有機スピントロニクス

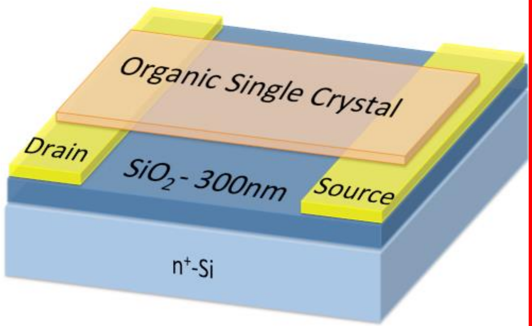
基礎工学研究科
大戸達彦

Molecular Architectonics Research Group

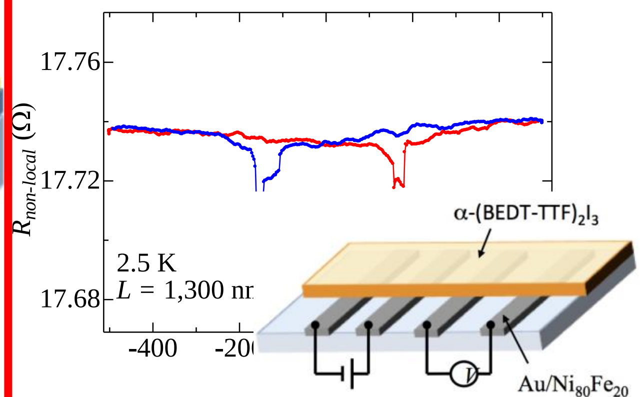
TADA Lab

http://molectronics.jp
http://molarch.jp

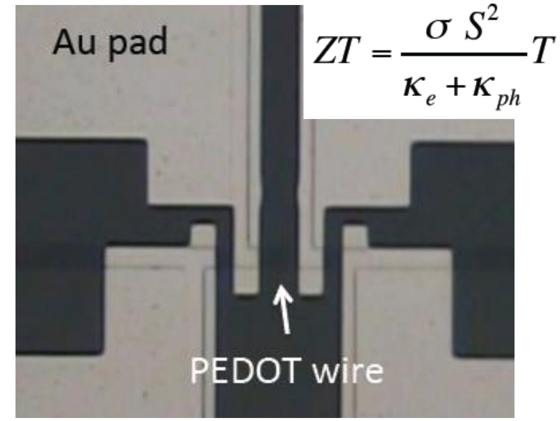
Thin Film



Electronics

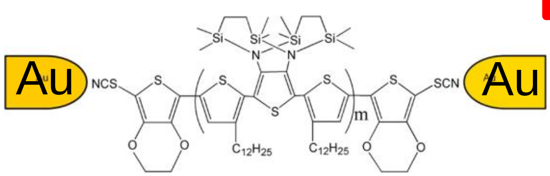


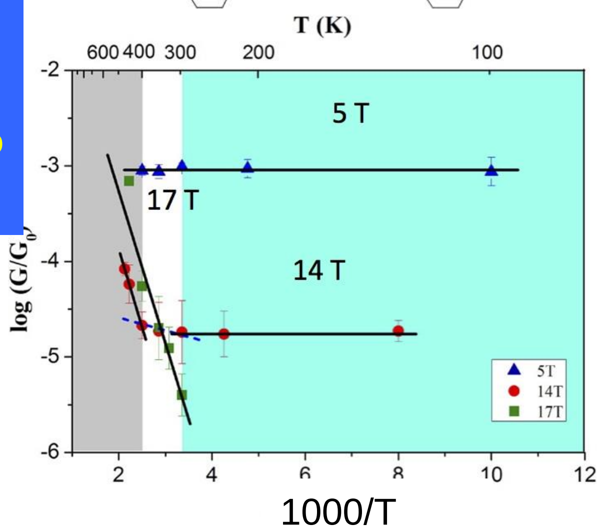
Spintronics

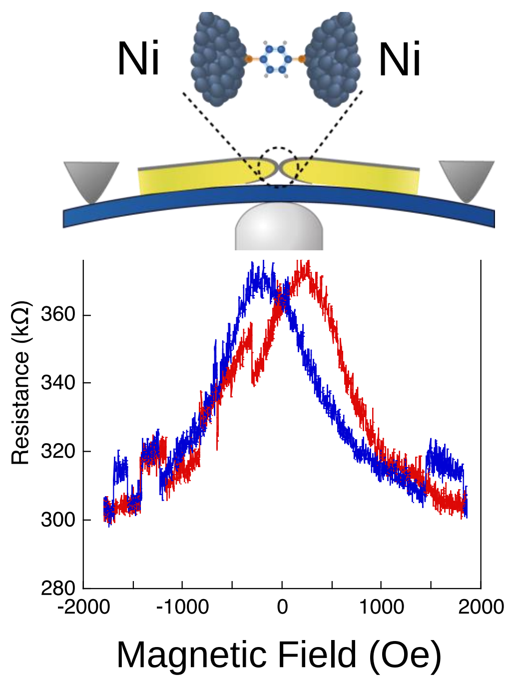


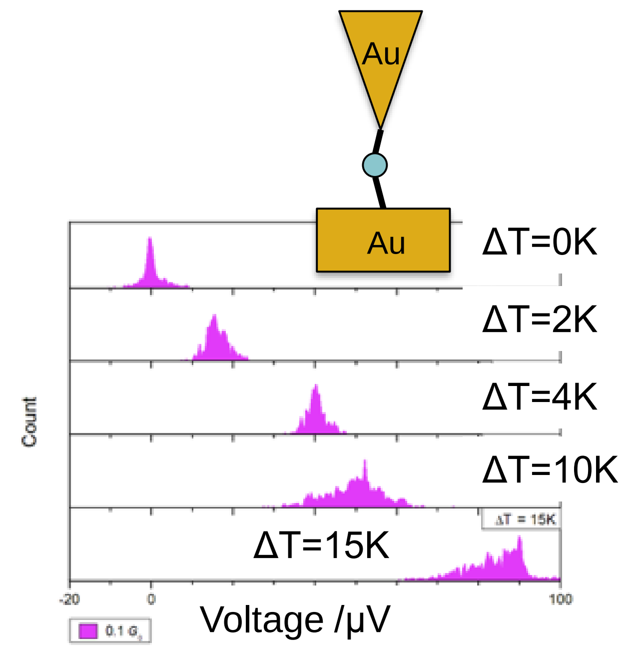
Thermoelectronics

Single Molecule



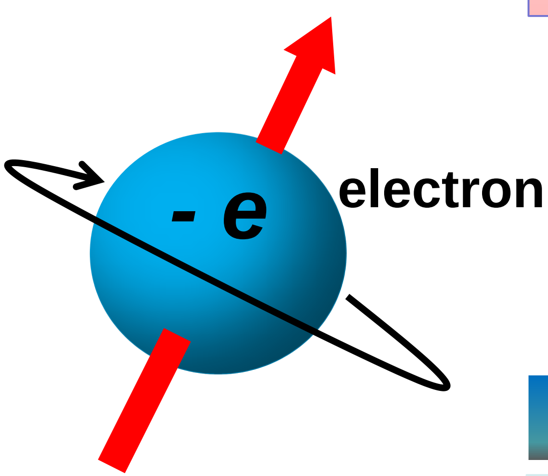






Spintronics

Spin



Electron

Magnetics

- Hard disk
- Magnet
- Sensor

etc…

Electronics

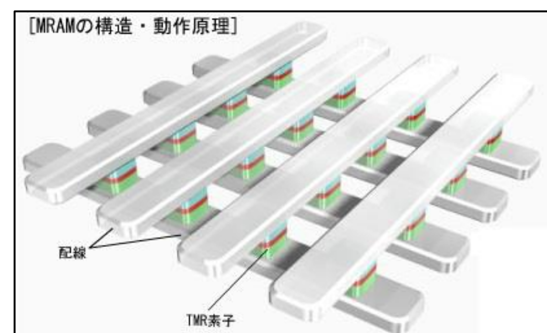
- Transistor
- Laser
- LSI

etc…

Spintronics

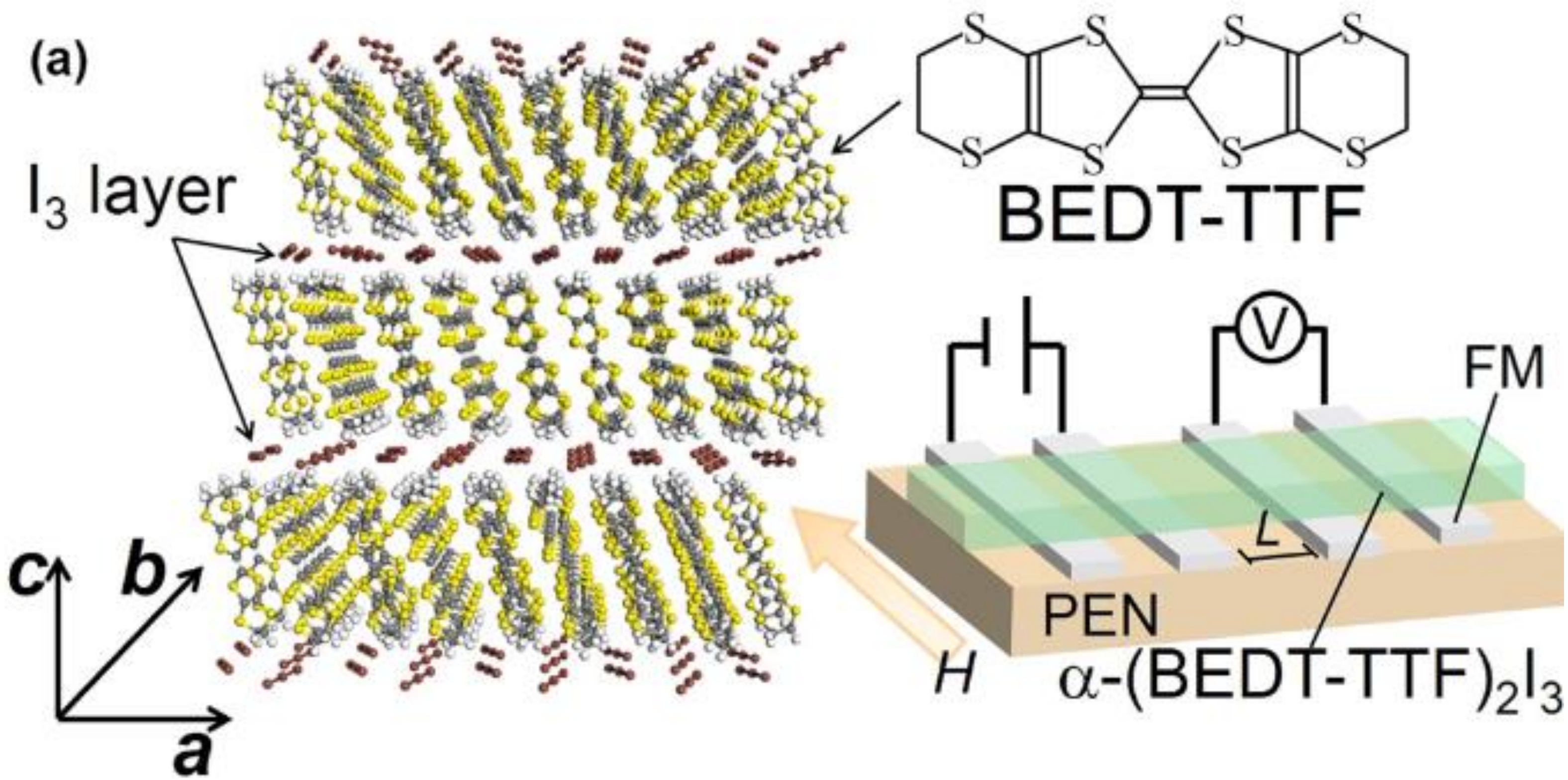
- TMR head
- ReRAM
- Spin Seebeck
- Spin Transistor

etc…



http://www.s-graphics.co.jp/nanoelectronics/index.html

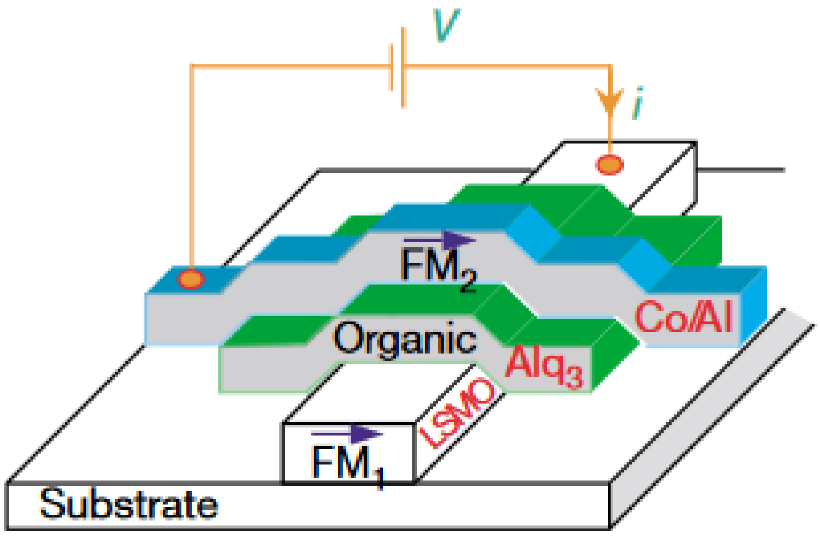
First report of lateral organic spin valve

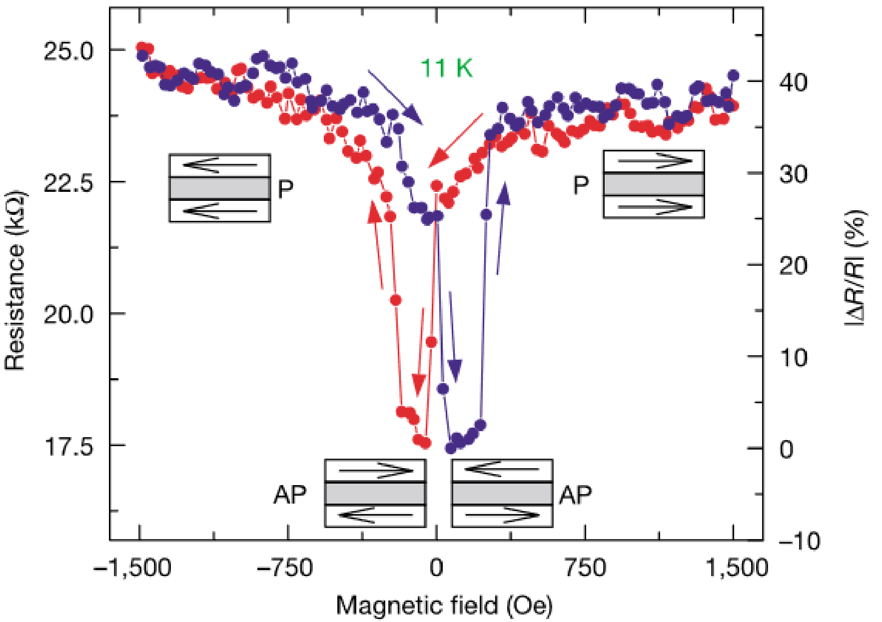


T. Kamiya *et al.* Phys. Rev. B **95** (2017) 085307

Organic Spin Valve

2004 Vardeny
Organic Spin Valve



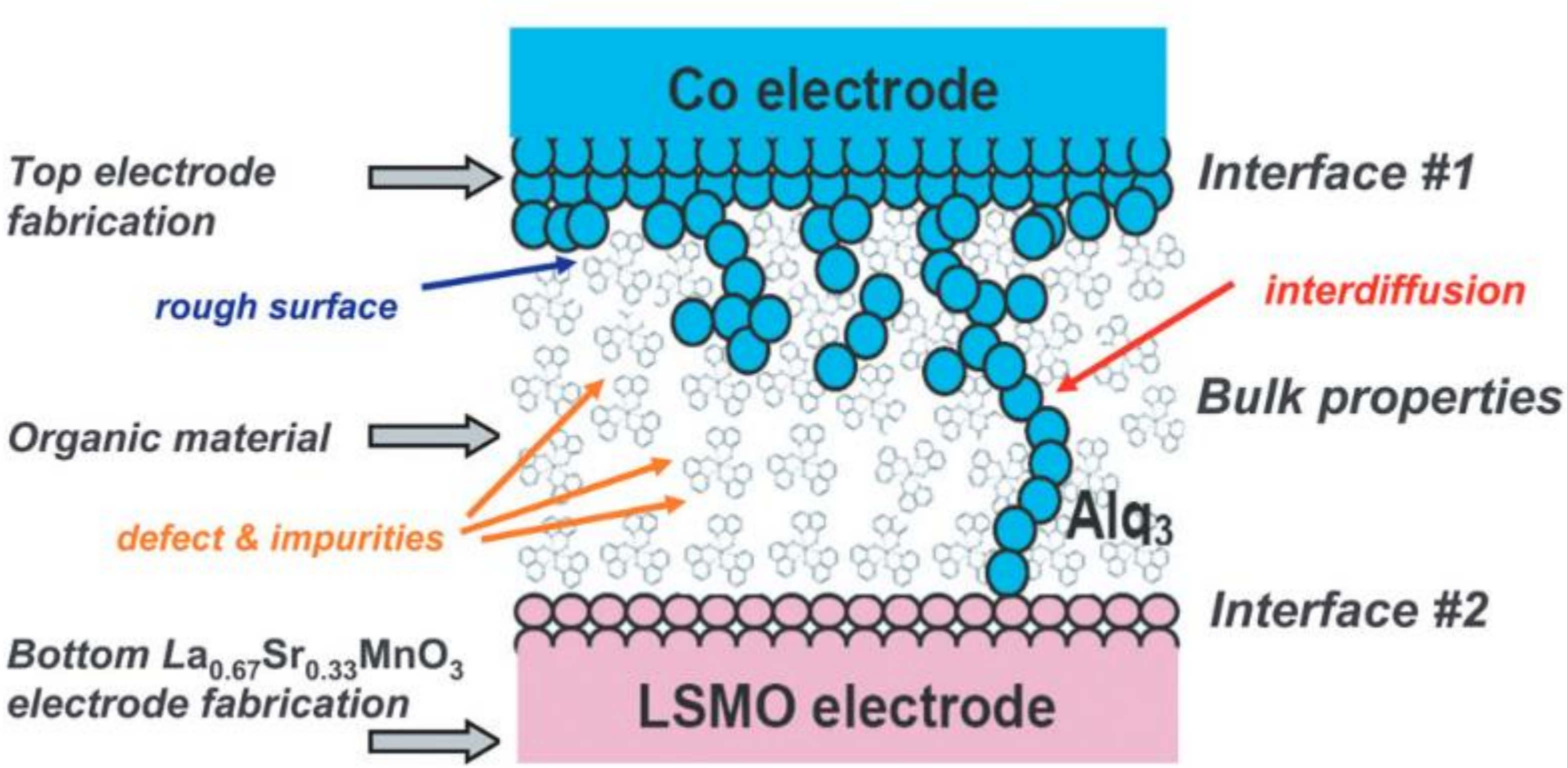


Xiong *et al.* Nature **427** (2004) 821

Weak spin-orbit interaction

Molecular design, light weight

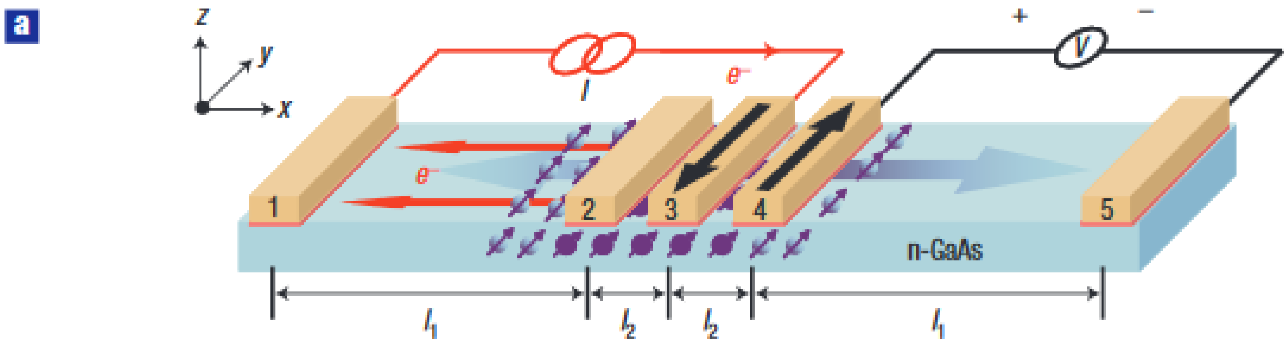
Problems of vertical devices?



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

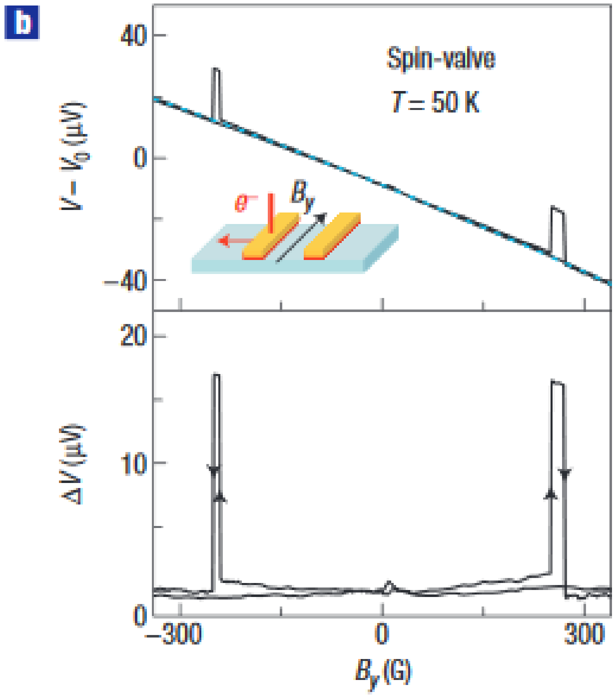
Can we inject spin into organic materials?

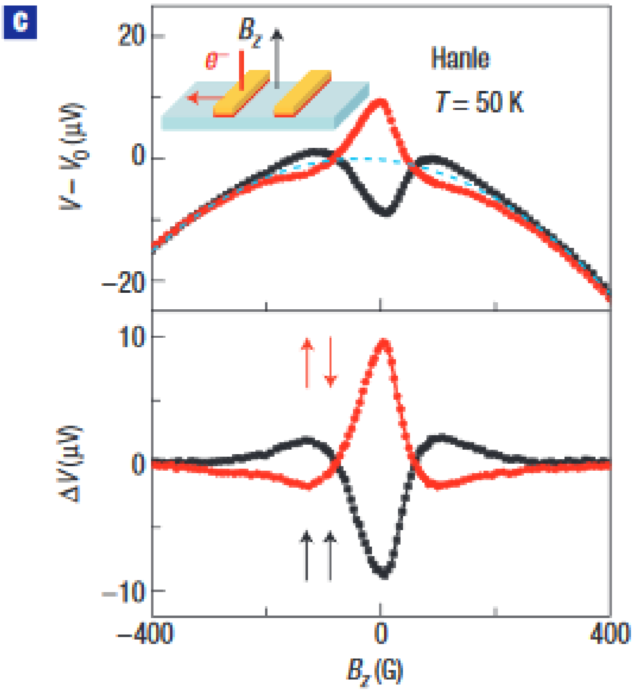
Lateral Device



Spin valve

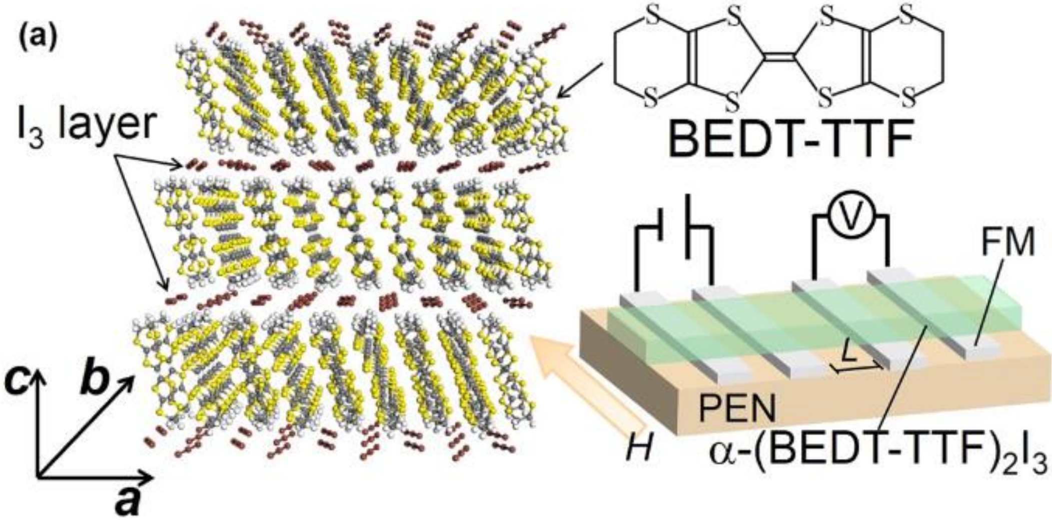
Hanle effect

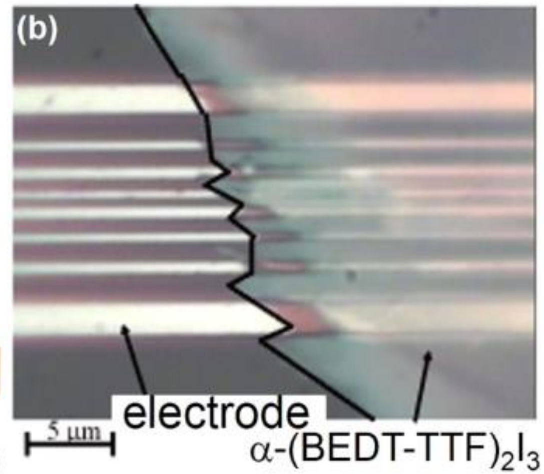


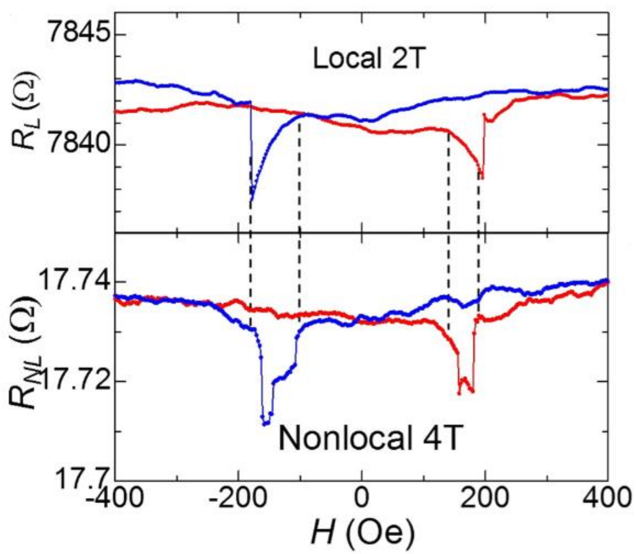


X. Lou *et al.* Nature Physics **3** (2007) 197

Lateral Organic Spin Valve







Pressured α-$(BEDT\text{-}TTF)_2I_3$ Crystal

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

Outline

1. Single Molecular Spin Valve

2. Introduction of Non-equilibrium Green's Function (NEGF) method

3. NEGF-DFT and its applications

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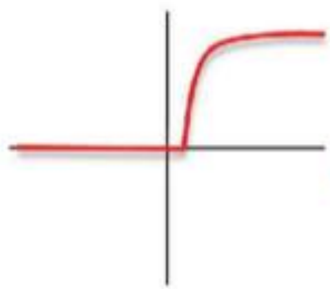
4. Organic Magetoresistance, OMAR

1. Single Molecular Spin Valve

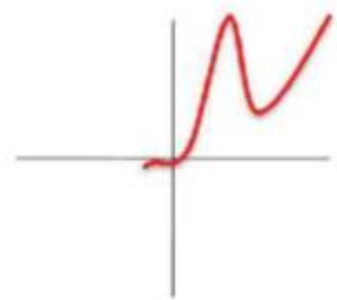
Single Molecular Electronics



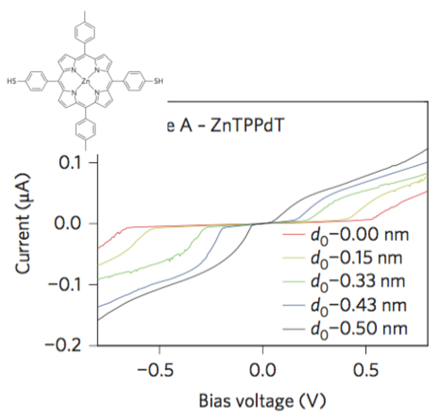
Threshold
*Coulomb blockade

Rectification
(Diode)

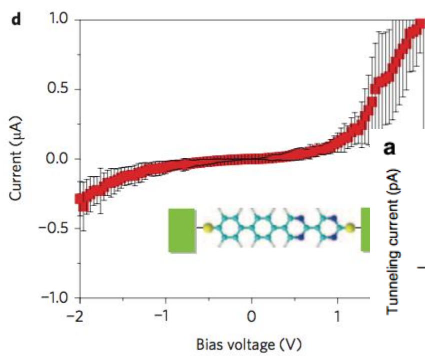
Hysteresis
(Memory/Switch)



Negative differential
resistance (NDR)

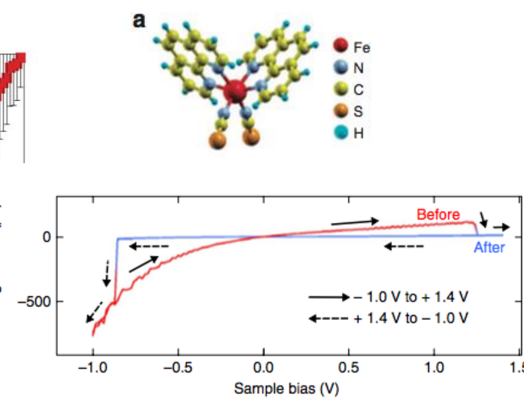


ML Perrin et al., Nature Nanotech. 8, 282 (2013).

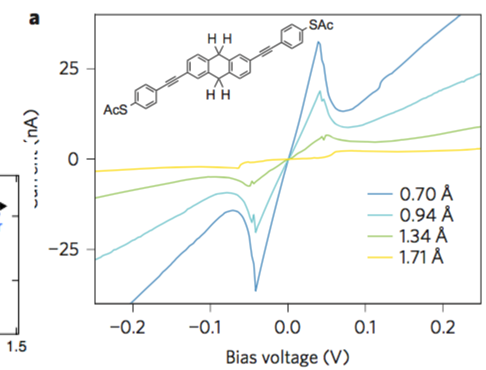


I. Diez-Perez et al., Nature Chem. 1, 635 (2009).

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

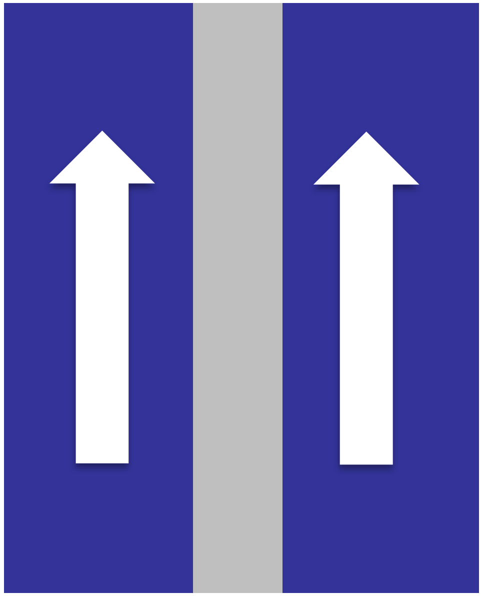


Spin-cross over; T. Miyamachi et al., Nature Comm. 3, 938 (2012)
Mg-Porphine; S. Saha et al., Apl. Mater&Inter., 7, 10085 (2015).

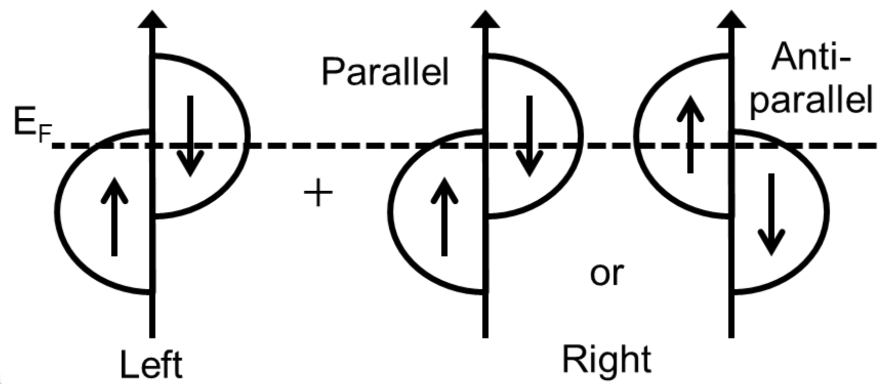


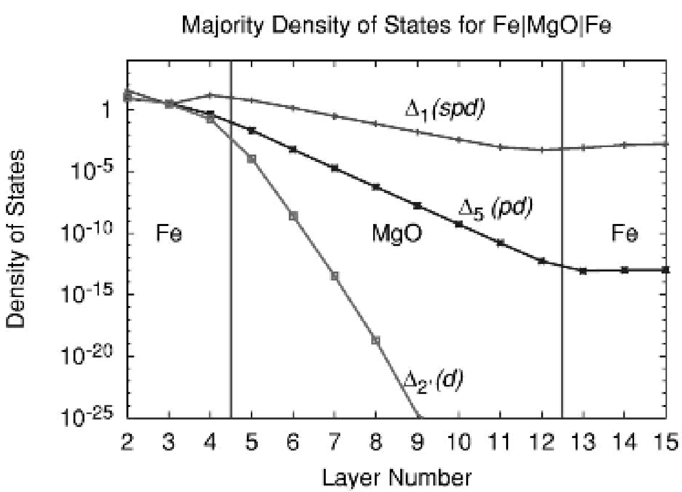
ML Perrin et al., Nature Nanotech. 9, 830 (2014). (Double barrier resonant tunneling)

Tunneling Magnetoresistance (TMR)



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

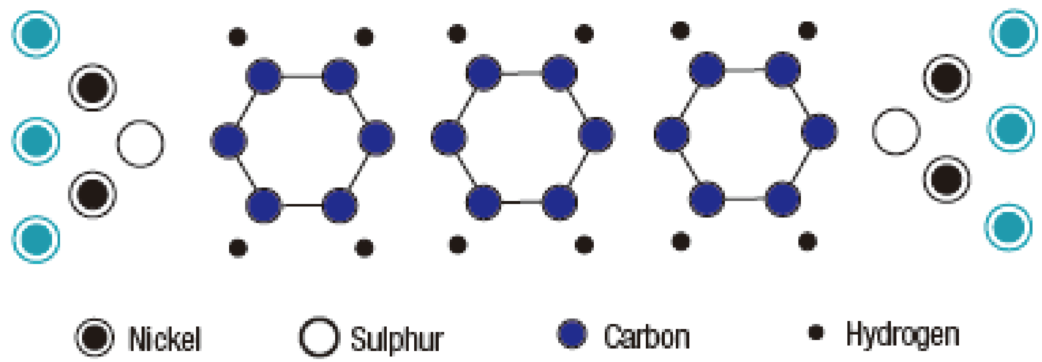




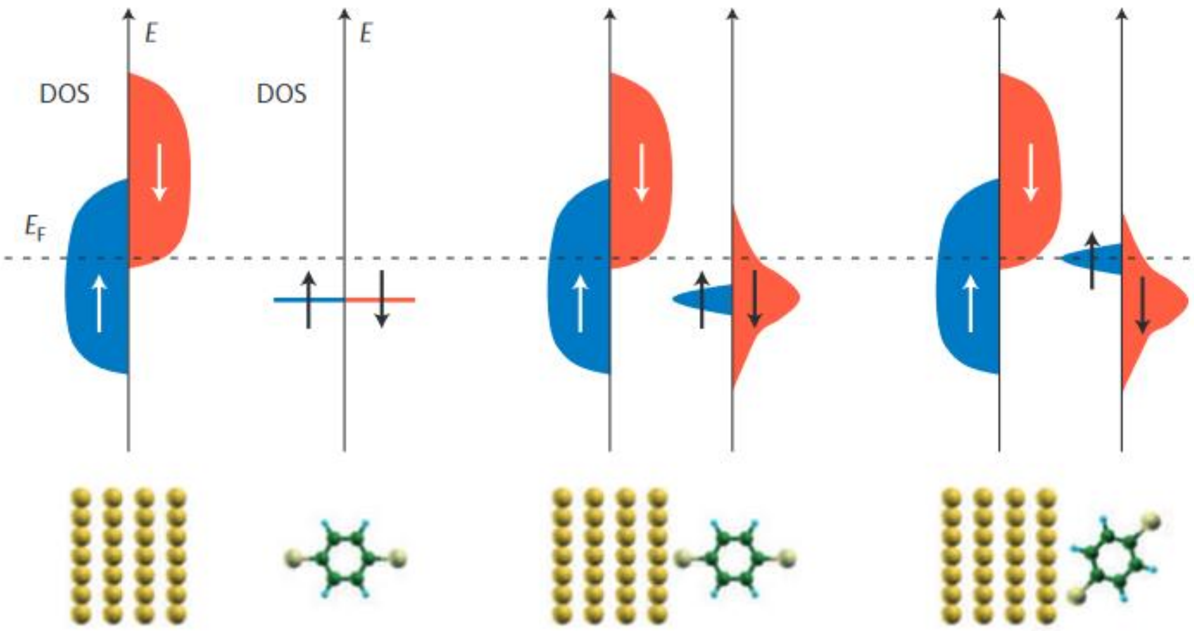
MgO crystal blocks d electron of majority spin

W. H. Butler et al. Phys. Rev. B **63** (2001) 054416

Single Molecular TMR Devices

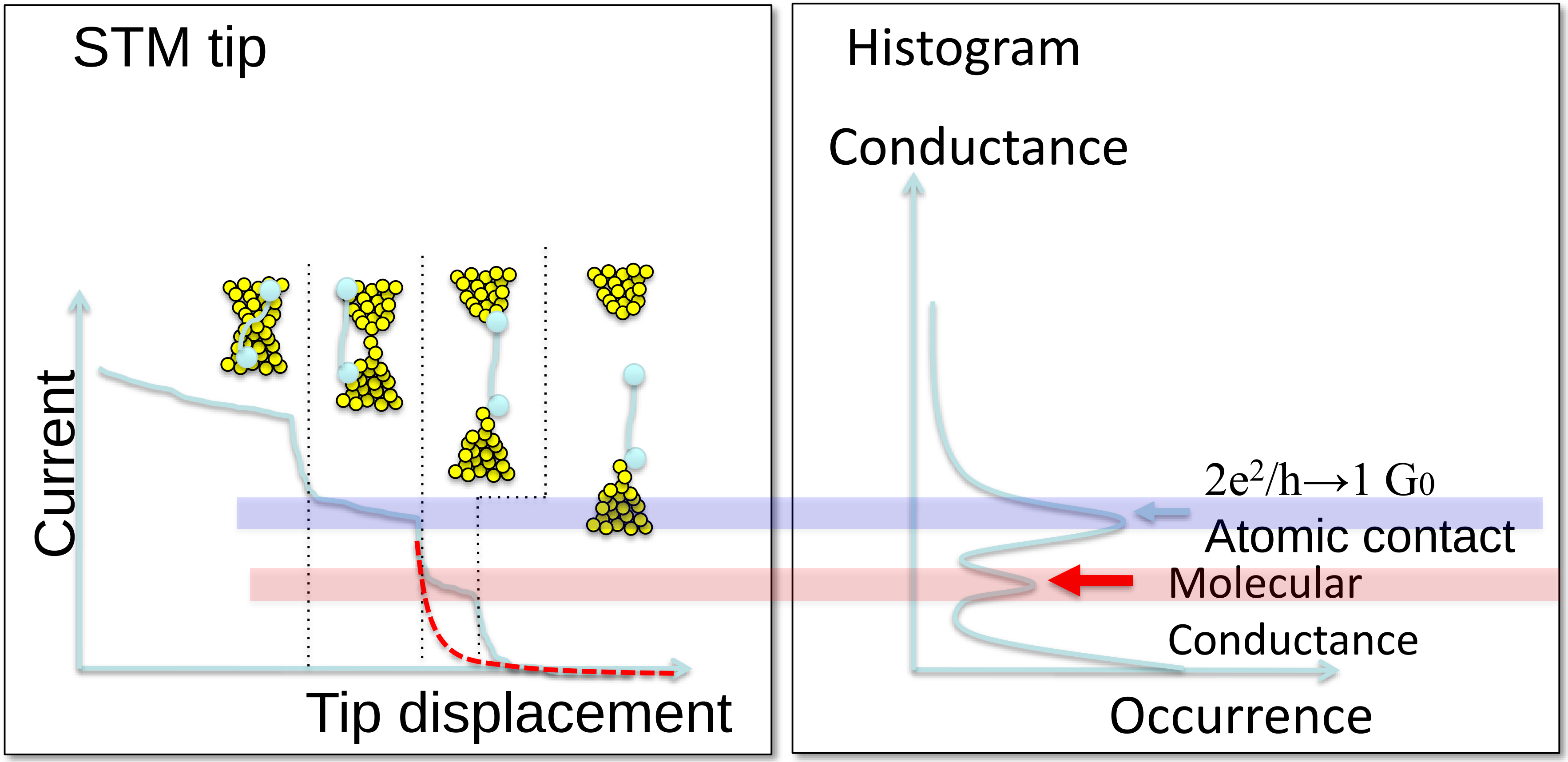


Rocha *et al.* Nat. Mater. **4** (2005) 335



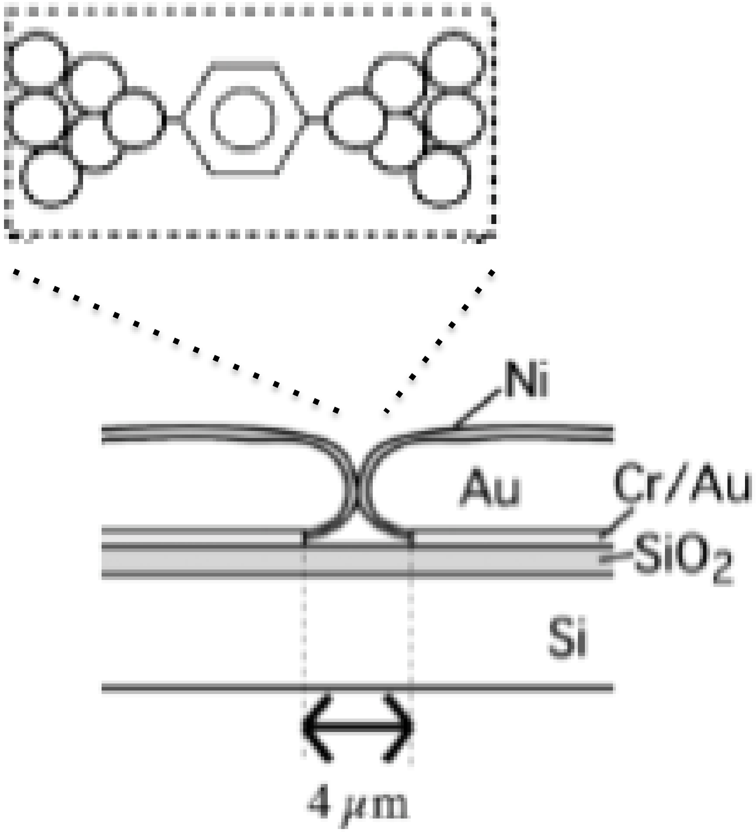
S. Sanvito Nat. Phys. **6** (2010) 562

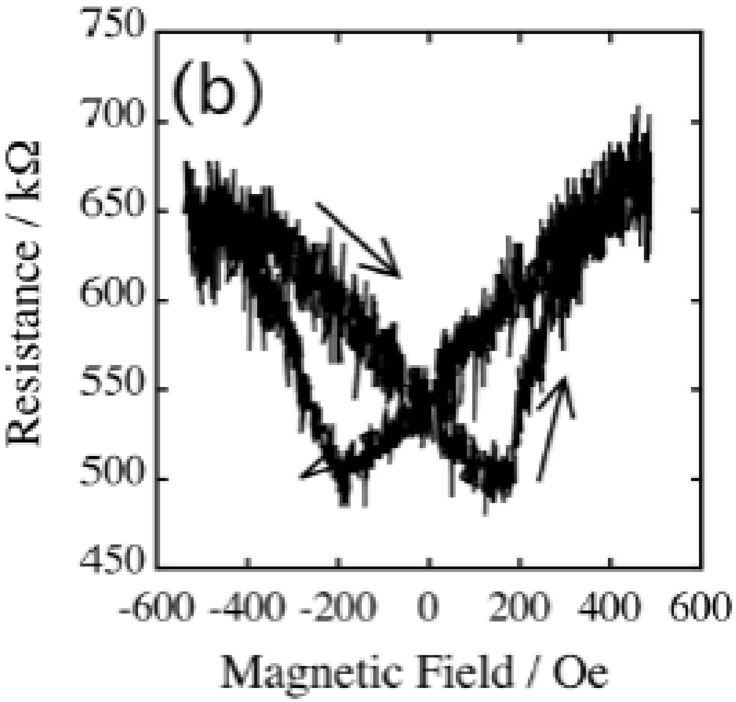
Experimental Methods



Break Junction (BJ) Method

Experimental Methods

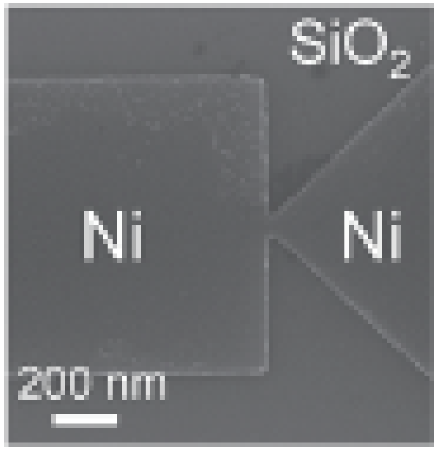


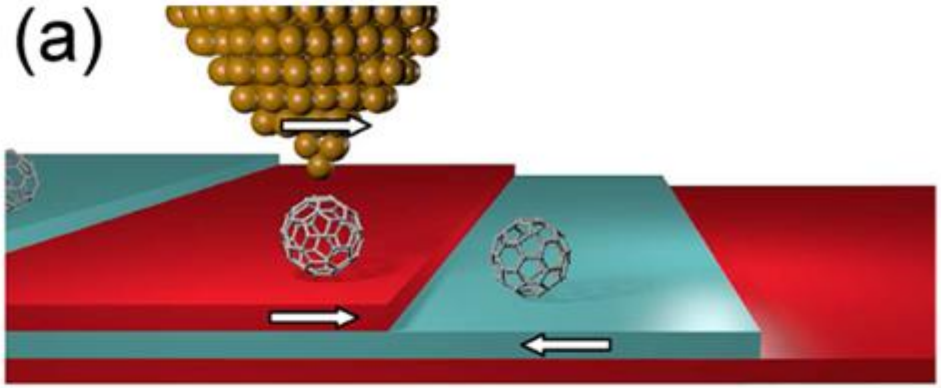


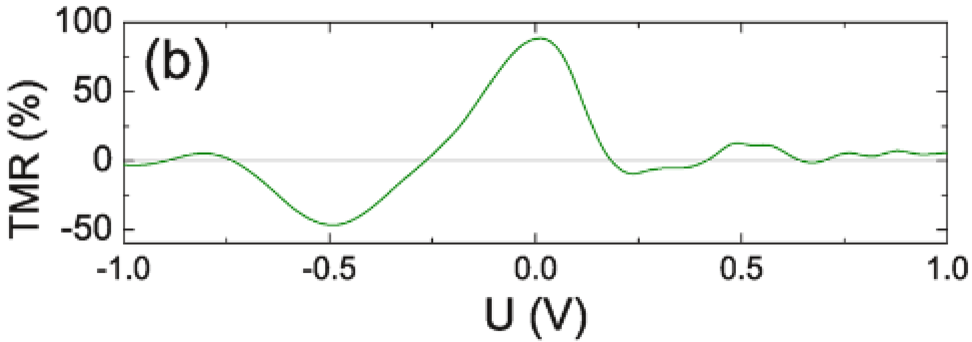
MCBJ with magnetic electrodes

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

Experimental Methods







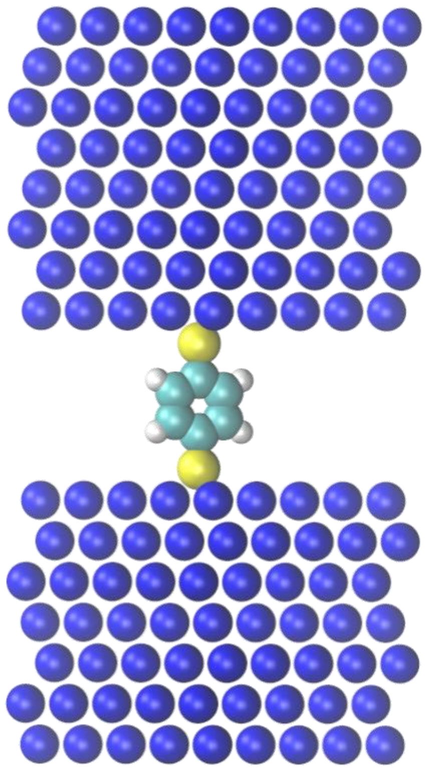
Electrical break junction method, C_{60}/Ni

Scanning tunneling microscopy (STM), C_{60}/Cr(001)

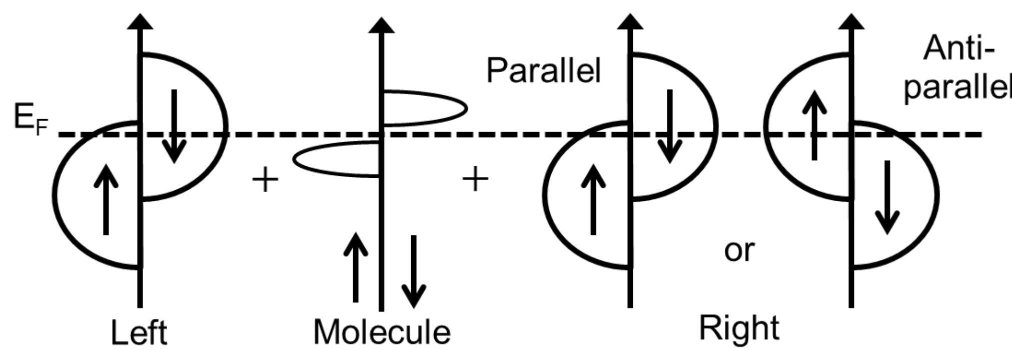
K. Yoshida *et al.* Nano Lett. **13** (2013) 481

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

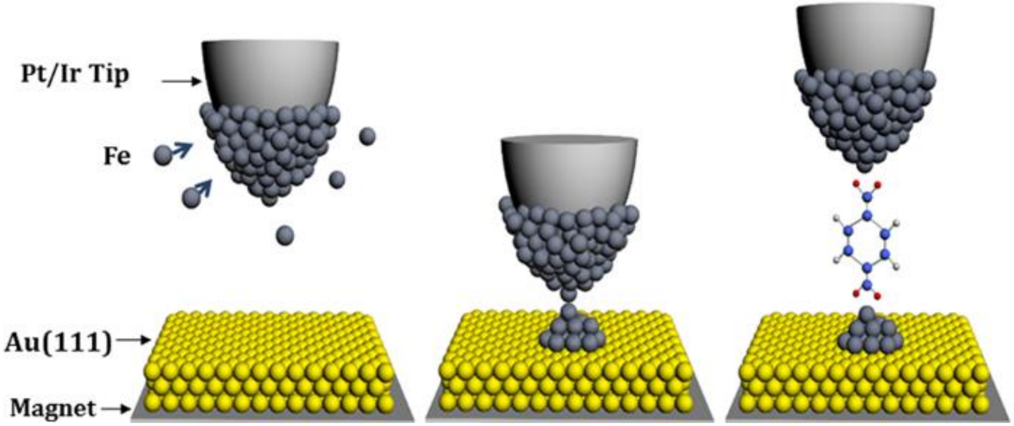
Theoretical Design of Molecular Spin Valve

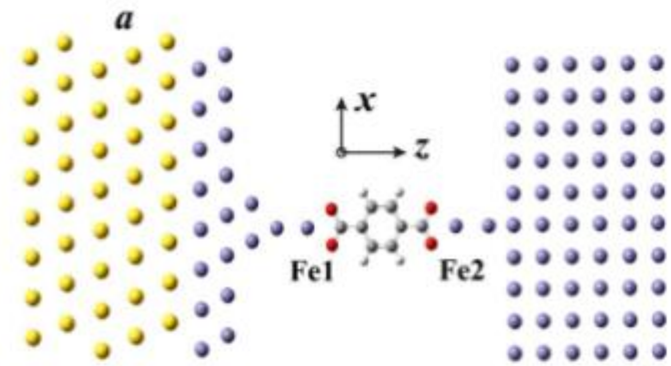


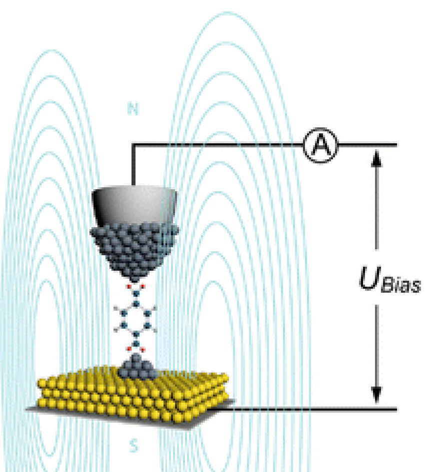
- Origin of magnetoresistance
  - TMR
  - TAMR
- Molecular structure
- Spin filter effect

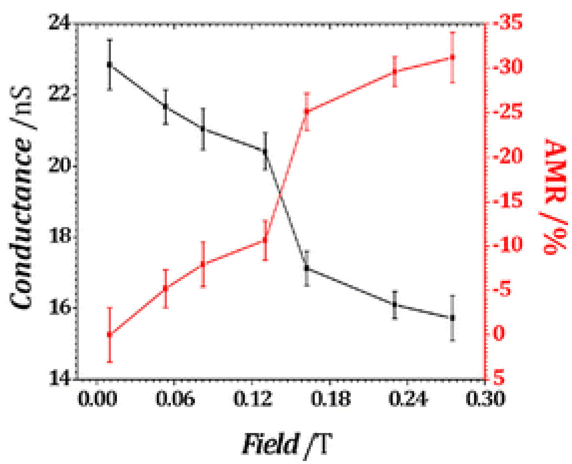


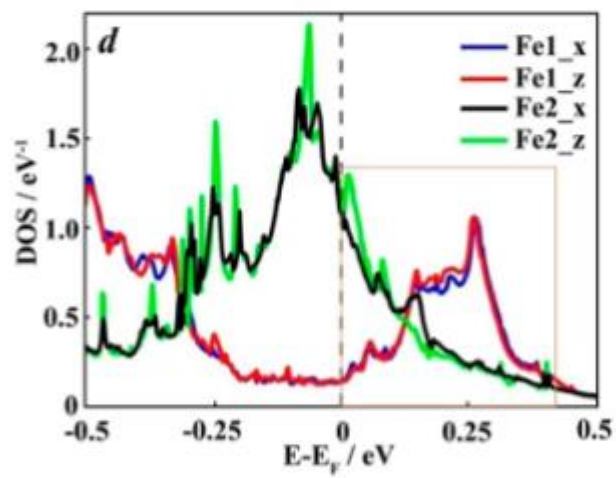
Tunneling Anisotropic MR (TAMR)











J.-J. Li *et al.* J. Am. Chem. Soc. **137** (2015) 5923

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

Programs

Atomic Orbial (SIESTA)

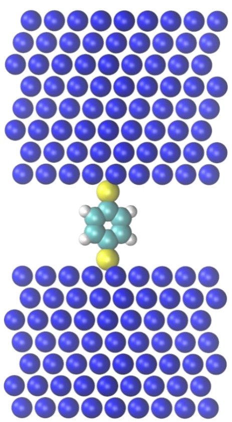
TranSIESTA（Spain, Denmark）
with SIESTA

ATK (Quantum Wise)
Commercial TranSIESTA

SMEAGOL（Ireland, UK）
Spin Transport

HiRUNE（Japan, AIST）
Electron-phonon

OpenMX（Japan）



molecule
10~100 atoms

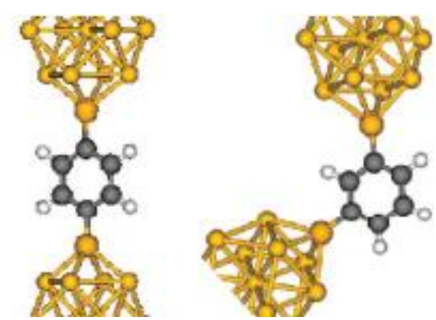
electrodes
8x8x6x2
=768 atoms(!)

Plane Wave

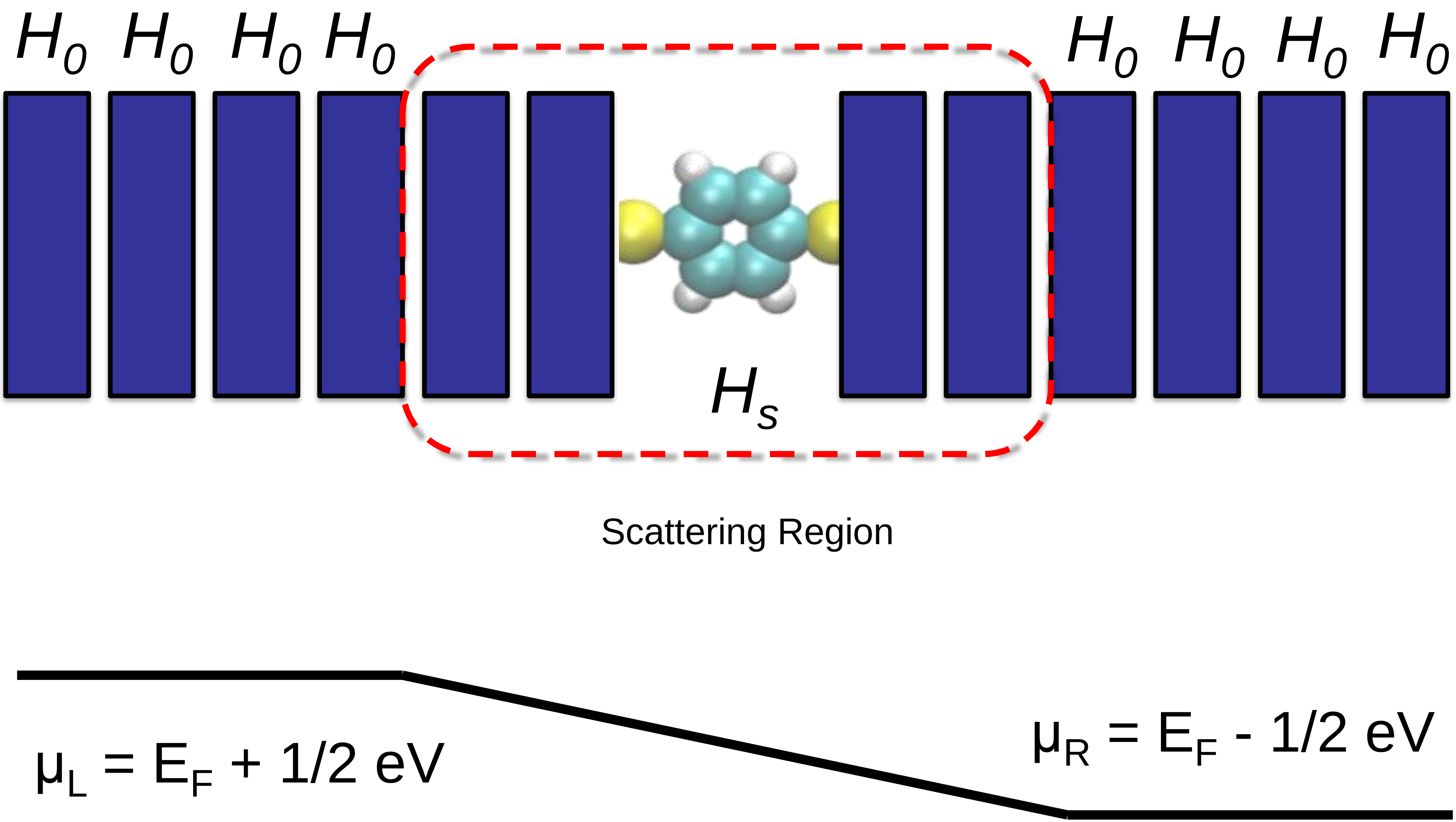
Quantum Espresso

Gaussian Basis

Turbomole

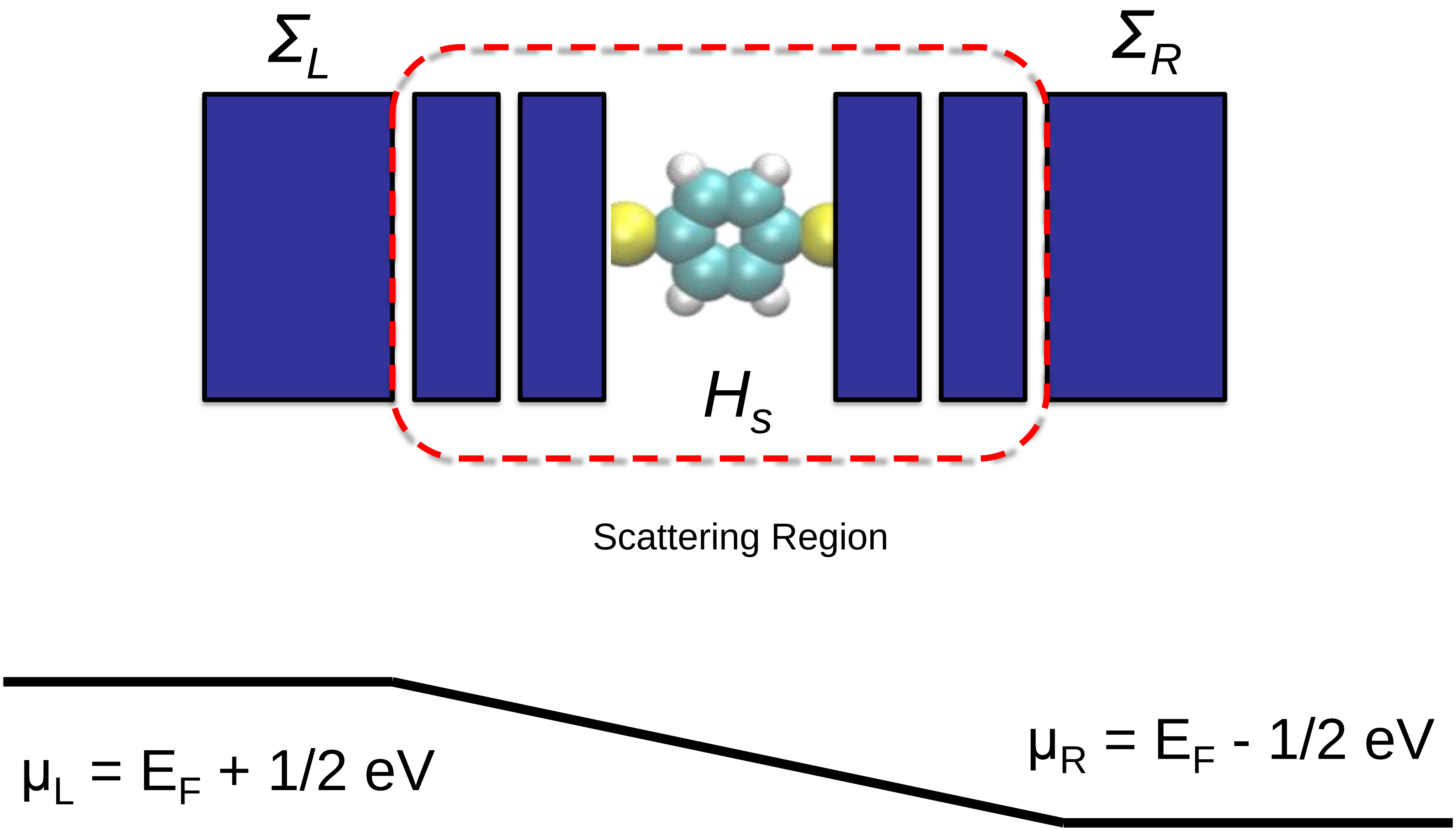


NEGF

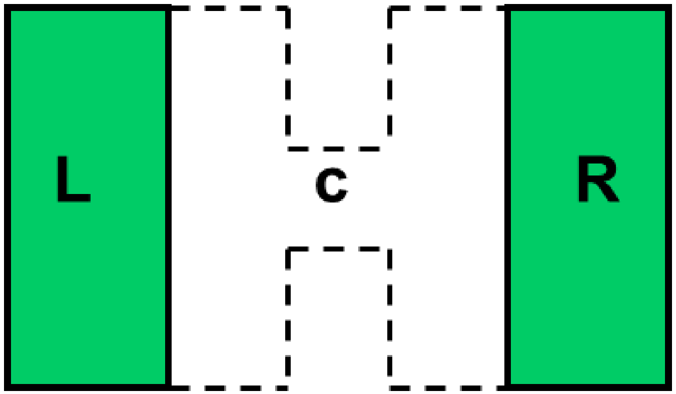


H_0 H_0 H_0 H_0
H_0 H_0 H_0 H_0
H_S
Scattering Region
$\mu_L = E_F + 1/2$ eV
$\mu_R = E_F - 1/2$ eV

NEGF



NEGF



Hermitian problem for an open infinite system

$$H = H_s + H_0 + H_0 + H_0 + \ldots$$

Non-Hermitian problem for a finite system

$$H = H_s + \Sigma_L + \Sigma_R$$

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

$$\mathbf{H}_{eff} = \mathbf{H} + \mathbf{\Sigma}_L(E) + \mathbf{\Sigma}_R(E)$$

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

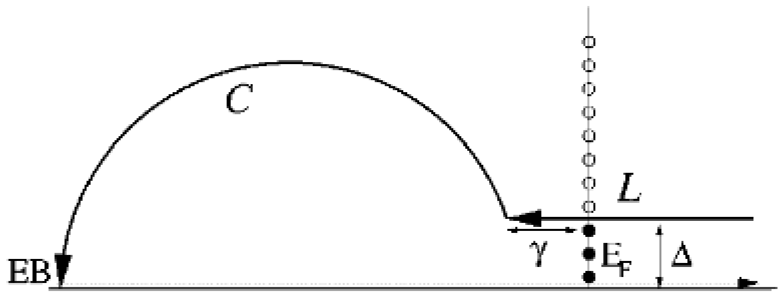
Surface Green's function

NEGF-SCF

"Lesser" Green's function

$$\mathbf{G}^{<}_{CC}(E) = \mathbf{G}_{CC}(E)\mathbf{\Sigma}^{<}\mathbf{G}^{\dagger}_{CC}(E)$$ *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

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

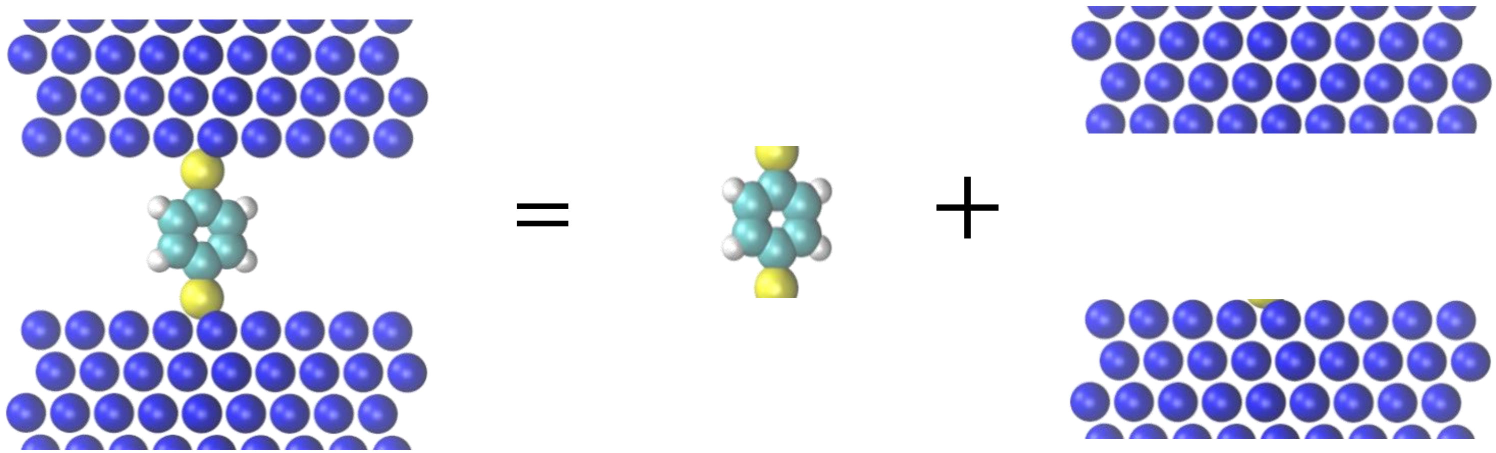
Convergence of density matrix

NEGF

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

$$G = G_0 + G_0 \Sigma\, G$$ Dyson Equation

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



$$G \qquad = \qquad G_0 \qquad + \qquad \Sigma = \Sigma_L + \Sigma_R$$

We can add any interactions through Σ

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

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

↑ lesser self energy

3. NEGF-DFT and its application

What we can obtain…

- Transmission Function

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

- TMR ratio

The ratio of the transmission function with parallel/antiparallel magnetization

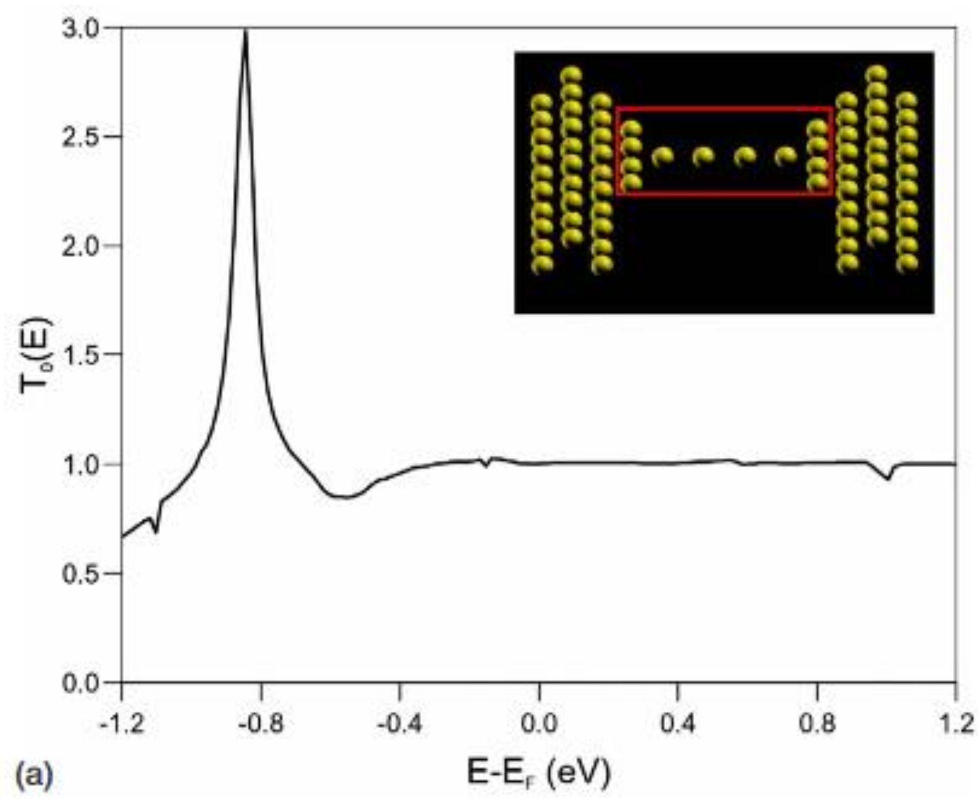
- Current voltage characteristics

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

- Spin Transfer Torque
- TAMR

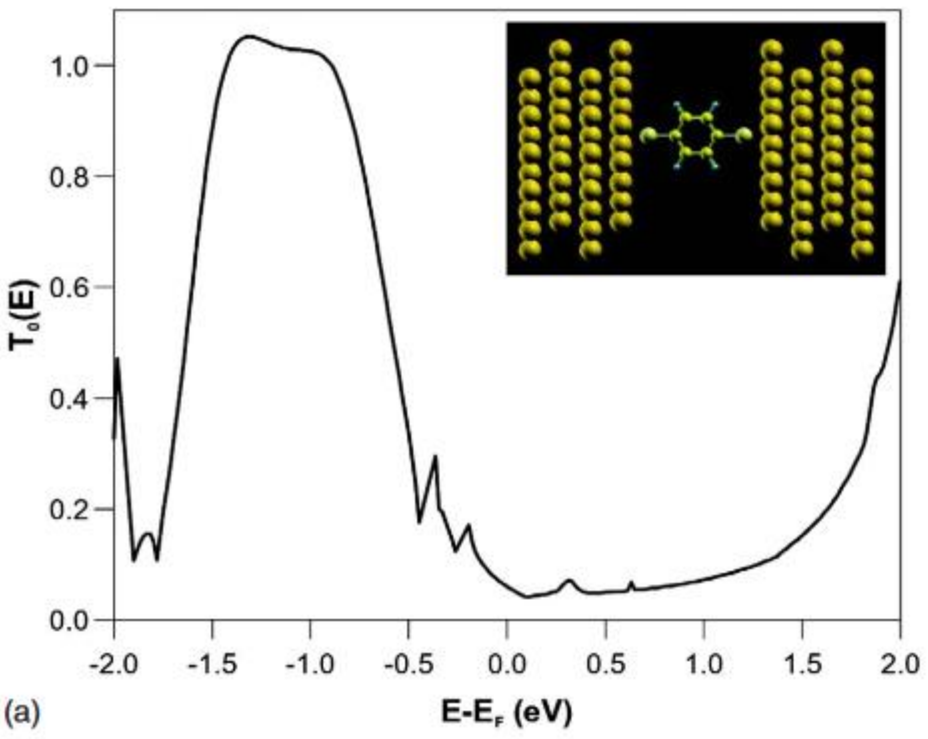
with SMEAGOL

Gold wire



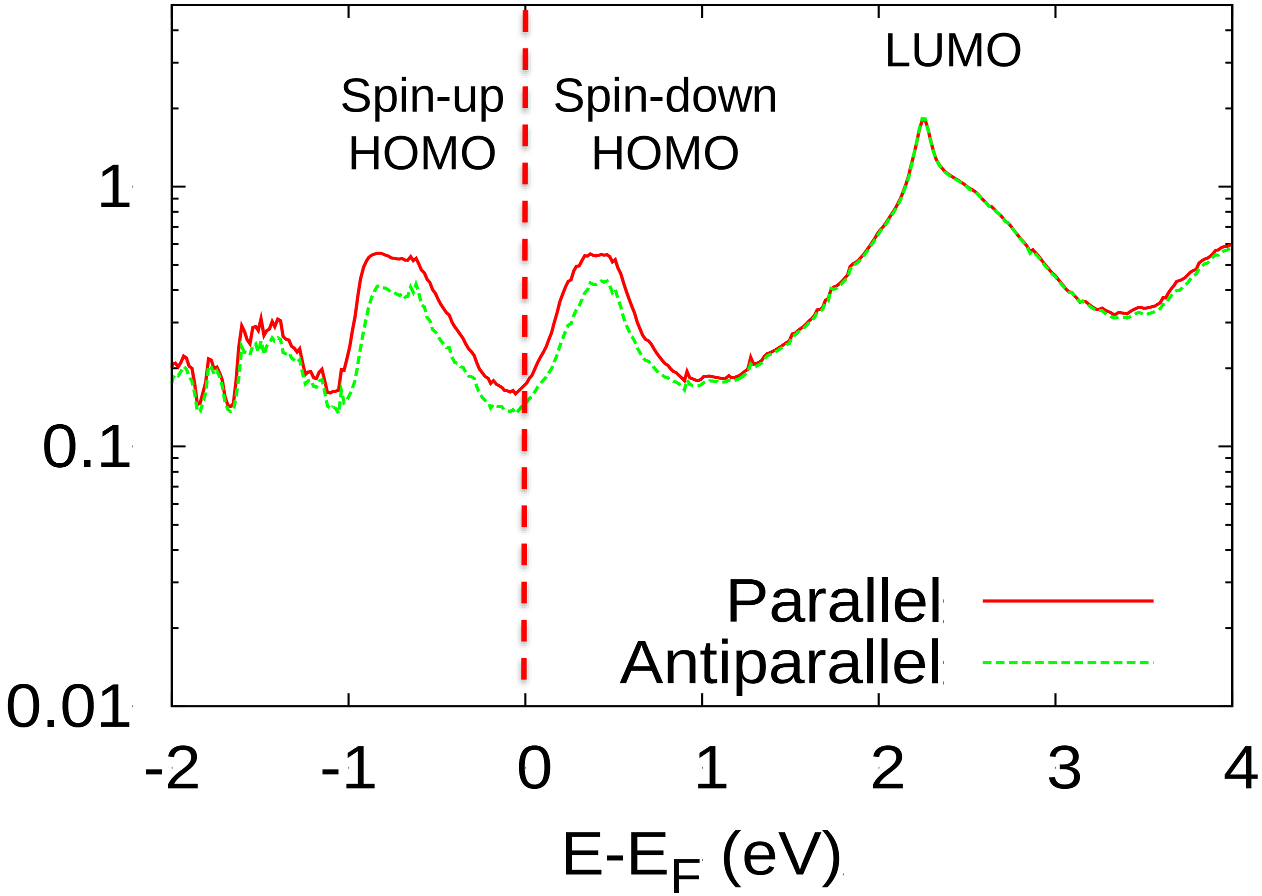
H. Nakamura *et al*. Phys. Rev. B **78** (2008) 235420

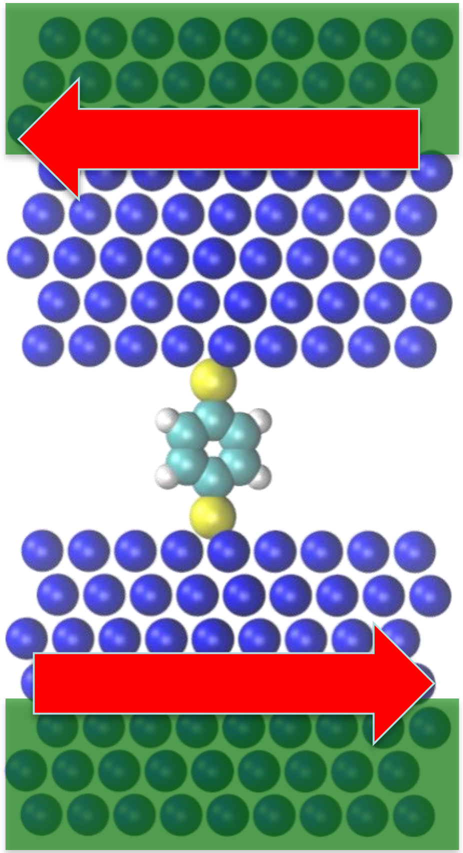
Au-BDT-Au



H. Nakamura *et al*. Phys. Rev. B **78** (2008) 235420

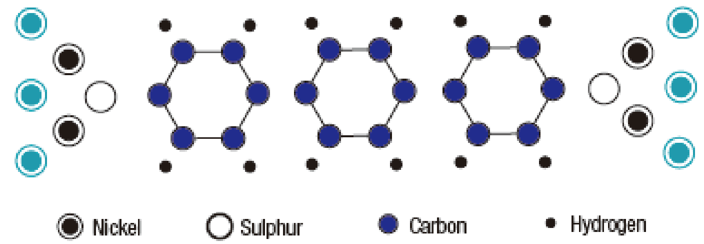
Ni-BDT-Ni

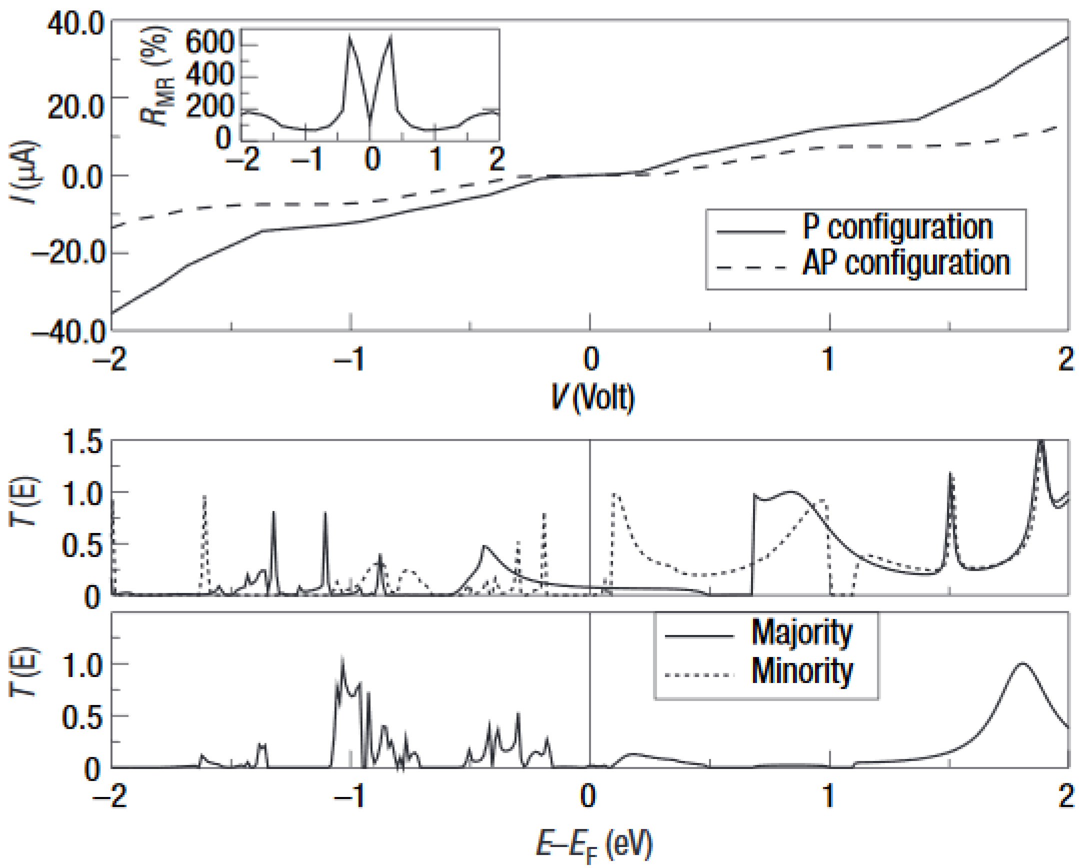




TMR~20%

Possibility of higher TMR





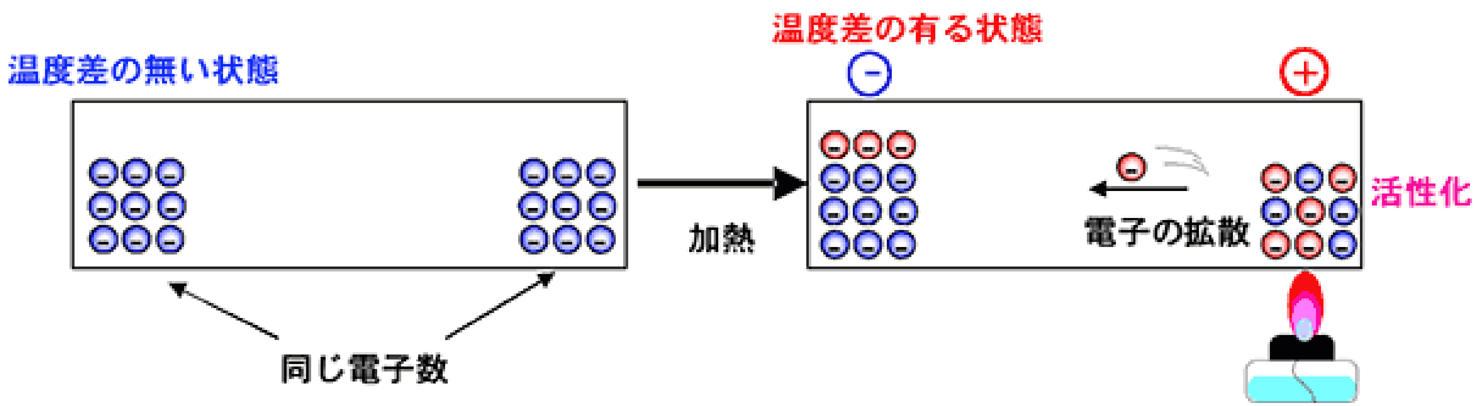
Rocha *et al.* Nat. Mater. **4** (2005) 335

Thermoelectric device

BioLite Inc.

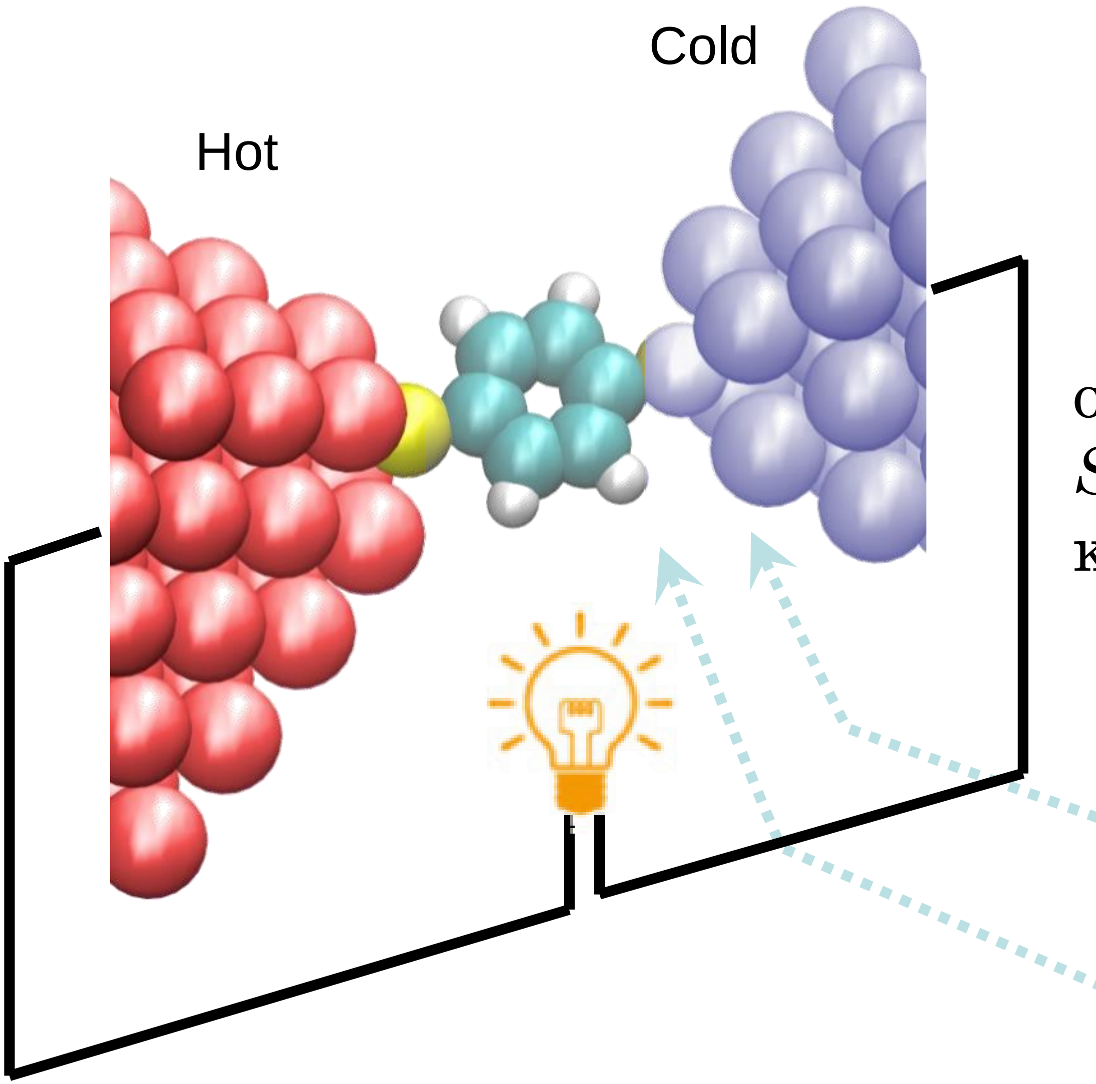
$$ZT = \frac{\sigma S^2}{\kappa} T$$

σ : 電気伝導度
S : ゼーベック係数
κ : 熱伝導度



https://www.aist.go.jp/pr20050531

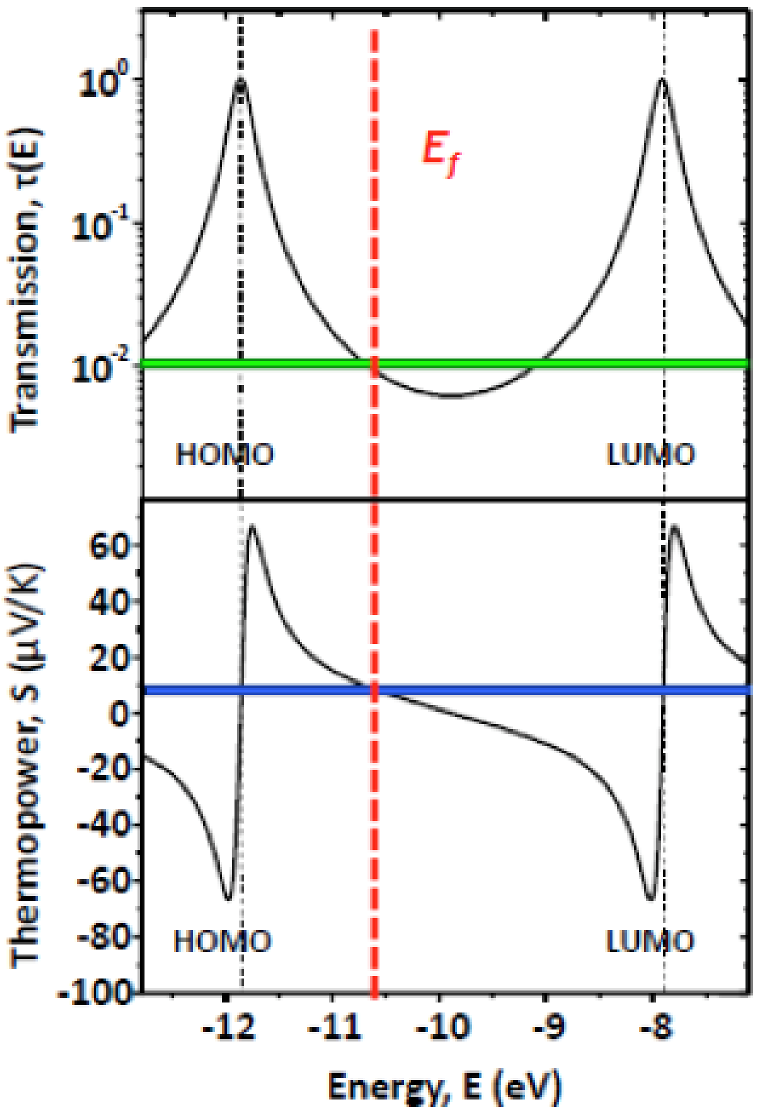
Molecular thermoelectric device



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

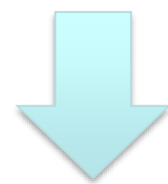
σ : Electrical conductance
S : Seebeck coefficient
κ : Thermal conductance

Themopower (Seebeck Coefficient)



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

Gradient of the contantance

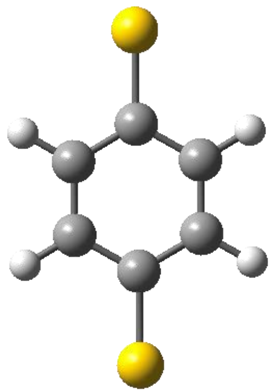


Electron or hole?

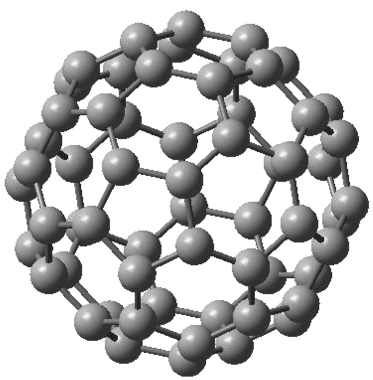
Calculation of T(E) from conductance and thermopower

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

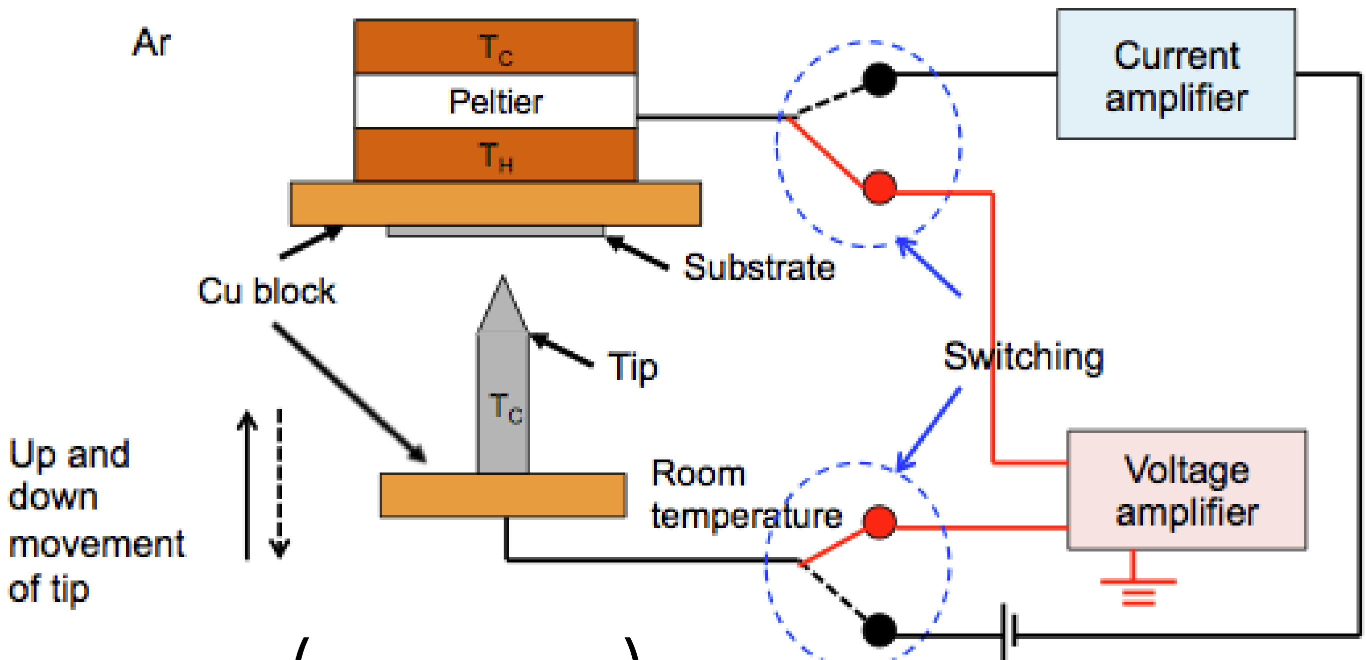
Thermopower measurement



BDT



C_{60}

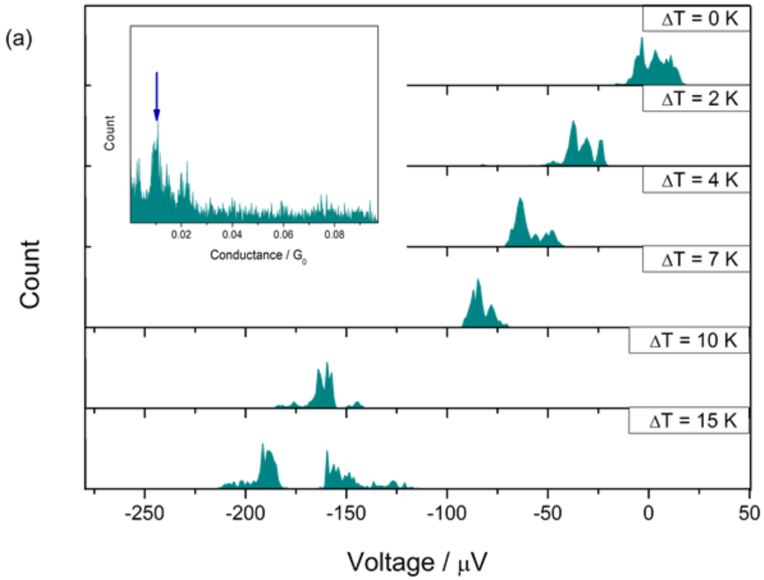


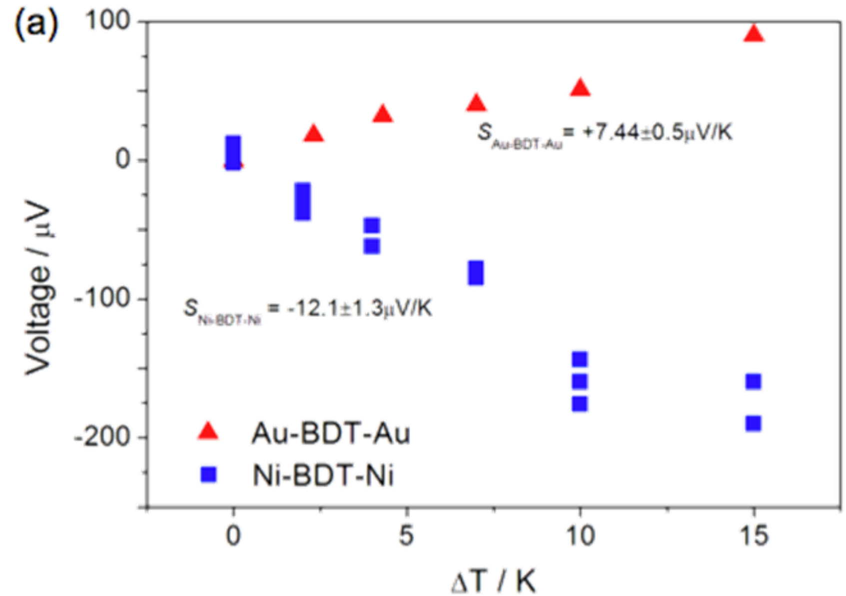
$$V = \left(S_{\mathrm{junction}} - S_{\mathrm{Cu}}\right)\Delta T$$

Substrate → Au and Ni

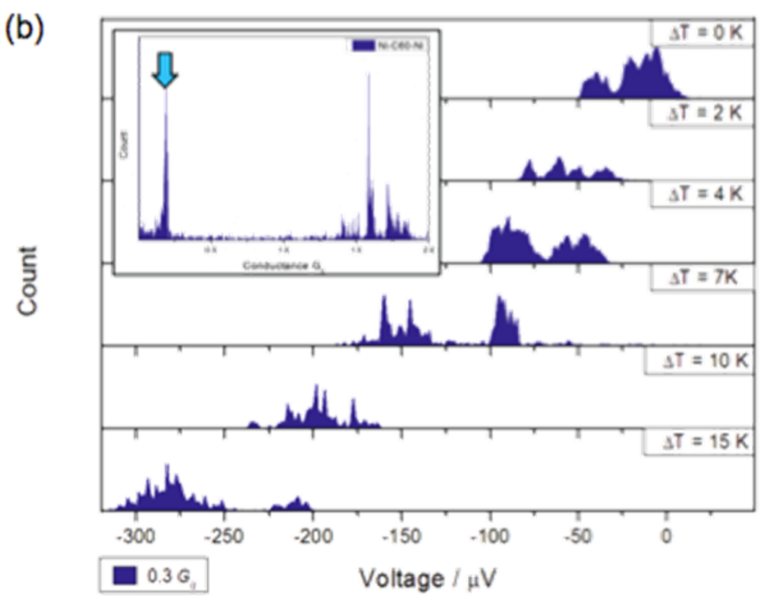
Lee, Ohto, *et al*. Nano Lett. **14**(2014)5276

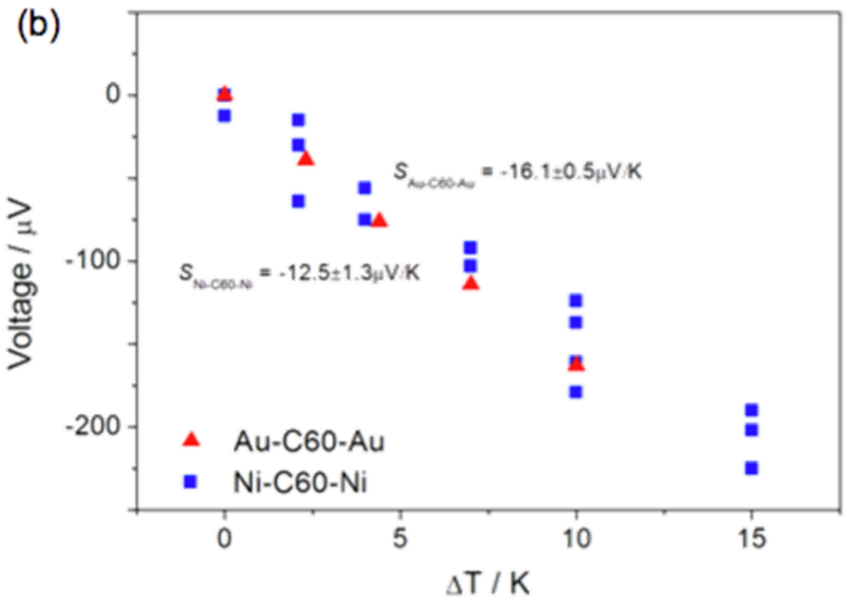
Thermopower measurement





BDT





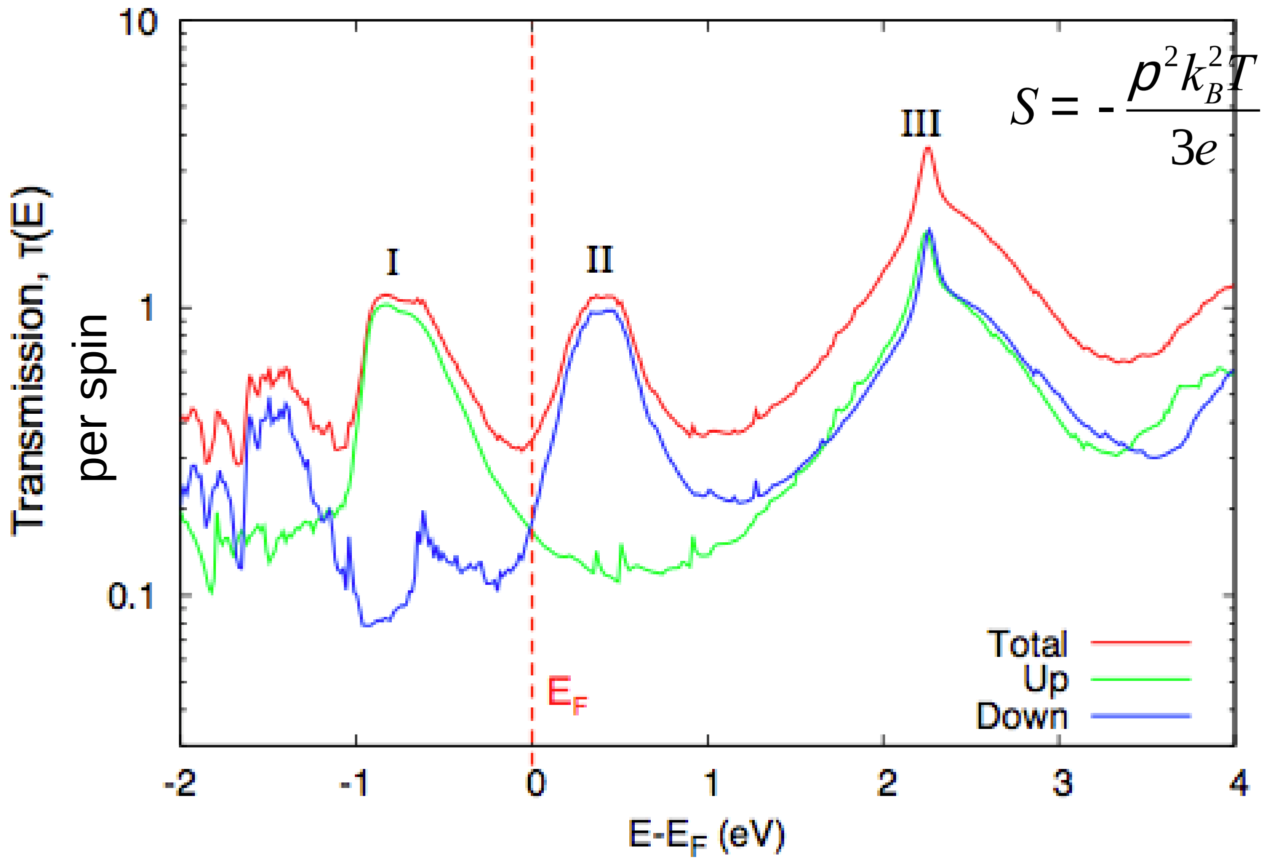
C_{60}

Lee, Ohto, *et al*. Nano Lett. **14**(2014)5276

Ni(111)-BDT-Ni(111)

SMEAGOL module (NEGF-DFT)，LDA functional

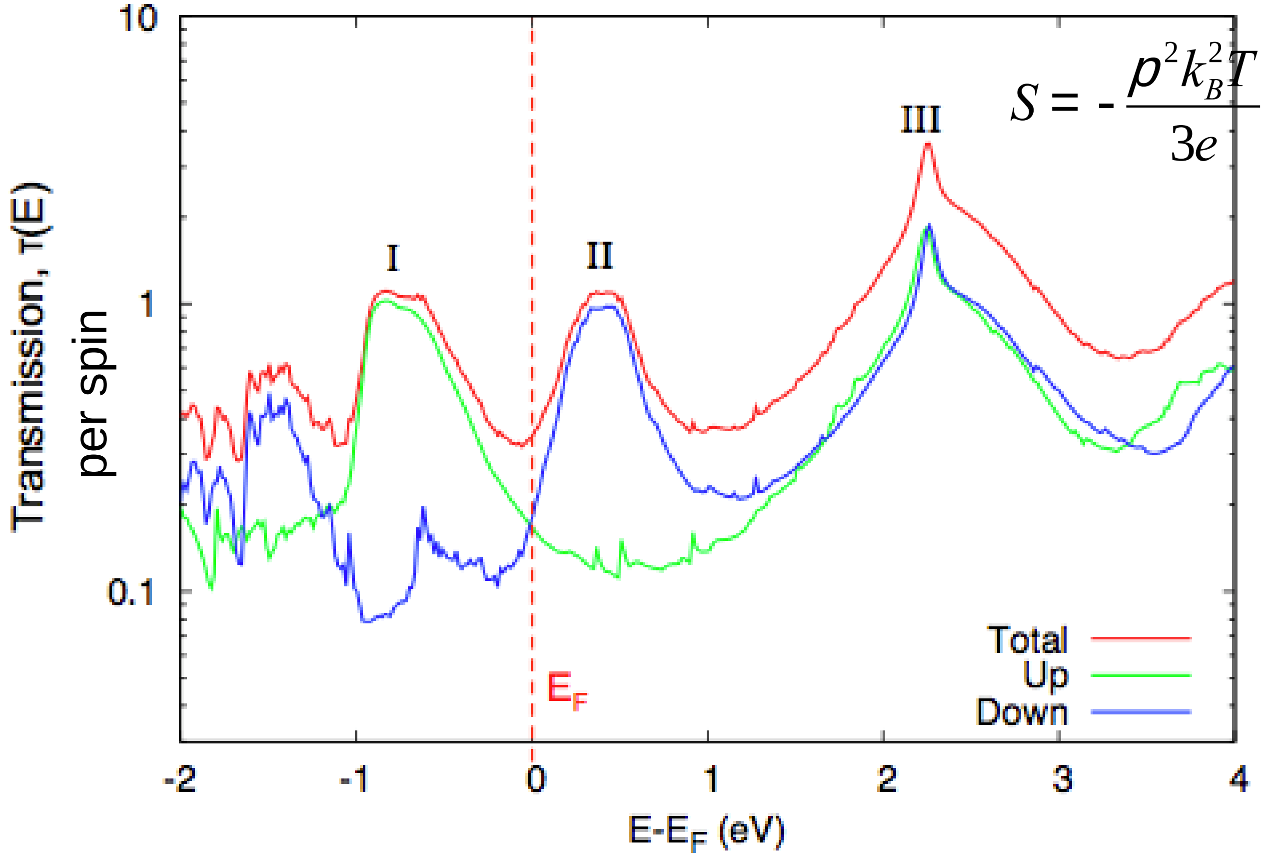
$$S = -\frac{p^2 k_B^2 T}{3e}\left(\frac{\partial \ln t(E)}{\partial E}\right)\Bigg|_{E=E_F}$$



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)

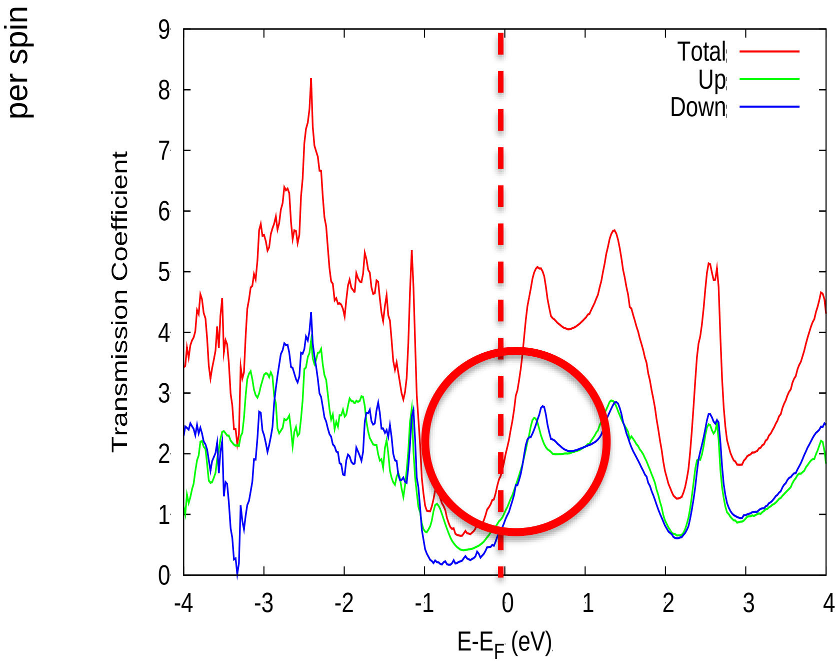
SMEAGOL module (NEGF-DFT), LDA functional



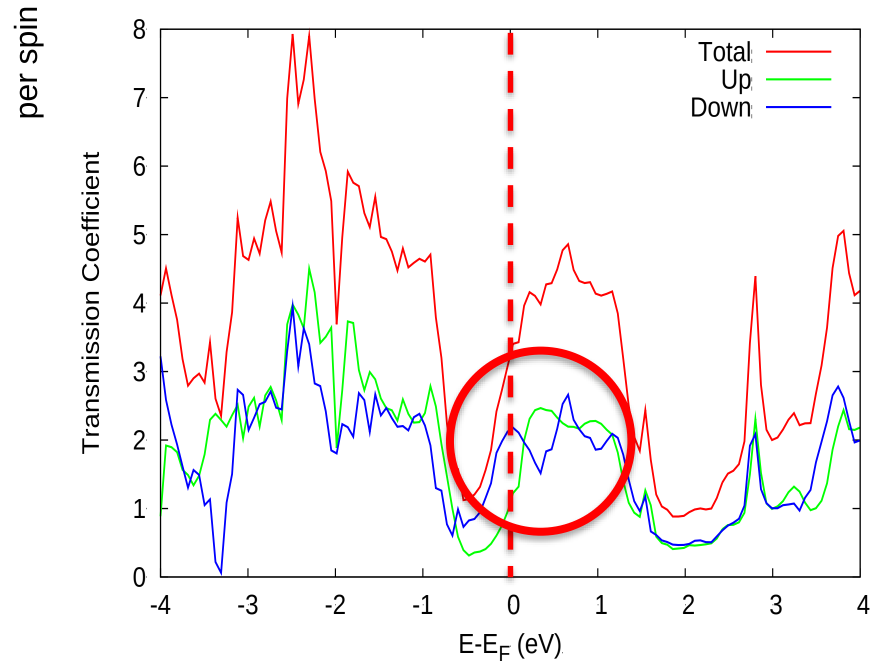
$$S = -\frac{p^2 k_B^2 T}{3e}\left(\frac{\partial \ln t(E)}{\partial E}\right)\Bigg|_{E=E_F}$$

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_{60}-Ni(111)



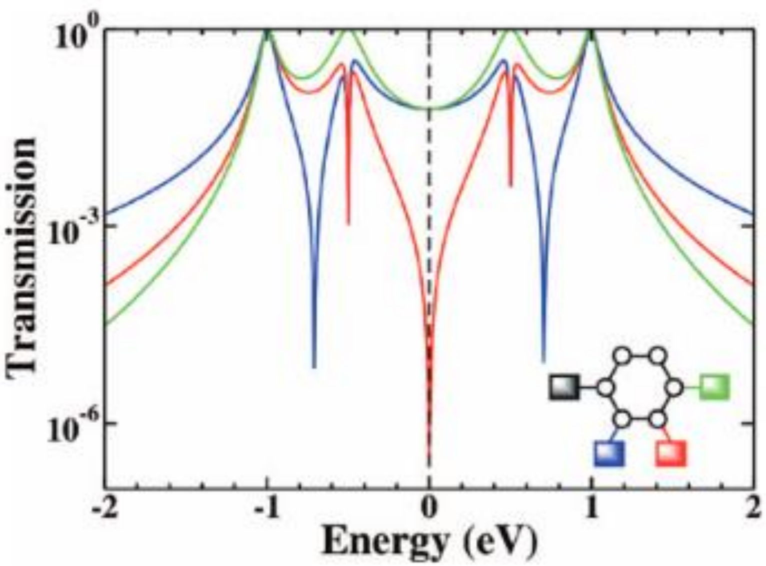
Hexa-faced structure
(most stable)



Penta-faced structure

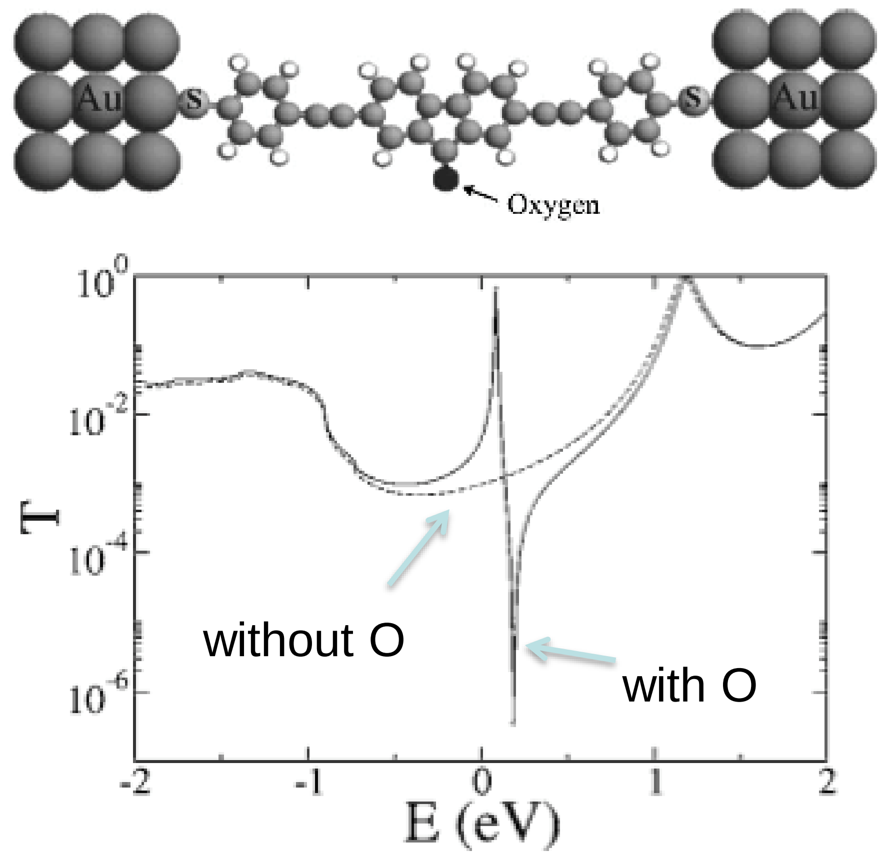
- 安定と考えられる構造ではいずれも負のゼーベック係数（実験結果を再現）
- フェルミ準位近くにあるLUMOが伝導に寄与（Au-C_{60}-Auと同様）
- スピン分極の様子は吸着構造によって異なるが、小さい

How to improve S?



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

Quantum Interference

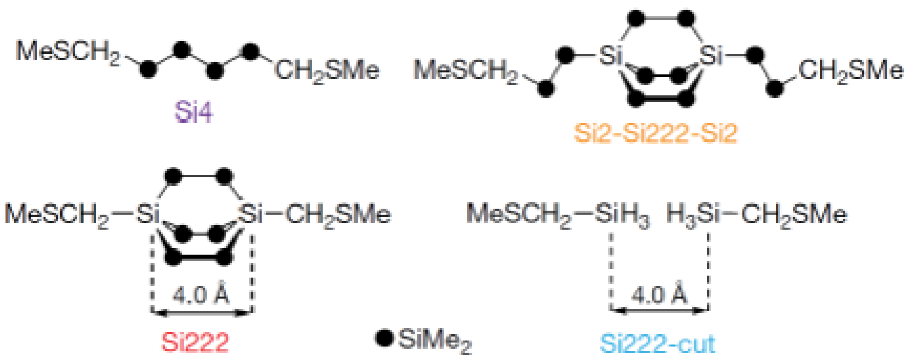


Papadopoulos *et al*. PRB **74**(2006)193306

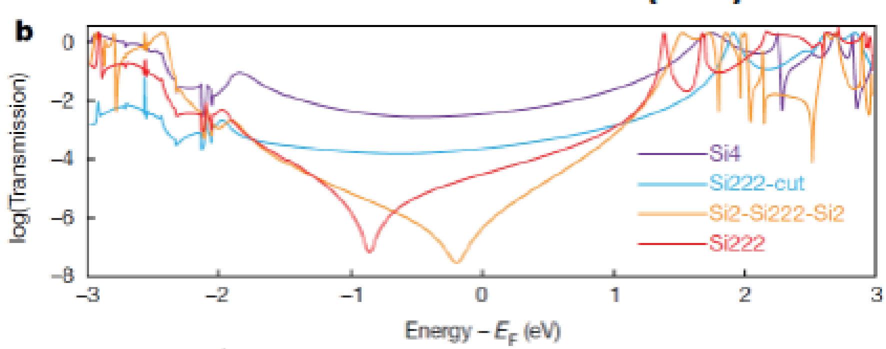
Fano Resonance

Singe Molecular QR

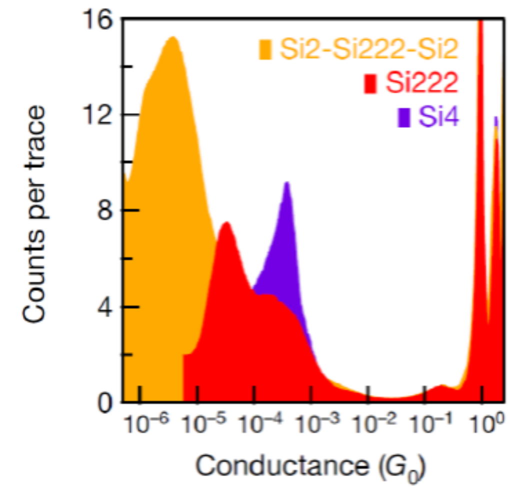
Molecular structures

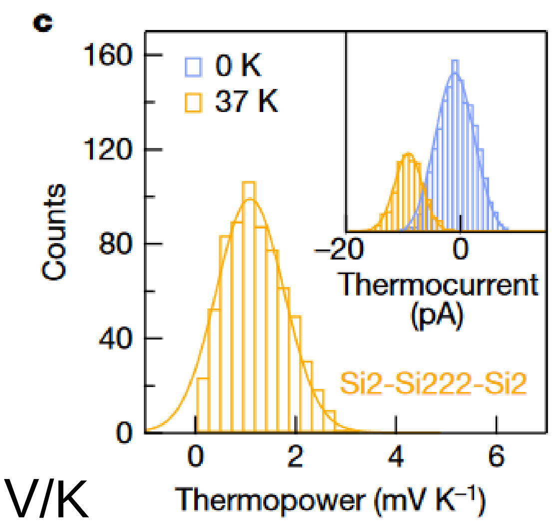


Theoretical transmission function (DFT)



Conductance histogram measured using STM BJ





S = 970 μV/K

M. H. Garner *et al*. Nature **558** (2018) 415

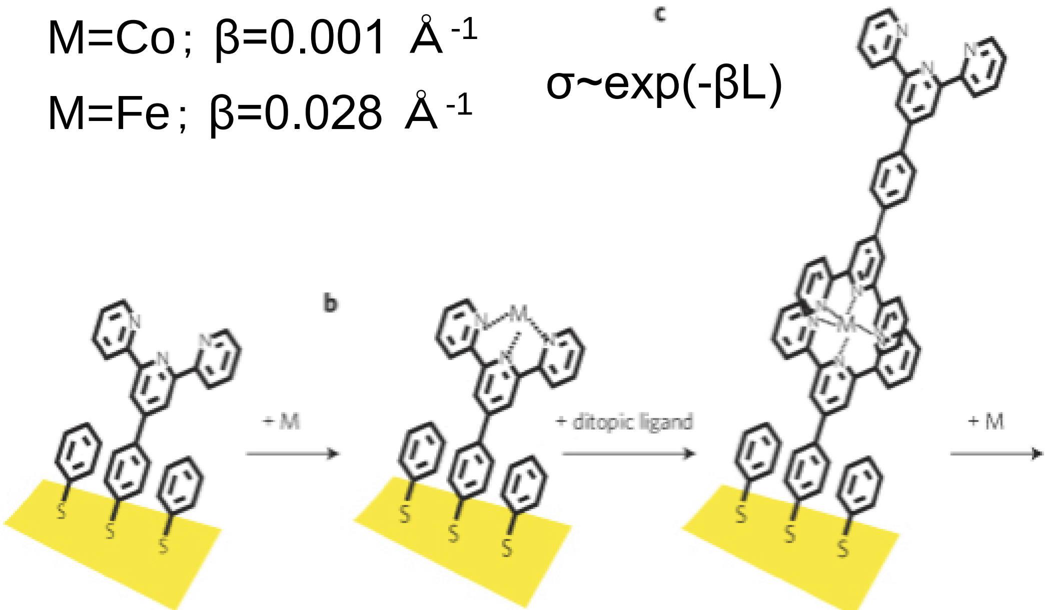
Long range transport wire

Bis(terpyridine)M

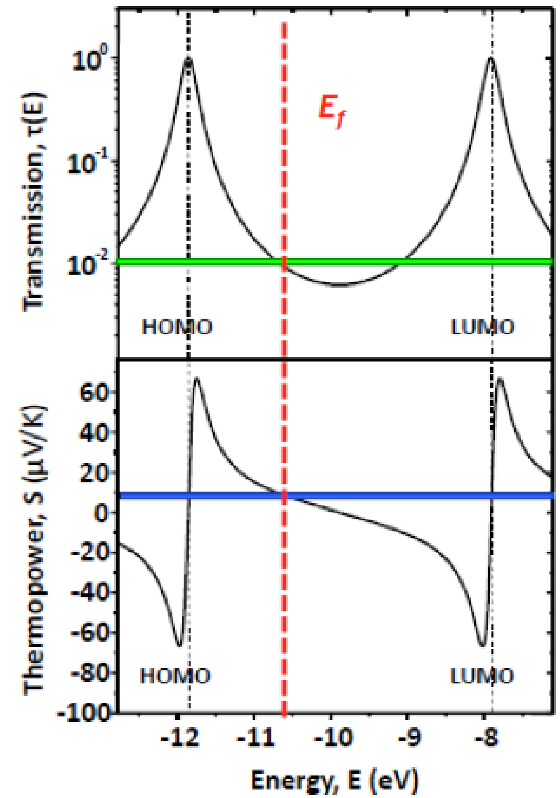
M=Co; β=0.001 Å^{-1}

M=Fe; β=0.028 Å^{-1}

σ~exp(-βL)



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



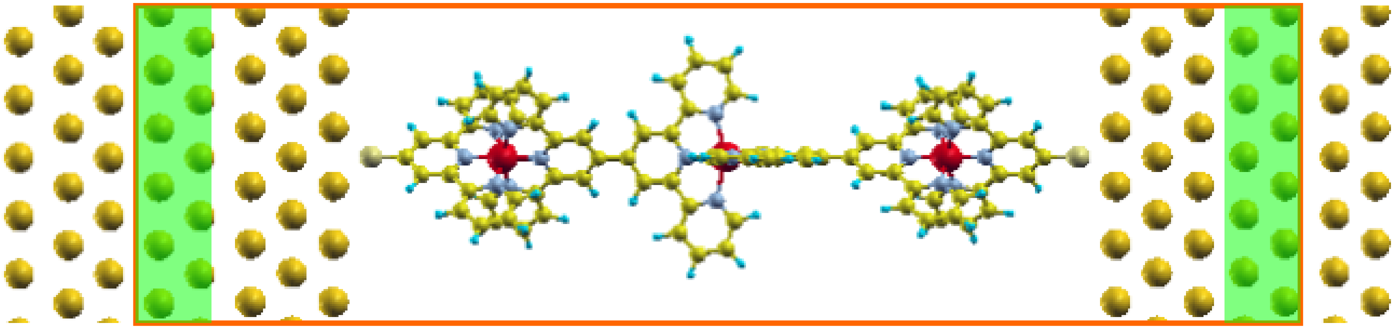
Reddy *et al*, Science **315**(2007) 1568

Resonant tunneling? → MO level is close to the Fermi level

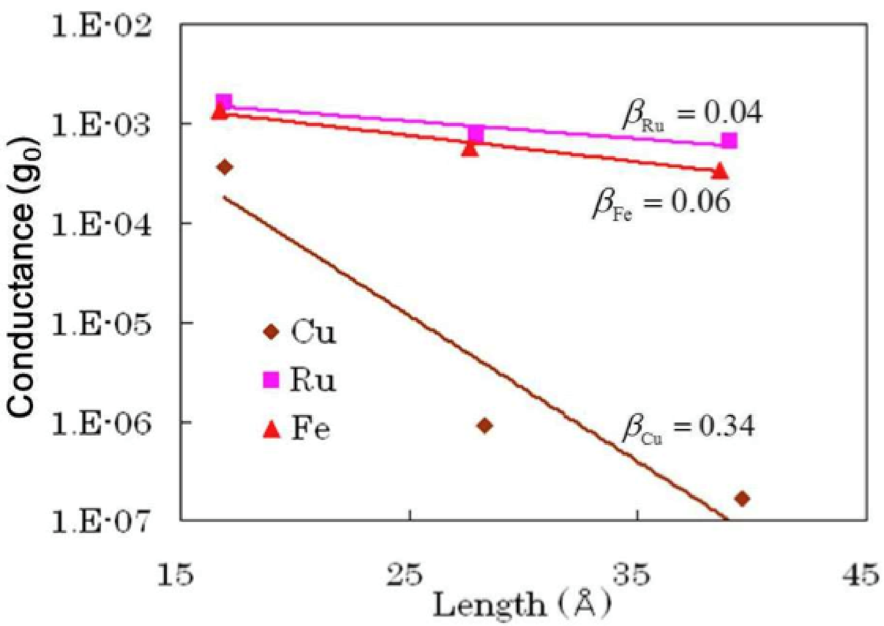
High S is expected

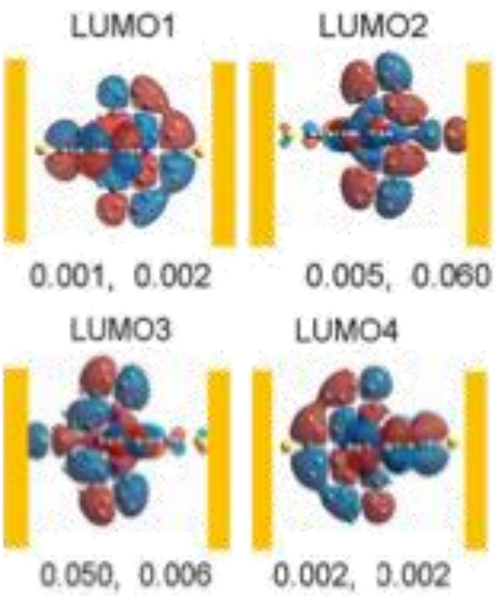
Transport calculations

HiRUNE module (NEGF-DFT), PBE functional



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

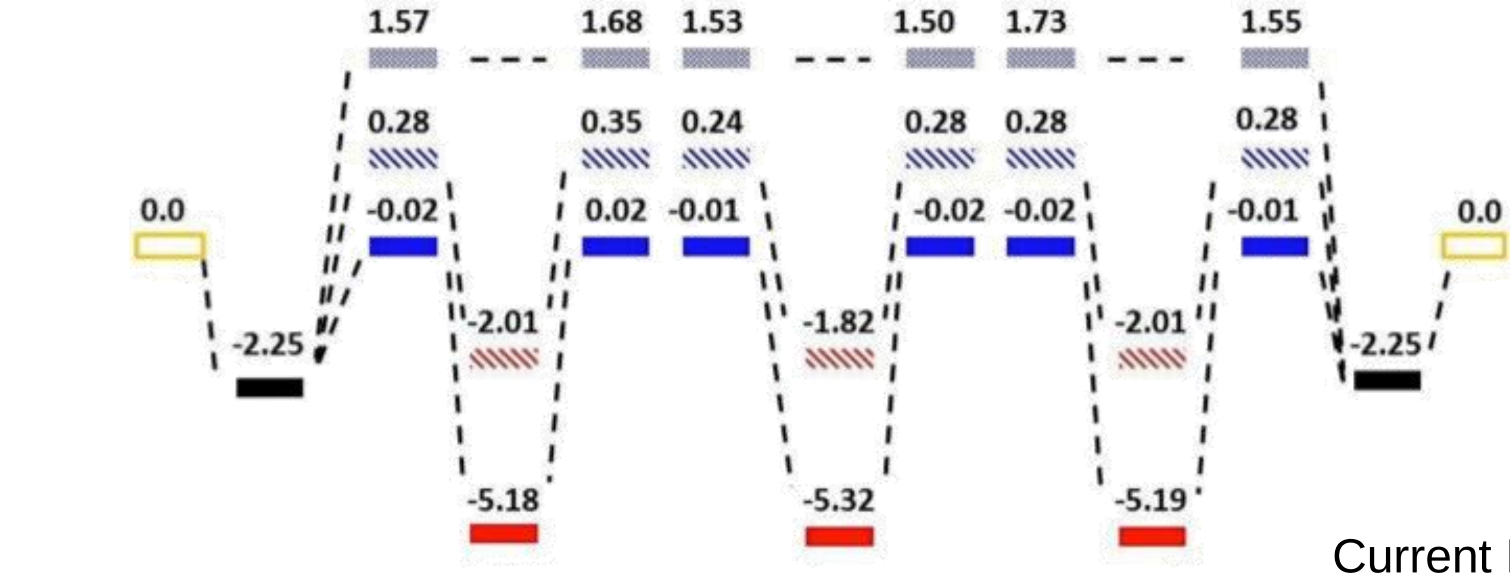




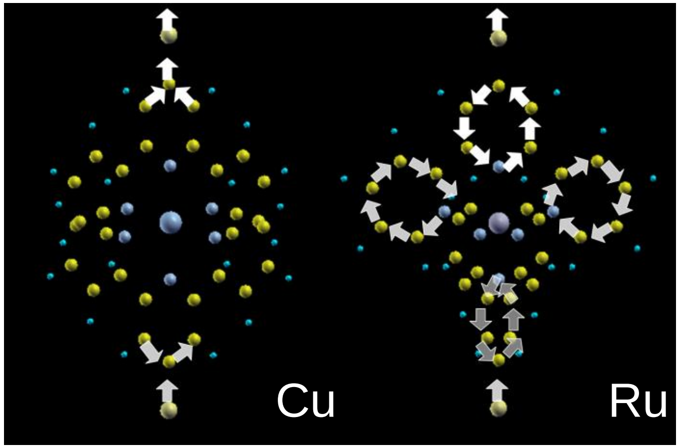
Υ_R, Υ_L

Nakamura, Ohto, *et al*. JACS **135**(2013)16545

Energy level diagram



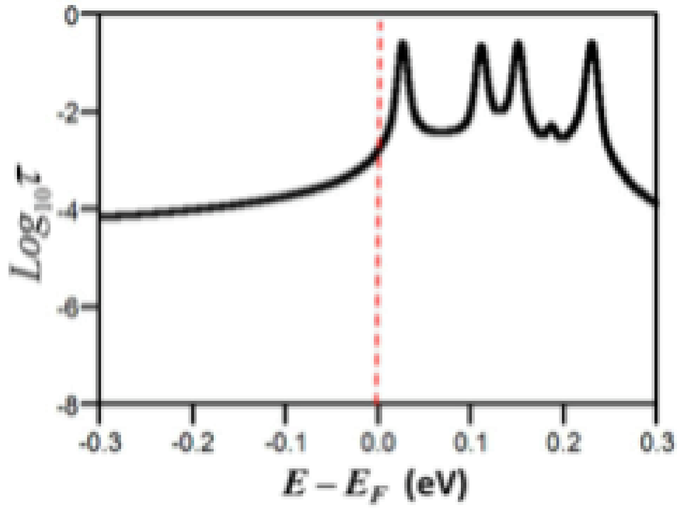
Current Profile

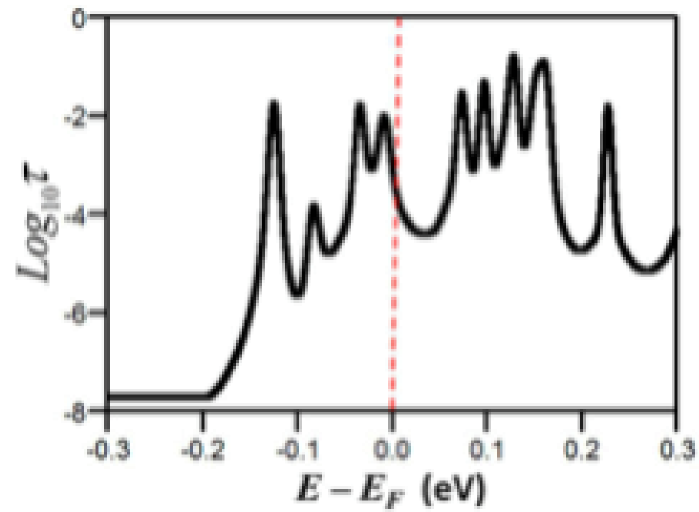


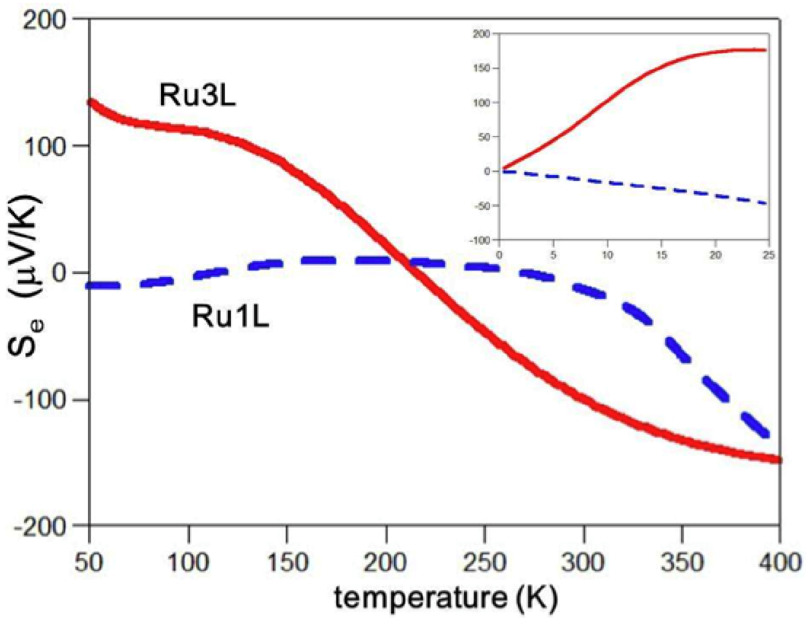
Resonant tunneling through MOs

Nakamura, Ohto, *et al*. JACS **135**(2013)16545

G and S





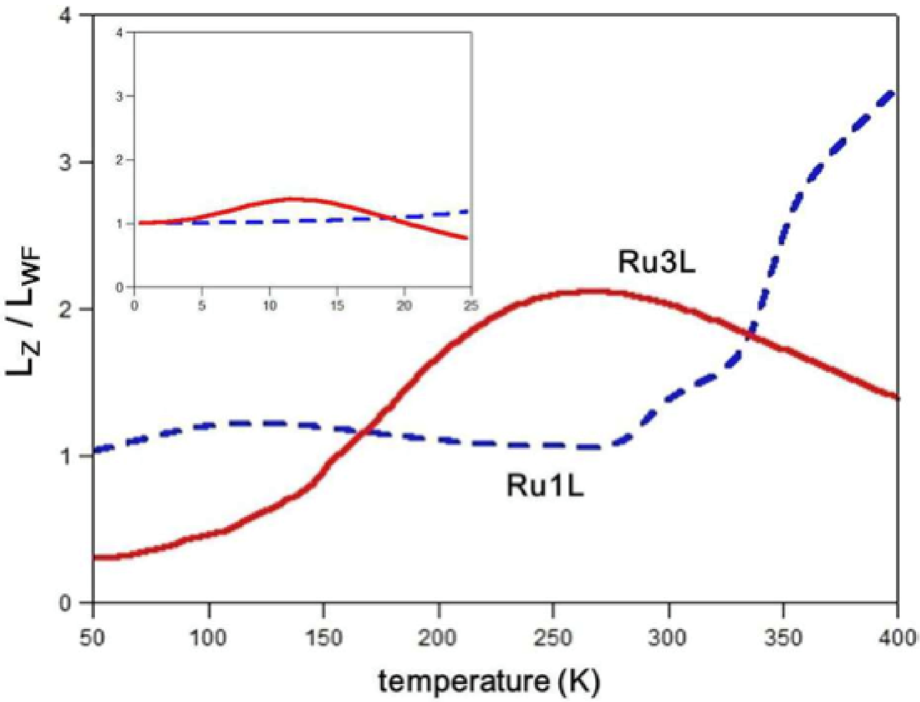


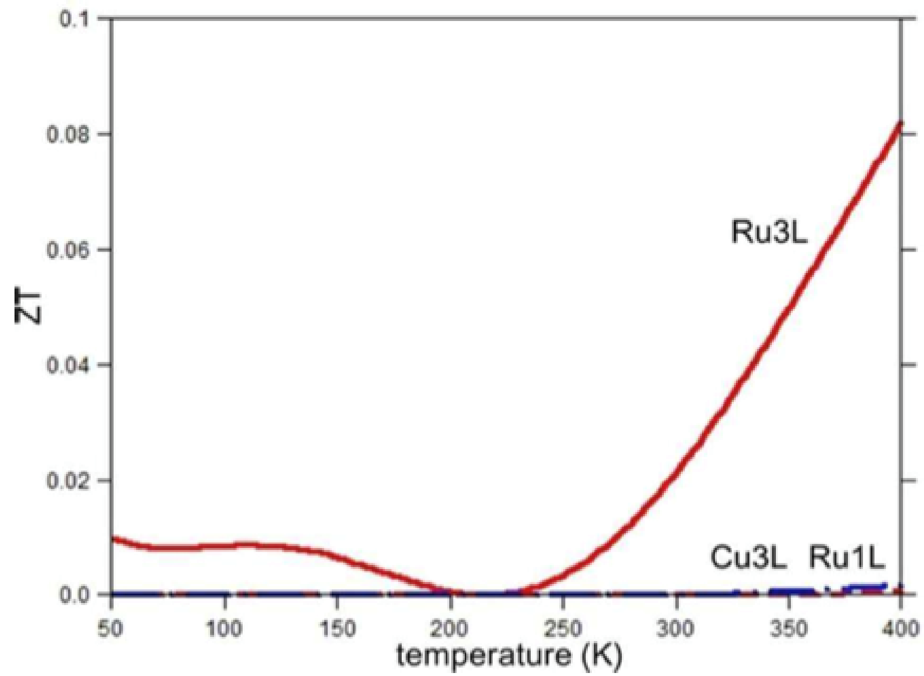
- Many narrow states
- Sign change of S

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

Nakamura, Ohto, *et al*. JACS **135**(2013)16545

Wiedemann-Franz and ZT





Wiedemann-Franz is broken

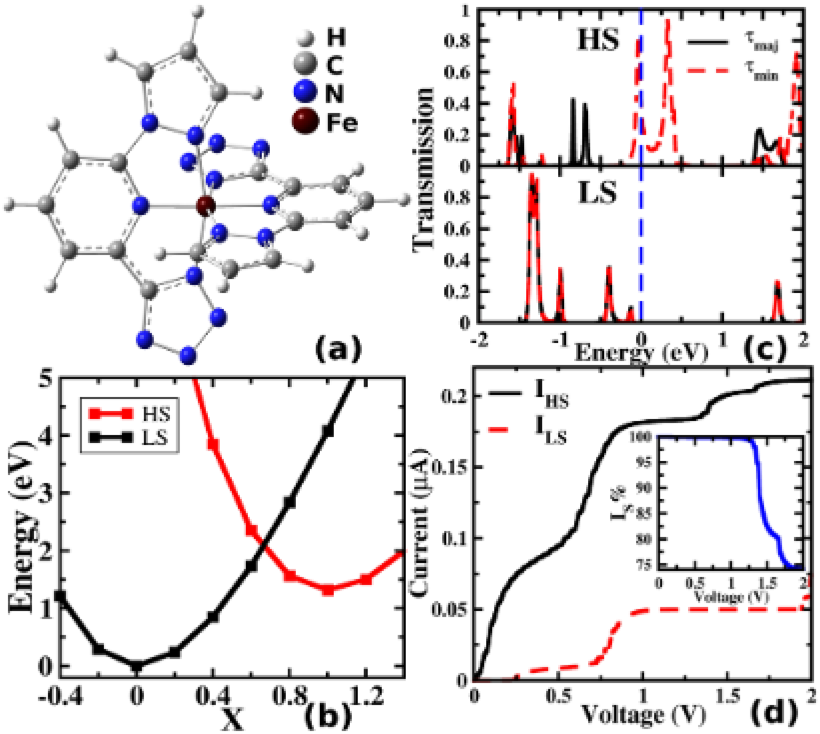
Wiedemann-Franz則

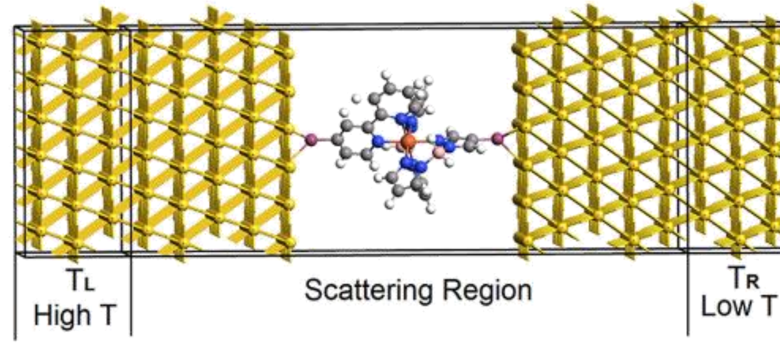
$$L_Z = \frac{k}{sT} = \text{const.} \qquad L_{WF} = \frac{p^2 k_B}{3}$$

At a temperature, ZT=0

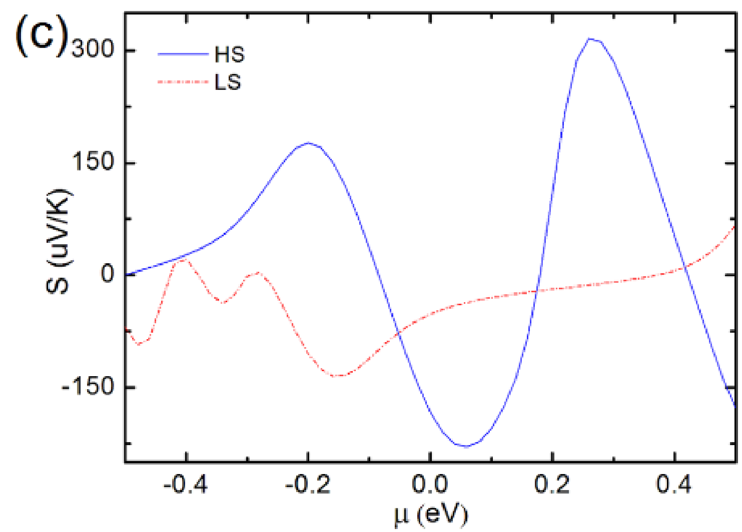
Nakamura, Ohto, *et al*. JACS **135**(2013)16545

Metal-complex-based thermoelectric devices





$Fe[(H_2Bpz_2)_2bipy]$



D. Ghosh *et al*.
Appl. Phys. Lett. **106** (2015) 193105

N. Liu *et al*.
J. Phys. D: Appl. Phys. **51** (2018) 145102

4. Organic Magnetoresistance

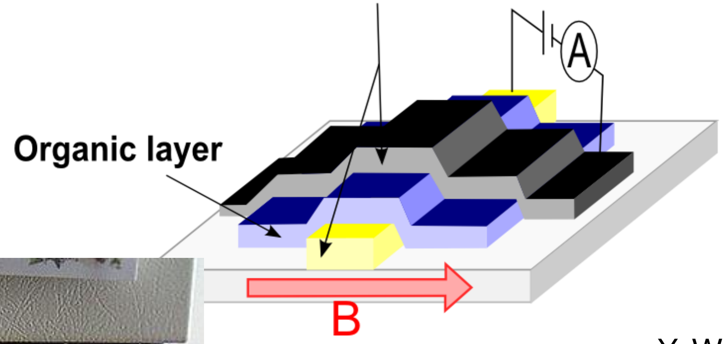
Organic magnetoresistance (OMAR)

Usual MR

MAGNETIC

GMR, TMR
Spinvalve.

Electrodes



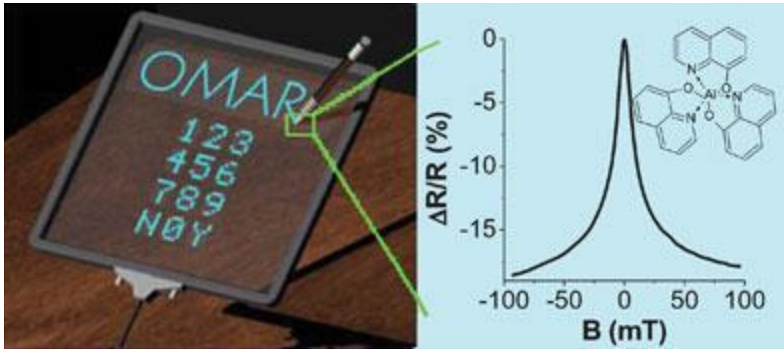
OMAR

NON MAGNETIC

Room temperature.
Low magnetic field (mT)

Up to several 1000%
Y. Wang et al. Phys. Rev. X 6, 011011 (2016)

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

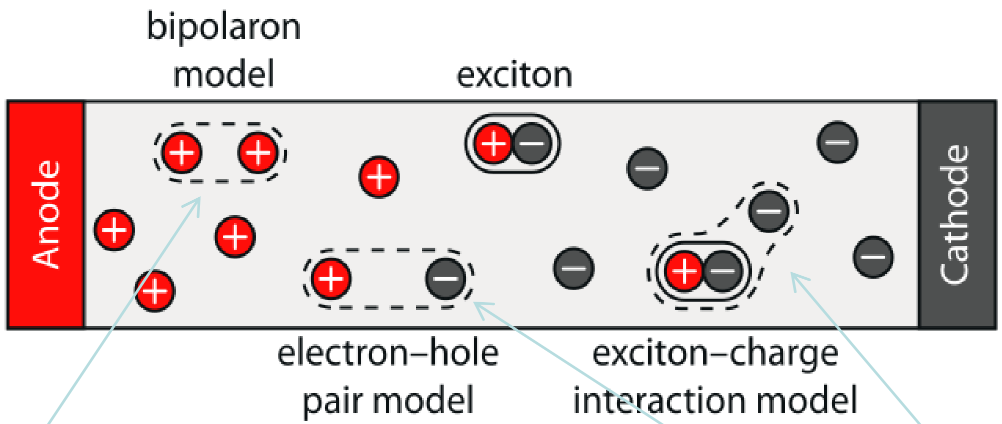


Nguyen et al. *J. Mater. Chem.* **17** (2007) 1995

MR: magnetoresistance

Theory: Single vs. Double carriers

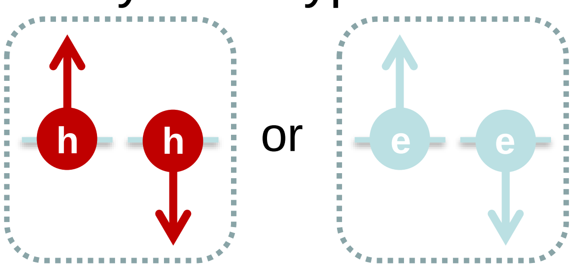
The magnetic field modifies
the ratio between SINGLET and TRIPLET



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

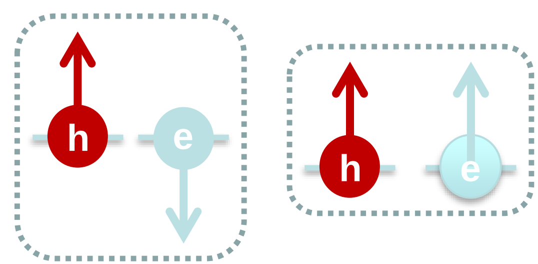
Single carriers

Only ONE type of carrier



Double carriers

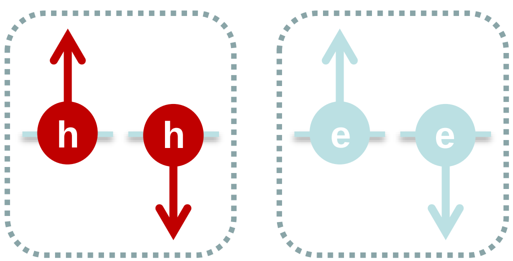
BOTH hole and electron are require



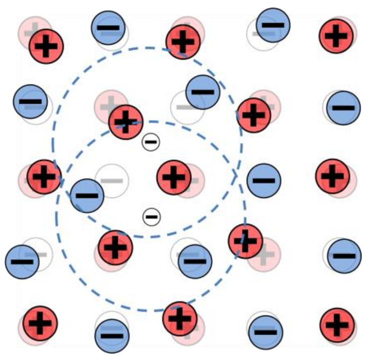
Theory: Single vs. Double carriers

The magnetic field modifies
the ratio between SINGLET and TRIPLET

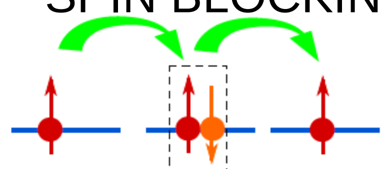
Single carriers



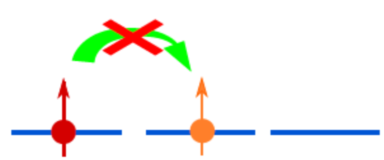
BIPOLARON



SPIN BLOCKING

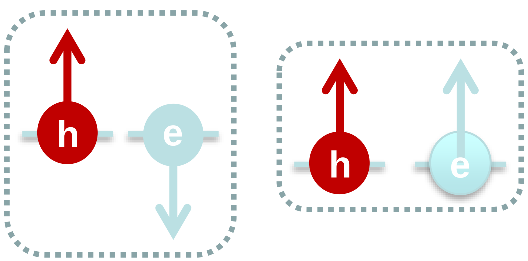


Singlet bipolaron allowed



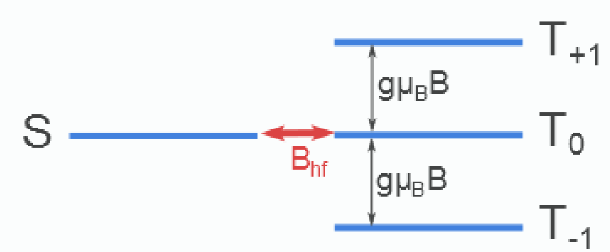
Triplet bipolaron forbidden

Double carriers



Singlet: Recombination/Dissociation

Triplet: Reaction with charge

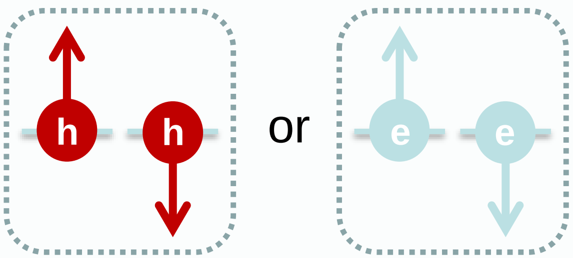


Modified **singlet to triplet ratio**

Theory: Single vs. Double carriers

Single carriers

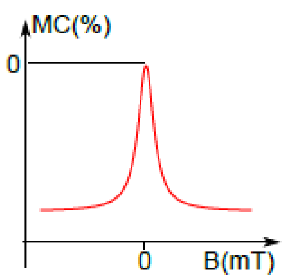
Bipolarons



***B* decreases the number of bipolarons**

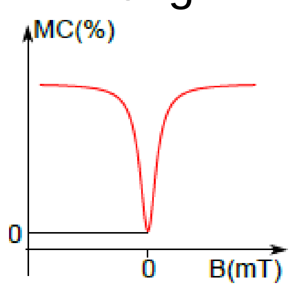
*Bipolaron **lifetime:***

short



-MC

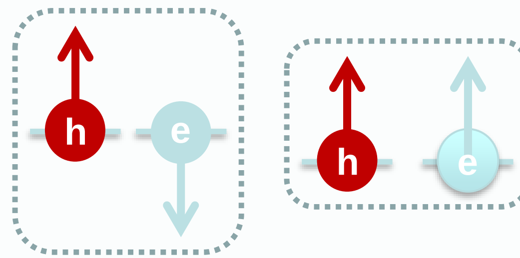
long



+MC

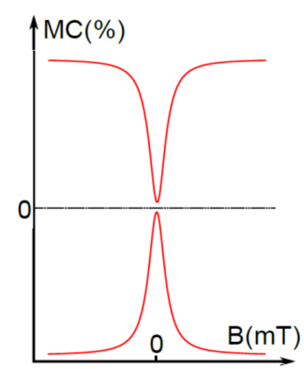
Double carriers

Excitons and e/h pairs



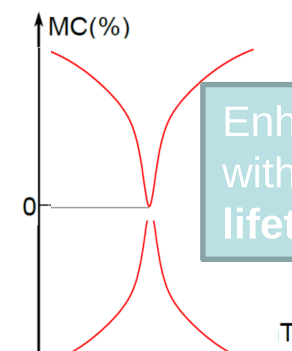
***B* changes the singlet/triplet ratio**

Singlet:
recombination



+MC or -MC

Triplet:
Reaction with charge

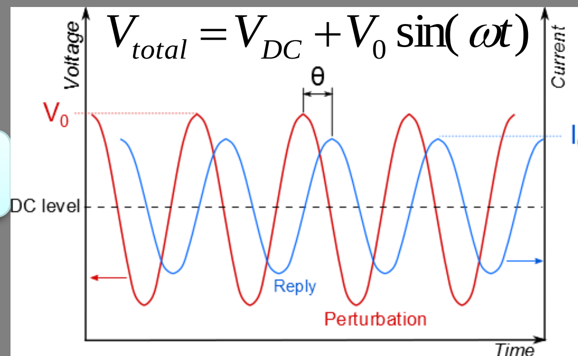


Enhanced with long **lifetime**

+MC or –MC
with HFE

Impedance spectroscopy

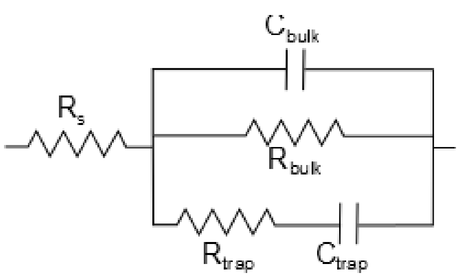
Measurement



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

Equivalent circuit

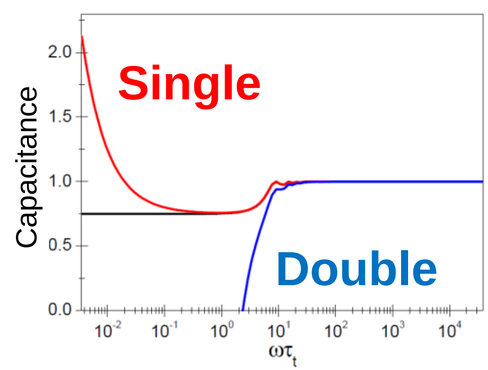
Fitting of the data



Nyquist diagram, Phase.

Give information on electronic processes

Capacitance vs frequency



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

Sign : type of injection

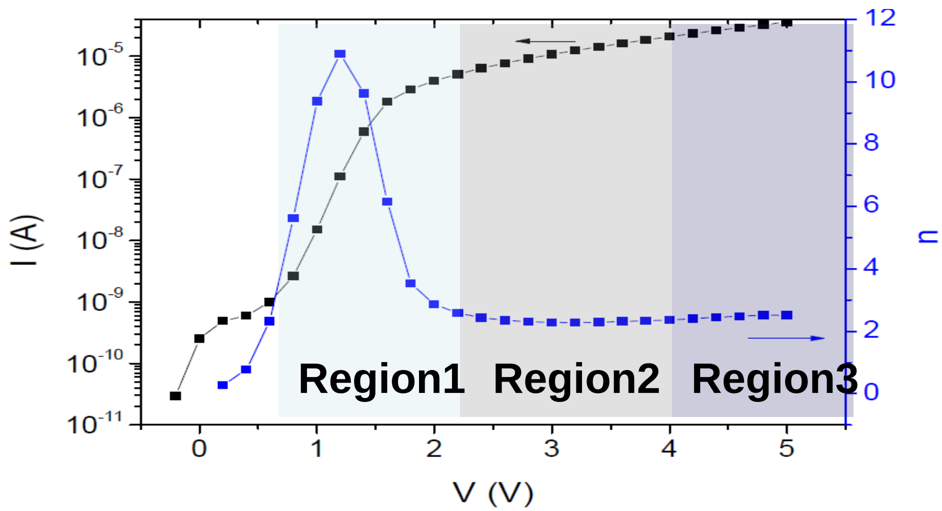
Value: traps characterization

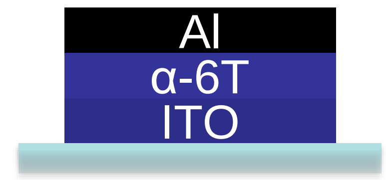
OMAR results

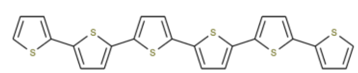
I-V characteristics:

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

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



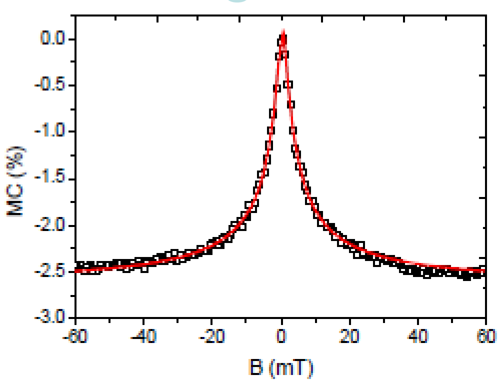




α-6T

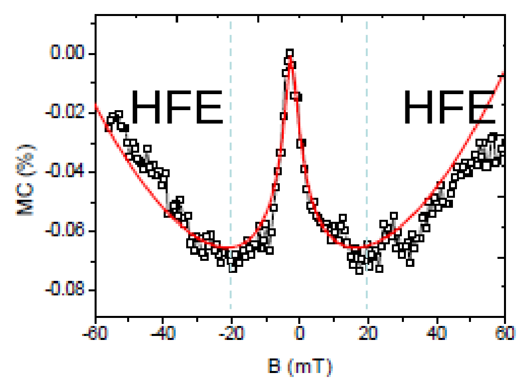
OMAR results:

Region 1



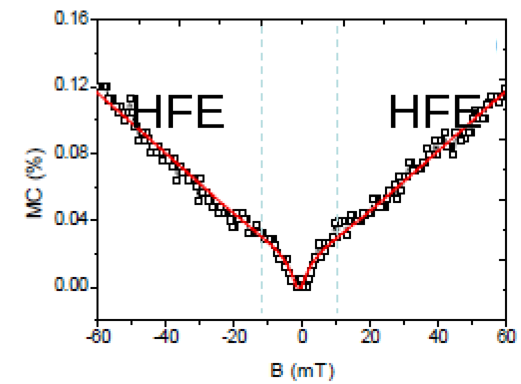
-MC

Region 2



–MC with HFE

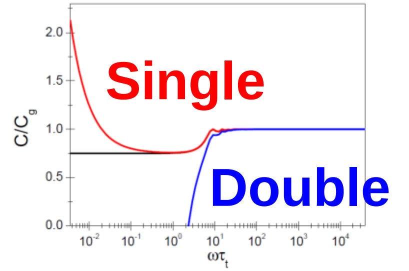
Region 3



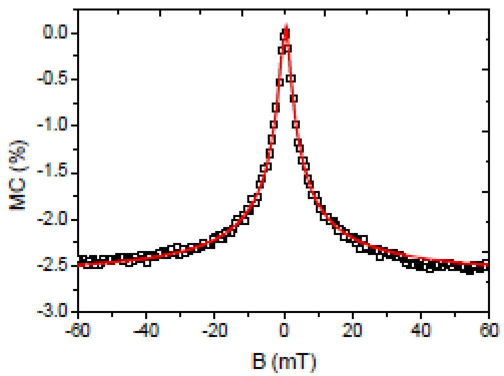
+MC with HFE

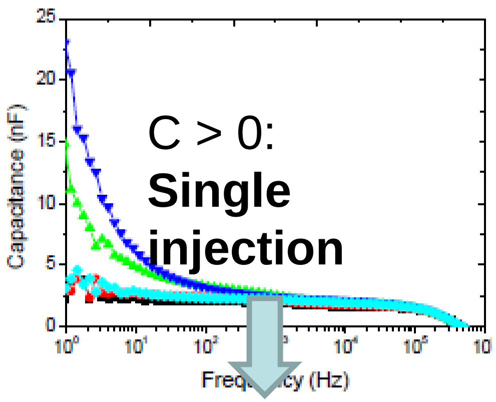
How to explain the various OMAR shapes?

Capacitance results



Region 1

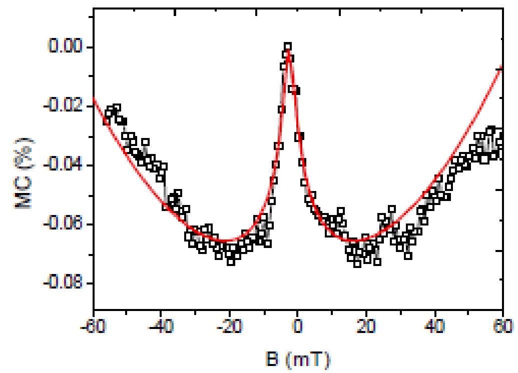


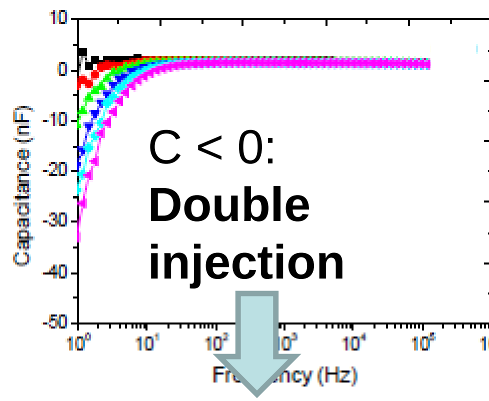


Bipolaron OMAR

Negative OMAR

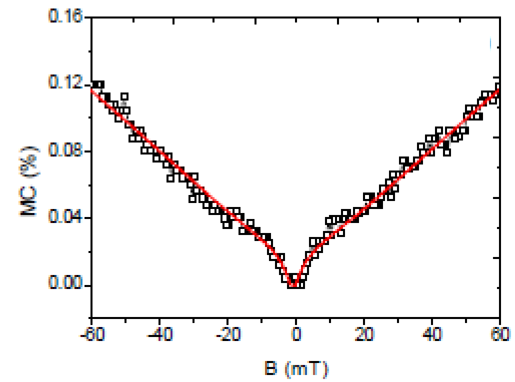
Region 2

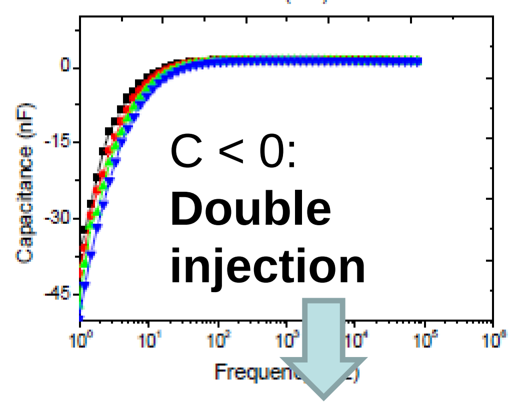




Transition: double + single carriers OMAR mix

Region 3

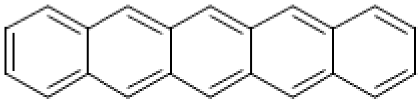




Double carriers OMAR

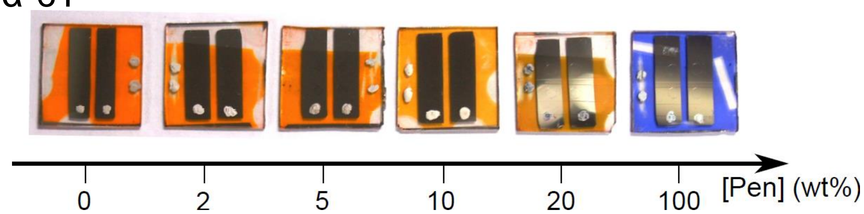
Positive OMAR

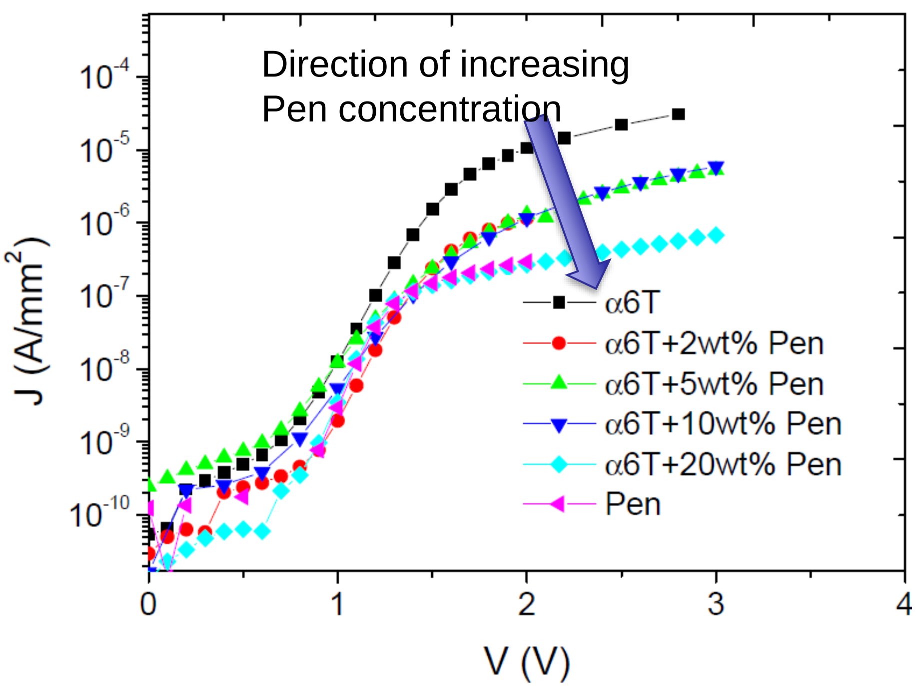
Pentacene (Pen)

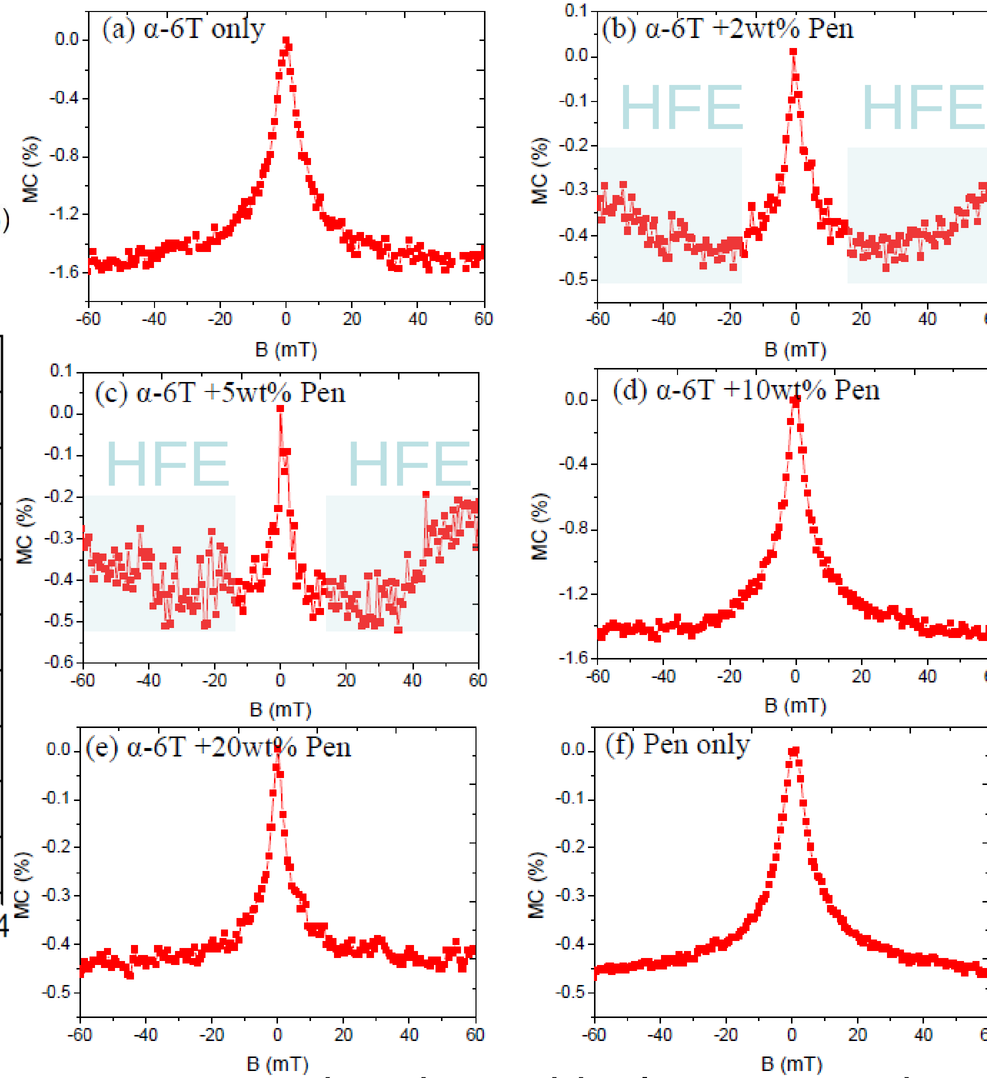


Pentacene doping

α-6T



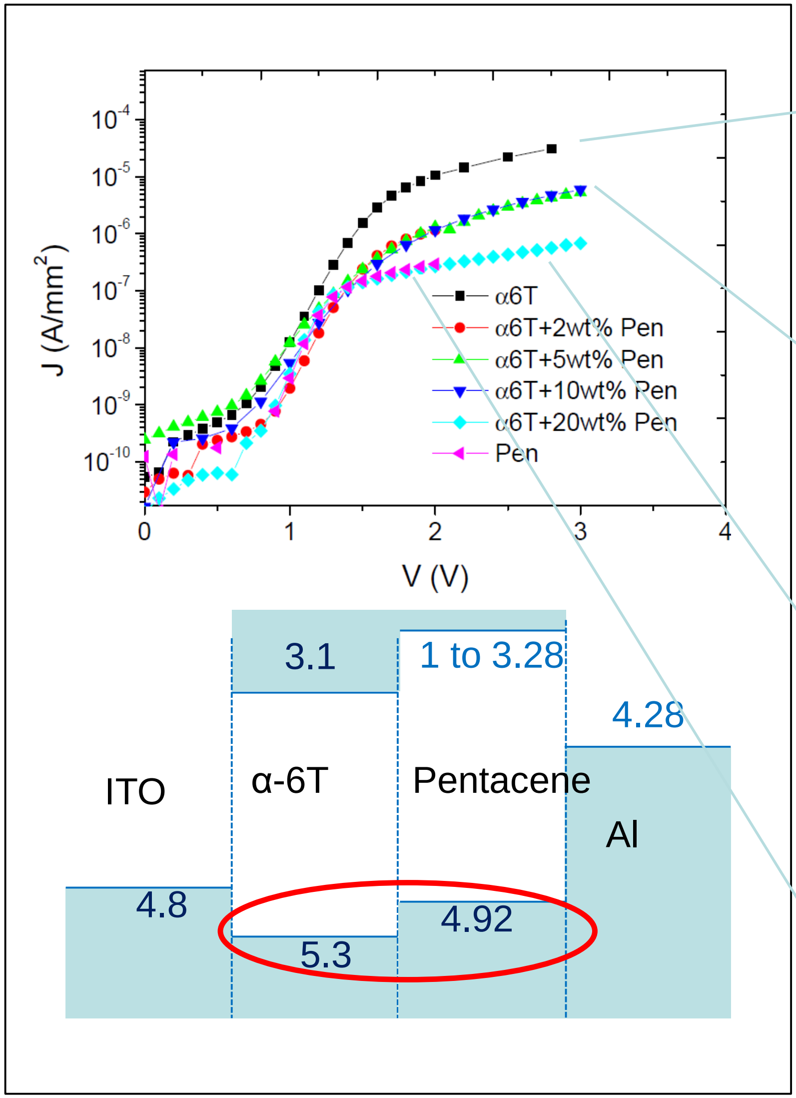


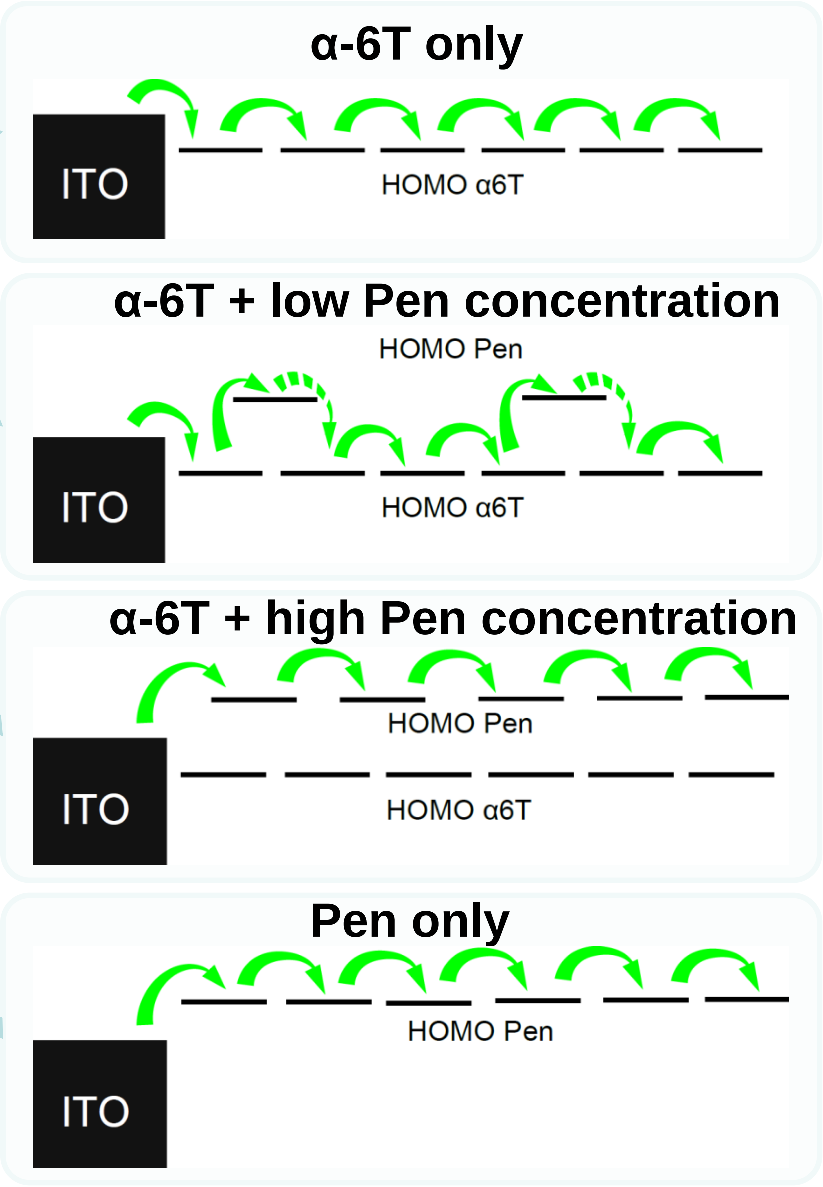


The current decreases with Pen.
At low Pen concentration only, HFE appears.

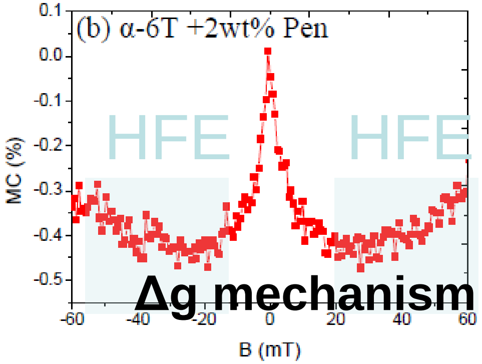
At 1.5 V (Region 1, bipolaron OMAR)

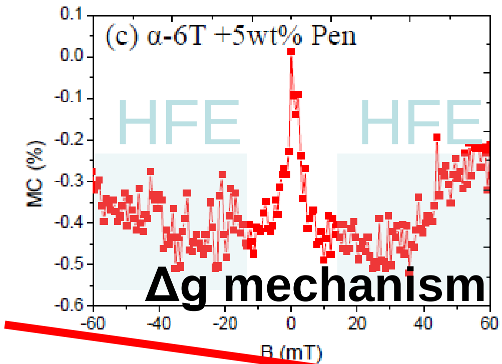
I-V chracteristics

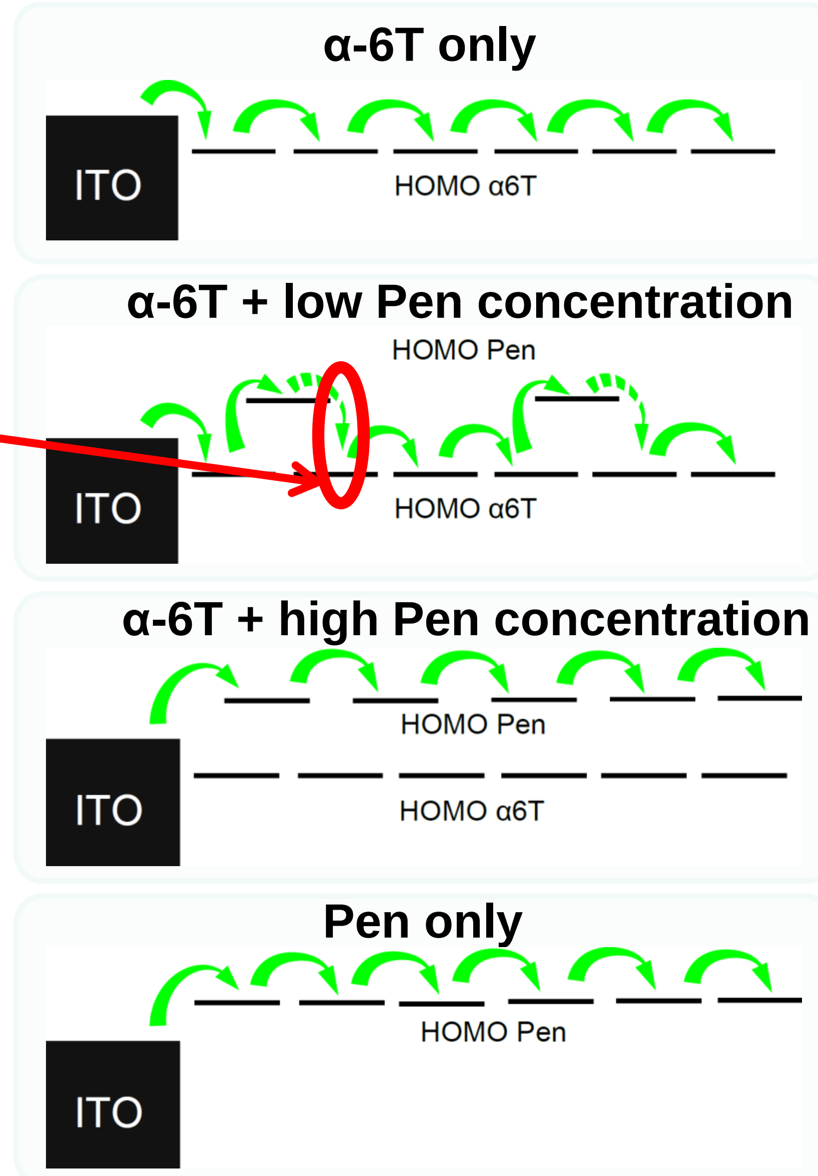




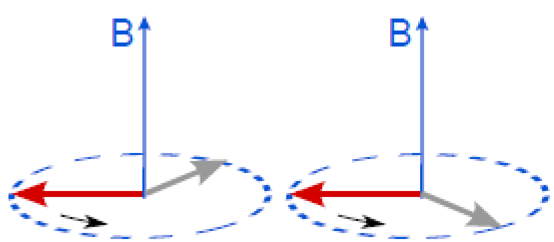
OMAR results







Different environment



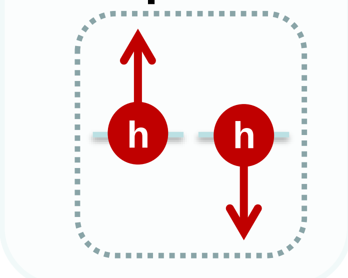
Δg ≠ 0

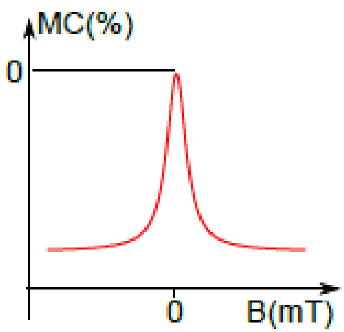
Spin precession out of phase. Cause an effect opposite to the effect at low field.

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

Summary

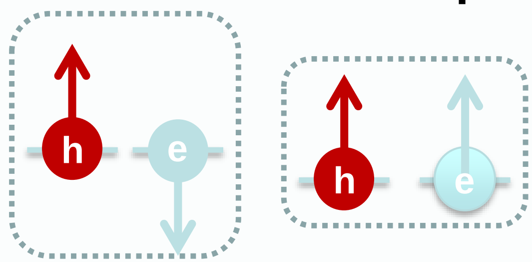
Single carriers

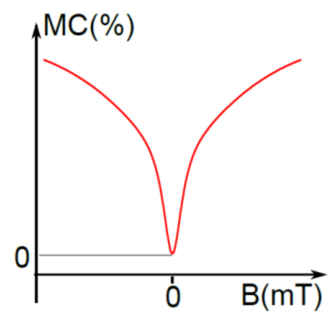




-MC

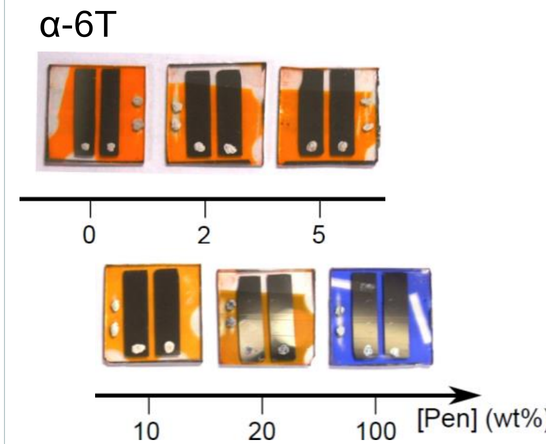
Double carriers

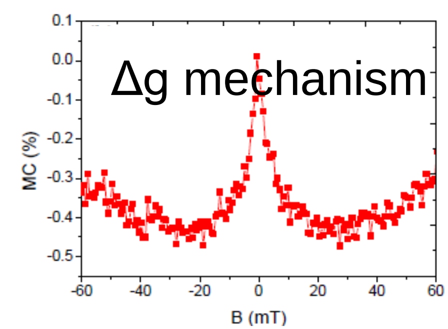




+MC with HFE

Disorder



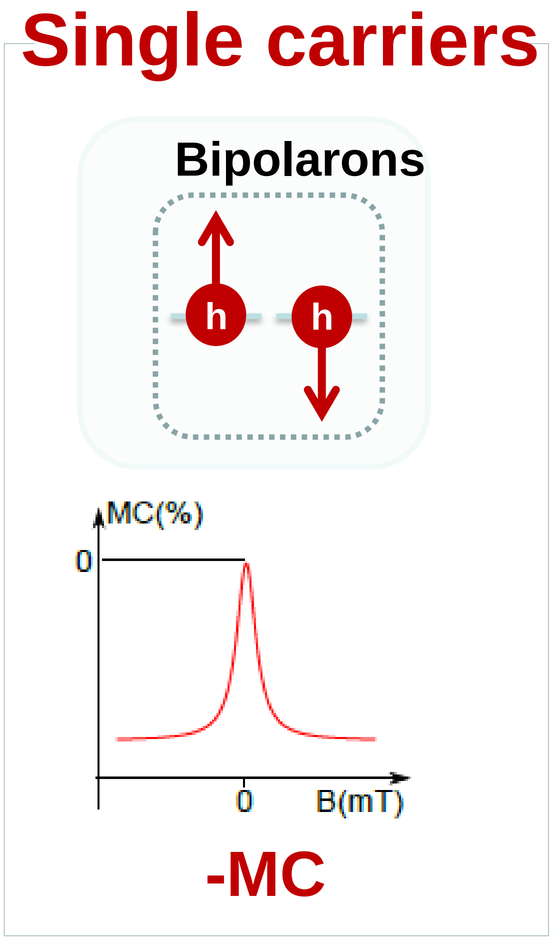


The mechanism is identified.

Magnitude and shape of OMAR is tuned.

Song-Toan Pham, Marine Fayolle, Tatsuhiko Ohto, Hirokazu Tada
Appl. Phys. Lett. **111**, 203303 (2017)

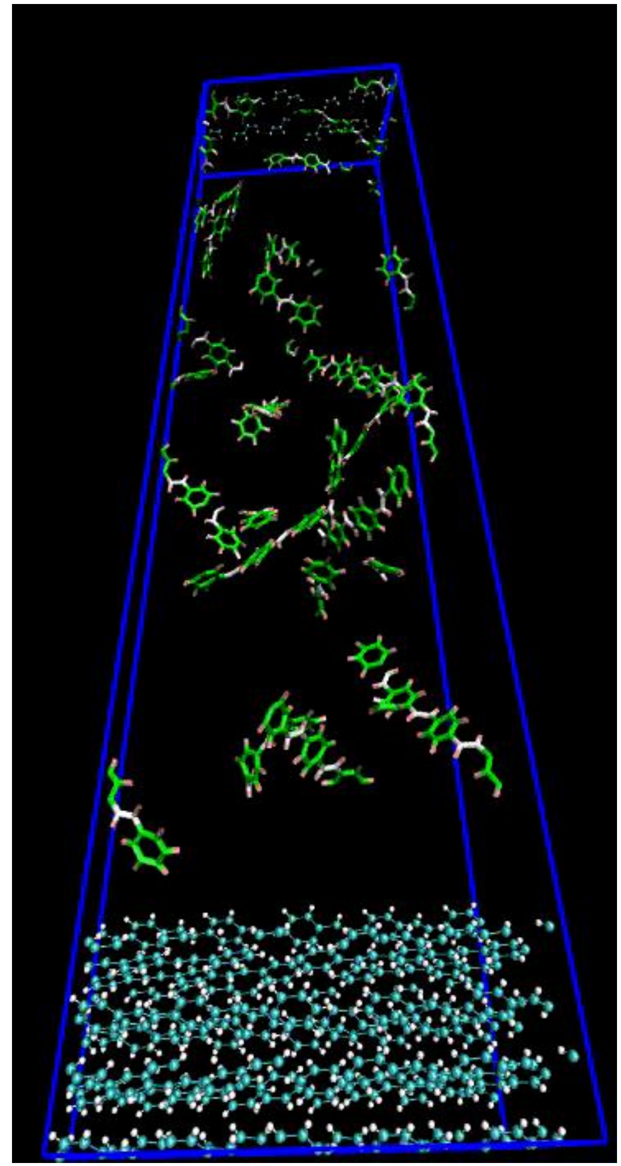
Perspective



▪Bipolaron is a deep mid-gap state

▪How much defective are organic semiconductors?

Realistic landscape
↓
Carrier dynamics simulation



W. Nie, et al, ***Adv. Sci.*, 2,** 1500024 (2015)

Summary

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

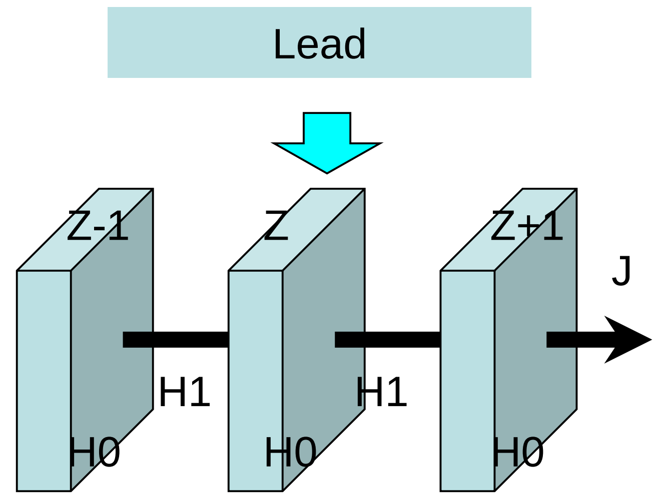
- Single Molecular Magnet
- OMAR and its mechanisms

Surface Green's Function

Recursive Method

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

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



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

$$\widetilde{t_0} = (E - H_0)^{-1} H_0 \qquad \widetilde{t_i} = (I - t_{i-1}\widetilde{t_{i-1}} - \widetilde{t_{i-1}} t_{i-1})^{-1} \widetilde{t_{i-1}^2}$$

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

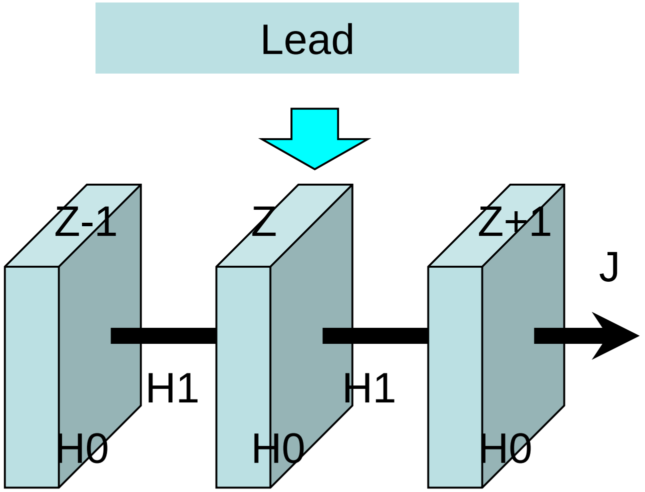
$$T = t_0 + \widetilde{t_0} t_1 + \widetilde{t_0}\widetilde{t_1} t_2 + \cdots + \widetilde{t_0} \ldots \widetilde{t_{n-1}} t_n$$

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

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

$$\sum_{l=1}^{M} \phi_{k_l} \tilde{\phi}_{k_l}^{\dagger} = \sum_{l=1}^{M} \phi_{\bar{k}_l} \tilde{\phi}_{\bar{k}_l}^{\dagger} = \mathrm{I} \qquad \tilde{\phi}_{k_l}^{\dagger} \phi_{k_h} = \tilde{\phi}_{\bar{k}_l}^{\dagger} \phi_{\bar{k}_l} = \delta_{lh}$$

Solution of H, φ…

→ Dual basis $\tilde{\varphi}$

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

Boundary condition $Z = Z_0$

$$g_L = \left[\mathrm{I} - \sum_{l,h=1}^{M} \phi_{\bar{k}_h} e^{i\bar{k}_h} \tilde{\phi}_{\bar{k}_h}^{\dagger} \phi_{k_l} e^{ik_l} \tilde{\phi}_{\bar{k}_l}^{\dagger} \right] \nu^{-1}$$

→ Semi-infinite (Surface Green's function)