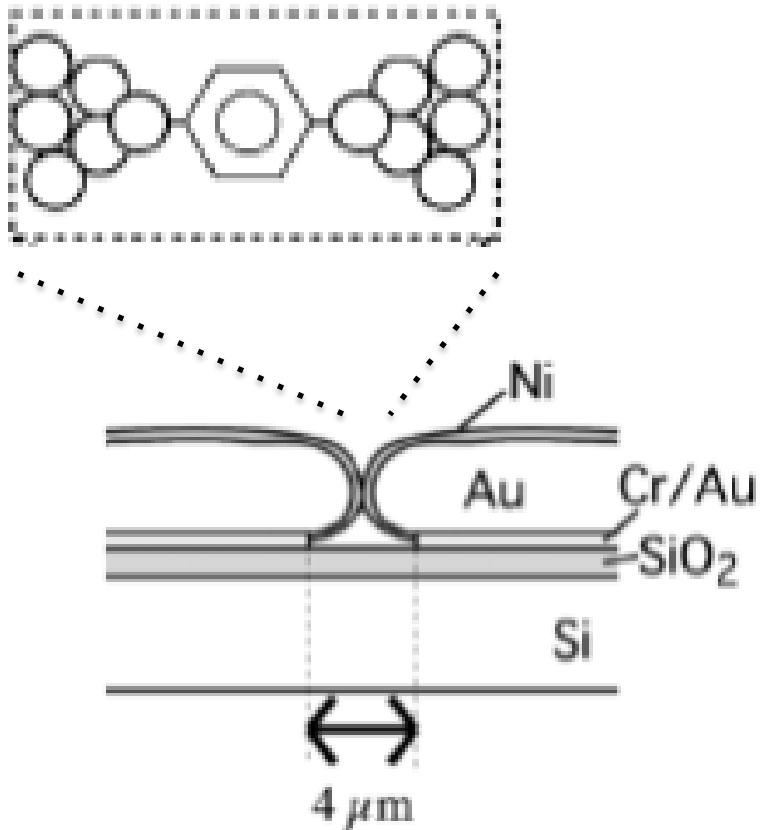
S. Sanvito Nat. Phys. **6** (2010) 562

# Experimental Methods



Break Junction (BJ) Method

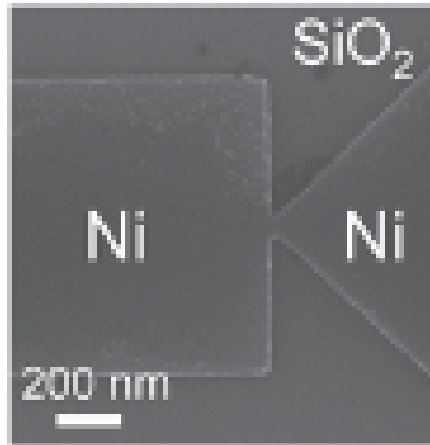
# Experimental Methods



MCBJ with magnetic electrodes

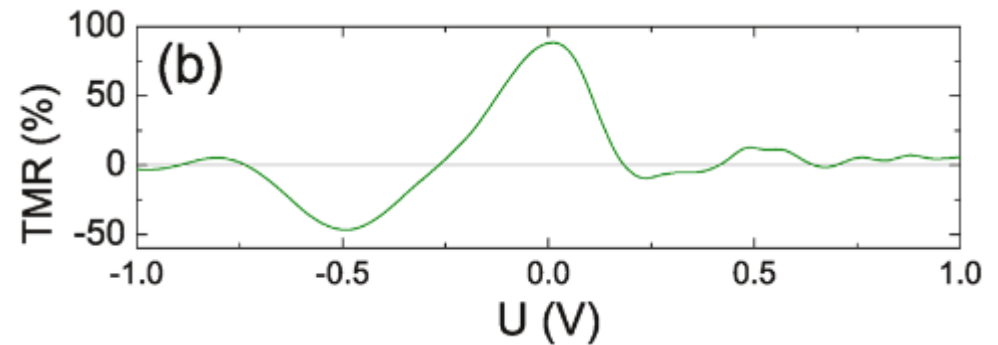
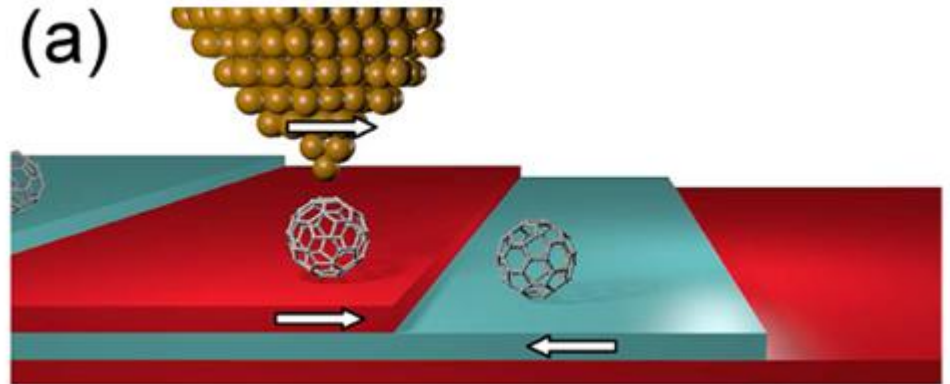
Yamada *et al.* APL **98** (2011) 053110

# Experimental Methods



Electrical break junction method,  
C<sub>60</sub>/Ni

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

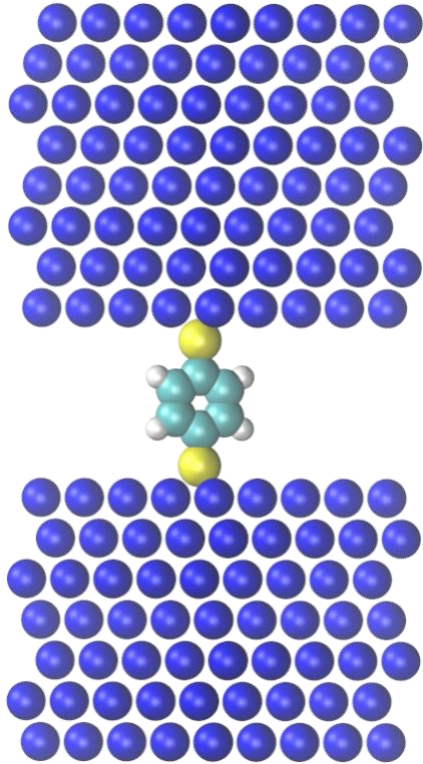


Scanning tunneling microscopy  
(STM), C<sub>60</sub>/Cr(001)

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



# Theoretical Design of Molecular Spin Valve



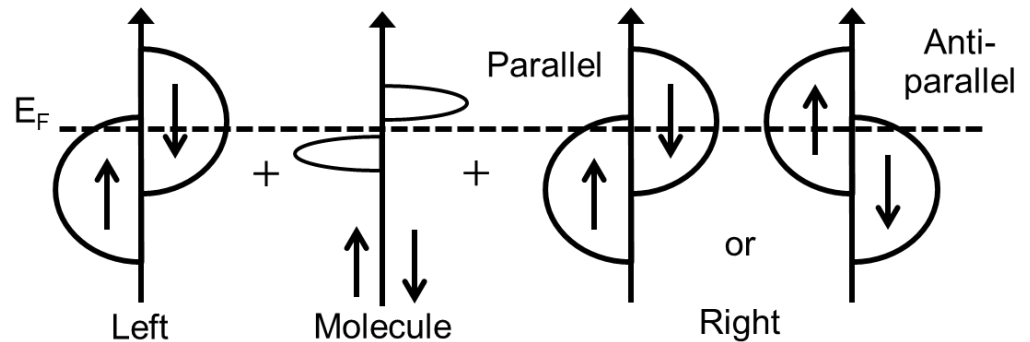
- Origin of magnetoresistance

  - TMR

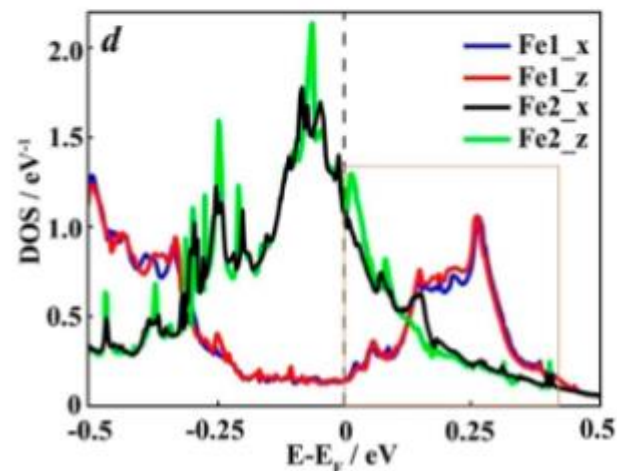
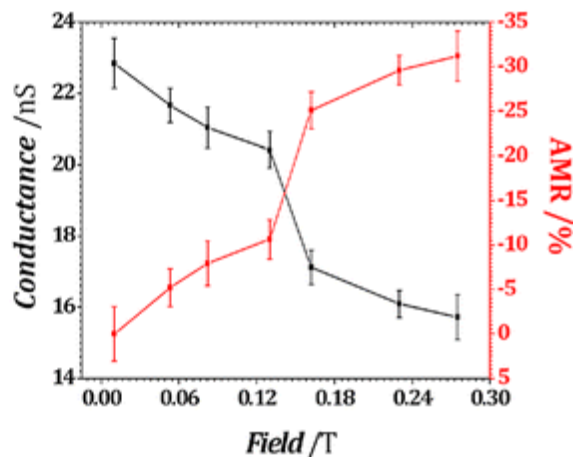
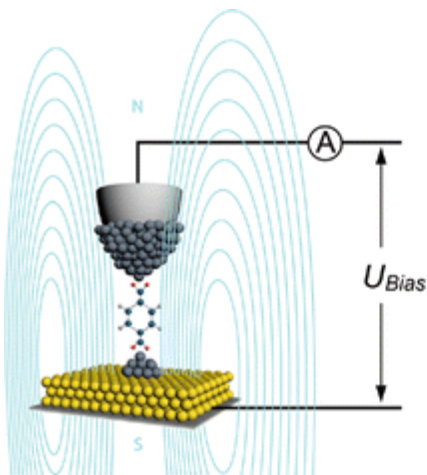
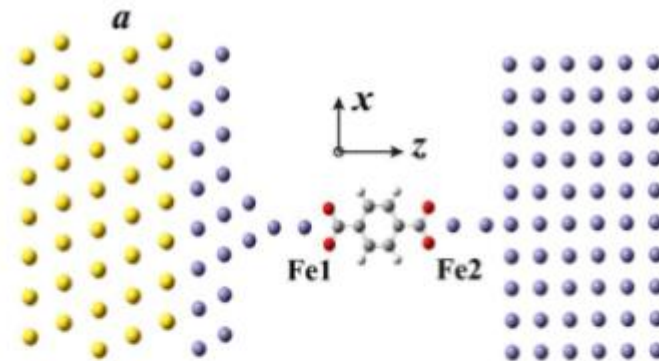
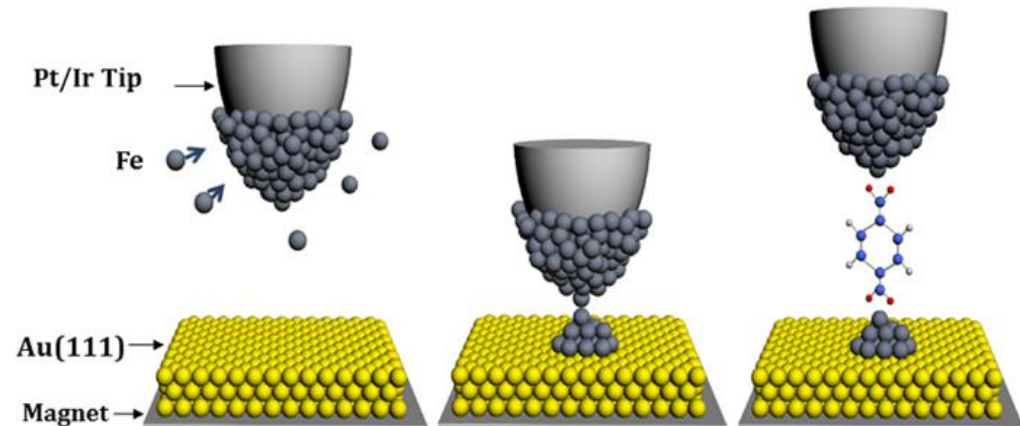
  - TAMR

- Molecular structure

- Spin filter effect



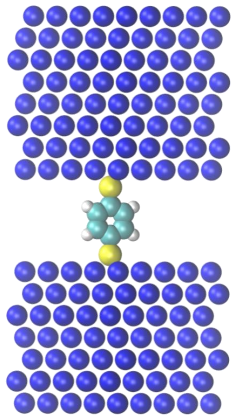
# Tunneling Anisotropic MR (TAMR)



## **2. 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

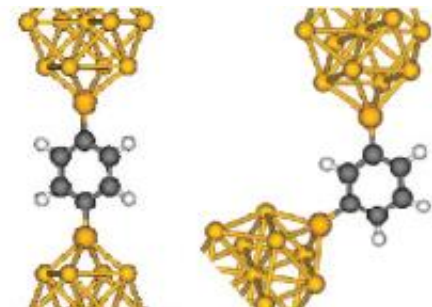
OpenMX (Japan)

## Plane Wave

Quantum Espresso

## Gaussian Basis

Turbomole





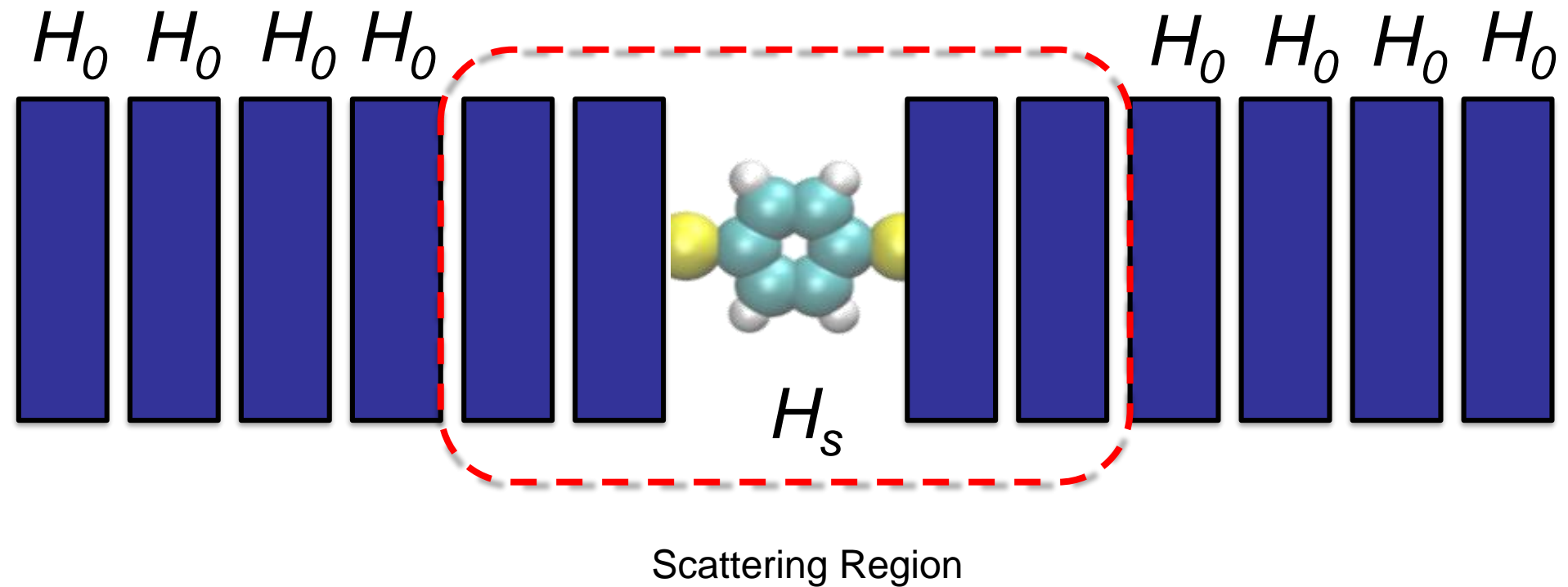
# *Smeagol*

**Non-equilibrium Electronic Transport**



*© 2003 New Line Productions, Inc. All Rights Reserved.*

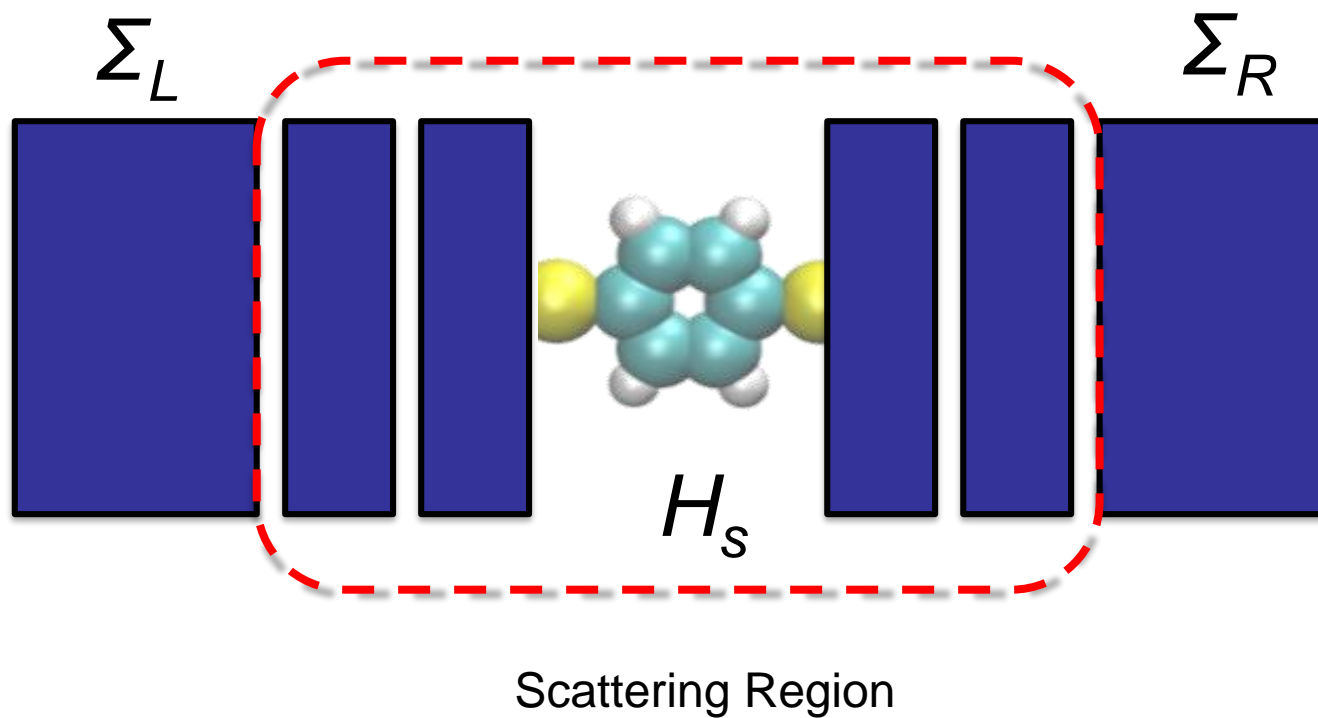
# NEGF



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

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

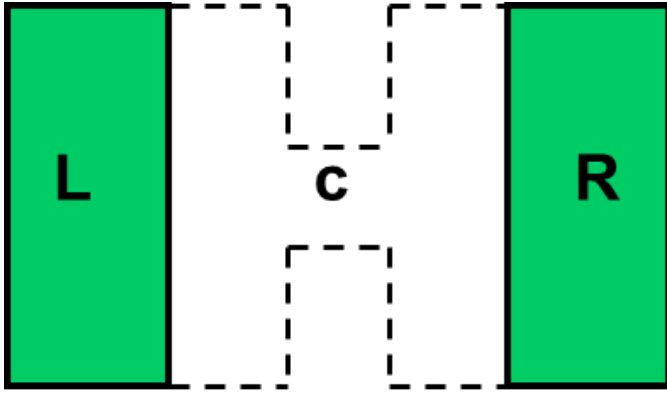
# NEGF



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

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

# 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

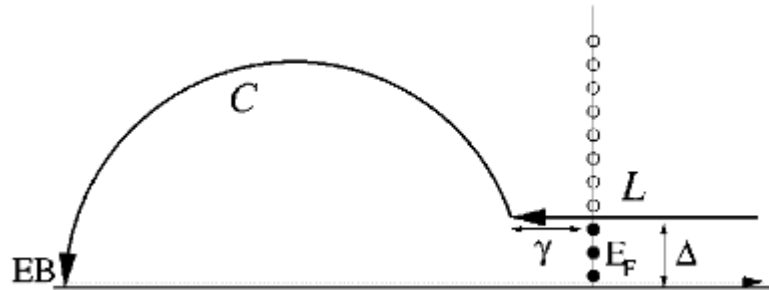


# NEGF-SCF

“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

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

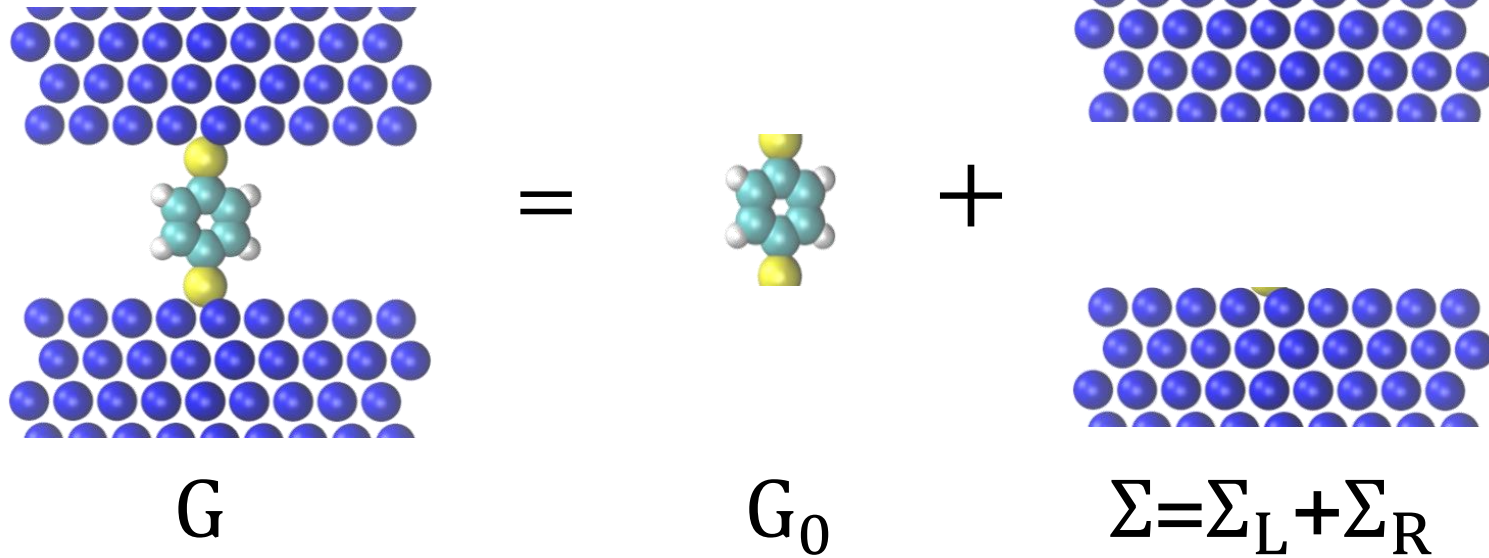
Convergence of density matrix

# 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  $\Sigma$

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

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

↑ lesser self energy

# **3. 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

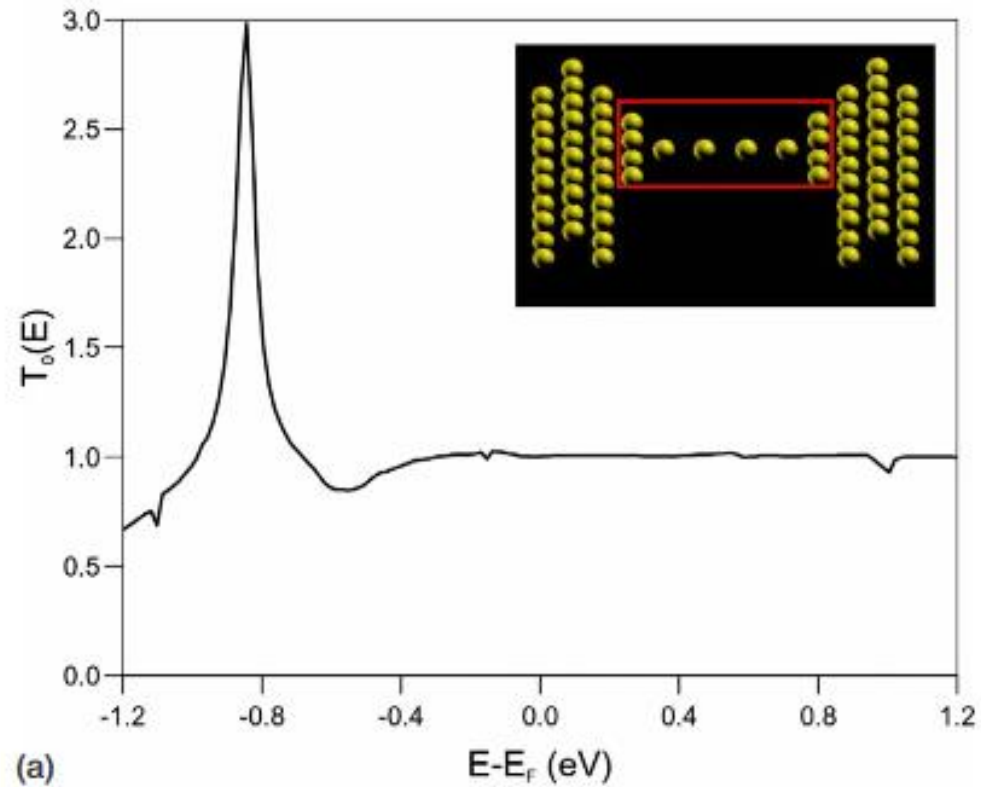
$$I(V_b) = \frac{1}{\pi} \int dE T(E, V_b) \left( f(E - \mu_L) - f(E - \mu_R) \right)$$

- Spin Transfer Torque

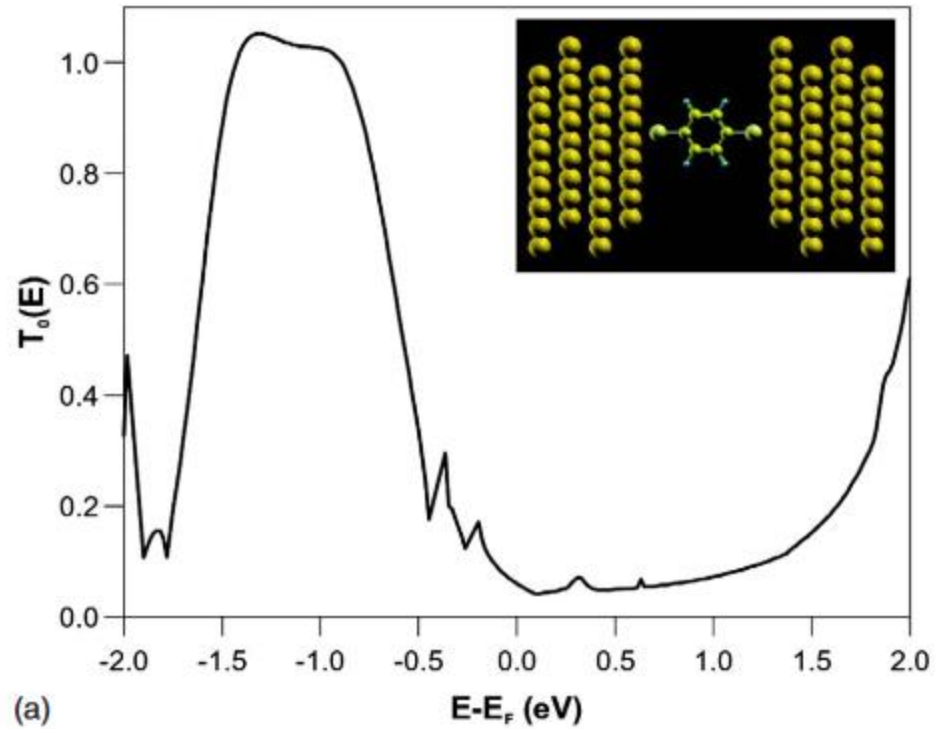
with SMEAGOL

- TAMR

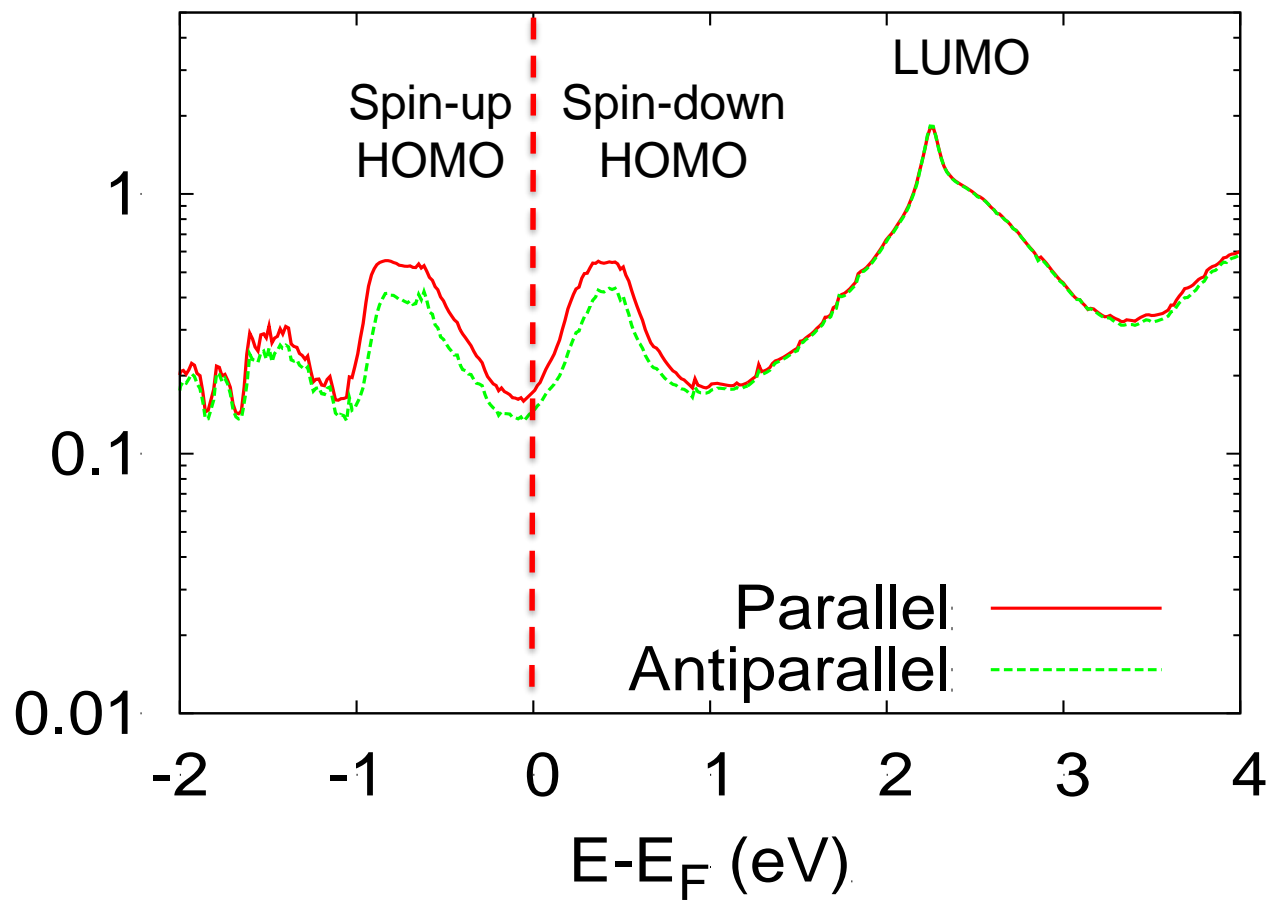
# Gold wire



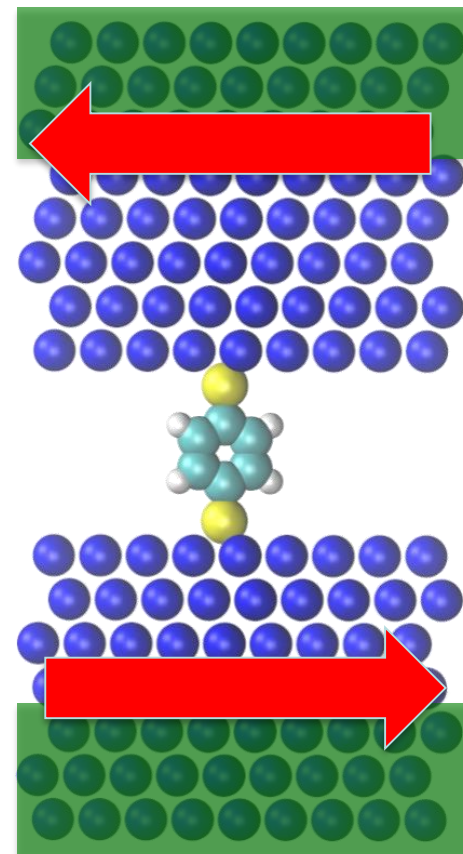
# Au-BDT-Au



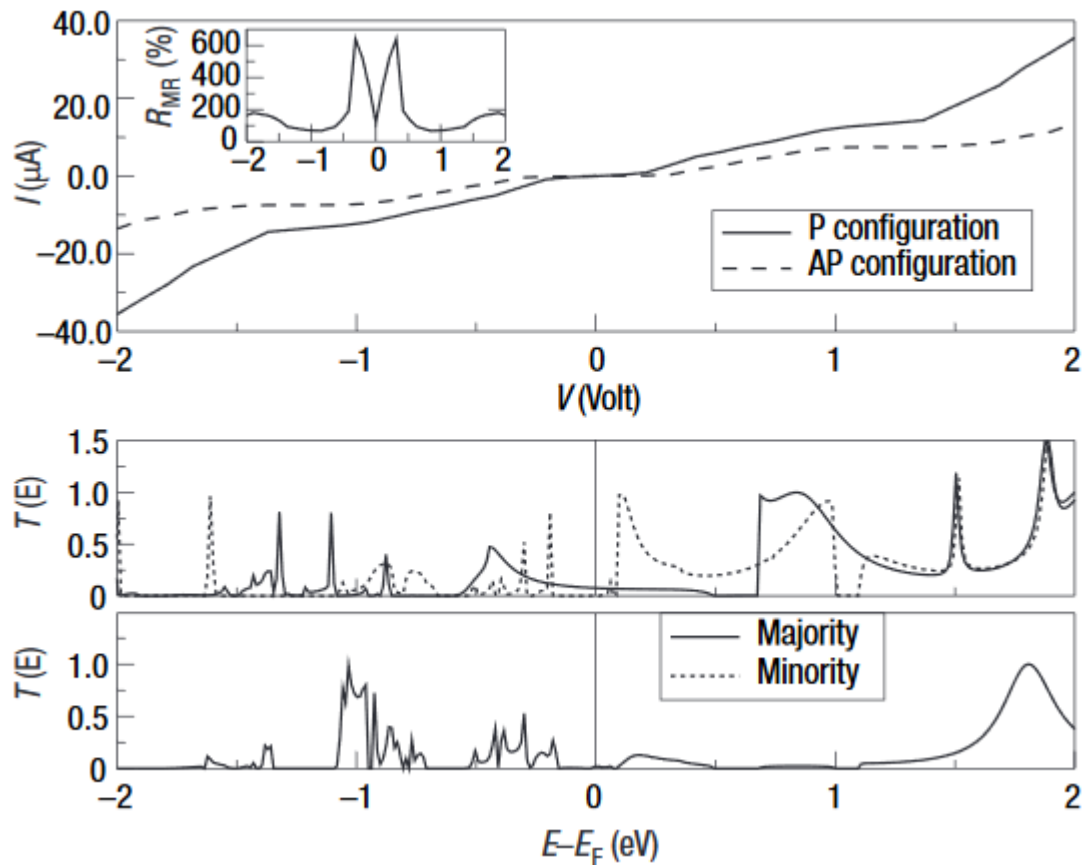
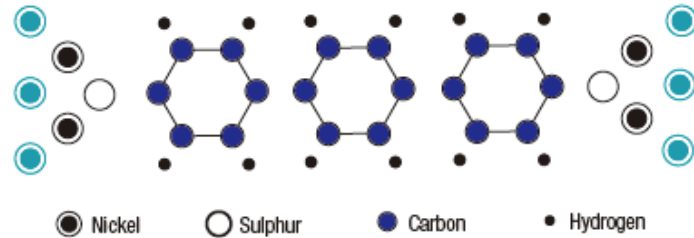
# Ni-BDT-Ni



TMR~20%



# Possibility of higher TMR





# Thermoelectric device



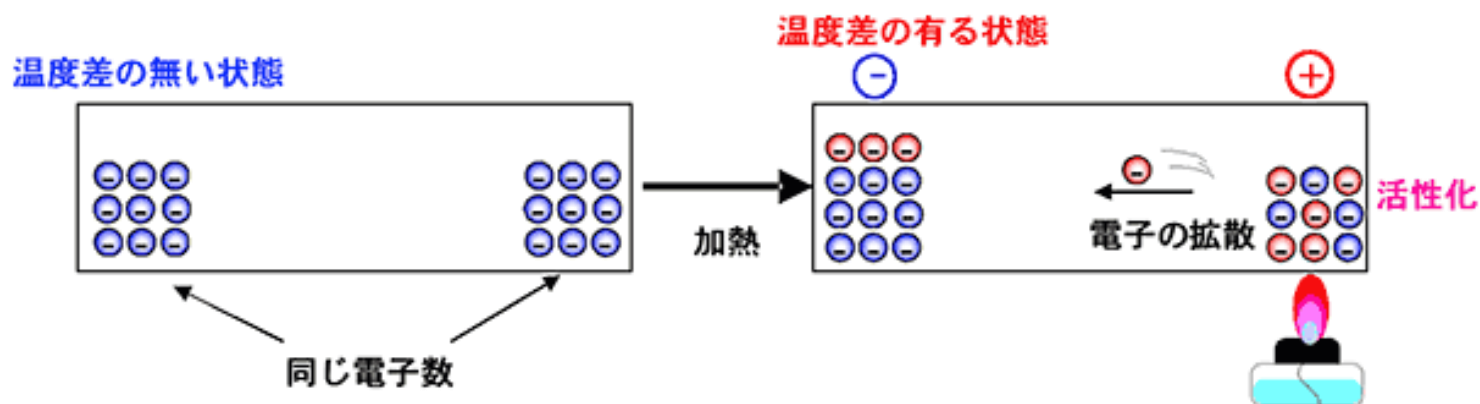
BioLite Inc.

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

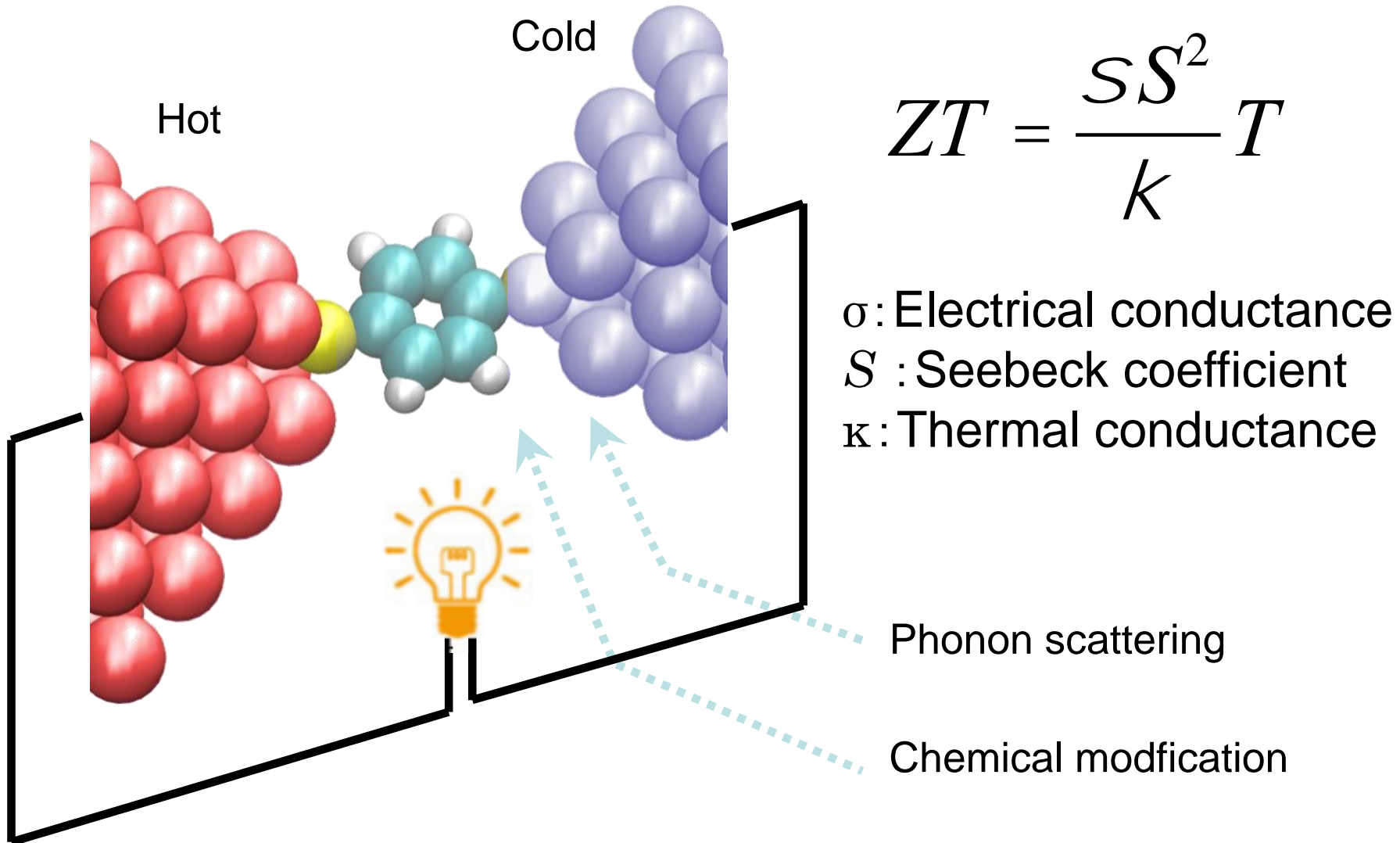
$\sigma$ : 電気伝導度

$S$ : ゼーベック係数

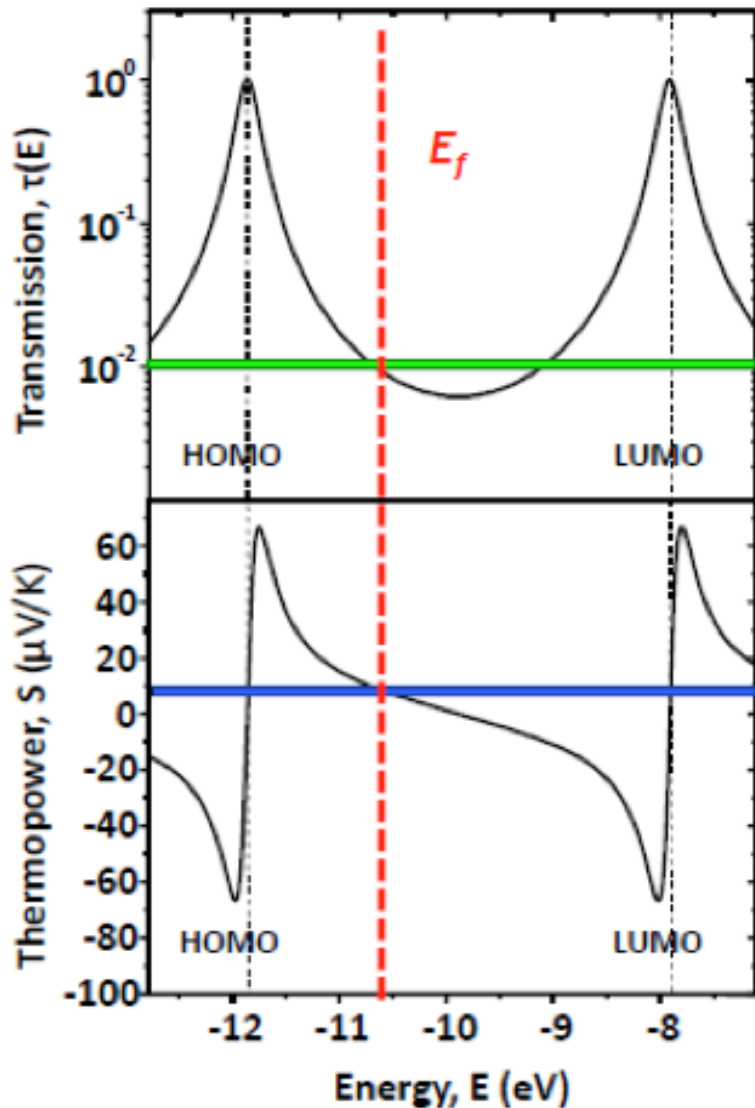
$k$ : 熱伝導度



# Molecular thermoelectric device



# Thermopower (Seebeck Coefficient)



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

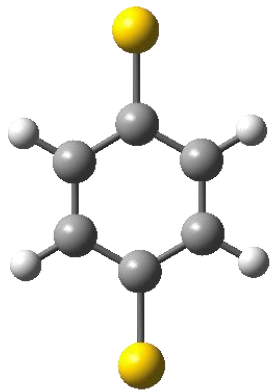
Gradient of the conductance



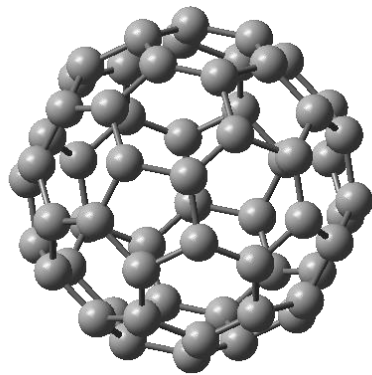
Electron or hole?

Calculation of  $T(E)$  from conductance and thermopower

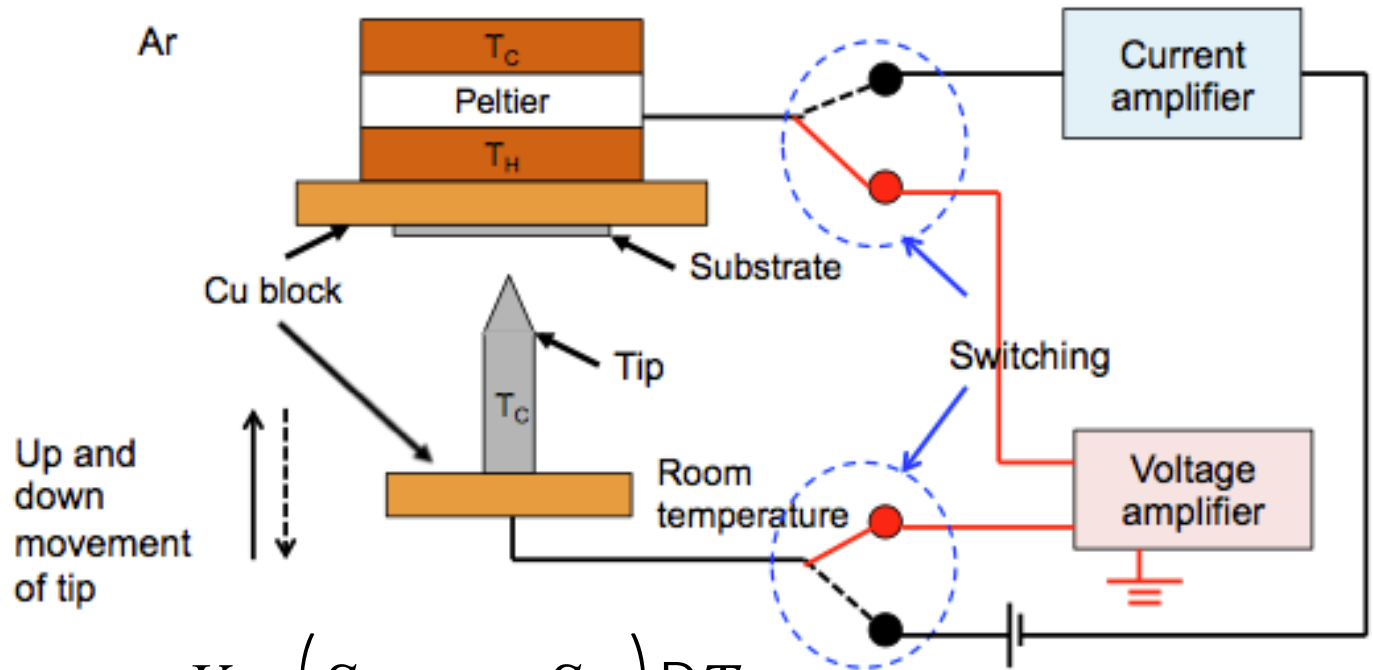
# Thermopower measurement



BDT



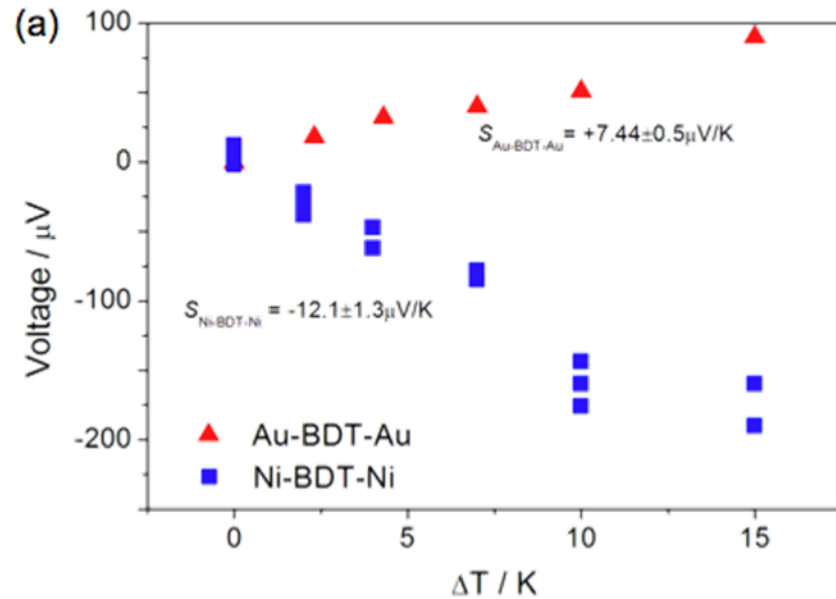
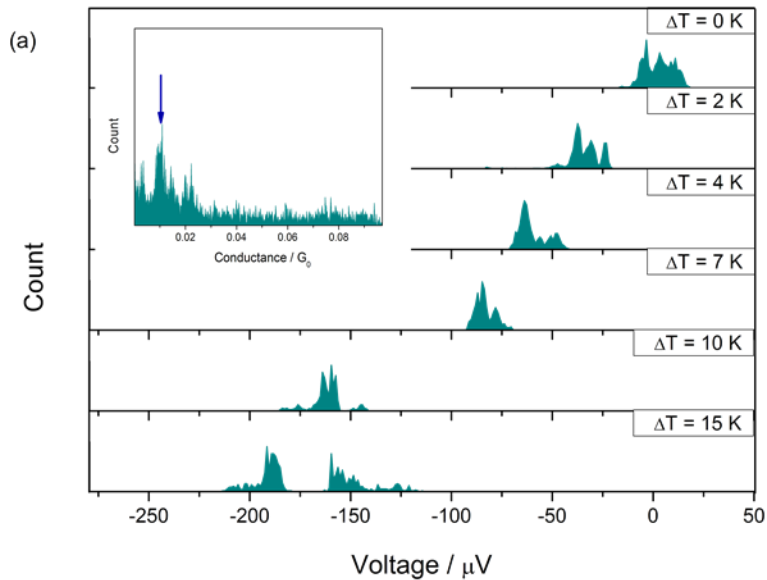
C<sub>60</sub>



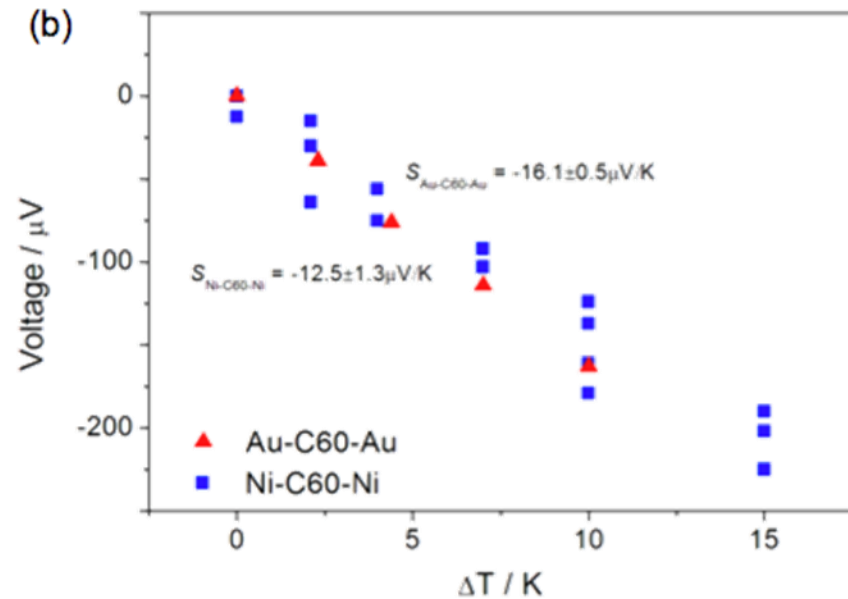
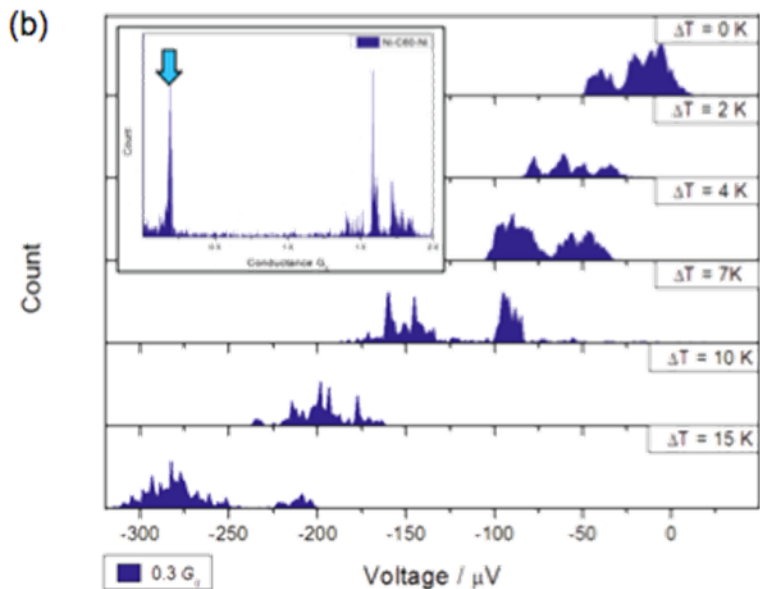
$$V = (S_{\text{junction}} - S_{\text{Cu}}) DT$$

Substrate → Au and Ni

# Thermopower measurement



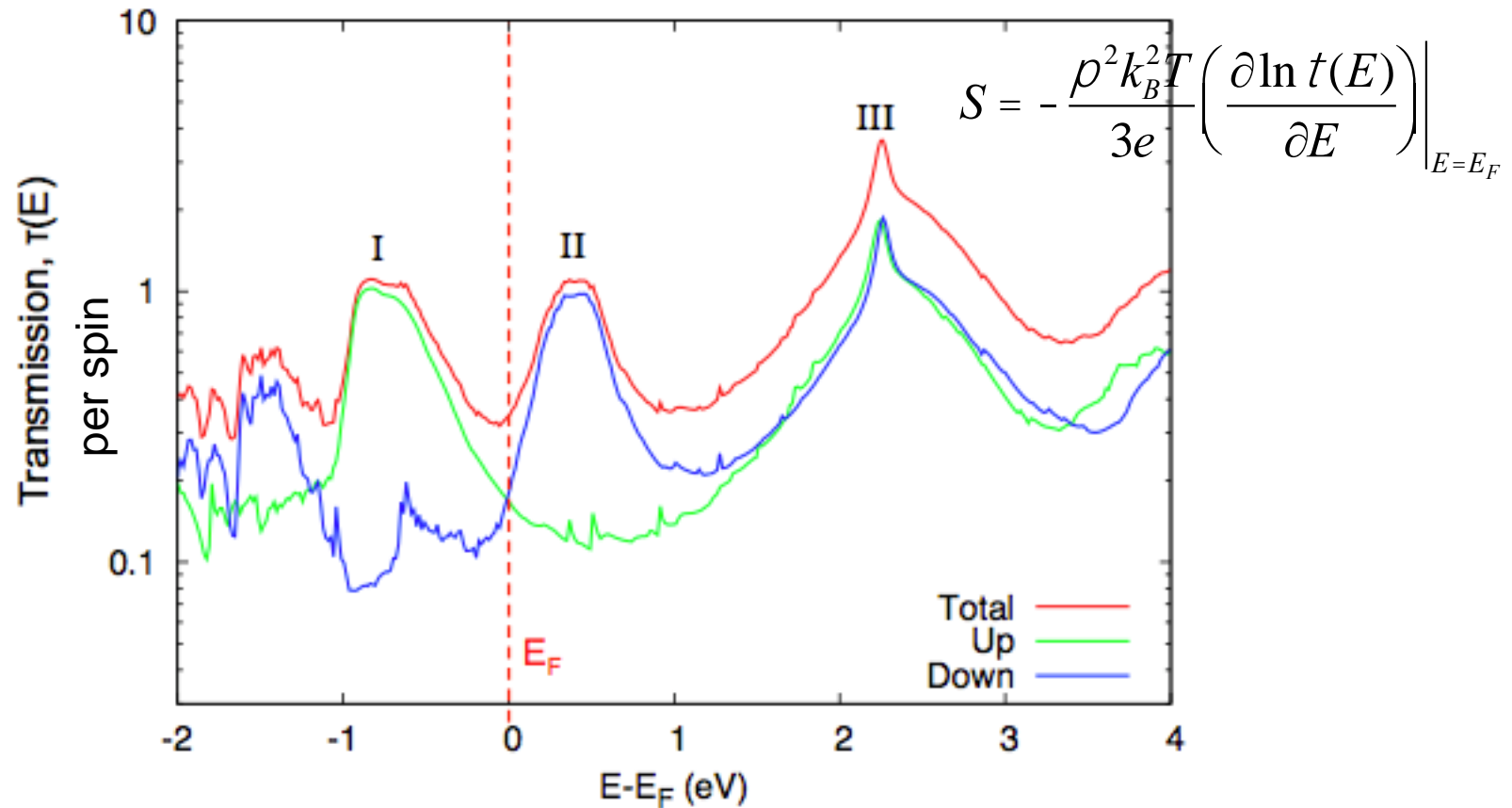
BDT



$C_{60}$

# Ni(111)-BDT-Ni(111)

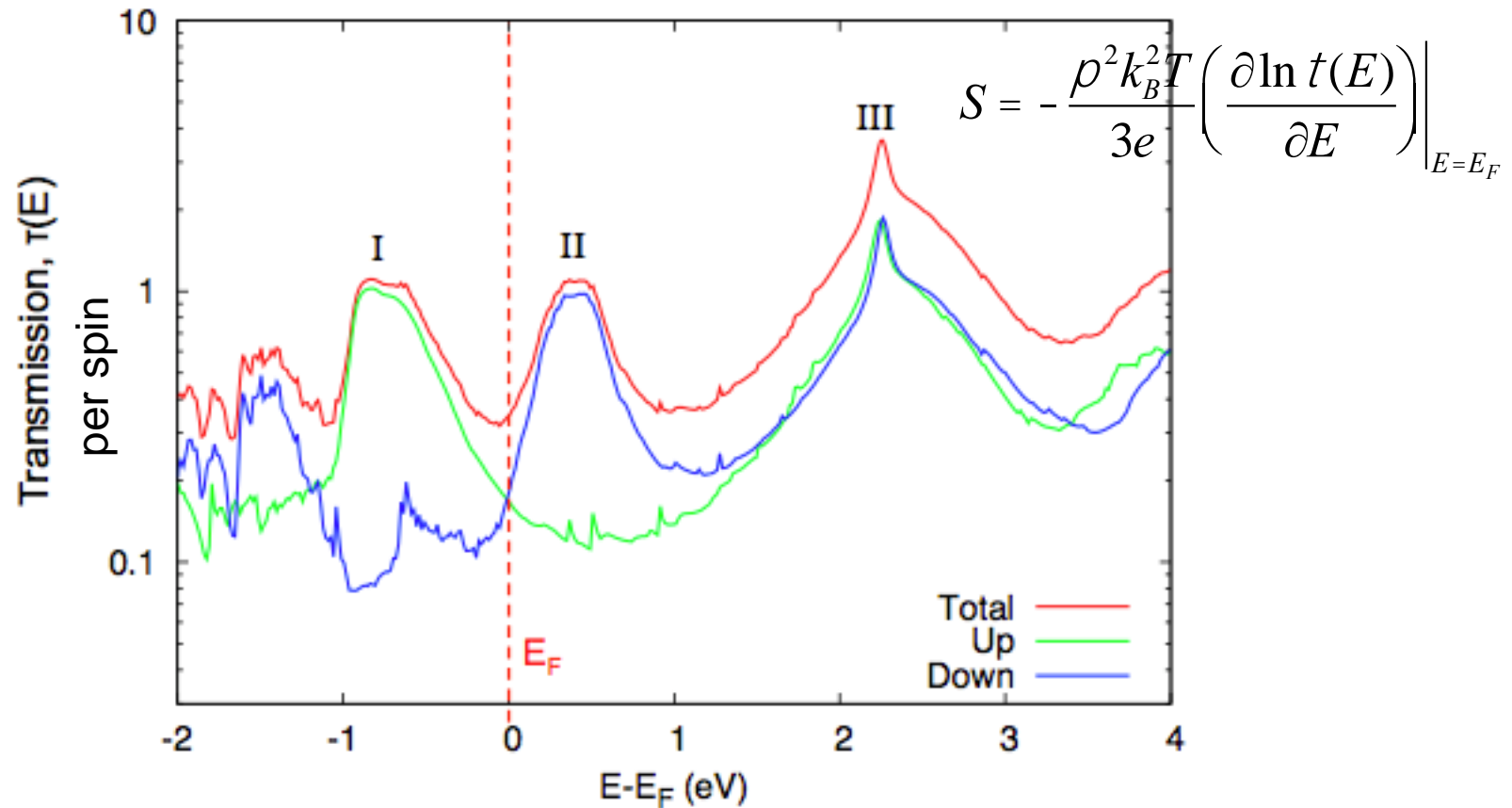
SMEAGOL module (NEGF-DFT), LDA functional



分子軌道 (HOMO) のスピン分極によりフェルミ準位より上に軌道が現れる  
⇒ゼーベック係数の符号が変わる

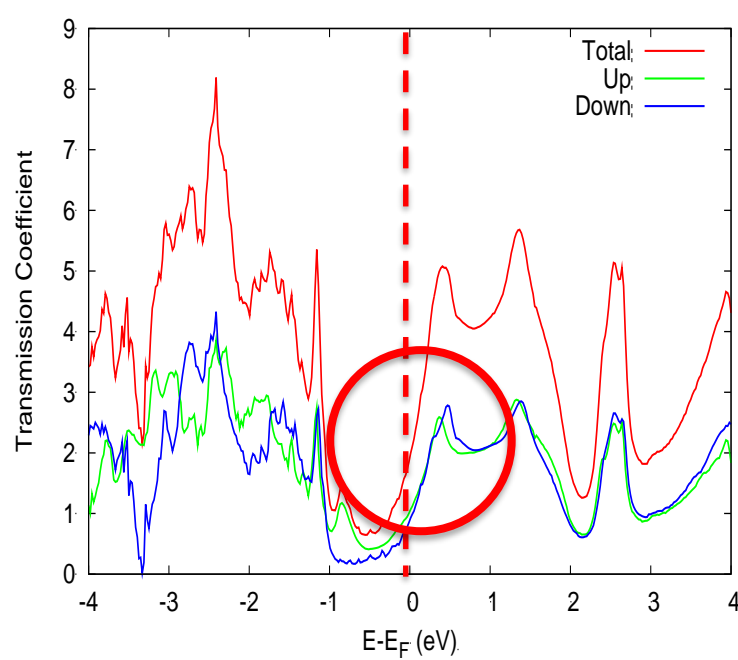
# Ni(111)-BDT-Ni(111)

SMEAGOL module (NEGF-DFT), LDA functional

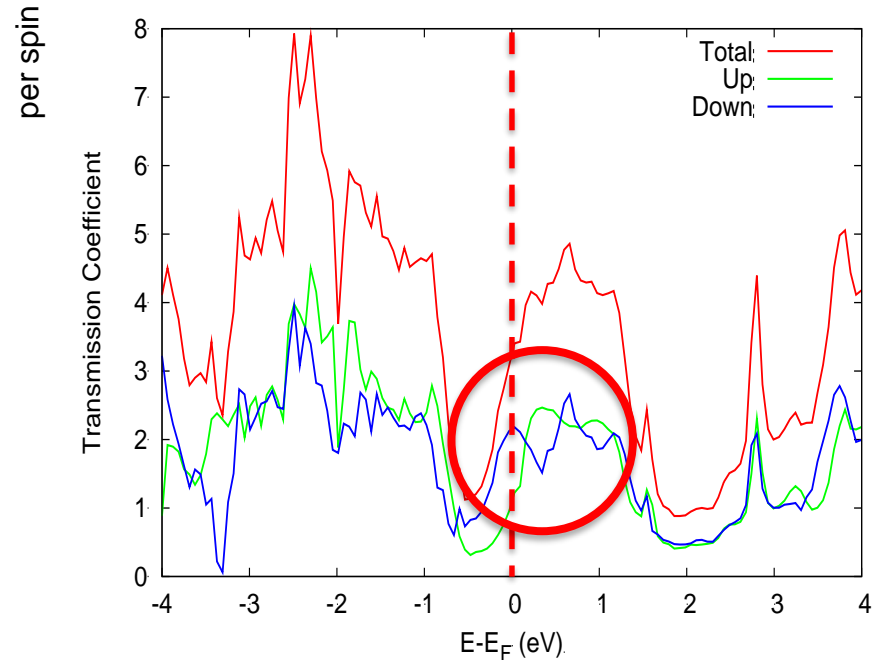


分子軌道 (HOMO) のスピン分極によりフェルミ準位より上に軌道が現れる  
⇒ゼーベック係数の符号が変わる

# Ni(111)-C<sub>60</sub>-Ni(111)



Hexa-faced structure  
(most stable)

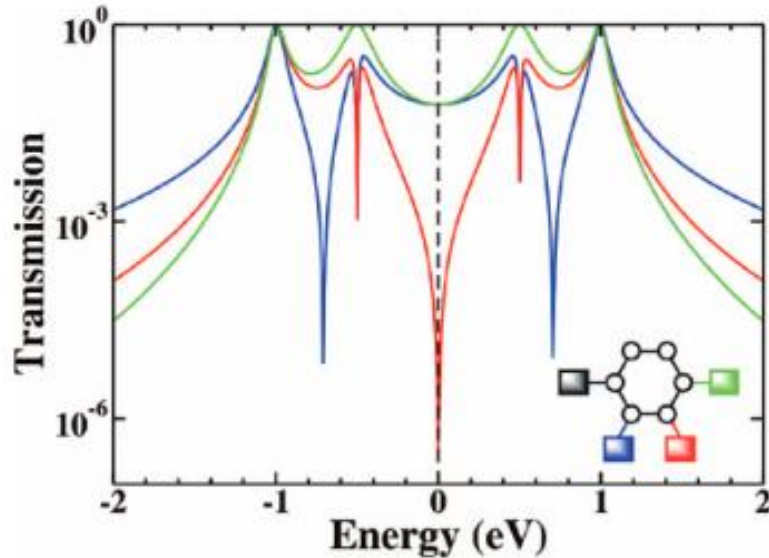


Penta-faced structure

- 安定と考えられる構造ではいずれも負のゼーベック係数(実験結果を再現)
- フェルミ準位近くにあるLUMOが伝導に寄与(Au-C<sub>60</sub>-Auと同様)
- スピン分極の様子は吸着構造によって異なるが、小さい

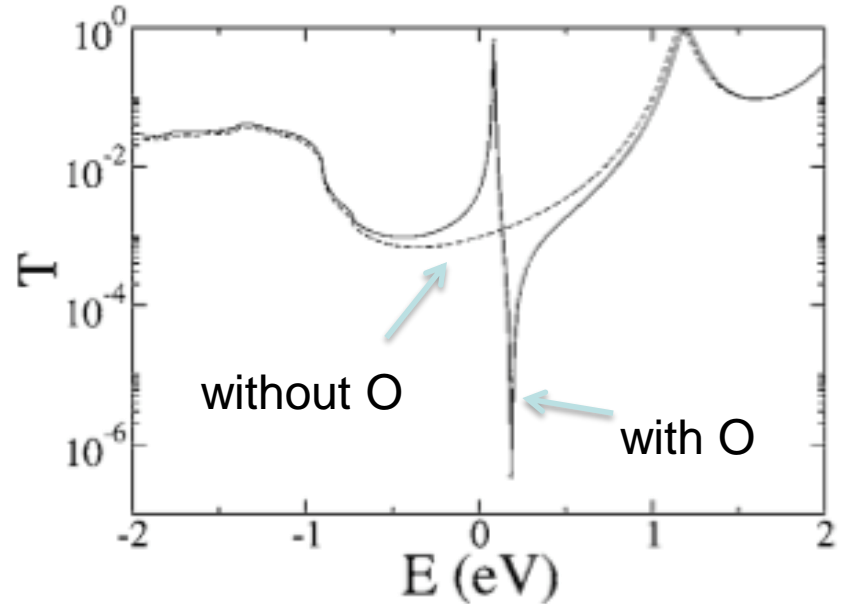
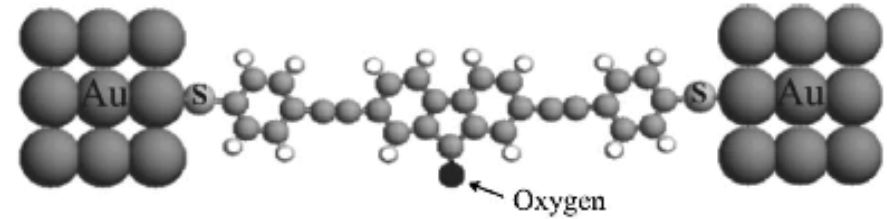


# 熱起電力向上に向けて



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

量子干渉効果

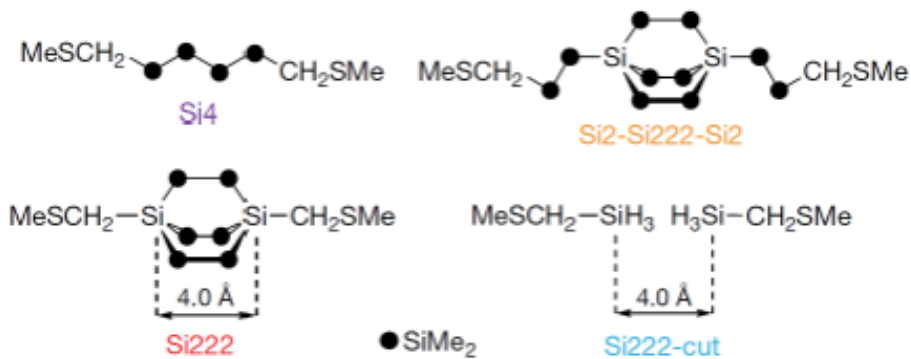


Papadopoulos *et al.* PRB **74**(2006)193306

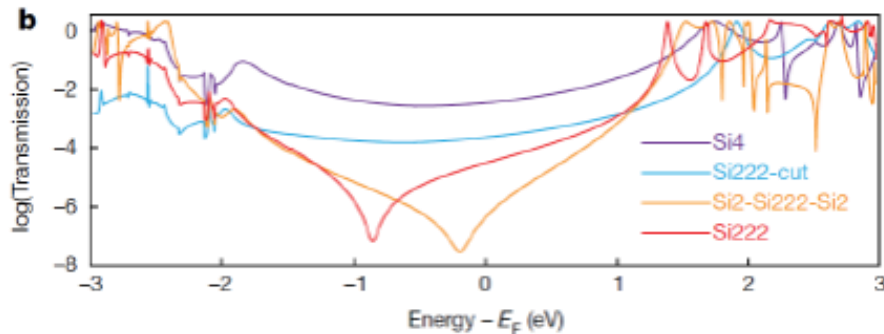
Fano共鳴

# 単一分子における量子干渉効果

## Molecular structures

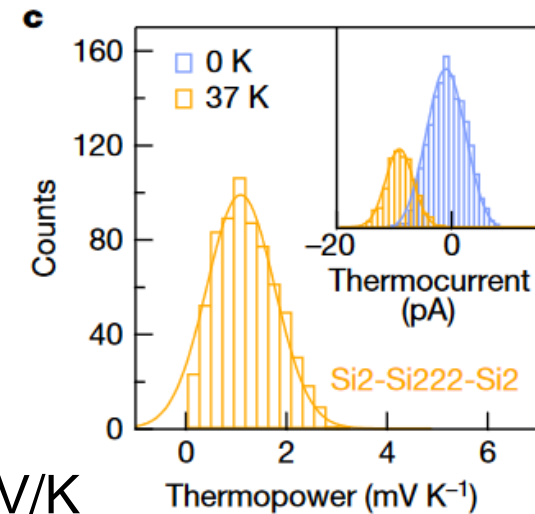
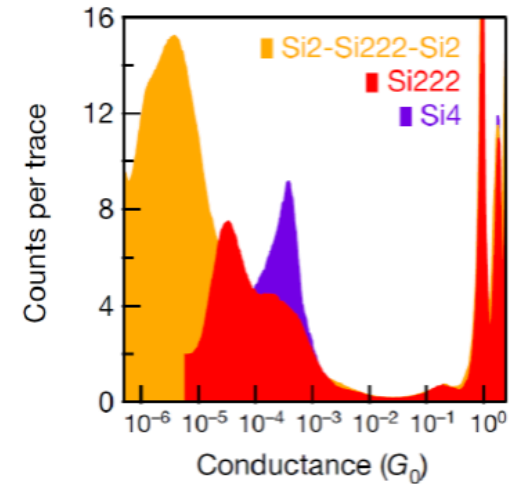


## Theoretical transmission function (DFT)



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

Conductance histogram measured using STM BJ



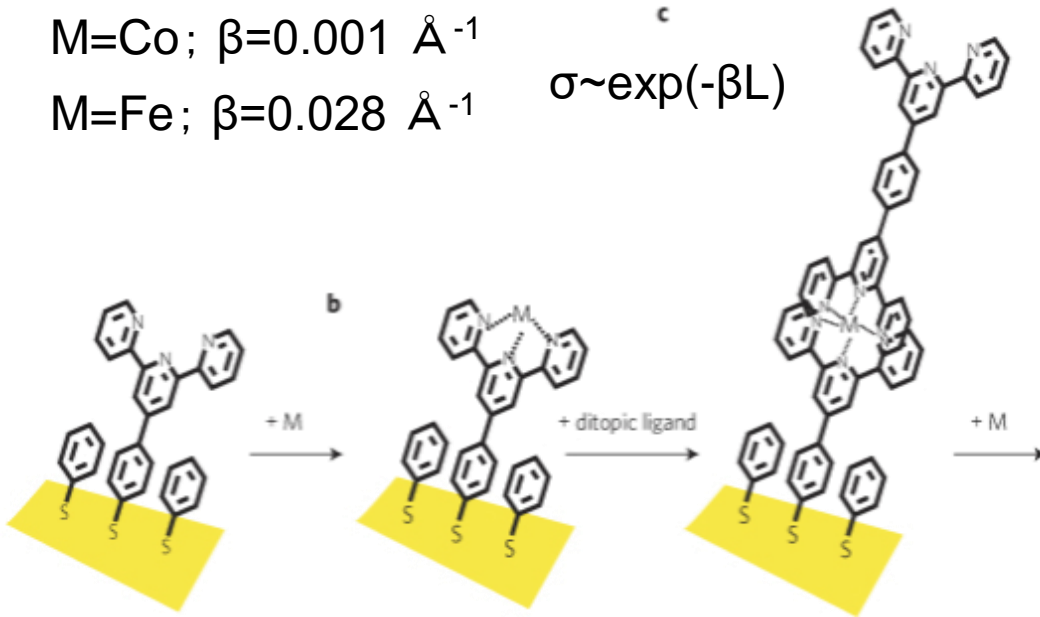
# 長距離伝導分子ワイヤー

Bis(terpyridine)M

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

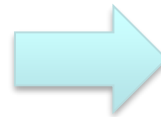
M=Fe;  $\beta=0.028 \text{ \AA}^{-1}$

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

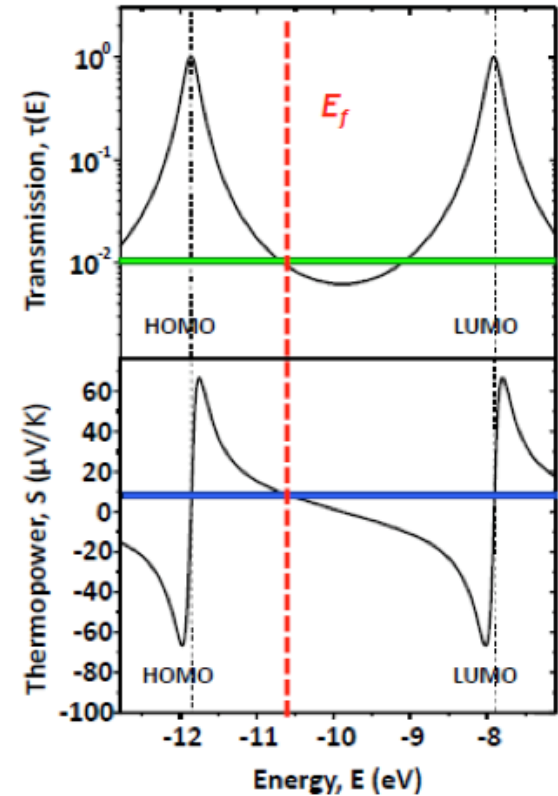


Tuccitto *et al*, Nat. Mat. **8**(2009) 41

共鳴トンネルによる長距離伝導？



分子軌道の位置が  
電極のフェルミ準位に非常に近い

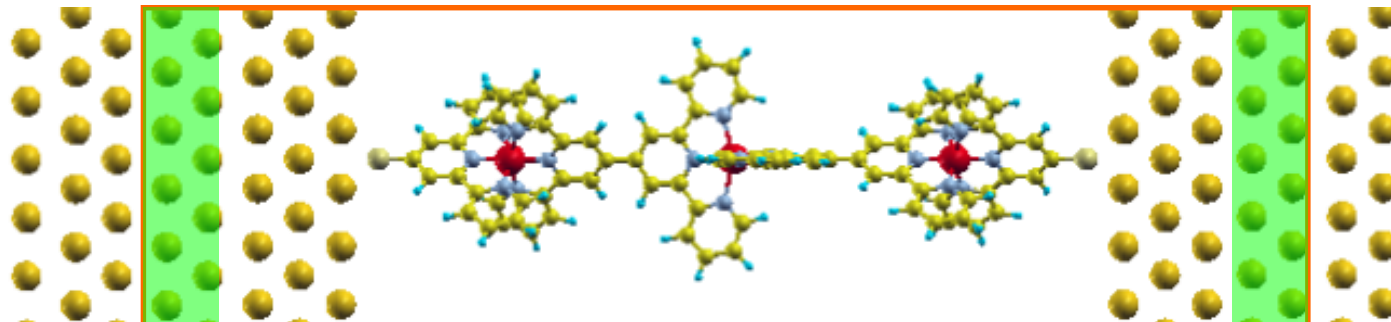


Reddy *et al*, Science **315**(2007) 1568

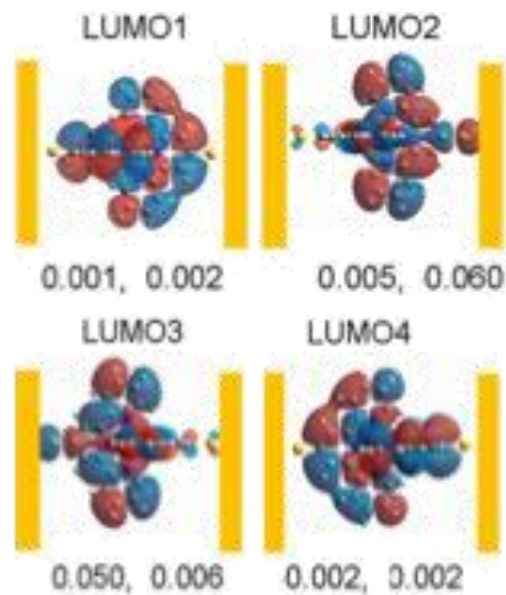
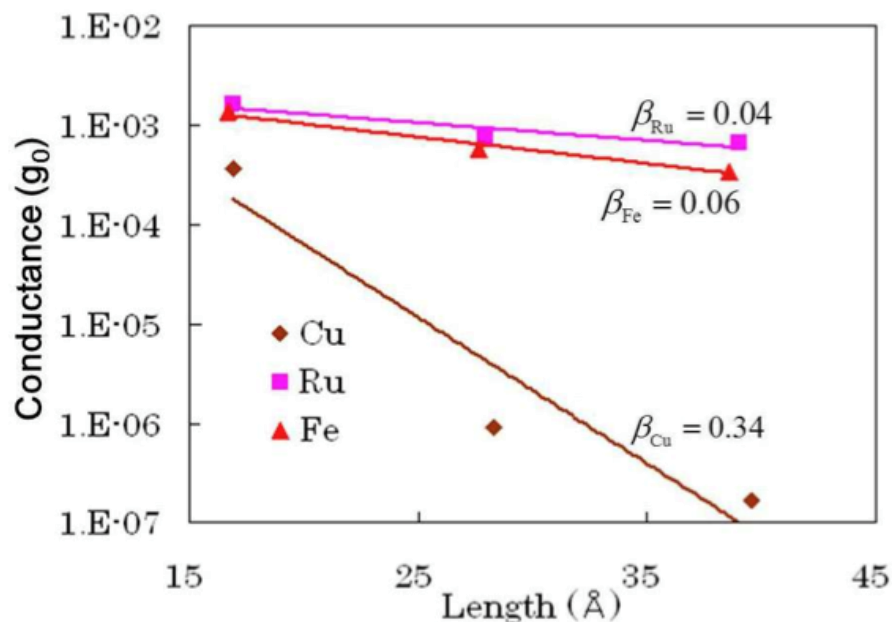
(共鳴トンネルなら)熱電材料として有望

# 電気伝導計算

HiRUNE module (NEGF-DFT), PBE functional

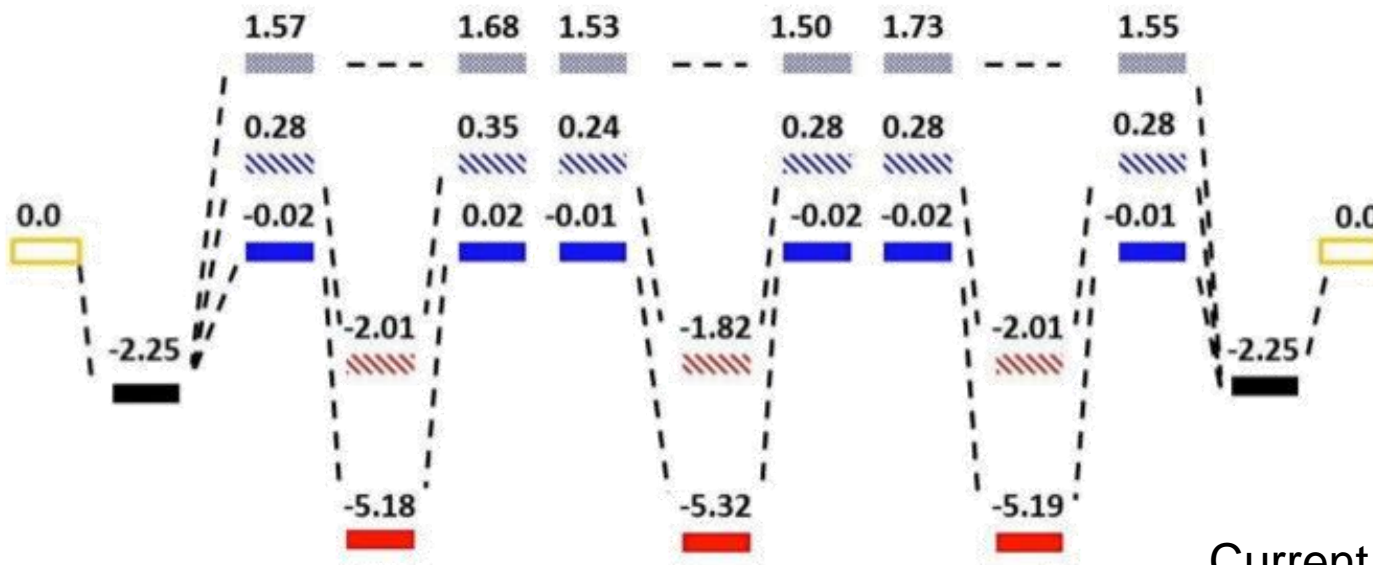


Au電極に架橋したBis-terPy(M) M=Cu, Fe, Ru, Vac etc.

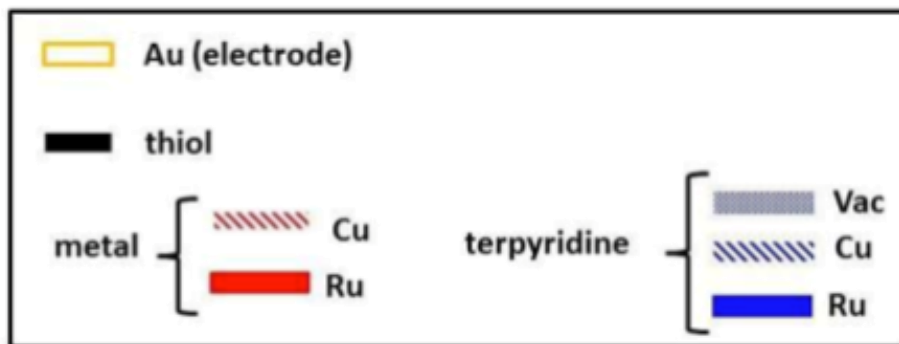
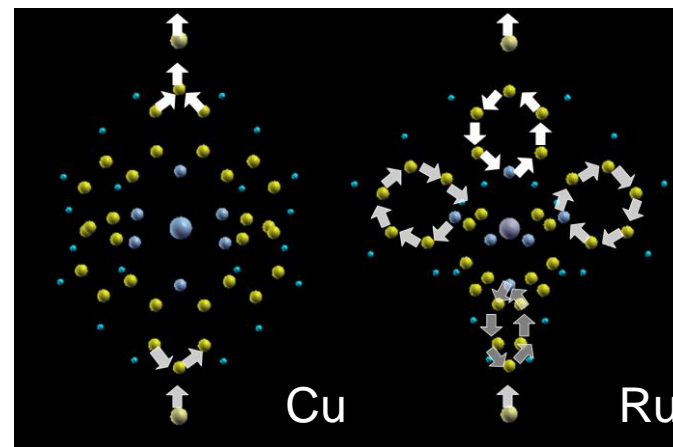


$Y_R, Y_L$

# 準位図

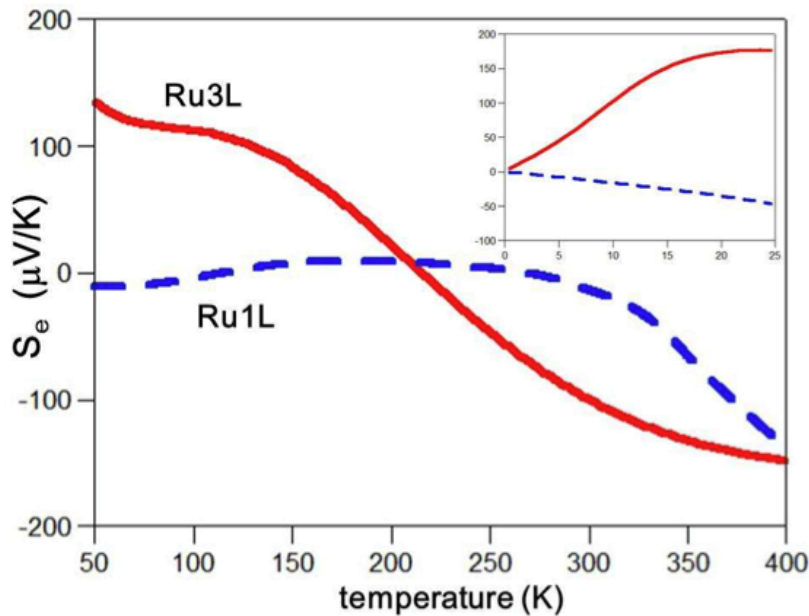
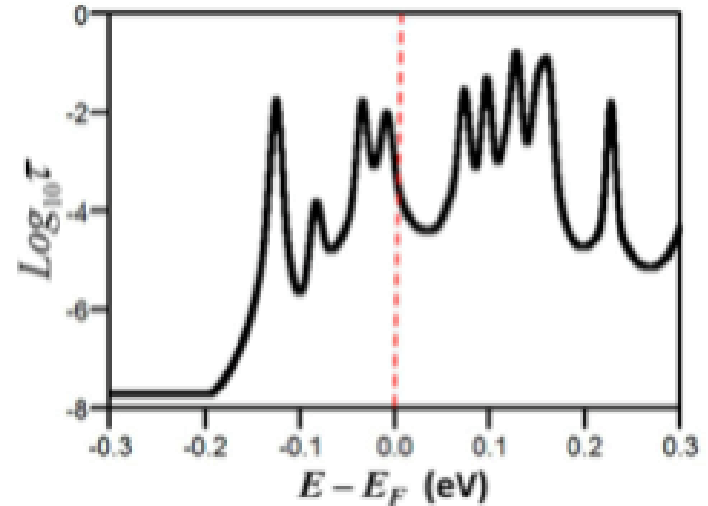
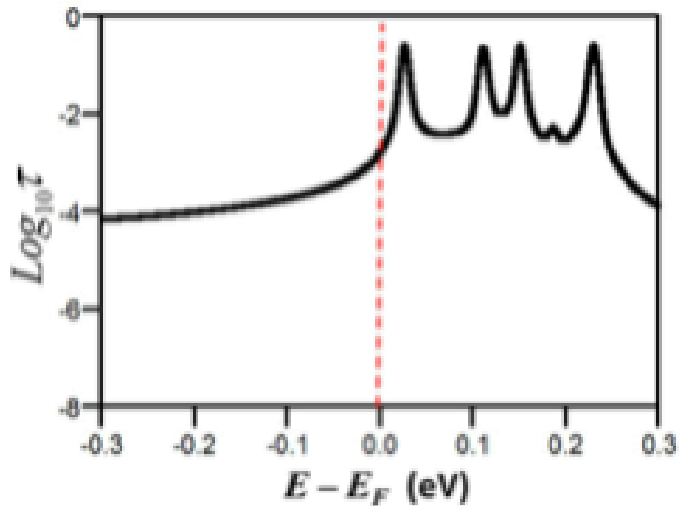


Current Profile



d-metalによってフェルミ準位まで下がった分子軌道による共鳴トンネル

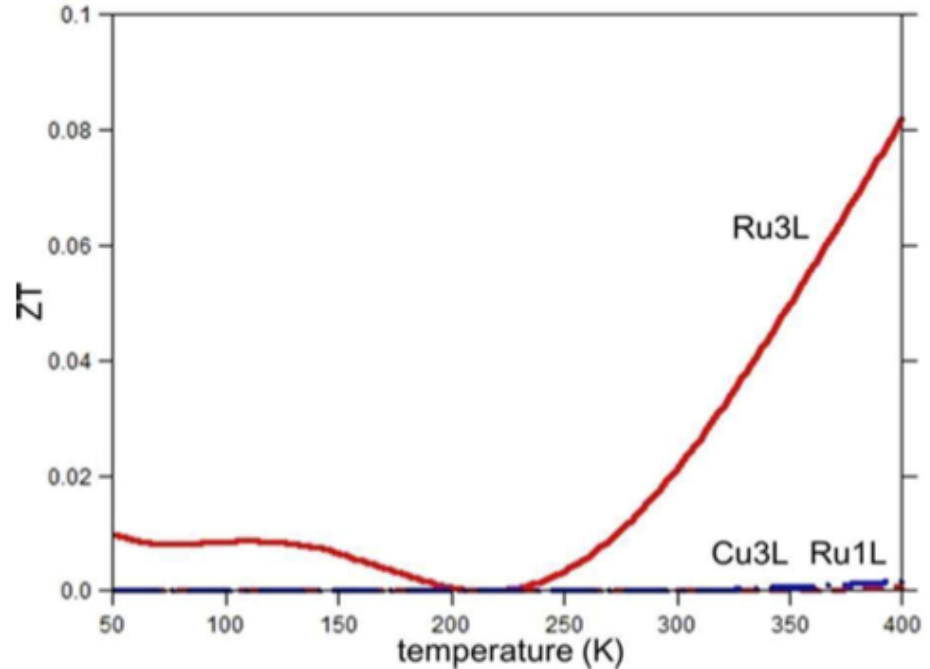
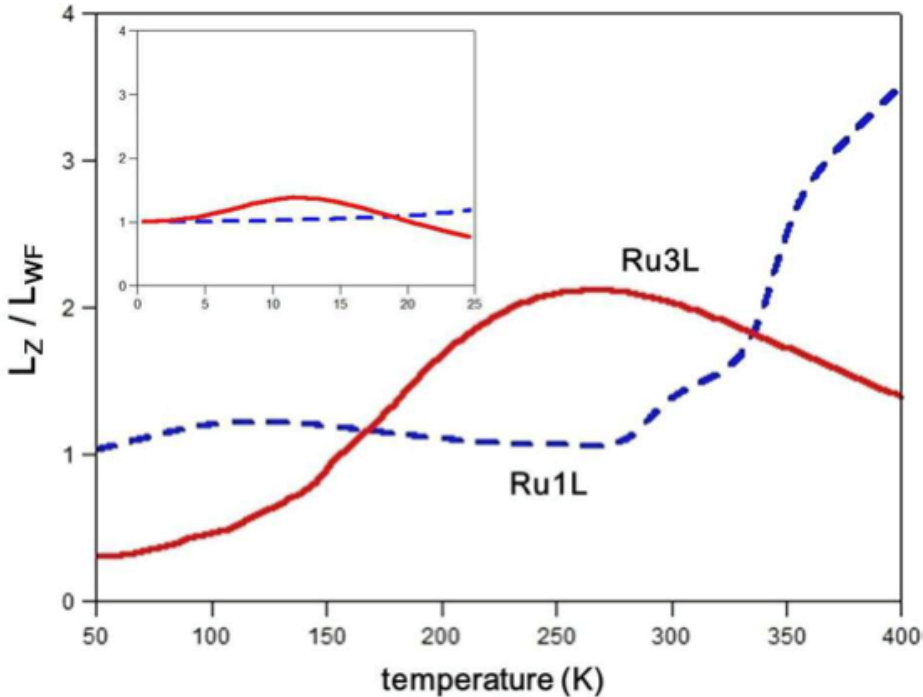
# 伝導度と熱起電力



- フェルミ準位付近に大量の状態
- 透過係数が鋭く、Sは大きい
- ある温度でSの符号が反転する

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

# Wiedemann-Franz則の破れとZT



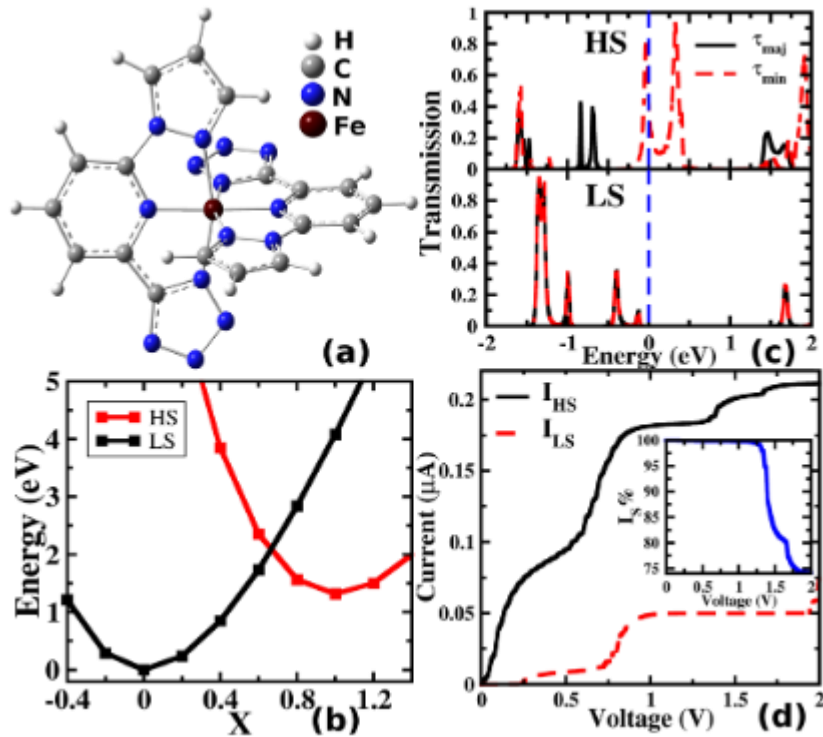
Wiedemann-Franz則

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

Wiedemann-Franz則の破れが  
大きなZTの一因

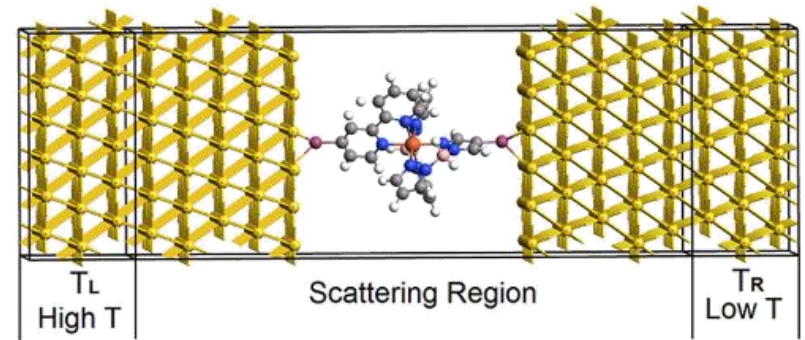
ZT=0となる温度が存在する

# 金属錯体分子を用いた熱電素子

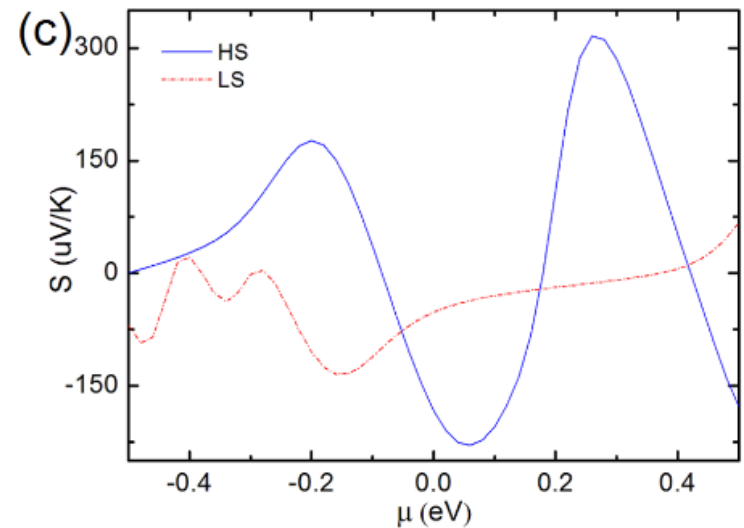


D. Ghosh *et al.*

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



Fe[(H<sub>2</sub>Bpz<sub>2</sub>)<sub>2</sub>bipy]



N. Liu *et al.*

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



# **4. Organic Magnetoresistance**

# Organic magnetoresistance (OMAR)

**Usual MR**

**MAGNETIC**

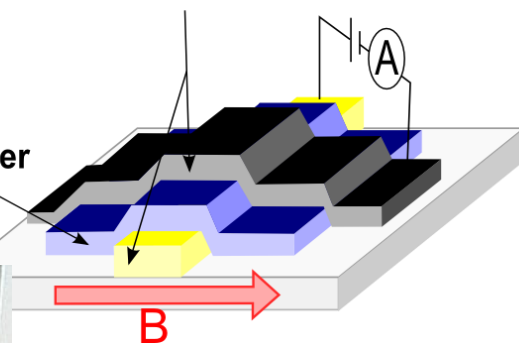
**Electrodes**

**OMAR**

**NON  
MAGNETIC**

GMR, TMR  
Spinvalve.

Organic layer



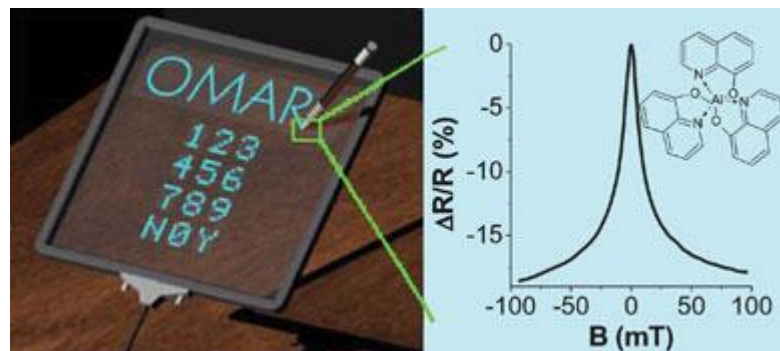
Room temperature.  
Low magnetic field (mT)

Up to several 1000%

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



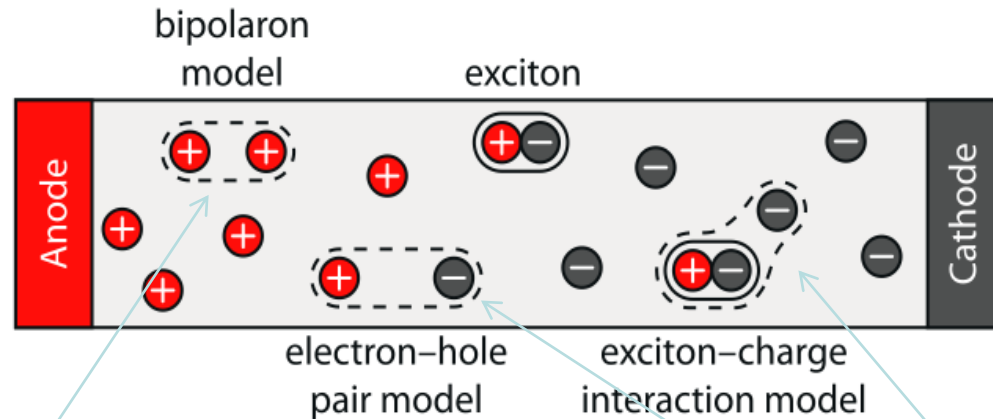
$$MC(\%) = \frac{I(B) - I(0)}{I(0)}$$



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

# Theory: Single vs. Double carriers

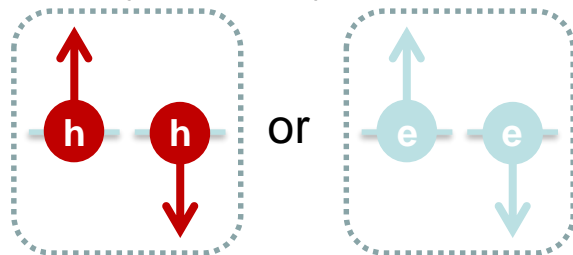
The magnetic field modifies the ratio between SINGLET and TRIPLET



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

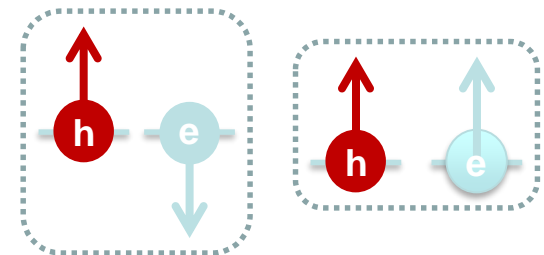
## Single carriers

Only **ONE** type of carrier



## Double carriers

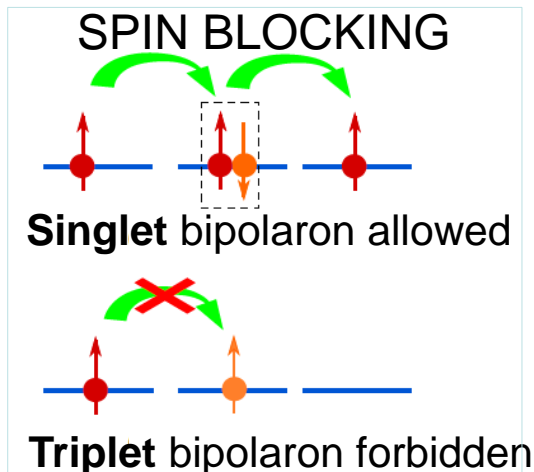
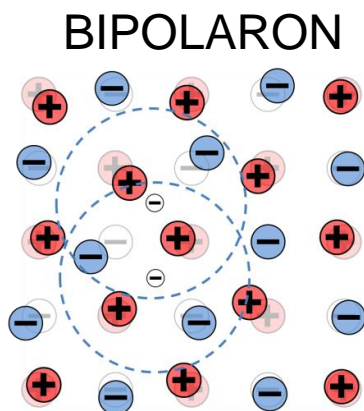
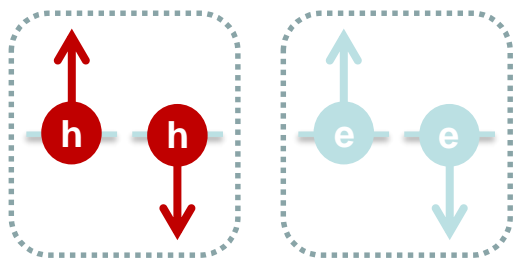
**BOTH** hole and electron are required



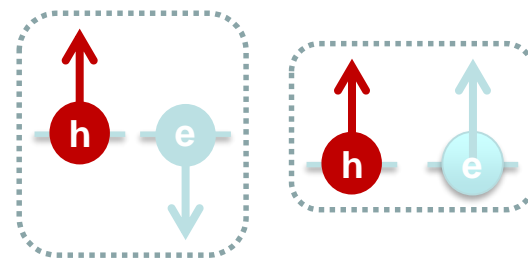
# Theory: Single vs. Double carriers

The magnetic field modifies the ratio between SINGLET and TRIPLET

## Single carriers

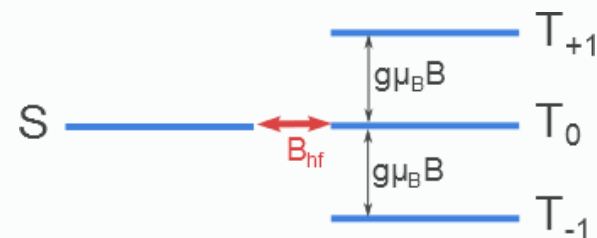


## Double carriers



**Singlet:** Recombination/Dissociation

**Triplet:** Reaction with charge

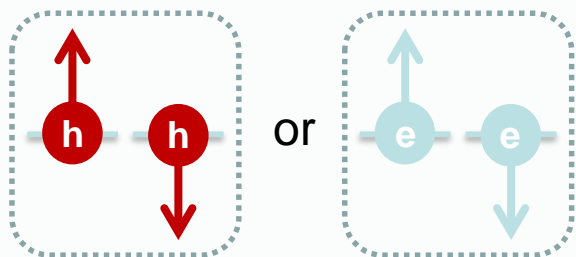


Modified **singlet to triplet ratio**

# Theory: Single vs. Double carriers

## Single carriers

### Bipolarons

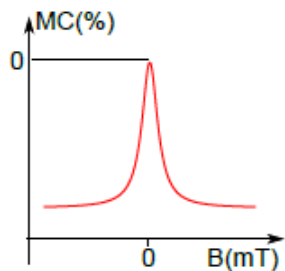


*B decreases the number of bipolarons*

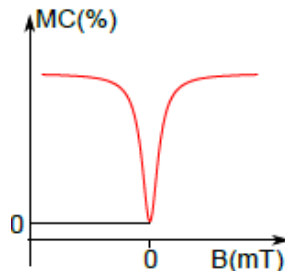
*Bipolaron lifetime*

short

long



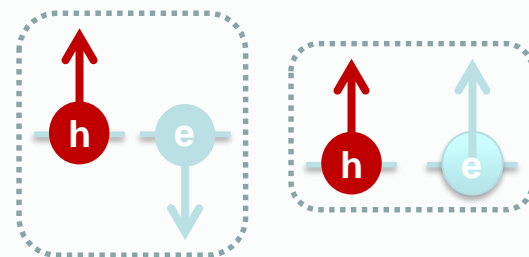
**-MC**



**+MC**

## Double carriers

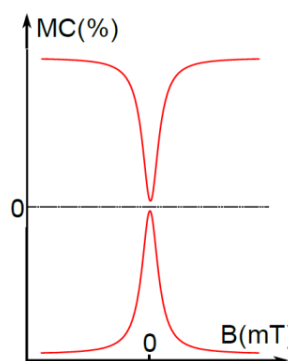
### Excitons and e/h pairs



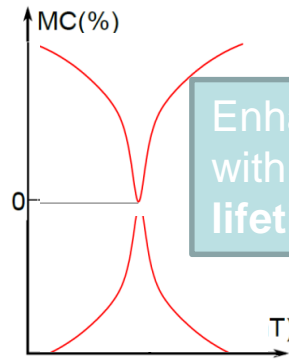
*B changes the singlet/triplet ratio*

Singlet:  
*recombination*

Triplet:  
*Reaction with charge*



**+MC or -MC**

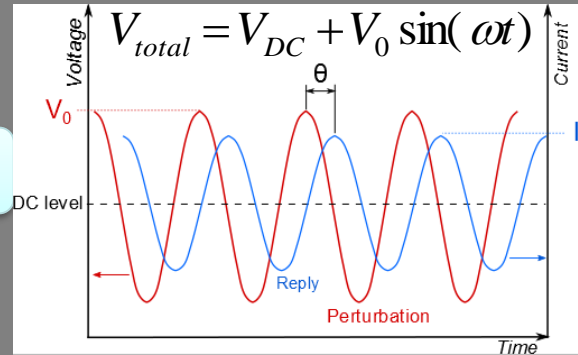


**+MC or -MC  
with HFE**

Enhanced  
with long  
lifetime

# Impedance spectroscopy

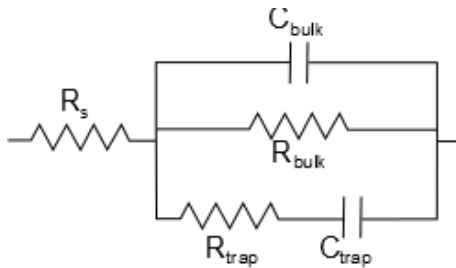
Measurement



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

## Equivalent circuit

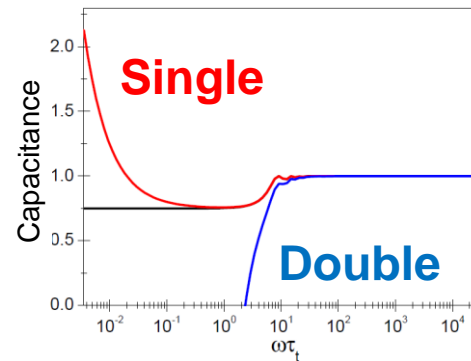
Fitting of the data



**Nyquist diagram, Phase.**

Give information on electronic processes

## Capacitance vs frequency



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

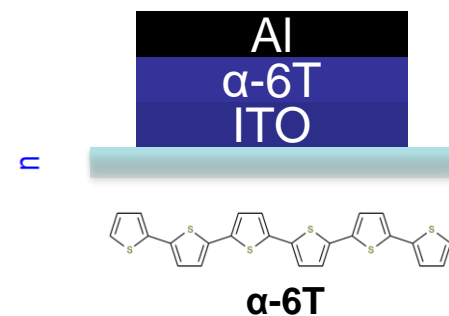
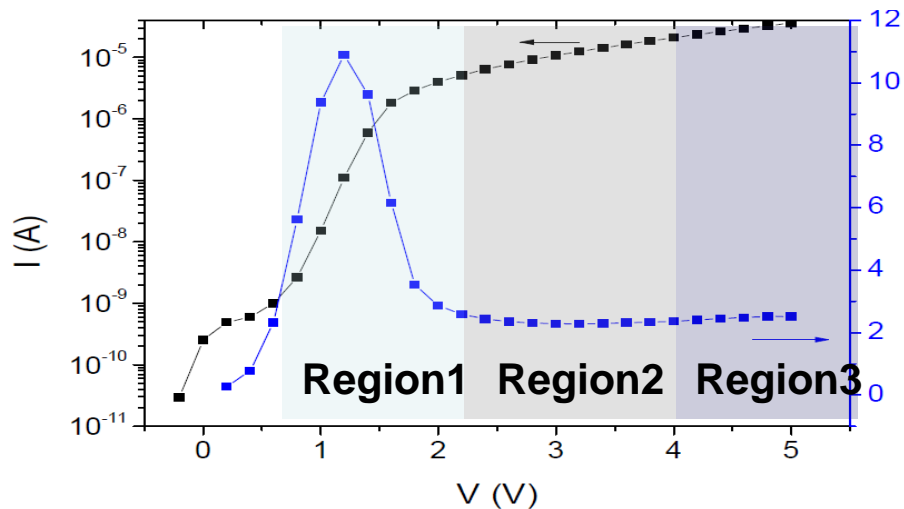
**Sign** : type of injection  
**Value** : traps characterization

# OMAR results

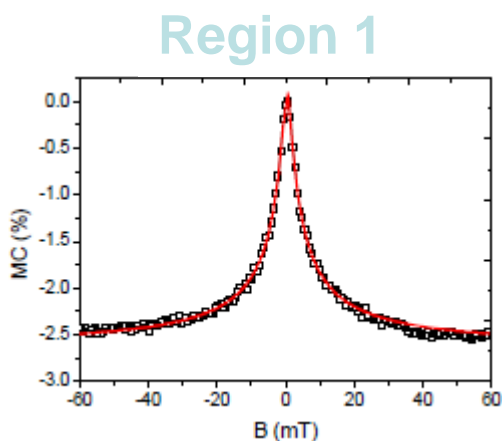
## I-V characteristics:

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

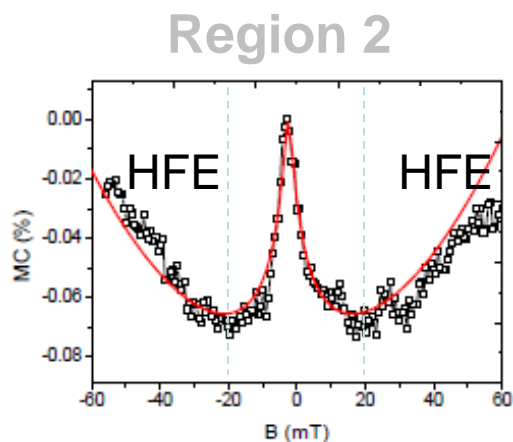
$$MC(\%) = \frac{I(B) - I(0)}{I(0)}$$



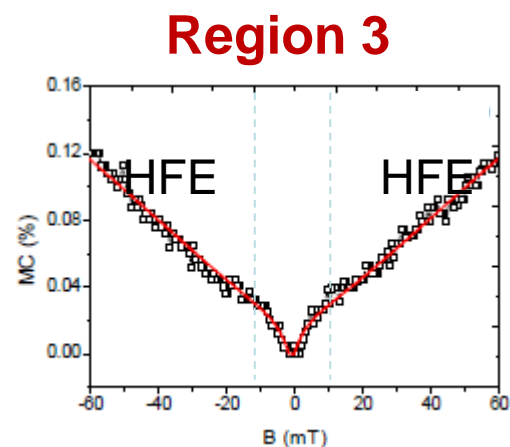
## OMAR results:



**-MC**



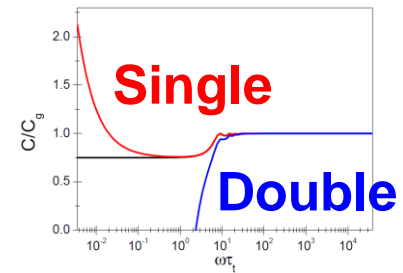
**-MC with HFE**



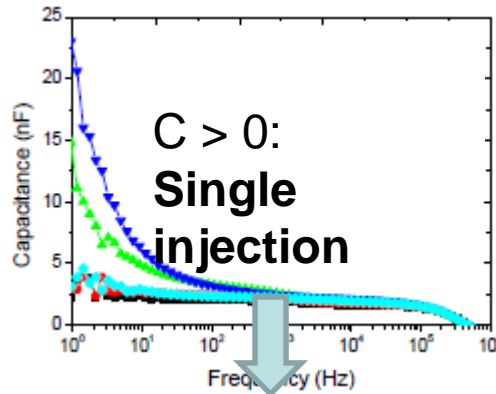
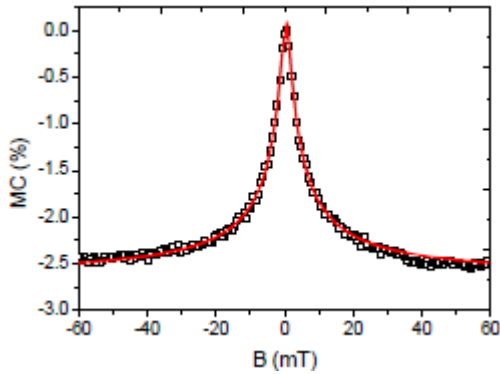
**+MC with HFE**

How to explain the various OMAR shapes?

# Capacitance results

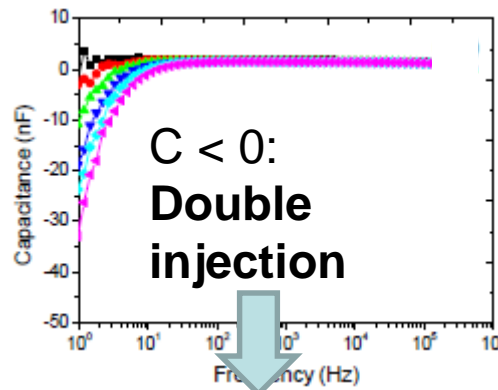
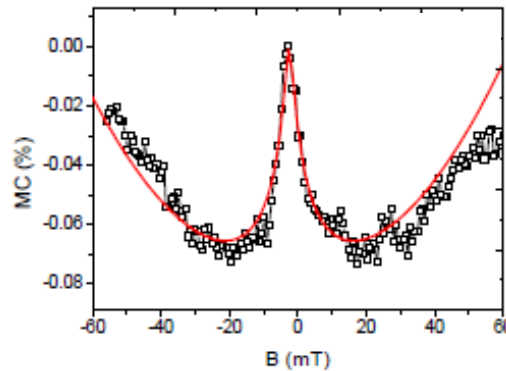


## Region 1



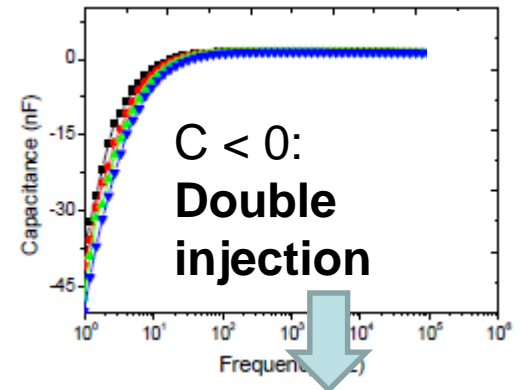
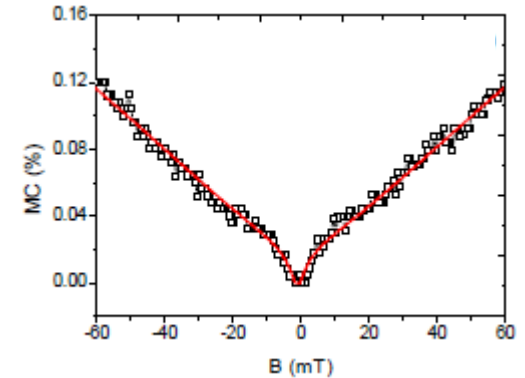
**Bipolaron OMAR**  
Negative OMAR

## Region 2



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

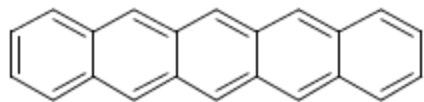
## Region 3



**Double carriers OMAR**  
Positive OMAR



Pentacene (Pen)

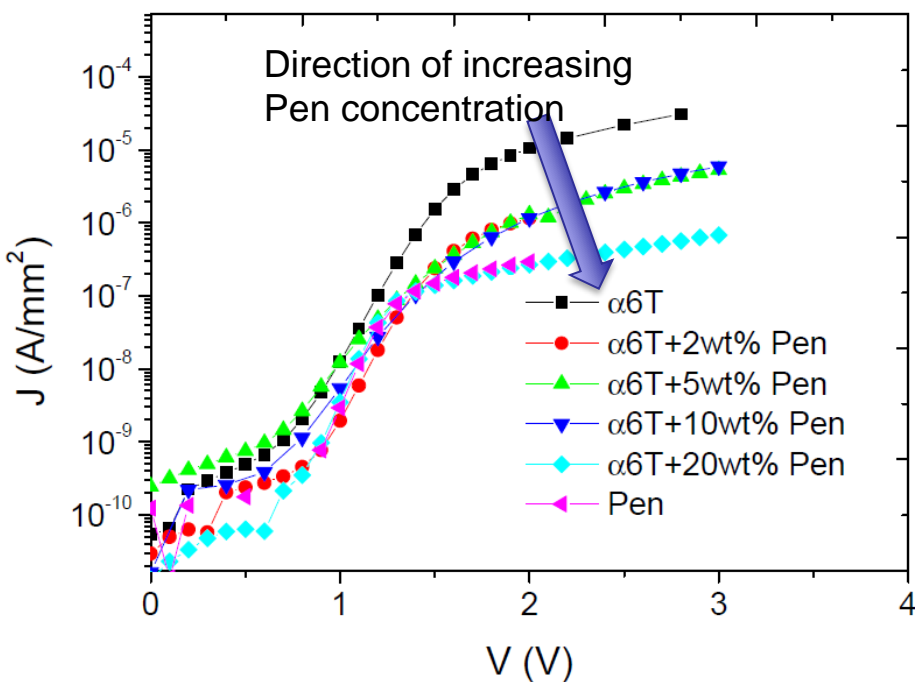


# Pentacene doping

$\alpha$ -6T

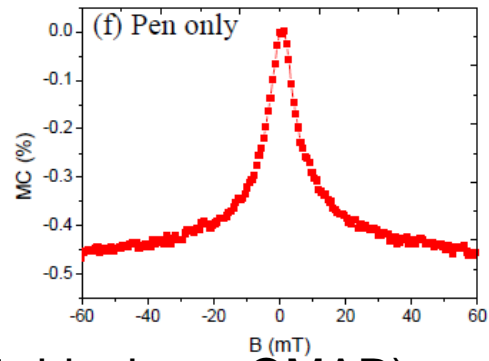
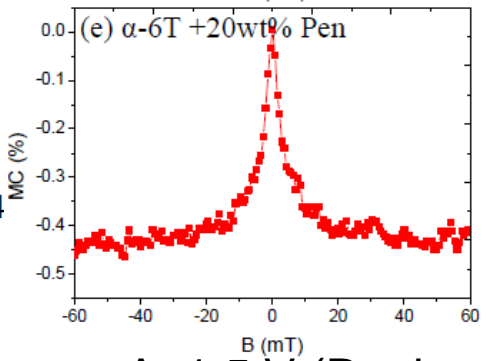
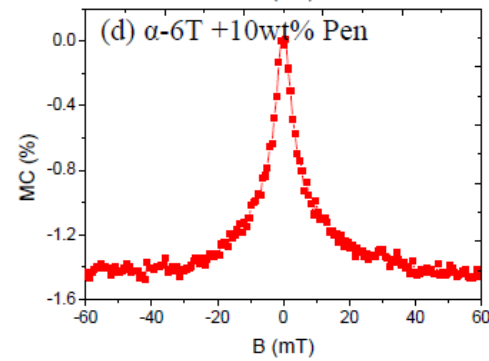
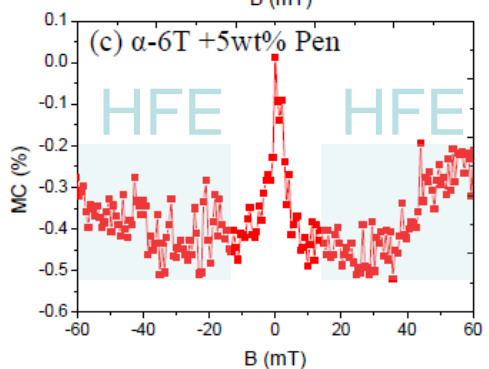
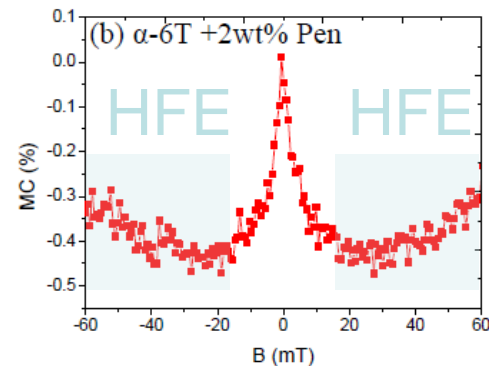
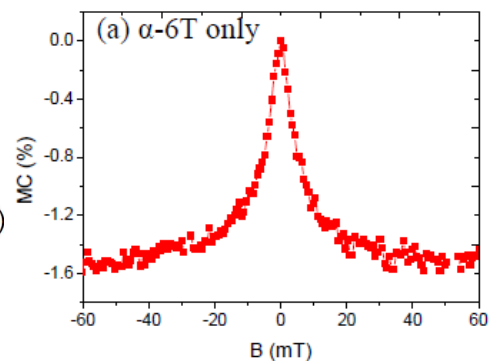


0 2 5 10 20 100 [Pen] (wt%)



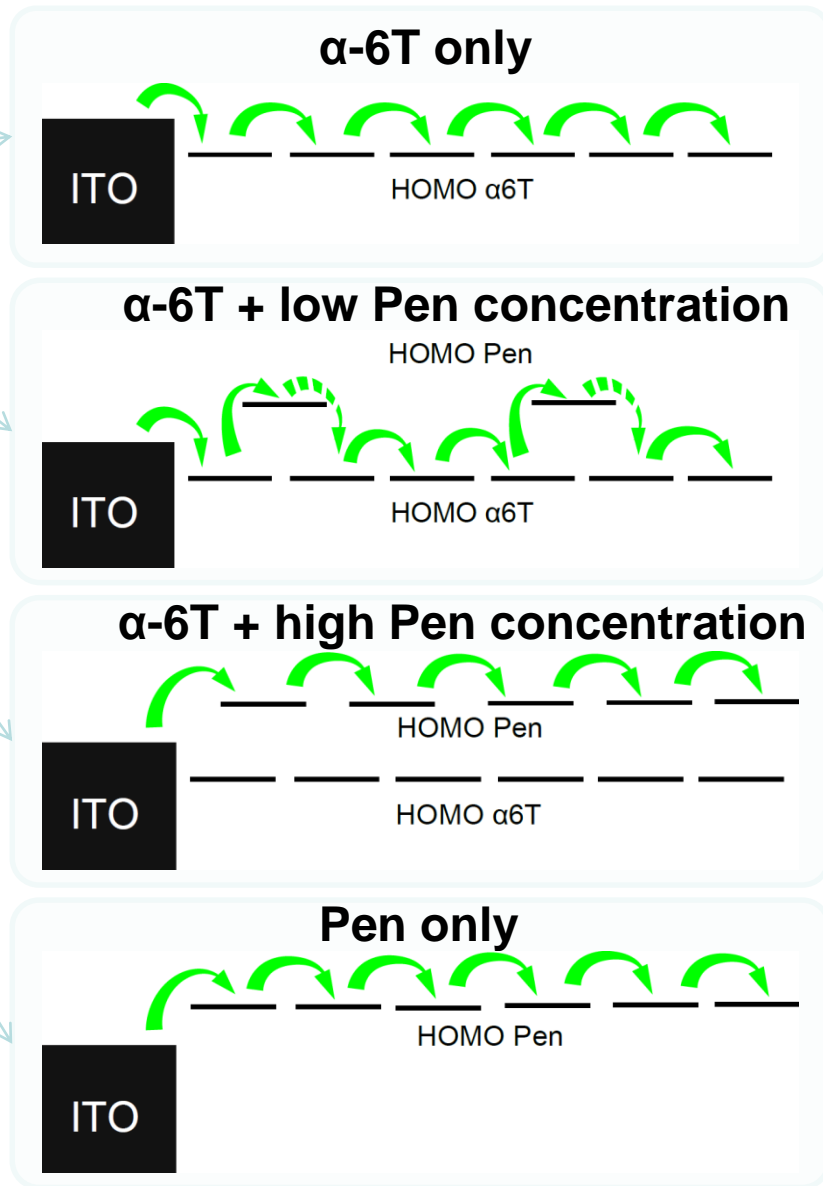
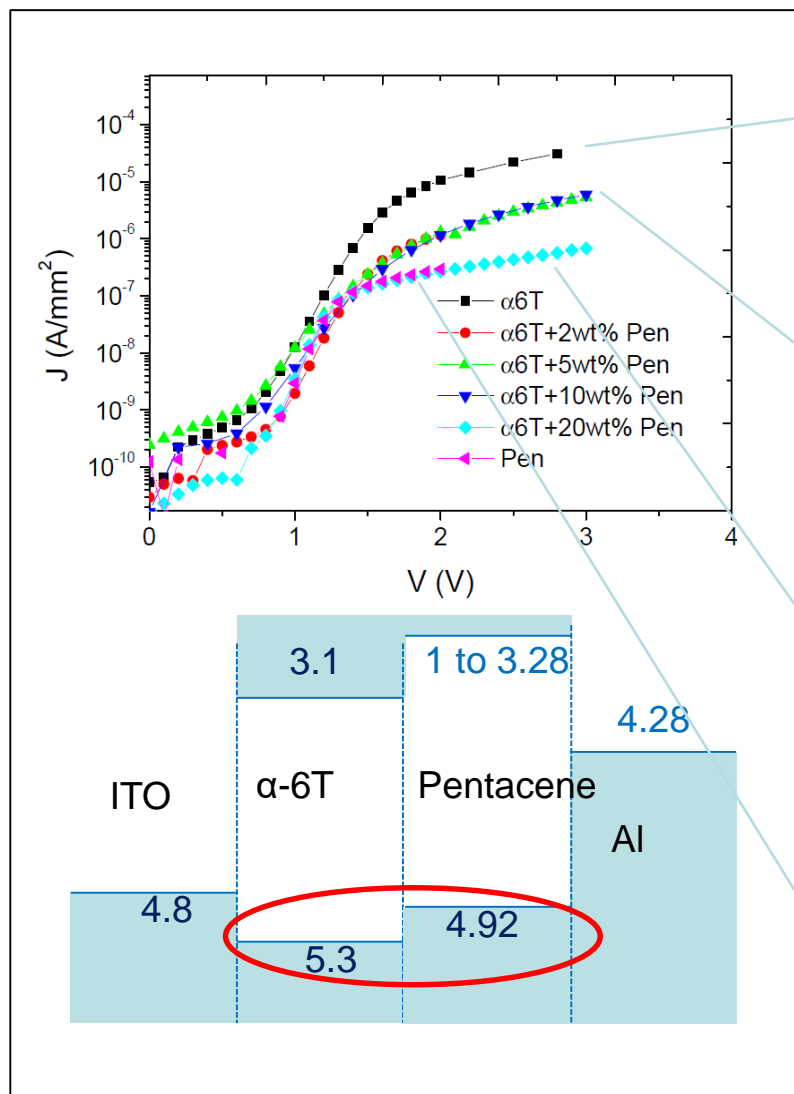
Direction of increasing Pen concentration

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

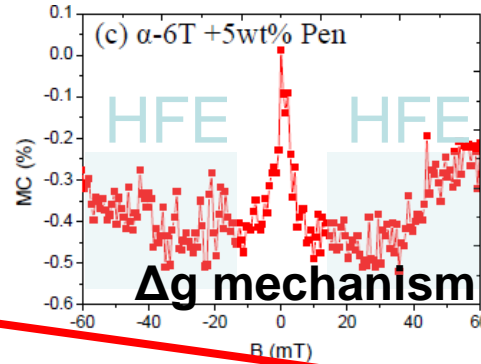
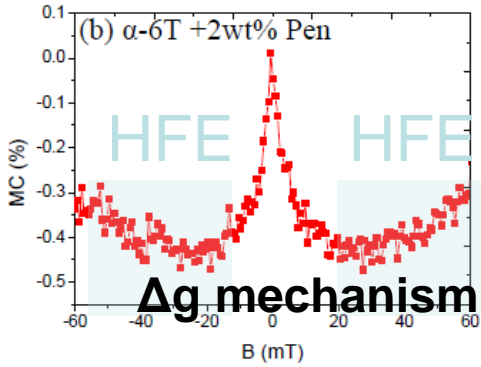


At 1.5 V (Region 1, bipolaron OMAR)

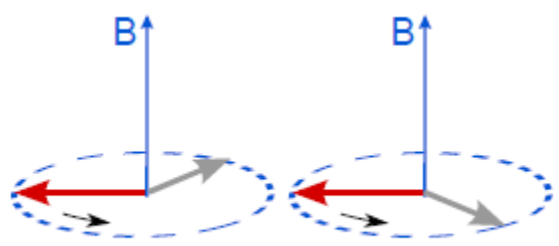
# I-V characteristics



# OMAR results

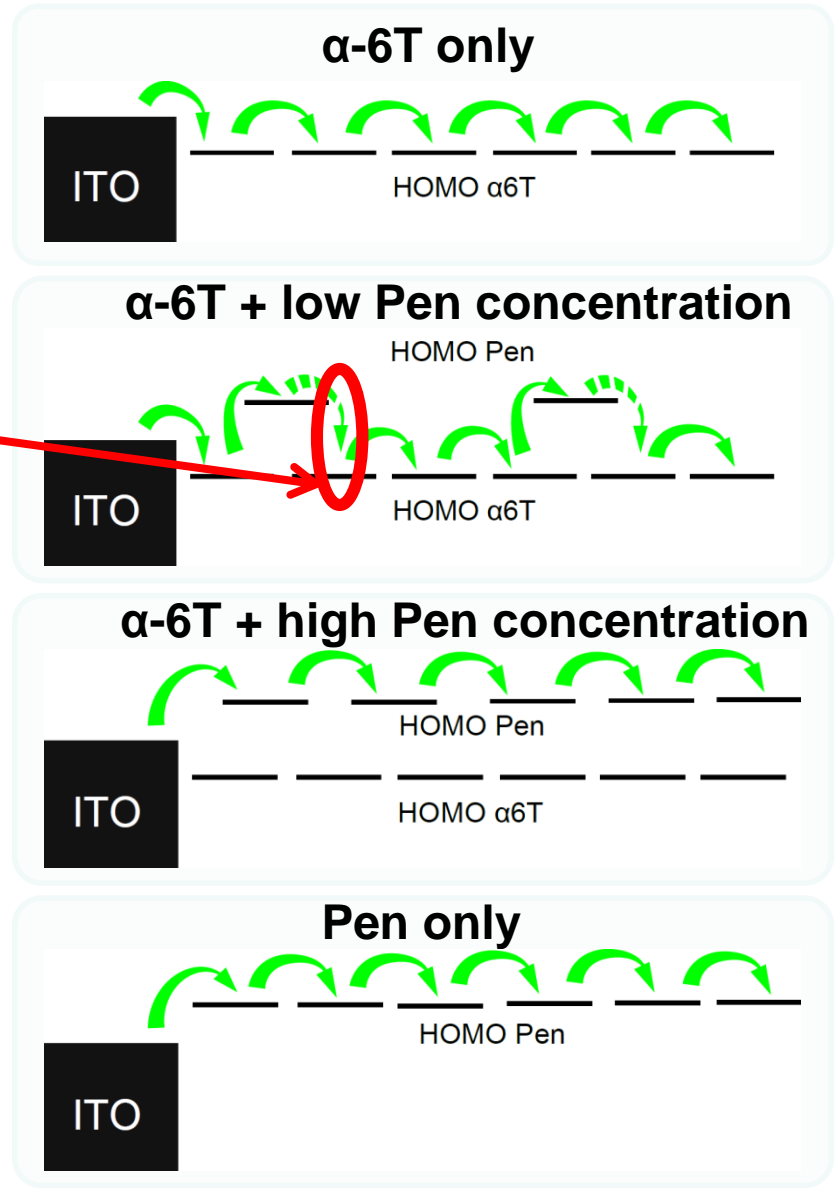


Different environment



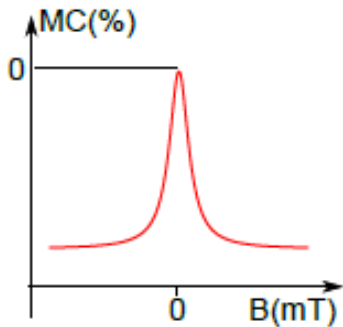
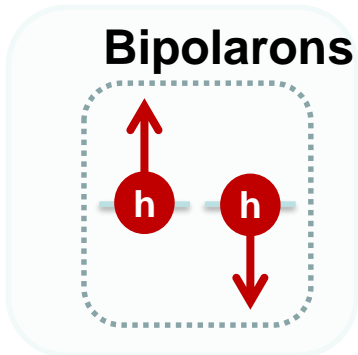
Spin precession out of phase. Cause an effect opposite to the effect at low field.

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



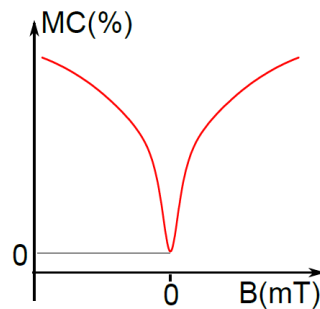
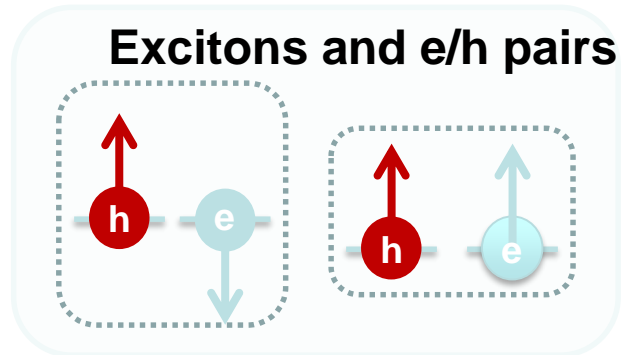
# Summary

## Single carriers



**-MC**

## Double carriers



**+MC with HFE**

## Disorder

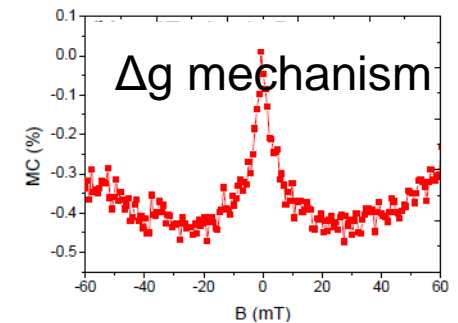
$\alpha$ -6T



0 2 5



10 20 100 [Pen] (wt%)

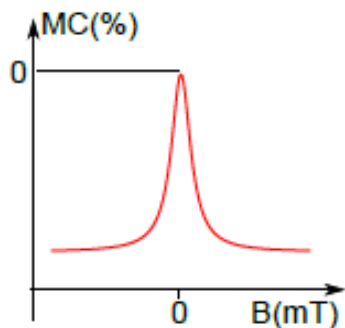
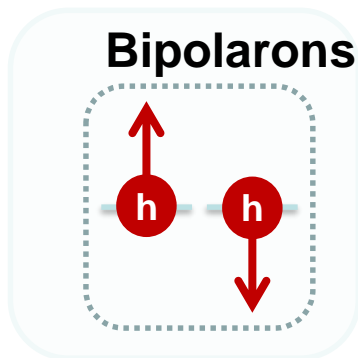


**The mechanism is identified.**

**Magnitude and shape of OMAR is tuned.**

# Perspective

## Single carriers



**-MC**

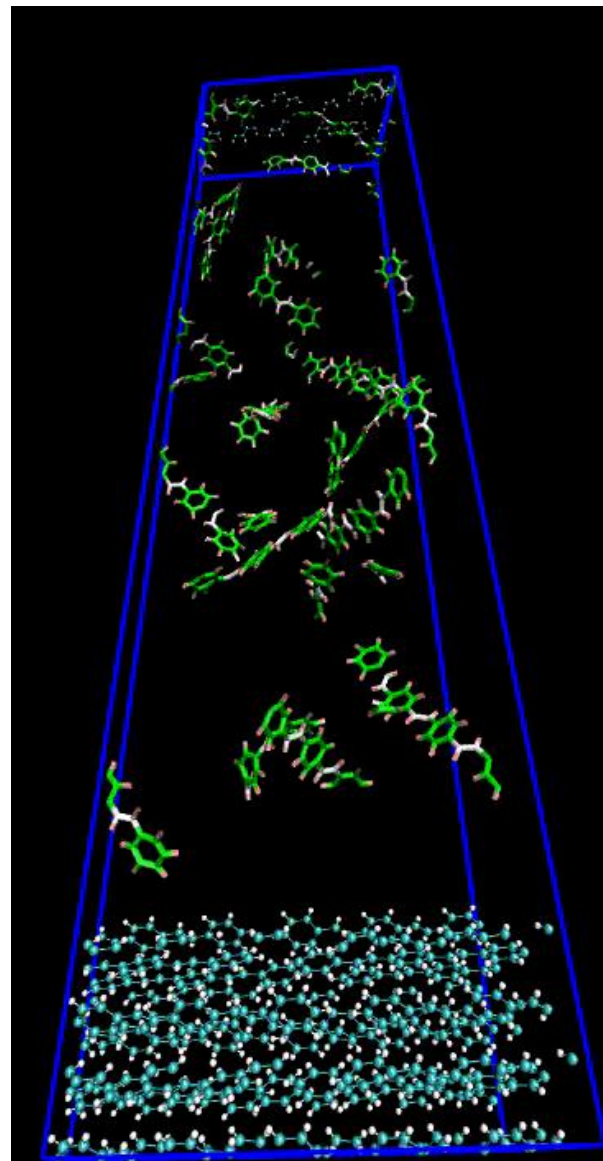
- Bipolaron is a deep mid-gap state

- How much defective are organic semiconductors?

Realistic landscape



Carrier dynamics simulation



# Summary

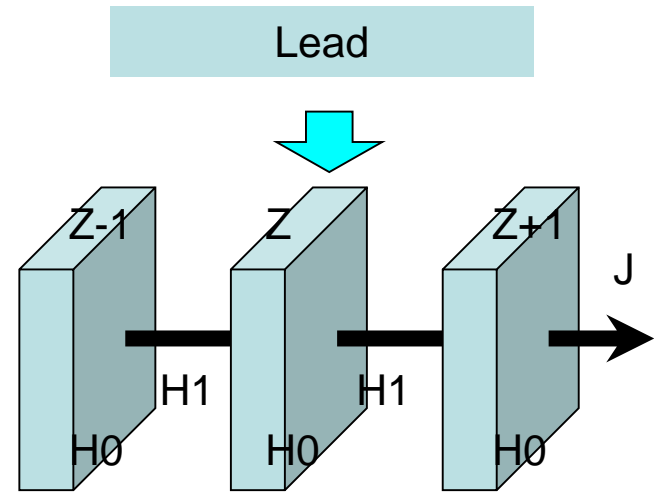
- Theoretical design of molecular spin valve
- NEGF-DFT and its application to spintronics and thermoelectronics
  
- Single Molecular Magnet
- OMAR and its mechanisms

# 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

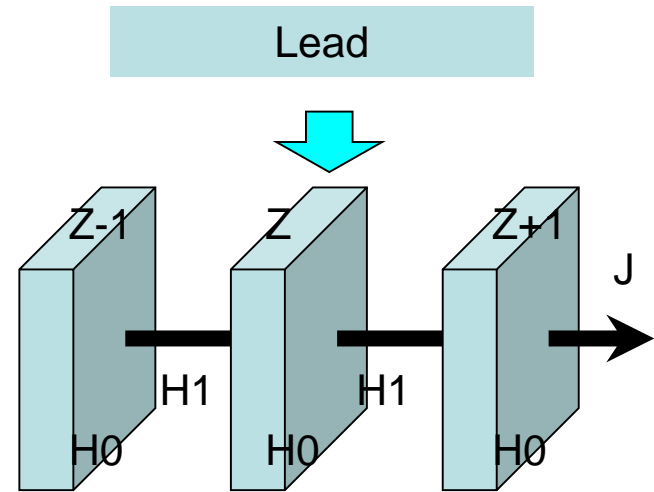
Tight Binding Layer (TBL) Method

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



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

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

Boundary condition  $Z = Z_0$

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