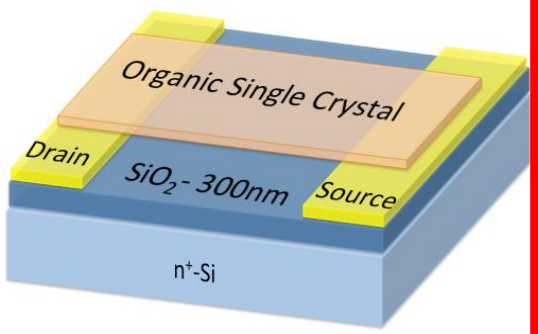
Organic Spintronics

Graduate School of Engineering Science
Tatsuhiko Ohto

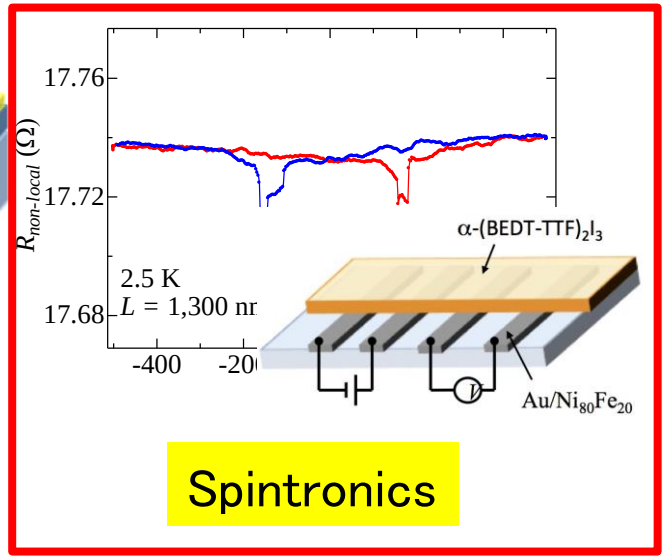
Molecular Architectonics Research Group

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

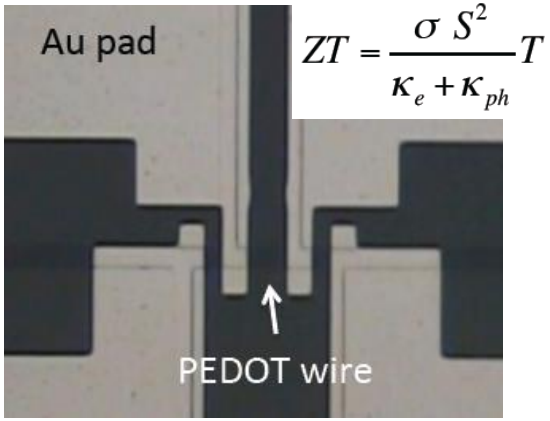
Thin Film



Electronics



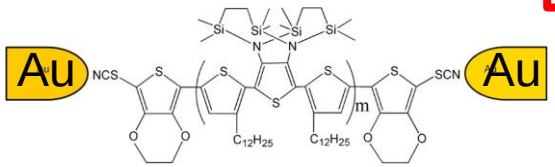
Spintronics

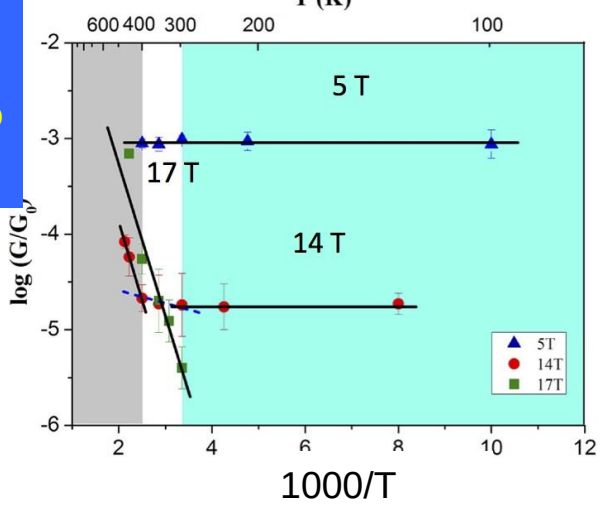


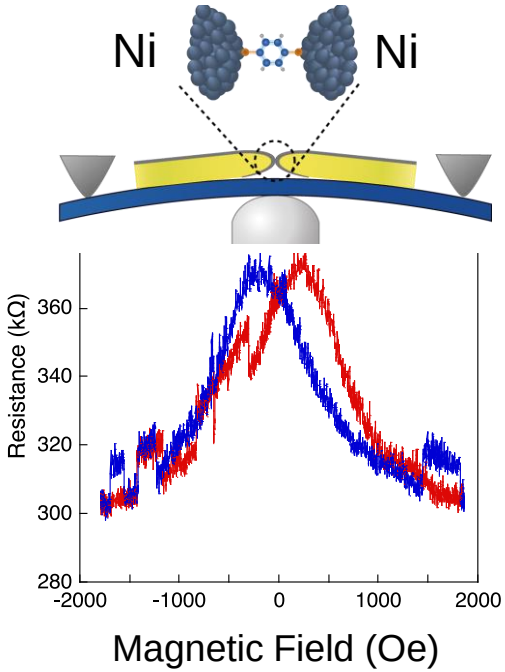
$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_{ph}} T$$

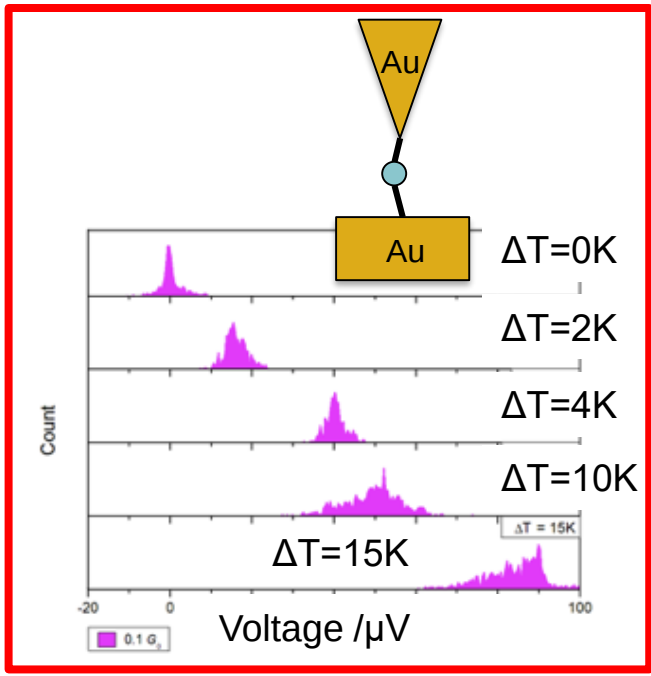
Thermoelectronics

Single Molecule

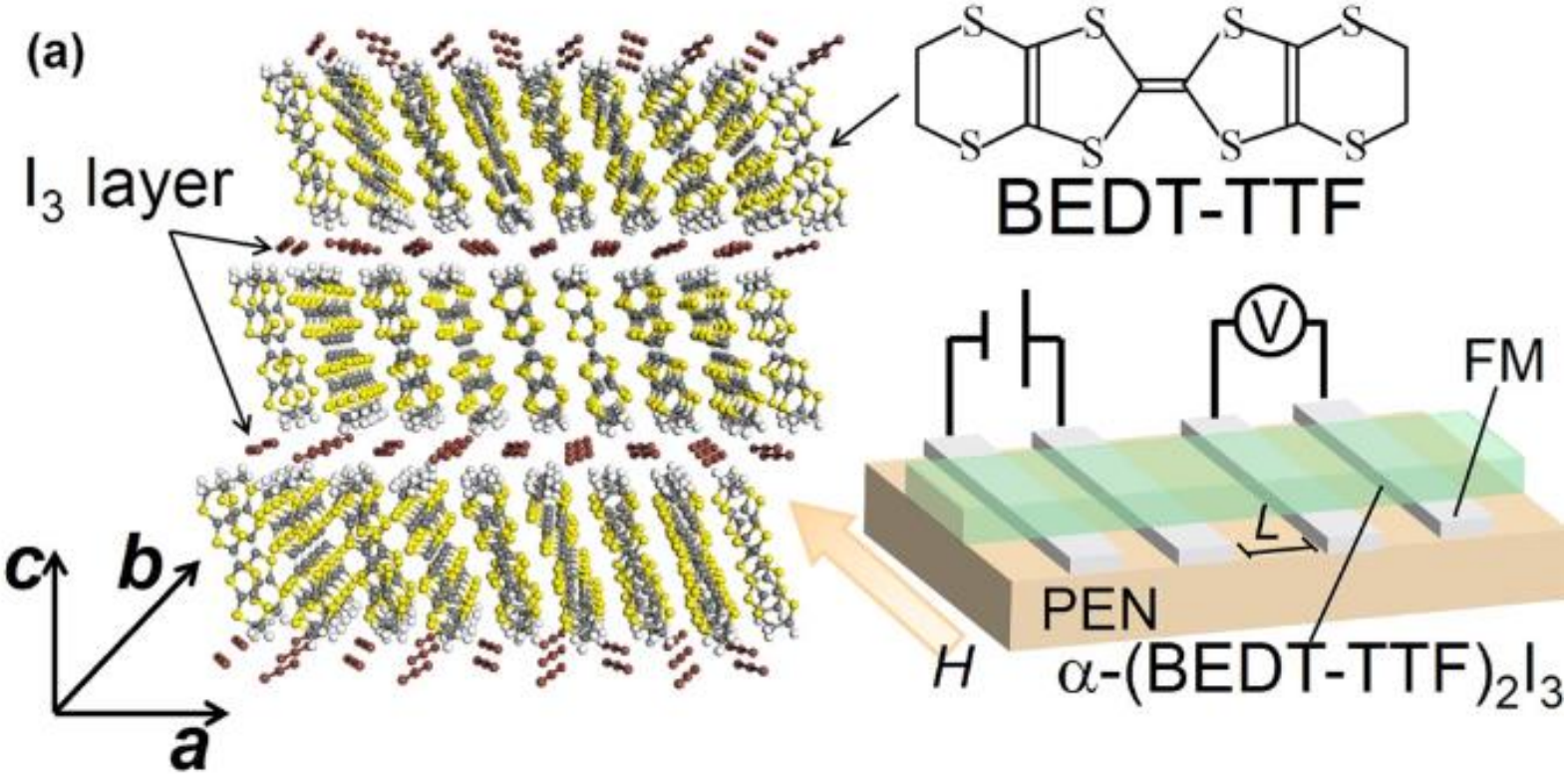








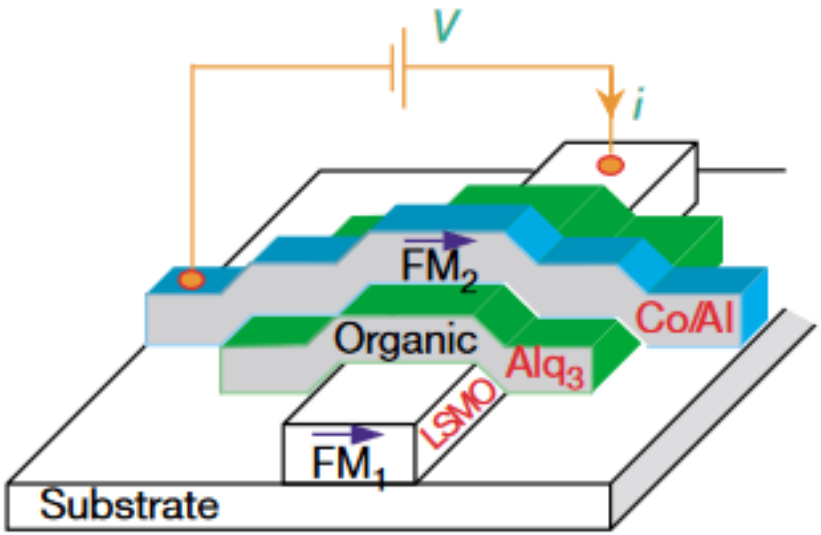
First report of lateral organic spin valve

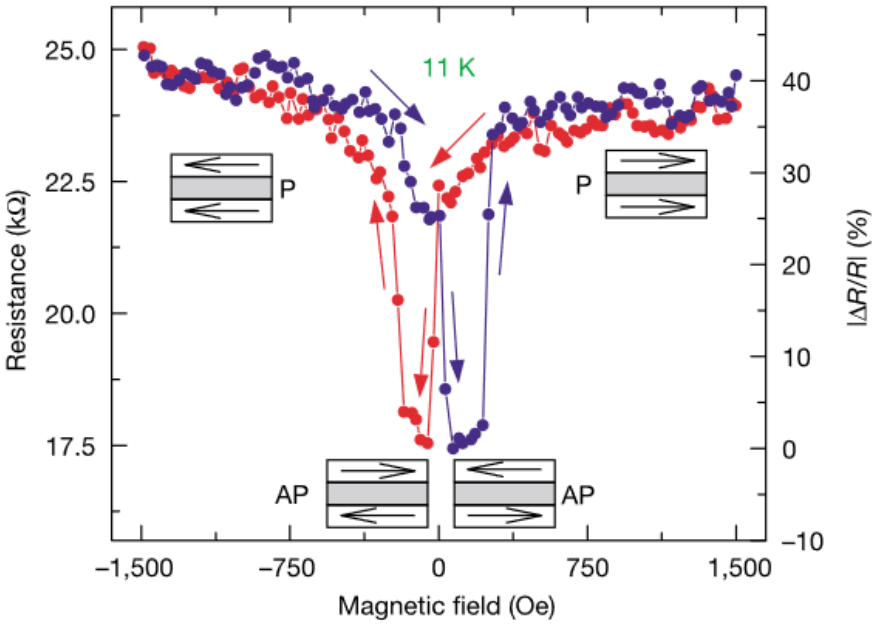


T. Kamiya *et al.* Phys. Rev. B **95** (2017) 085307

Organic Spin Valve

2004 Vardeny
Organic Spin Valve



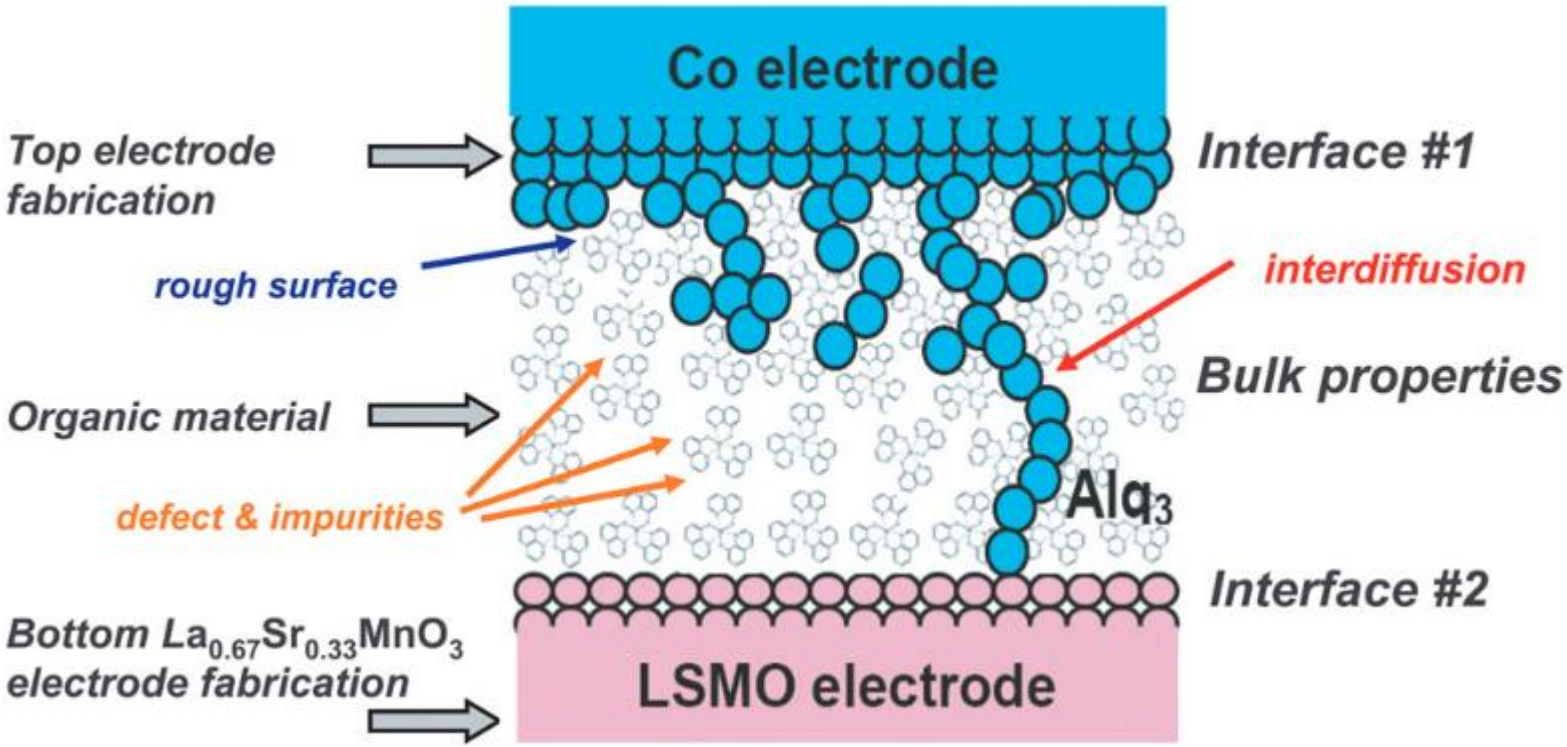


Xiong *et al.* Nature **427** (2004) 821

Weak spin-orbit interaction

Molecular design, light weight

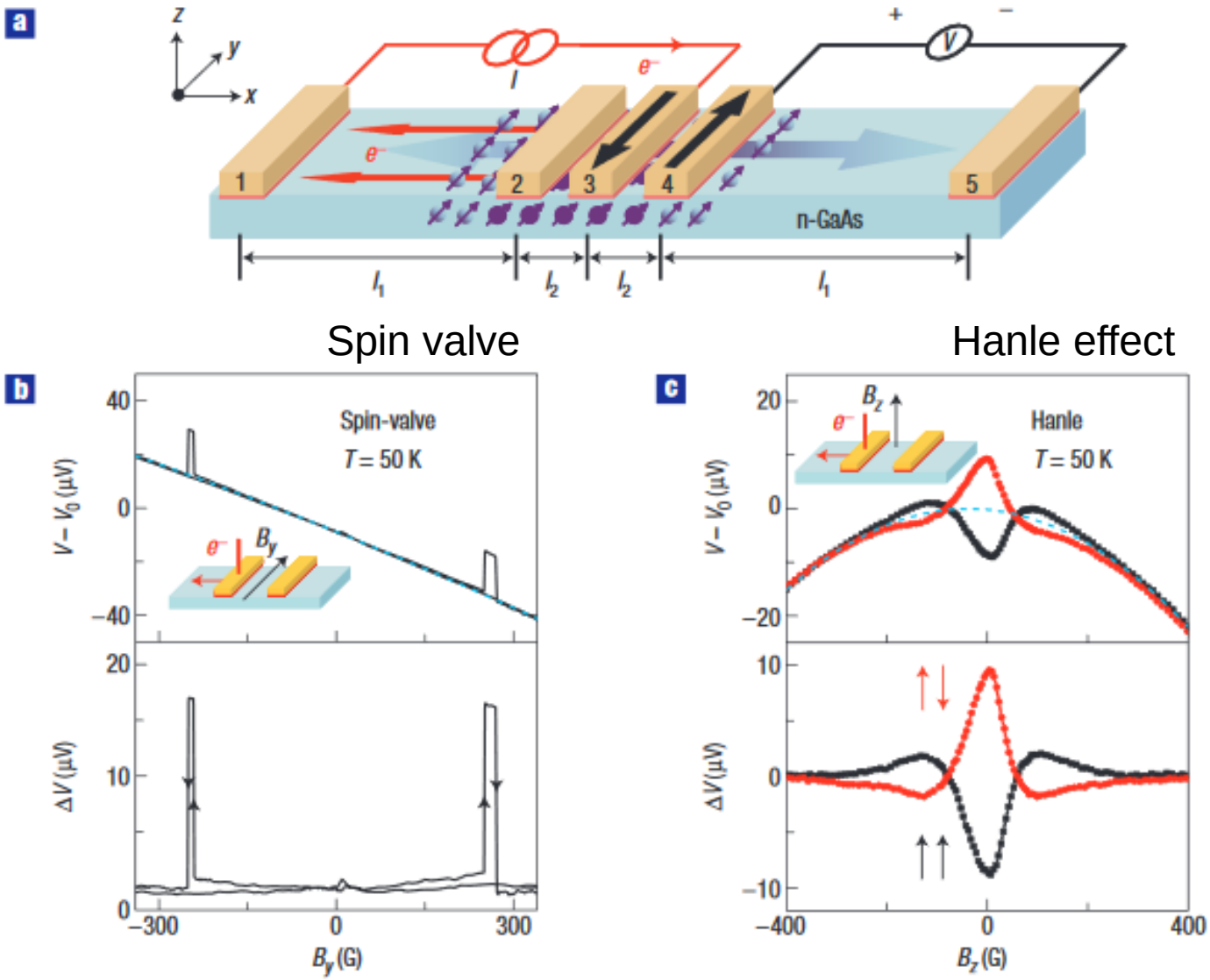
Problems of vertical devices?



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

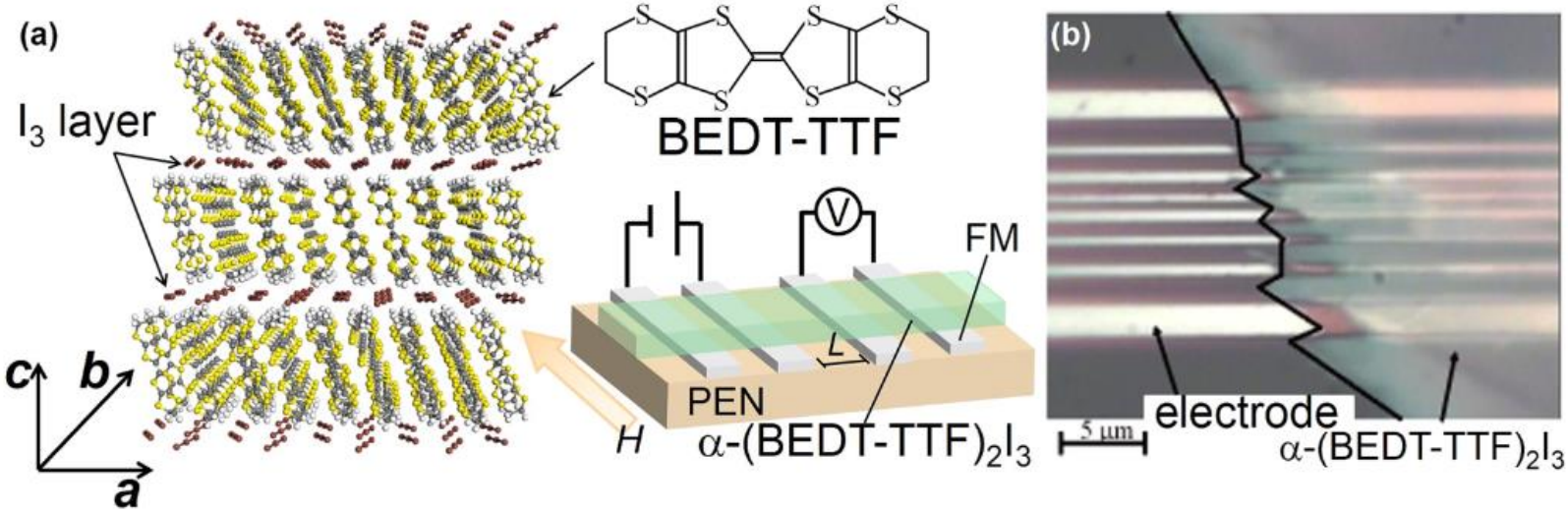
Can we inject spin into organic materials?

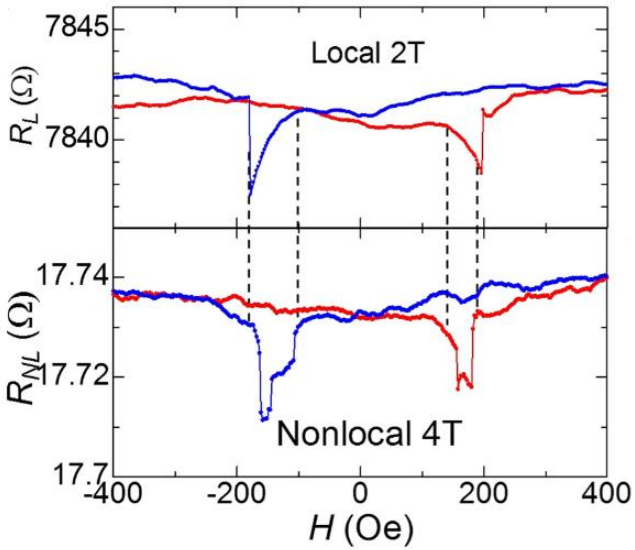
Lateral Device



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

Lateral Organic Spin Valve

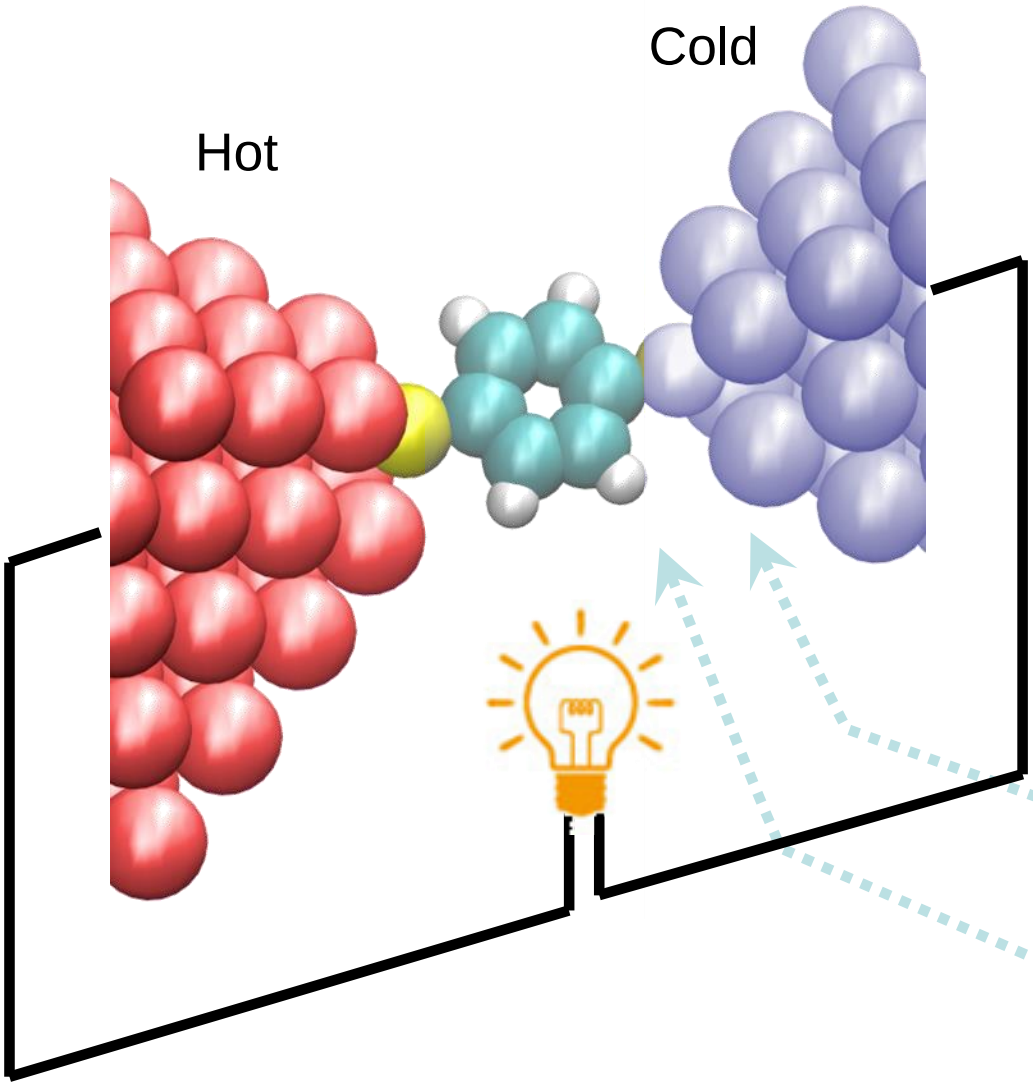




Pressured α-(BEDT-TTF)$_2$I$_3$ Crystal

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

Molecular thermoelectric device



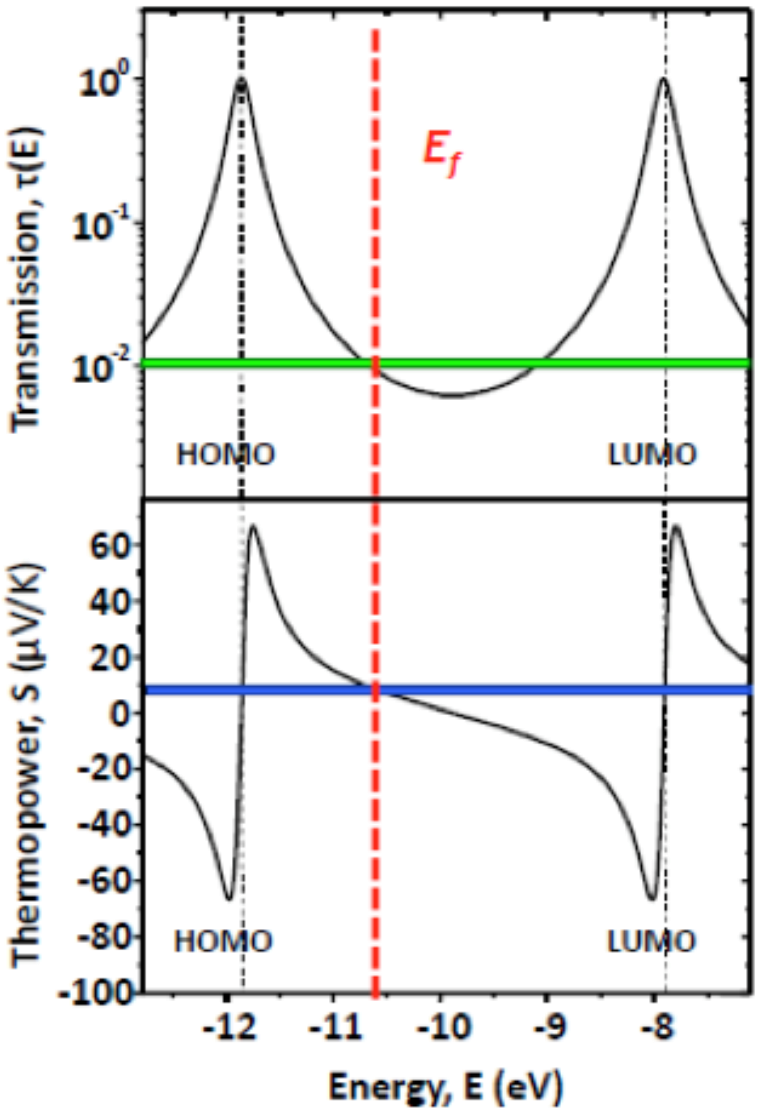
$$ZT = \frac{\sigma S^2}{k} T$$

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

Phonon scattering

Chemical modfication

Themopower (Seebeck Coefficient)



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

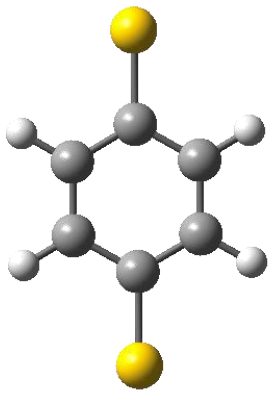
$$S = -\frac{p^2 k_B^2 T}{3e}\left(\frac{\partial \ln t(E)}{\partial E}\right)\Bigg|_{E=E_F}$$

Gradient of the contantance

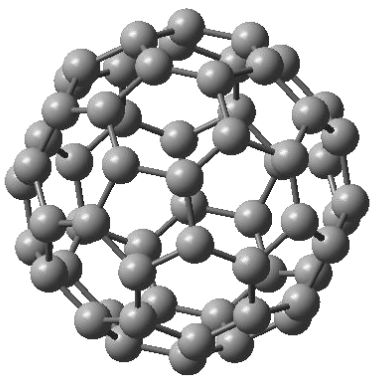
Electron or hole?

Calculation of T(E) from conductance and thermopower

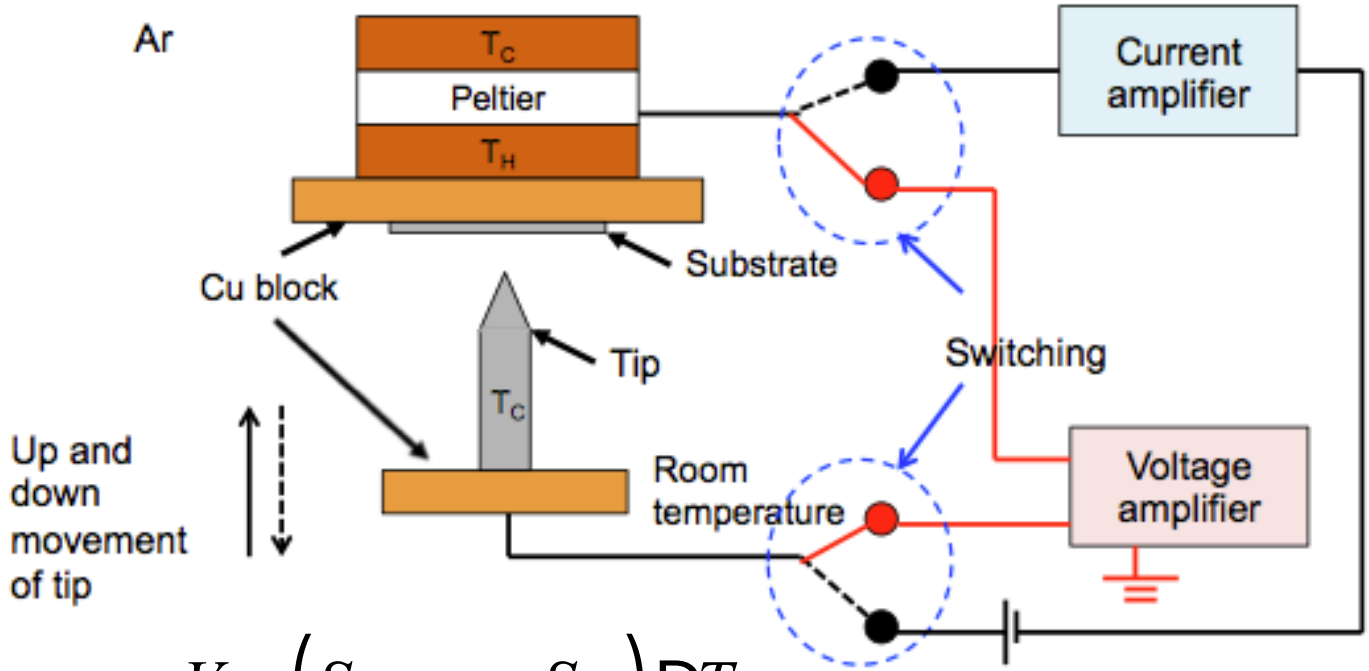
Thermopower measurement



BDT



C_{60}

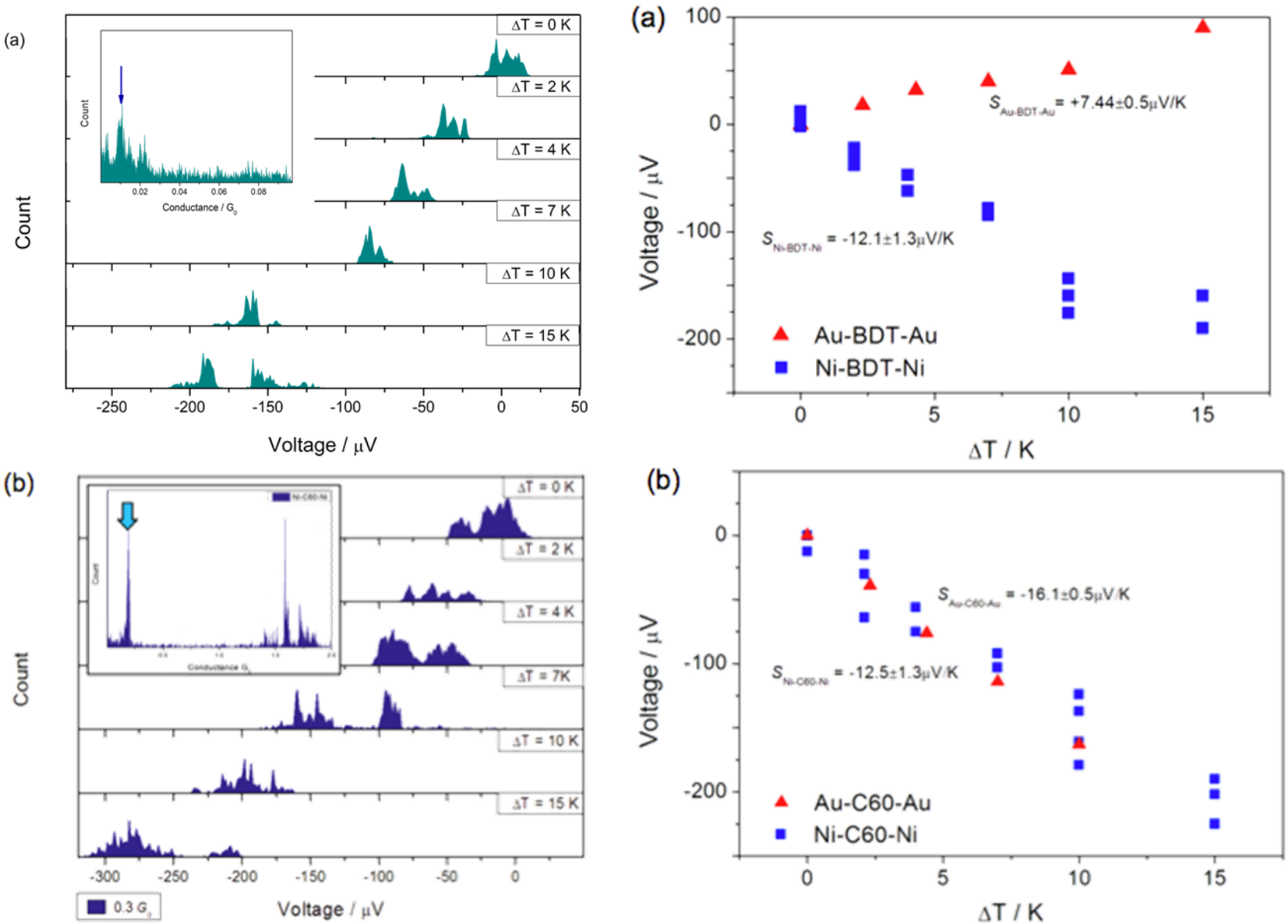


$$V = \left(S_{\text{junction}} - S_{\text{Cu}}\right) \mathrm{D}T$$

Substrate → Au and Ni

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

Thermopower measurement



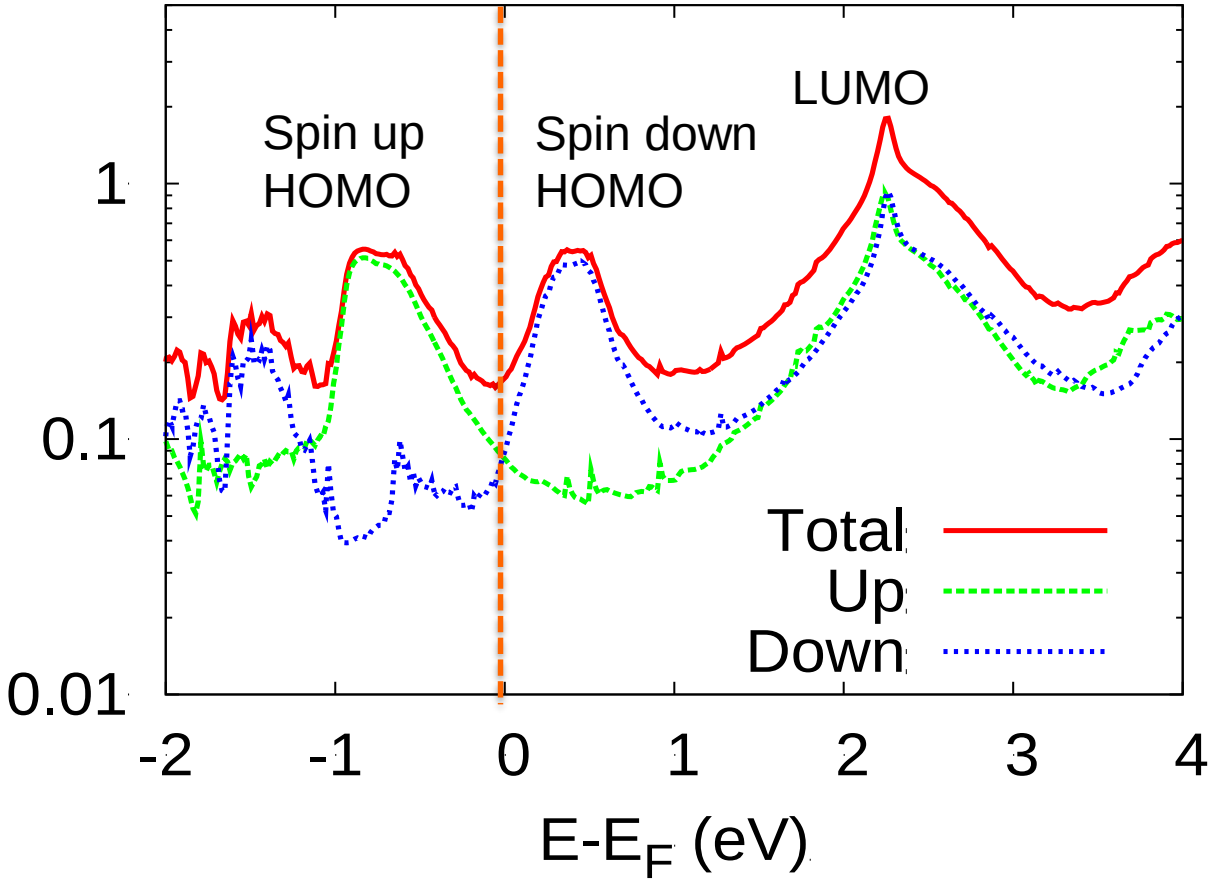
BDT

C_{60}

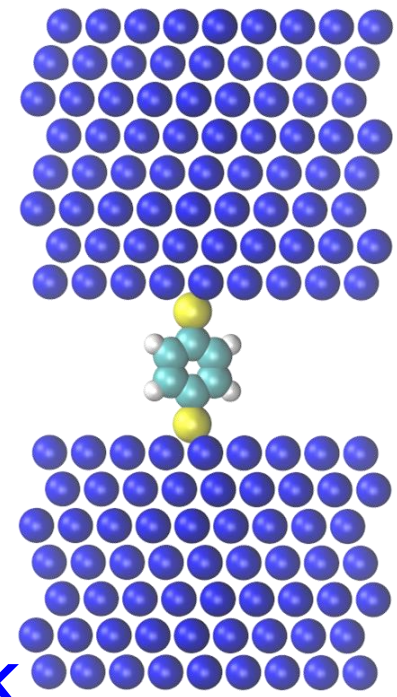
Lee, Ohto, *et al*. Nano Lett. **14**(2014)5276

Ni(111)-BDT-Ni(111)

SMEAGOL module (NEGF-DFT), LDA functional



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



$S_{Ni\text{-}BDT\text{-}Ni}$=-14.2 (calc), -12.1±1.3 (exp) μV/K

Splitting of HOMO due to the spin polarization

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

Outline

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

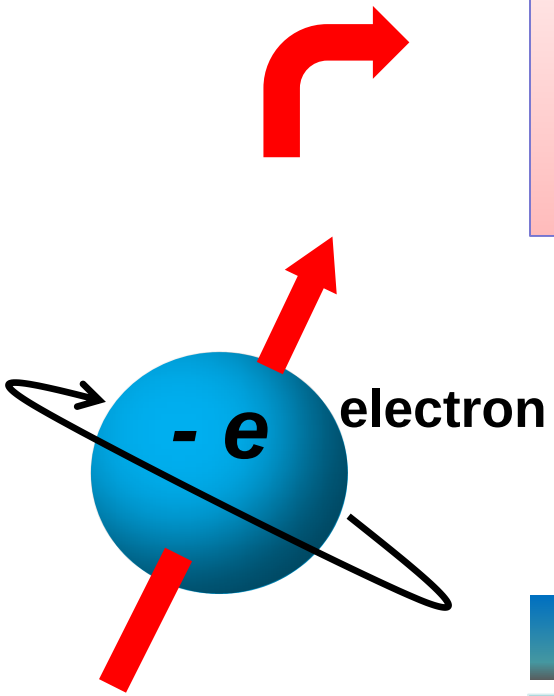
Beyond NEGF-DFT

4. Single molecular magnet and supramolecular spin valve
5. Organic Magetoresistance, OMAR

1. Molecular Spin Valve

Spintronics

Spin



Electron

Magnetics

- Hard disk
- Magnet
- Sensor

etc…

Electronics

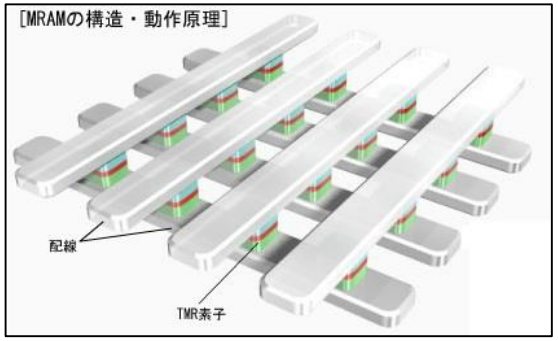
- Transistor
- Laser
- LSI

etc…

Spintronics

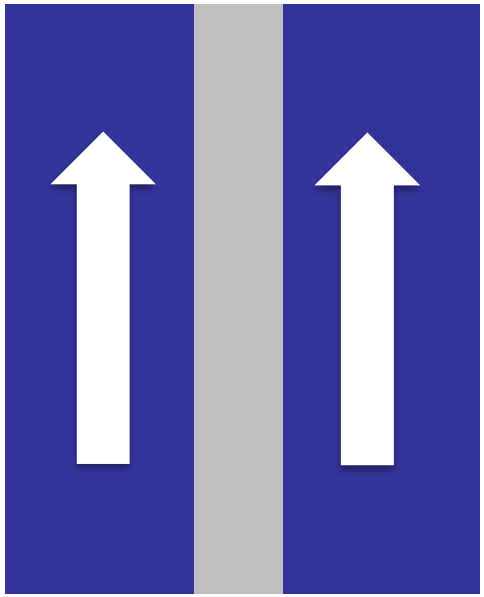
- TMR head
- ReRAM
- Spin Seebeck
- Spin Transistor

etc…

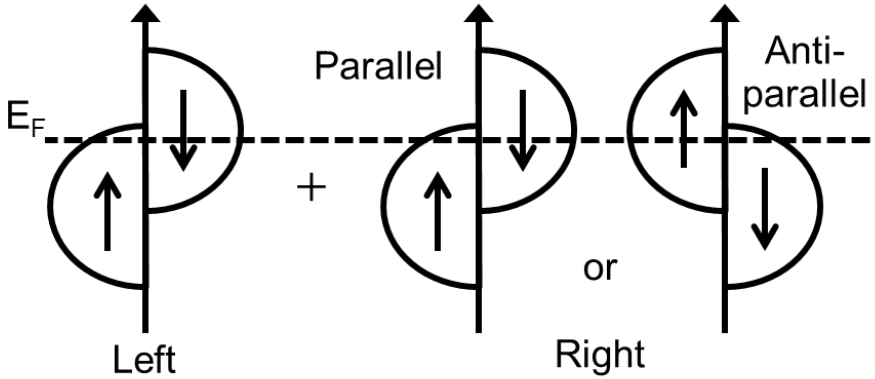


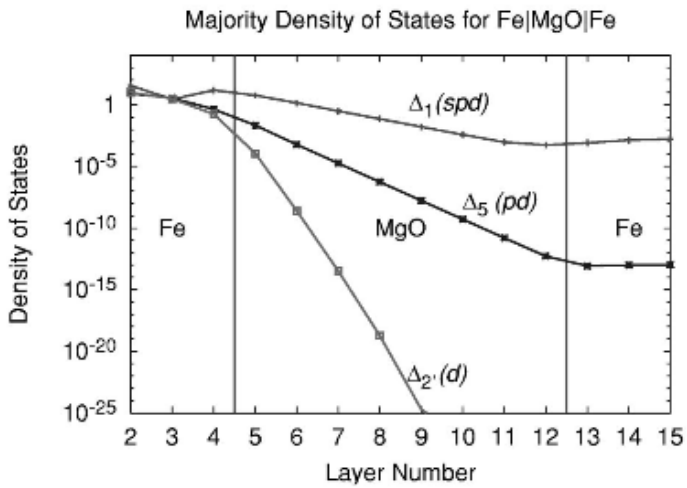
http://www.s-graphics.co.jp/nanoelectronics/index.html

Tunneling Magnetoresistance (TMR)



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

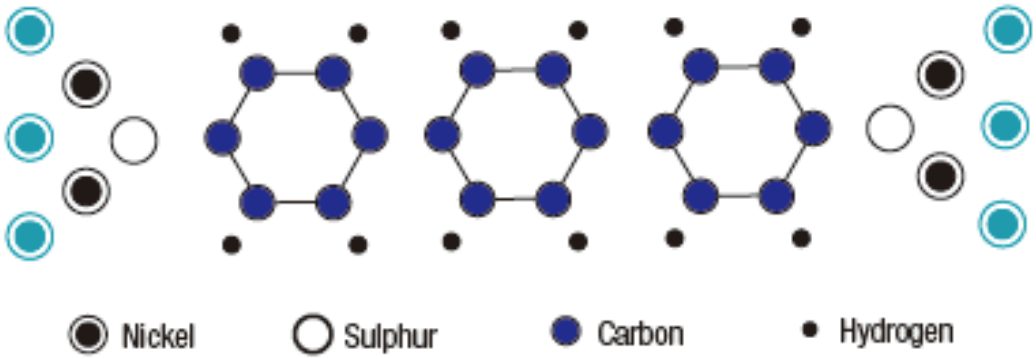




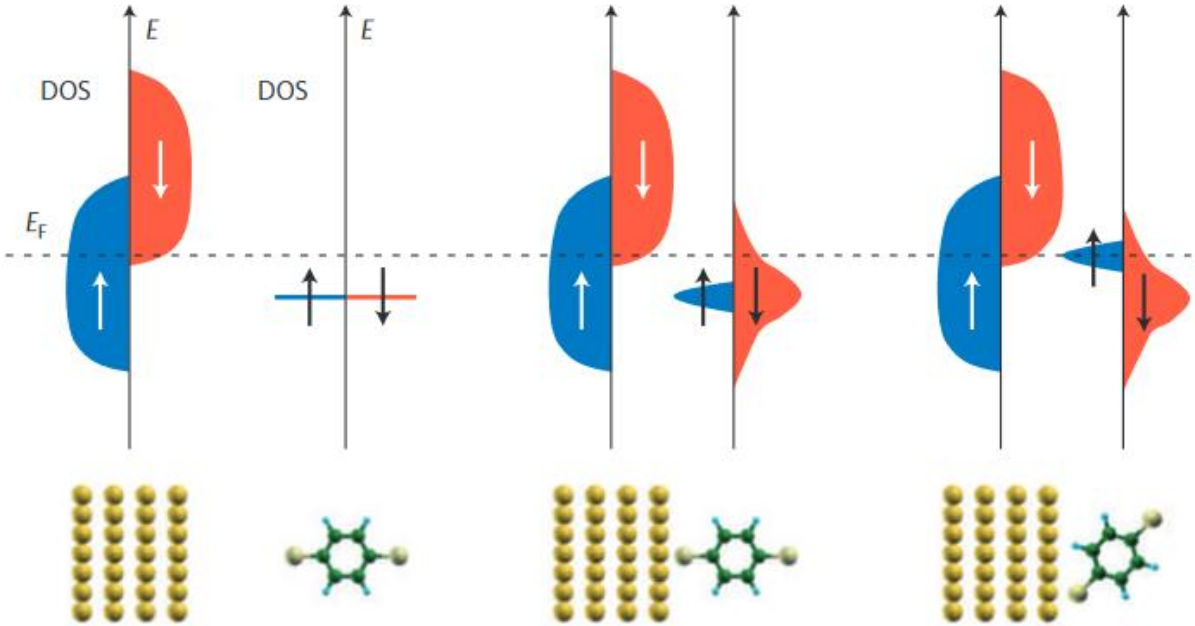
MgO crystal blocks d electron of majority spin

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

Single Molecular TMR Devices

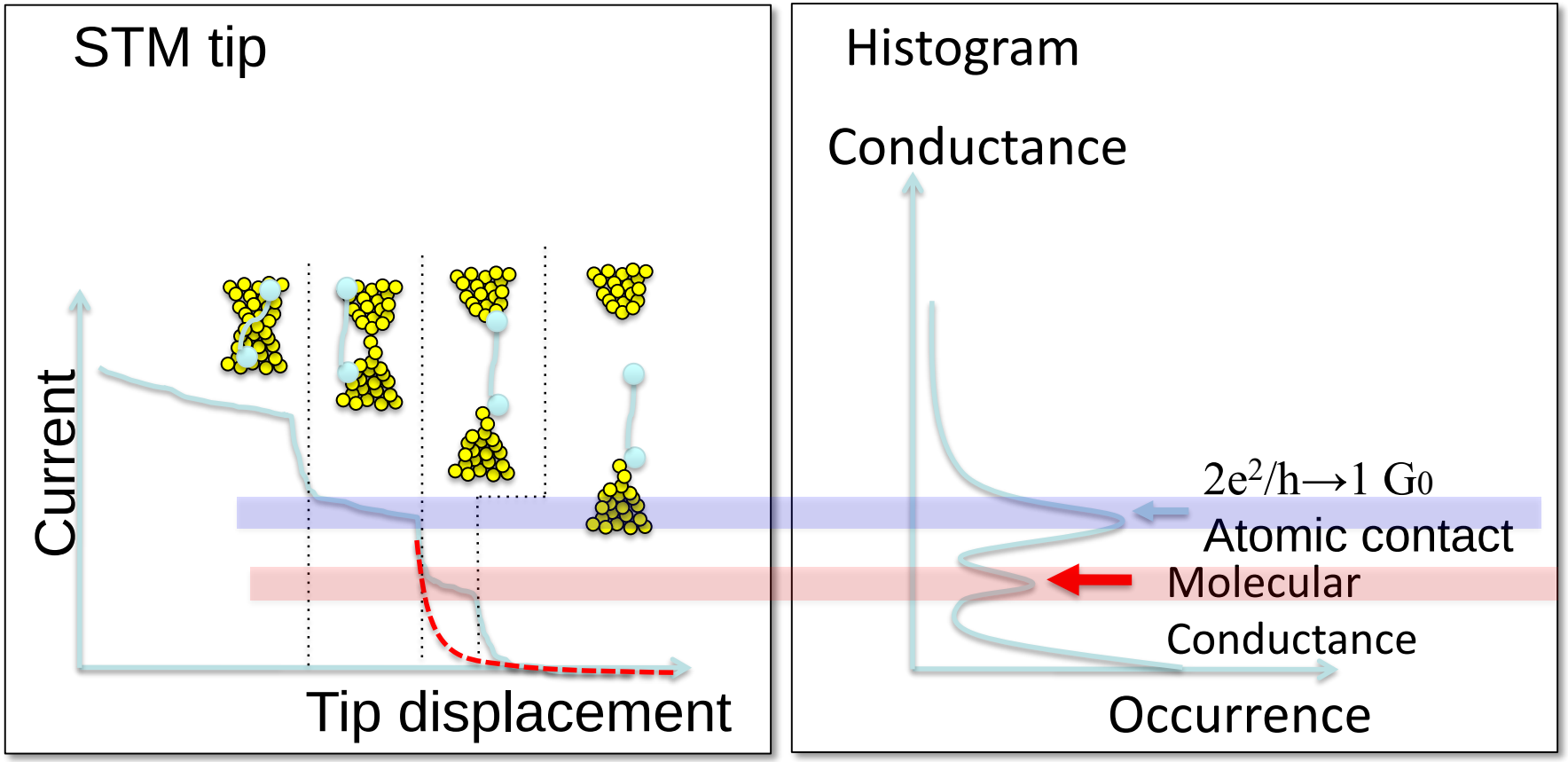


Rocha *et al.* Nat. Mater. **4** (2005) 335



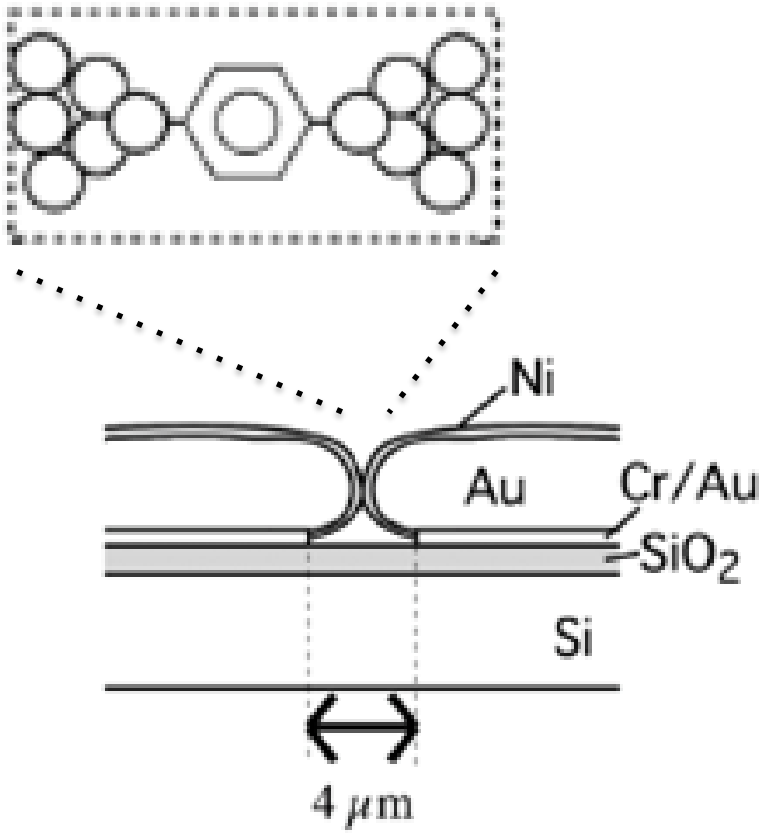
S. Sanvito Nat. Phys. **6** (2010) 562

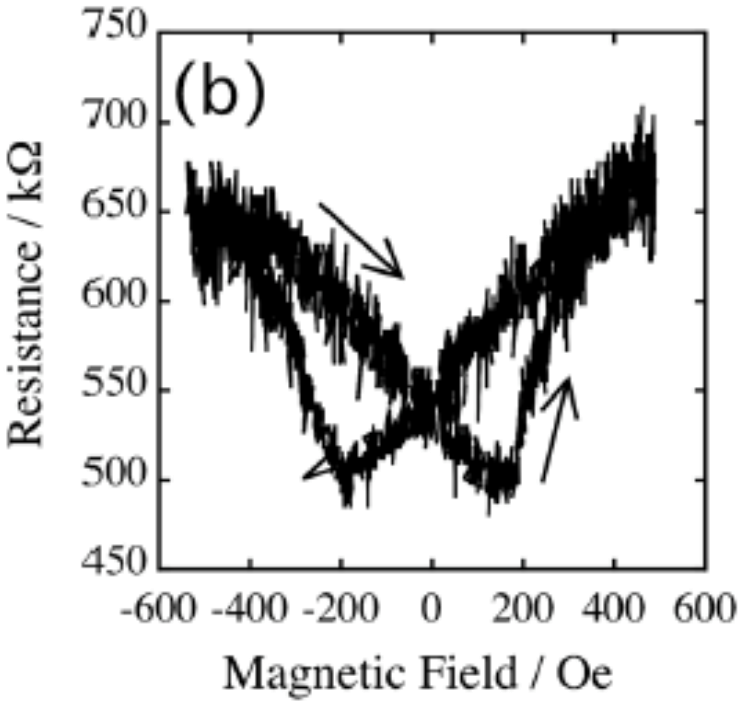
Experimental Methods



Break Junction (BJ) Method

Experimental Methods

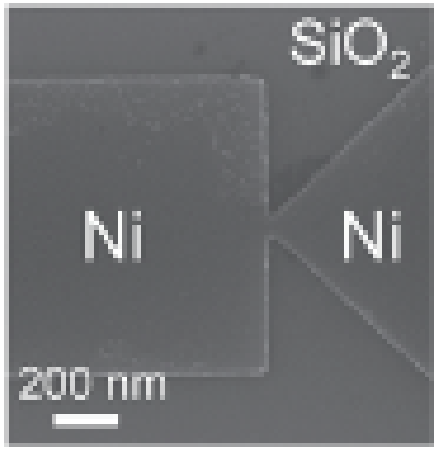


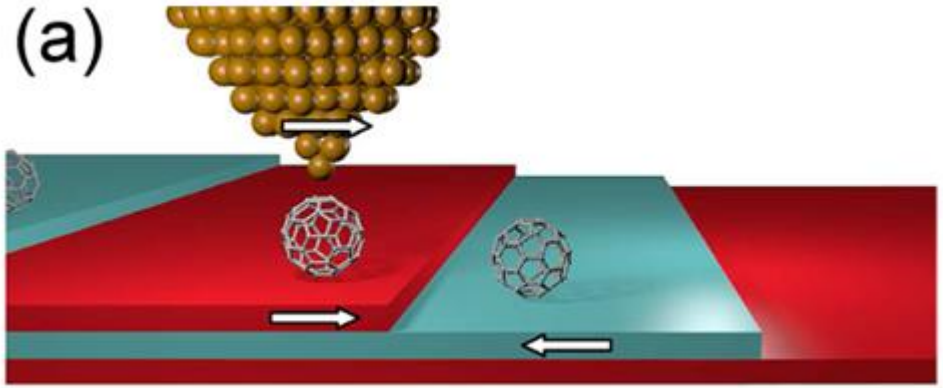


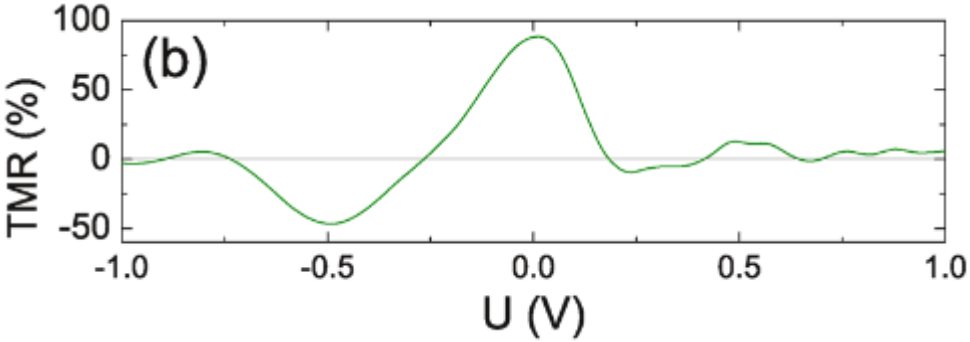
MCBJ with magnetic electrodes

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

Experimental Methods







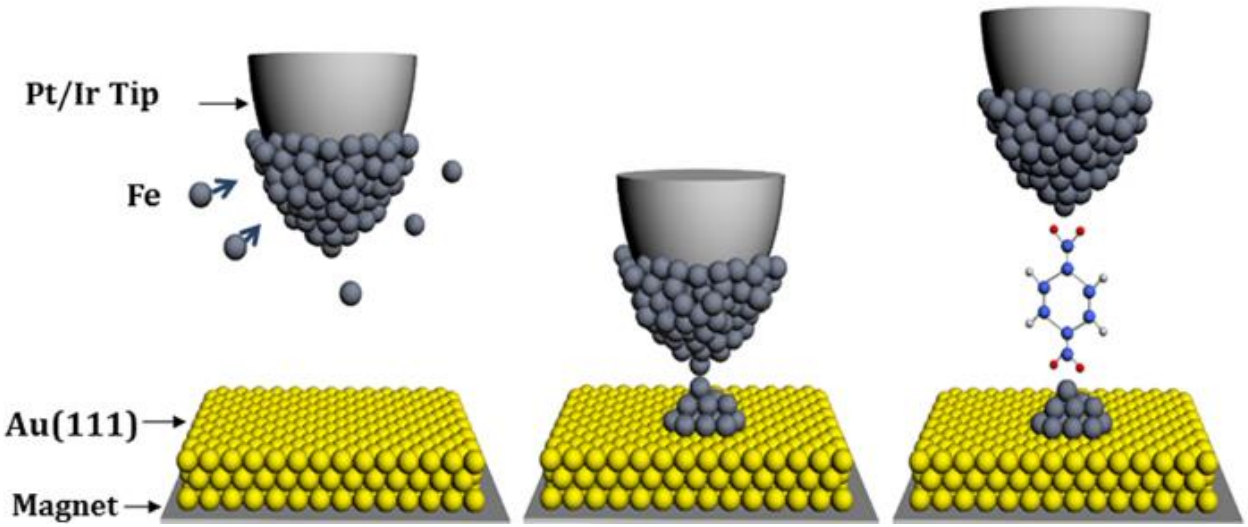
Electrical break junction method, C_{60}/Ni

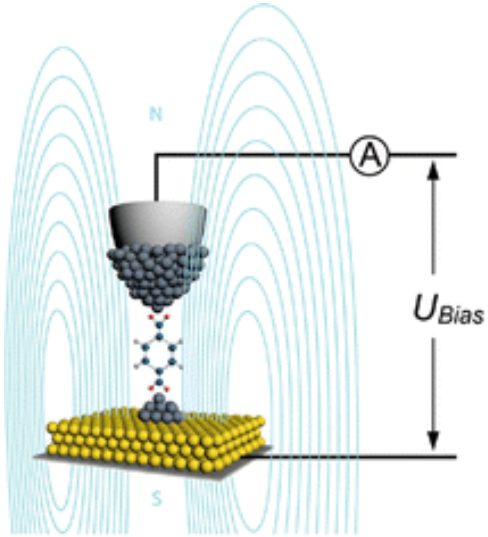
K. Yoshida *et al.* Nano Lett. **13** (2013) 481

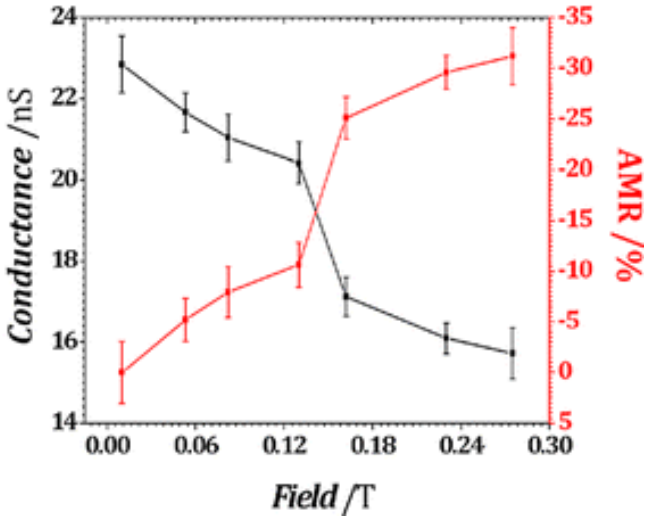
Scanning tunneling microscopy (STM), C_{60}/Cr(001)

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

Tunneling Anisotropic Magnetoresistance (TAMR)

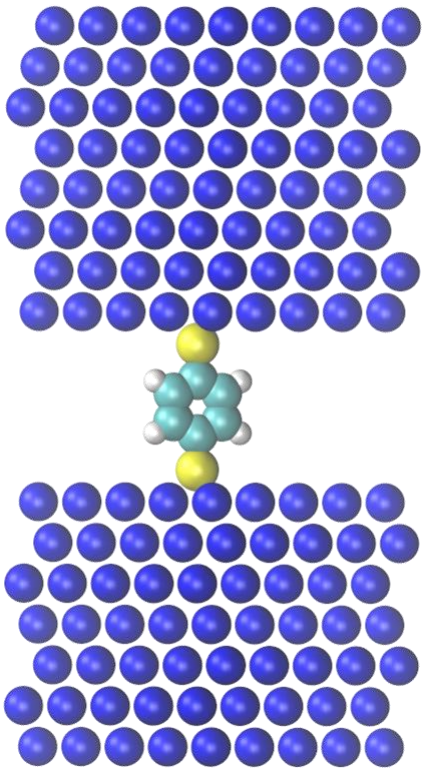




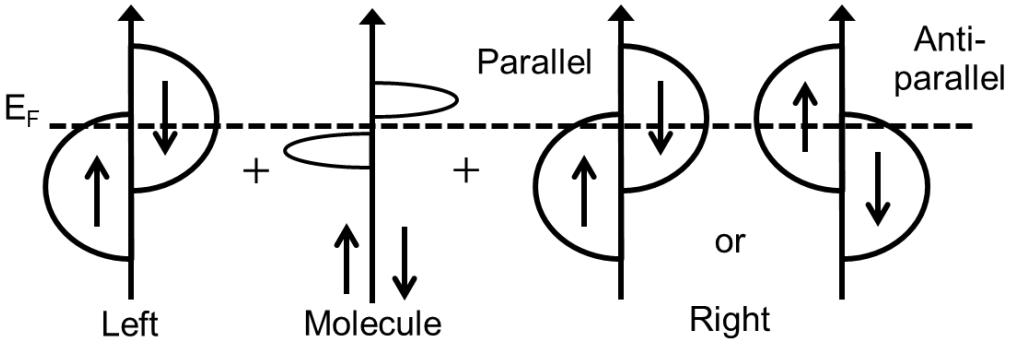


J.-J. Li *et al.* J. Am. Chem. Soc. **137** (2015) 5923

Theoretical Design of Molecular Spin Valve



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



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

Programs

Atomic Orbial (SIESTA)

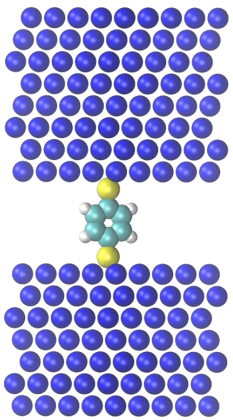
TranSIESTA（Spain, Denmark）
with SIESTA

ATK (Quantum Wise)
Commercial TranSIESTA

SMEAGOL（Ireland, UK）
Spin Transport

HiRUNE（Japan, AIST）
Electron-phonon

OpenMX（Japan）



molecule
10~100 atoms

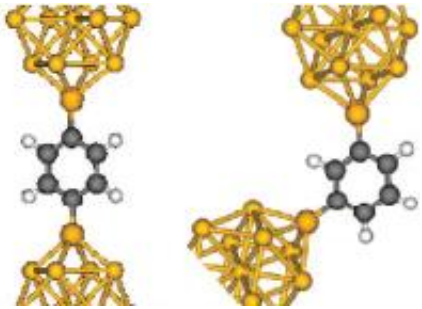
electrodes
8x8x6x2
=768 atoms(!)

Plane Wave

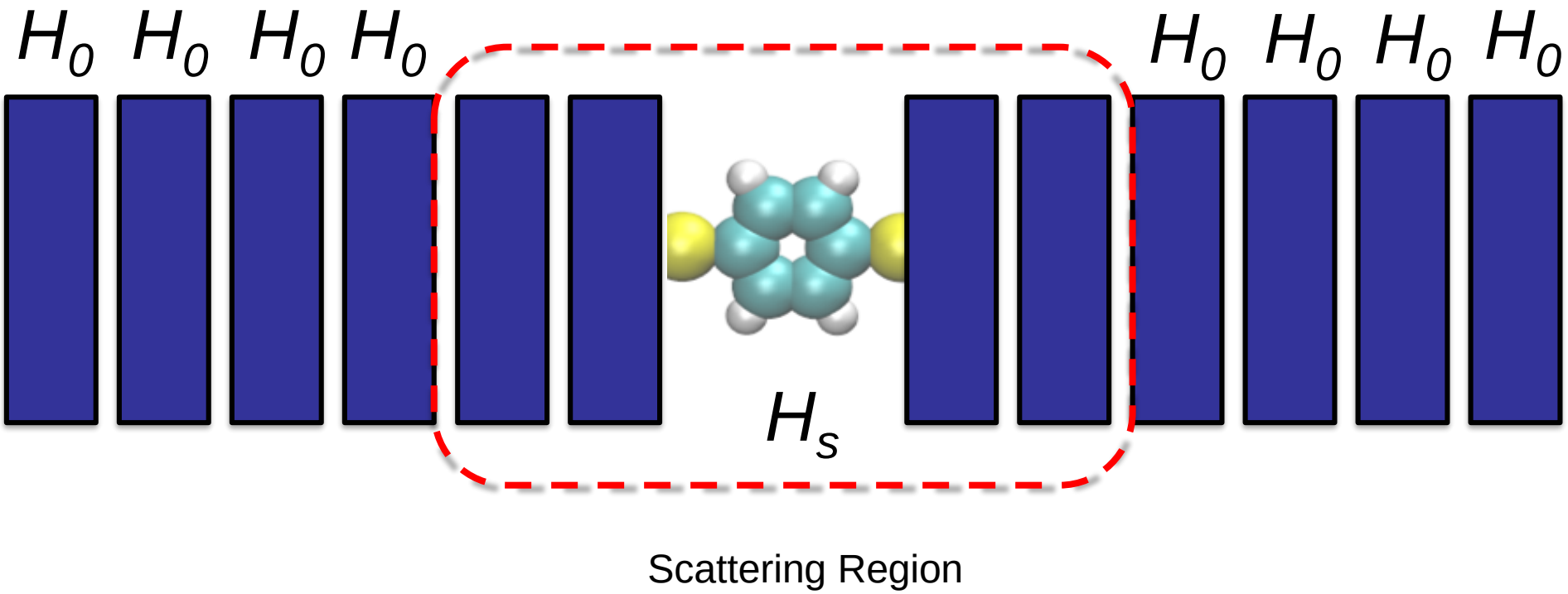
Quantum Espresso

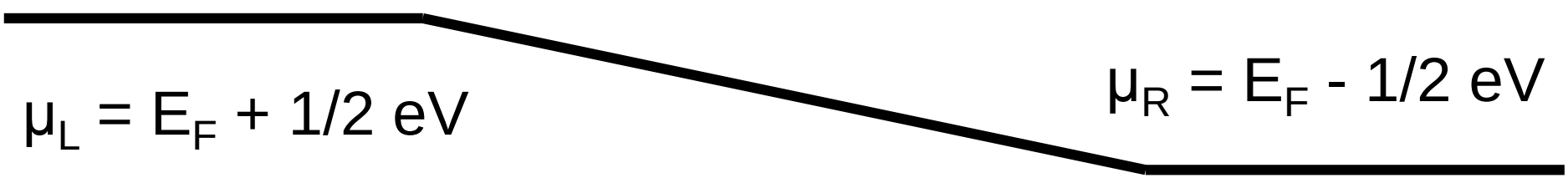
Gaussian Basis

Turbomole

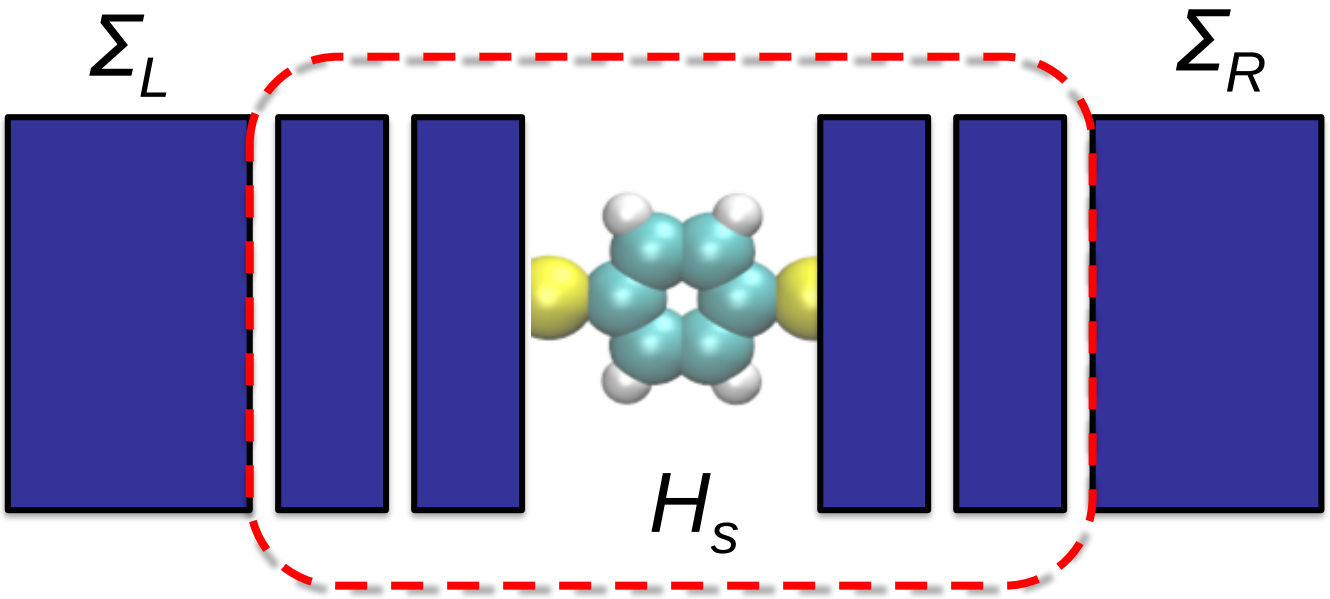


NEGF

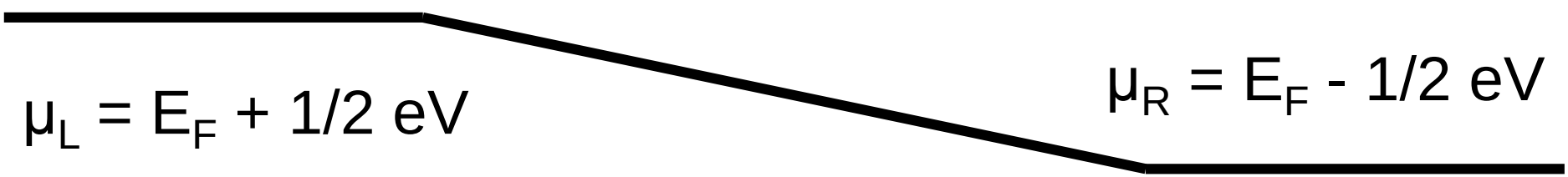

H_0 H_0 H_0 H_0
H_0 H_0 H_0 H_0
H_s
Scattering Region


$\mu_L = E_F + 1/2$ eV
$\mu_R = E_F - 1/2$ eV

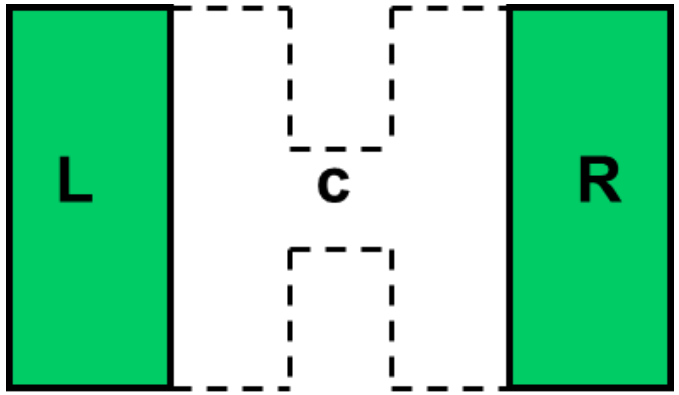
NEGF



Scattering Region



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

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

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

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

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

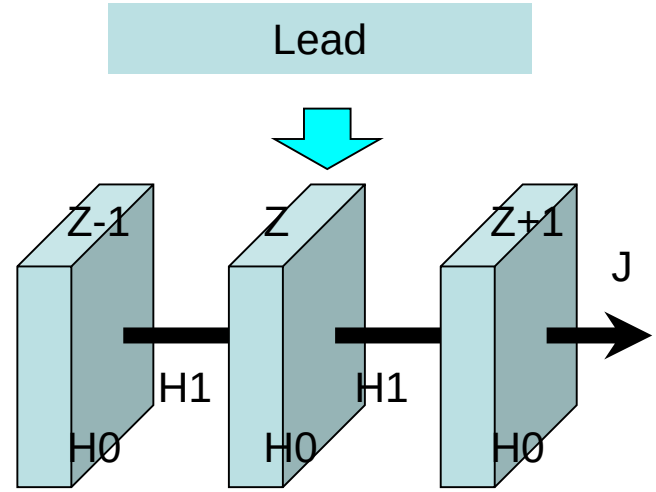
Surface Green's function

Surface Green's Function

Tight Binding Layer (TBL) Method

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

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

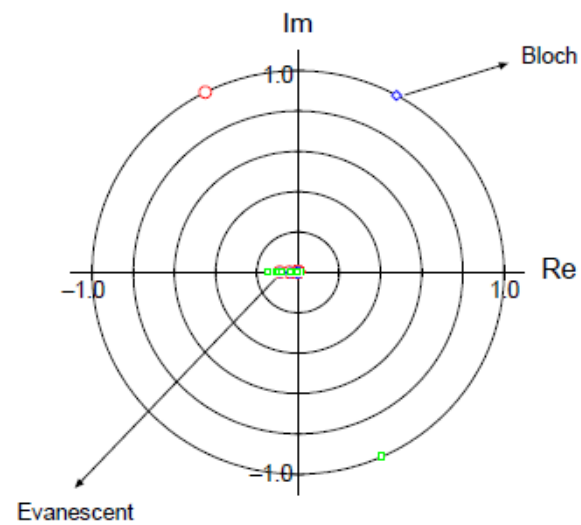


$$\psi_Z = n_{k_\perp}^{1/2} e^{ik_\perp z} \phi_{k_\perp}$$

M…degrees of freedom

$$\left(H_0 + H_1 e^{ik\perp} + H_{-1} e^{-ik\perp} - SE\right)\phi_{k_\perp} = 0$$

$$\mathrm{H} = \begin{pmatrix} -H_1^{-1}\left(H_0 - SE\right) & -H_1^{-1} H_{-1} \\ \mathrm{I} & 0 \end{pmatrix}$$



Sign of the group velocity

→ Bloch, Evanescent States

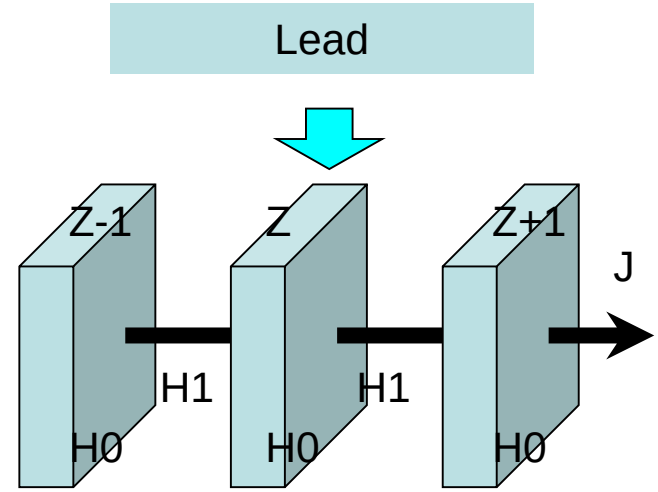
Surface Green's Function

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 $\tilde{\varphi}$

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

Boundary condition $Z = Z_0$

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

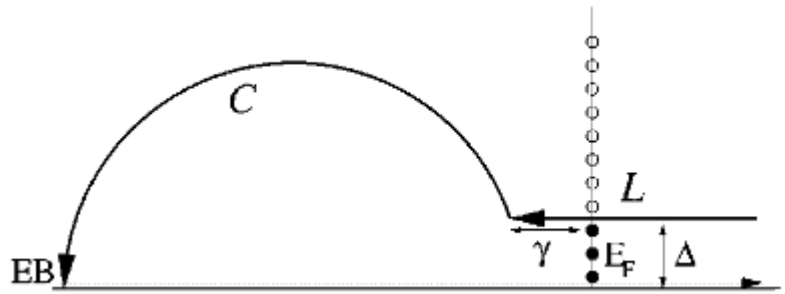
→ Semi-infinite (Surface Green's function)

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

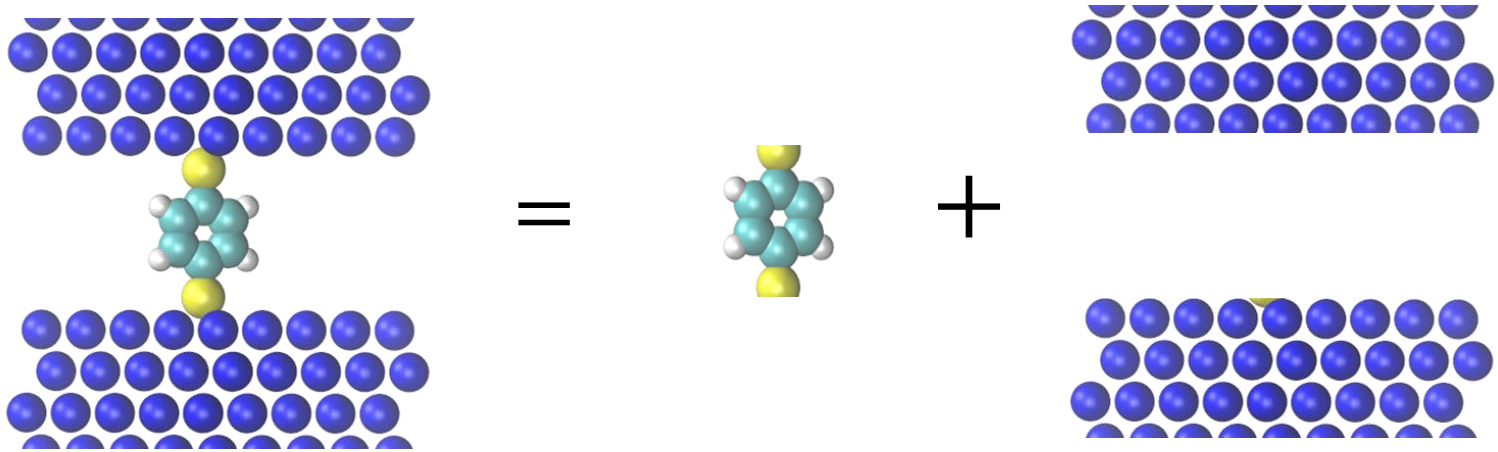
NEGF

$$\mathbf{\Gamma}_L(E) = i\left(\mathbf{\Sigma}_L(E) - \mathbf{\Sigma}_L^{\dagger}(E)\right)$$

$$\mathrm{G} = \mathrm{G}_0 + \mathrm{G}_0 \Sigma\, \mathrm{G}$$

Dyson Equation

$$T = \mathrm{Tr}[\mathrm{G}\Gamma_{\mathrm{L}}\mathrm{G}^{\dagger}\Gamma_{\mathrm{R}}]$$



G $\quad$ G_0 $\quad$ $\Sigma = \Sigma_{\mathrm{L}} + \Sigma_{\mathrm{R}}$

We can add any interactions through Σ

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

$$\mathrm{G}^{<} = \mathrm{G}\Sigma^{<}\mathrm{G}^{\dagger}$$

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

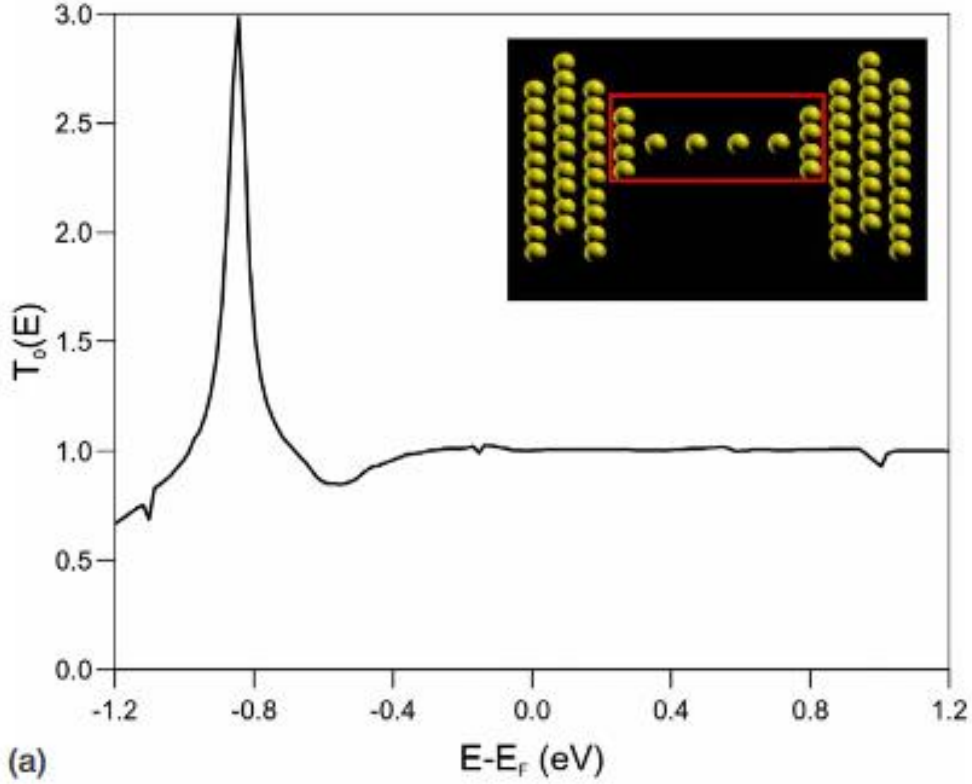
$$I(V_b)=\frac{1}{\pi}\int dE\,T(E,V_b)\left(f\left(E-\mu_L\right)-f\left(E-\mu_R\right)\right)$$

・Spin Transfer Torque

with SMEAGOL

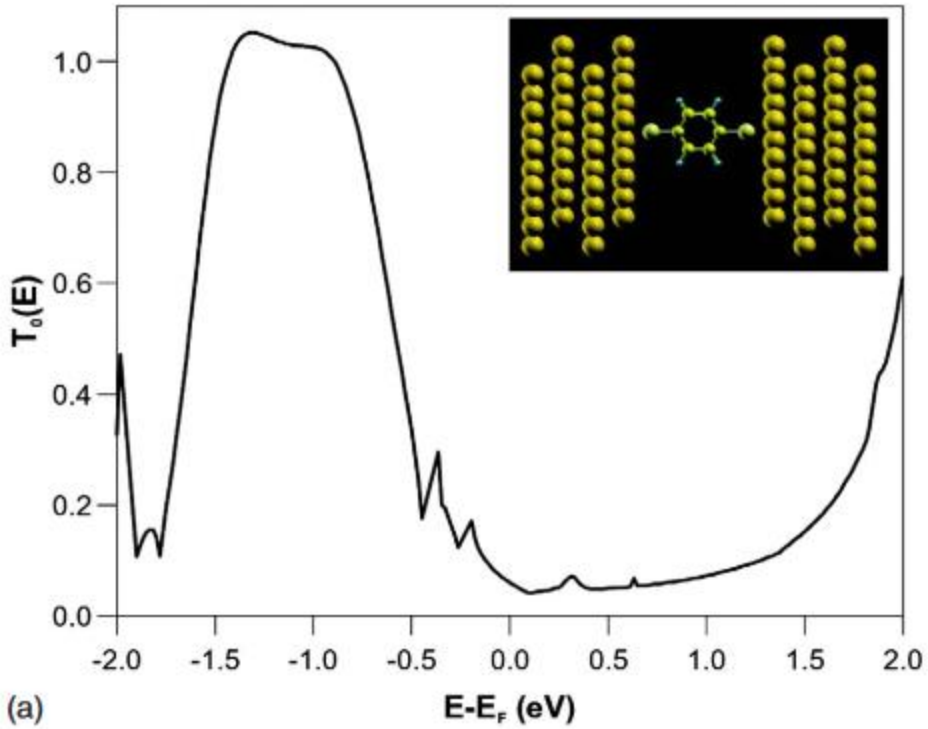
・TAMR

Gold wire



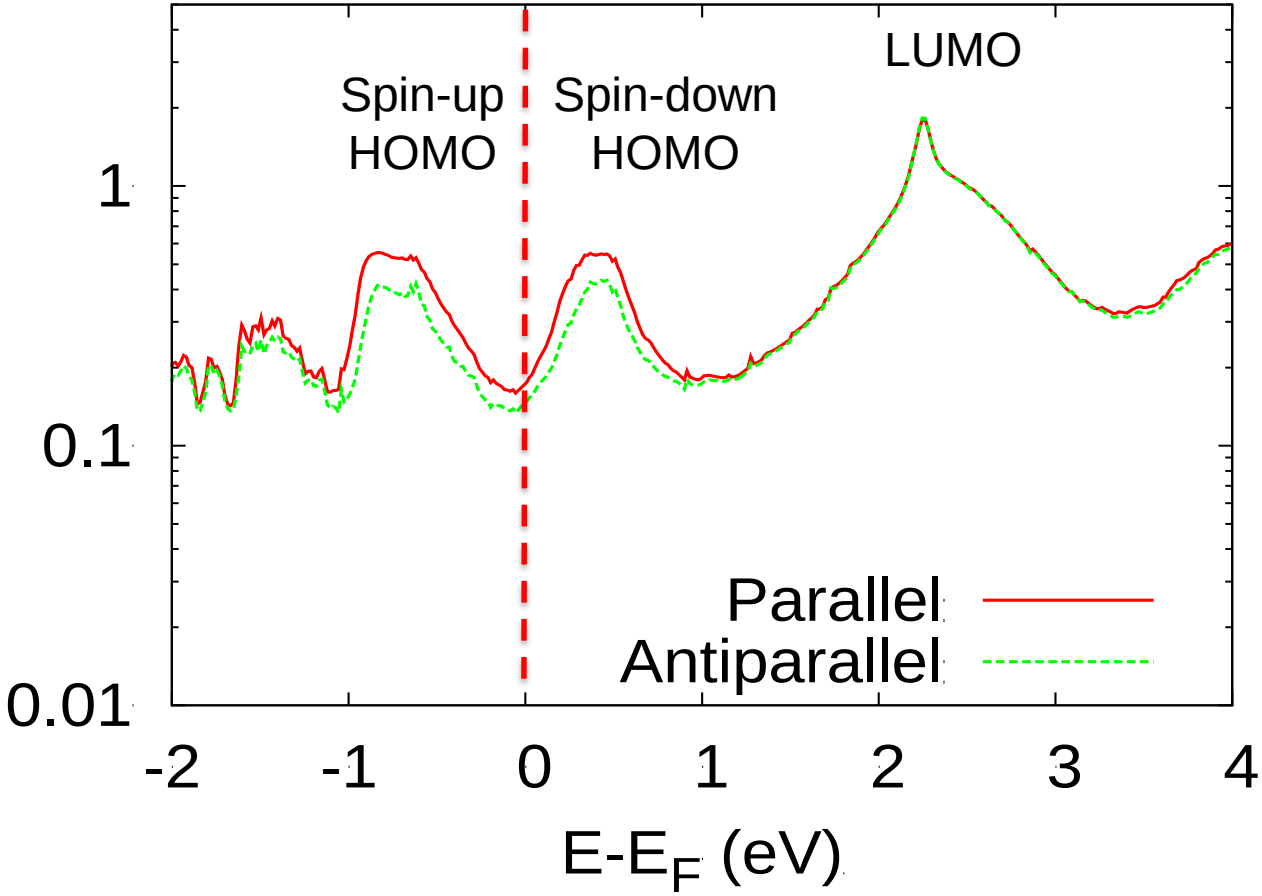
H. Nakamura *et al*. Phys. Rev. B **78** (2008) 235420

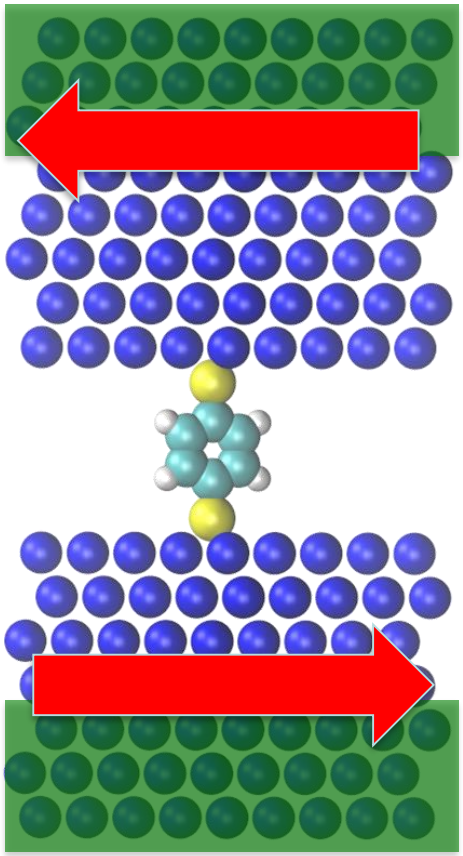
Au-BDT-Au



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

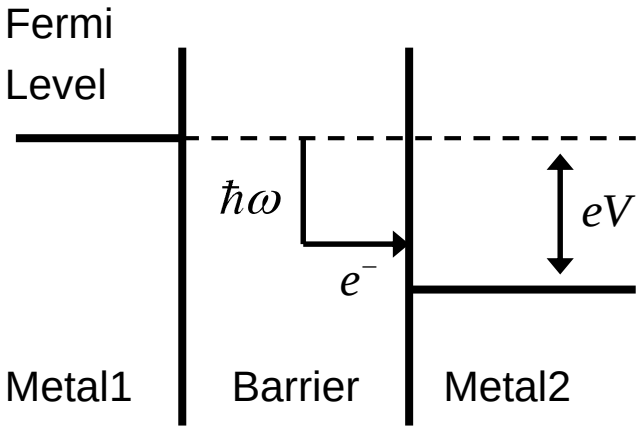
Ni-BDT-Ni





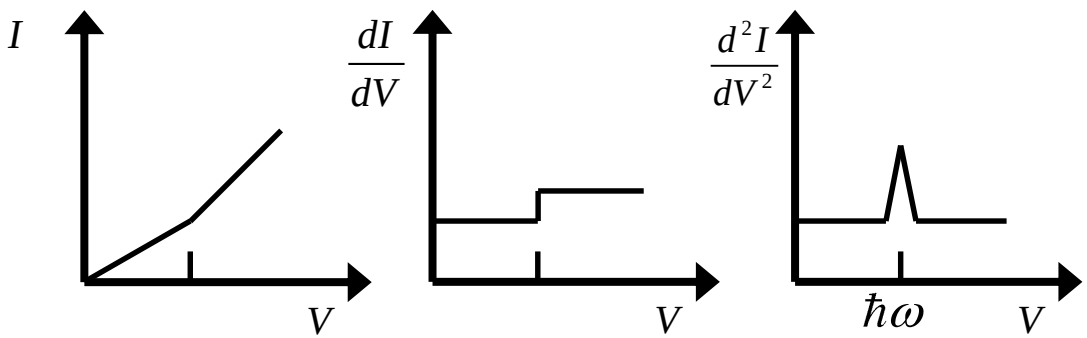
TMR~20%

Electron-Phonon Coupling



Electron-Phonon Self-energy

$$\mathbf{\Sigma}^{<}_{e-ph;\lambda}(E) = i\int_{-\infty}^{\infty}\frac{dE'}{2\pi}\mathbf{M}^{\lambda}\mathbf{G}^{<}_{CC}(E')\mathbf{M}^{\lambda}$$



Current-voltage

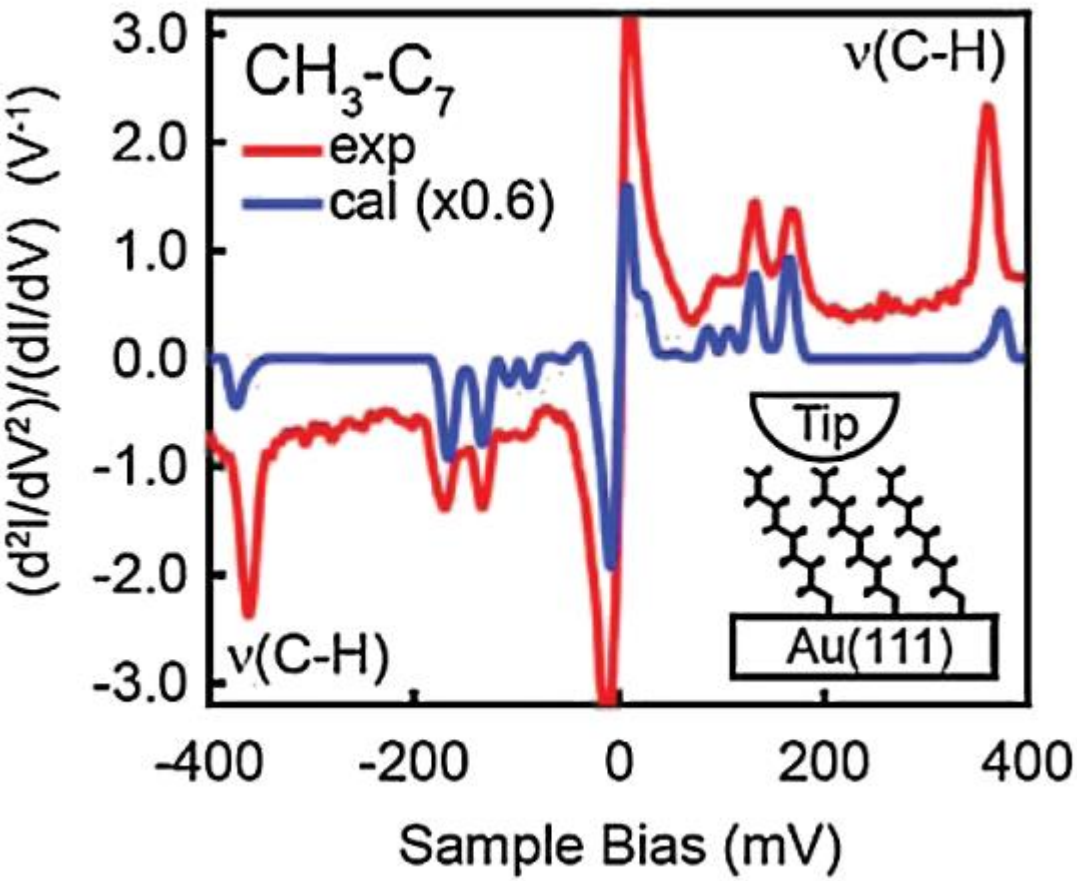
Transmission (Conductance)

Inelastic Electron Tunneling Spectroscopy (IETS)

IETS

Packages:

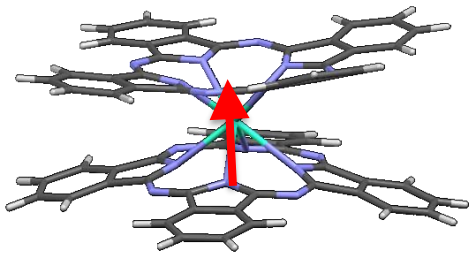
Inelasitica
HiRUNE
SMEAGOL



N. Okabayashi *et al*. Phys. Rev. Lett. **104** (2010) 077801

4. Single Molecular Magnet (SMM) and supramolecular spin valve

Single molecular magnet

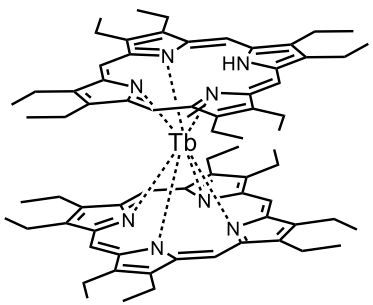


Tb(III) Double decker complex

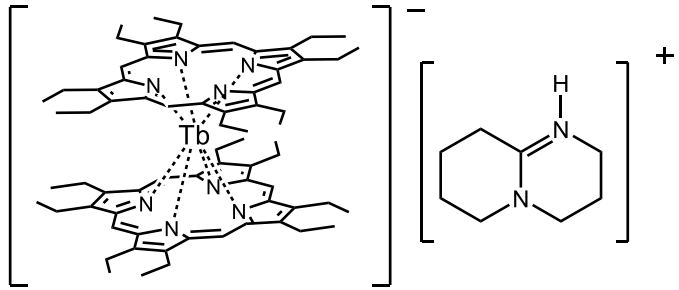
High blocking temperature (T_b ~ 52 K)

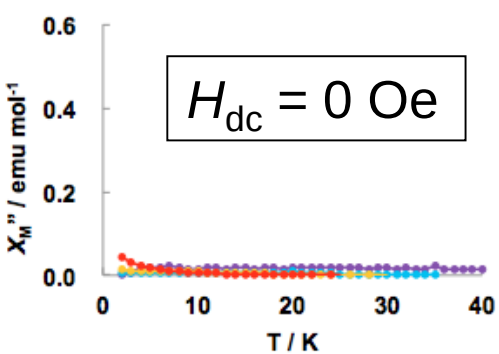
T. Ishikawa, *Inorg. Chem*. **2007**, 46 , 7250−7252

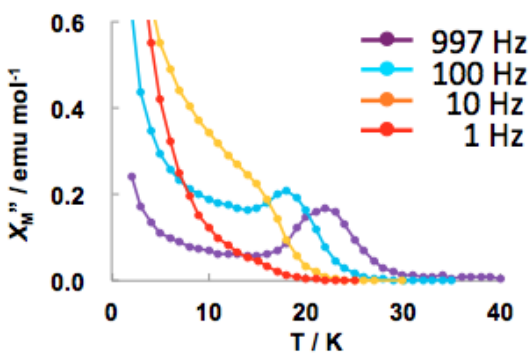
Protonated form

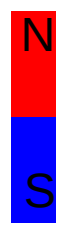


Anionic form

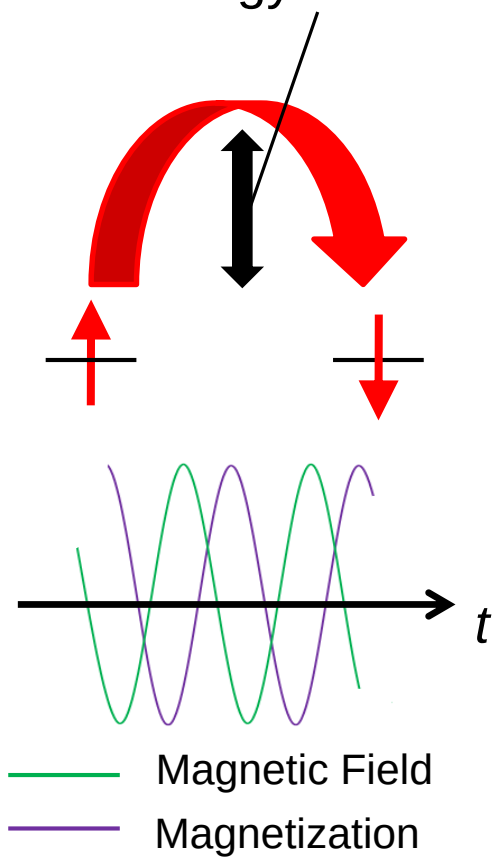








Energy barrier

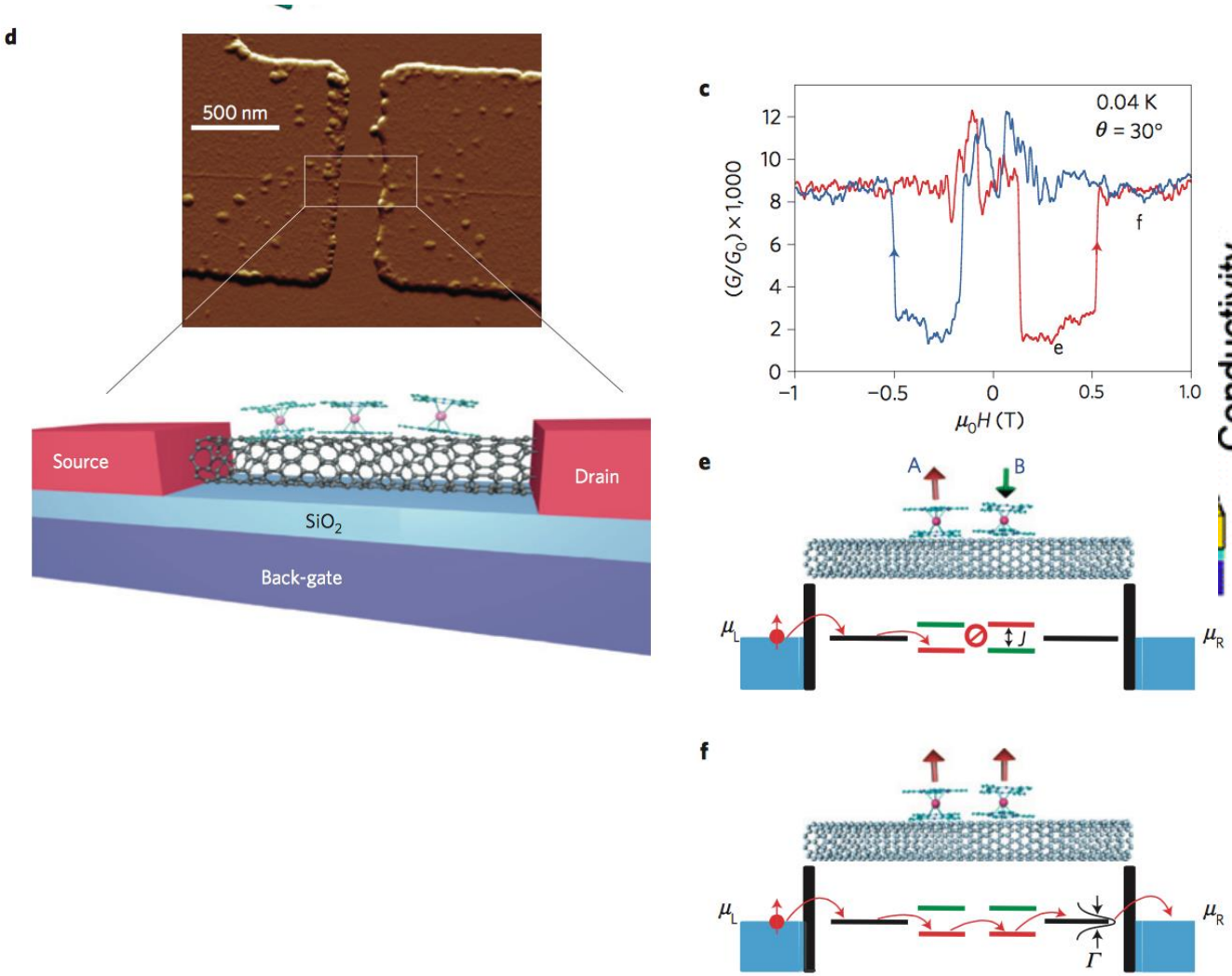


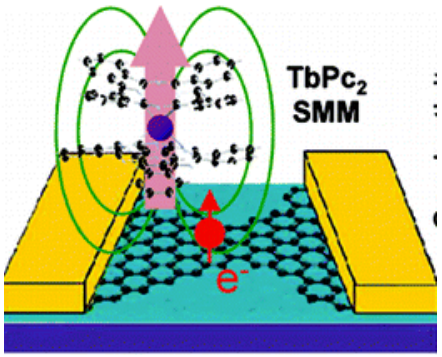
D. Tanaka et al., *Chem. Commun.*, **2012**, 48 7796−7798

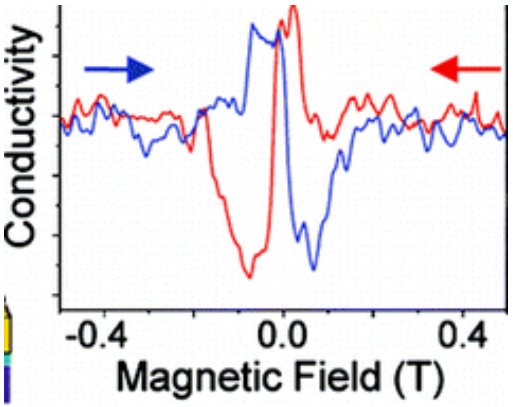
nature materials
LETTERS
PUBLISHED ONLINE: 19 JUNE 2011 | DOI: 10.1038/NMAT3050

Supramolecular spin valves

M. Urdampilleta[1], S. Klyatskaya[2], J-P. Cleuziou[1], M. Ruben[2,3]* and W. Wernsdorfer[1]*

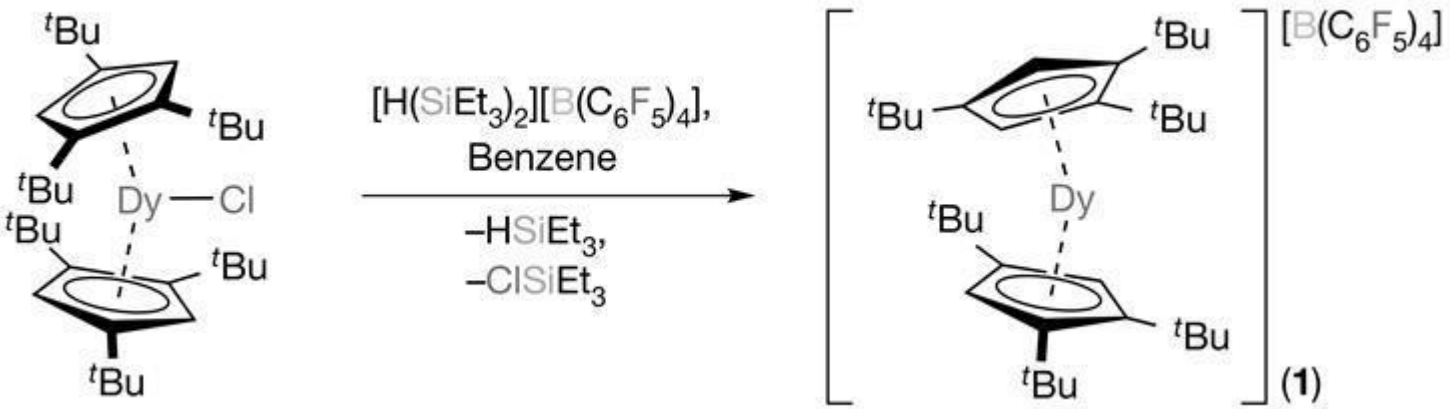






Candini et al. Nano Lett., **2011**, *11* (7), pp 2634–2639

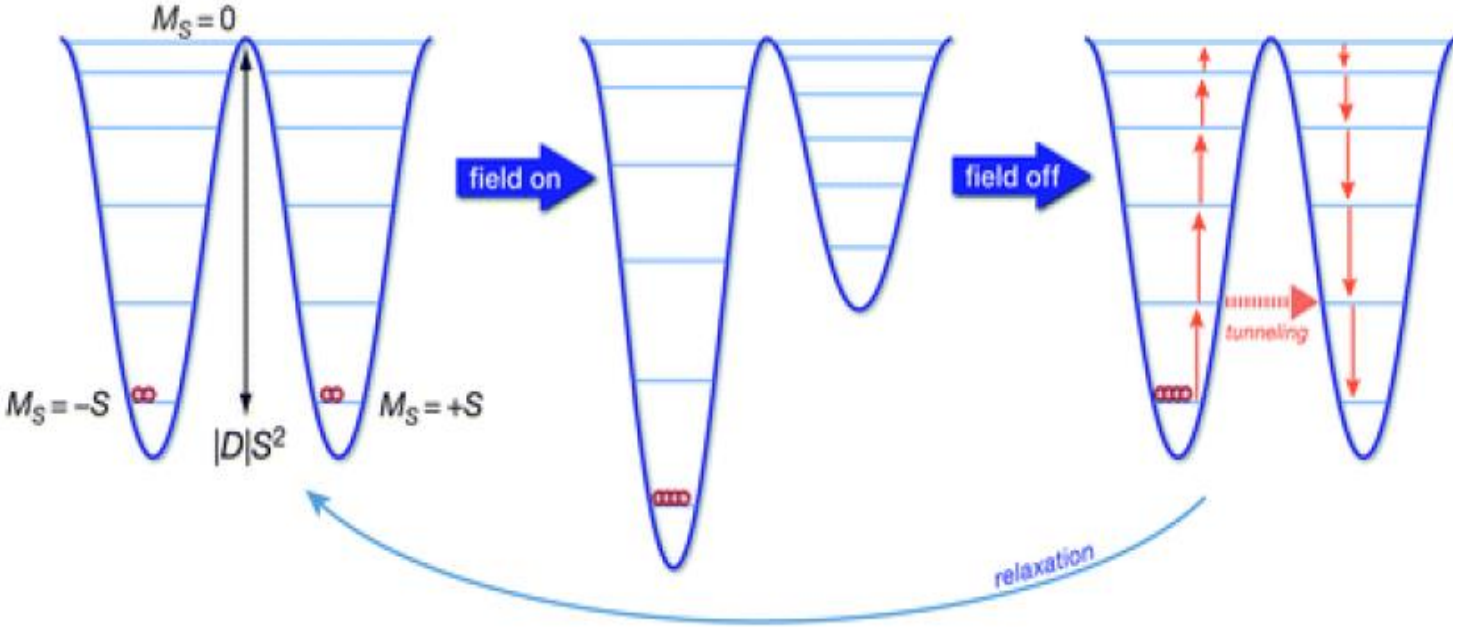
Single molecular magnet

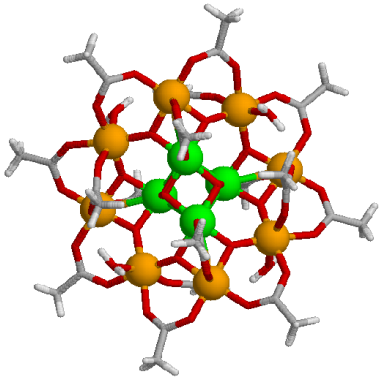


C. A. P. Goodwin et al., Nature 548, 439–442 (24 August 2017)

Hysteresis at 60K!

Estimation of the blocking temperature





Mn12

F. Neese, et al. *Faraday Discuss.*, **148**, 229238 (2011)

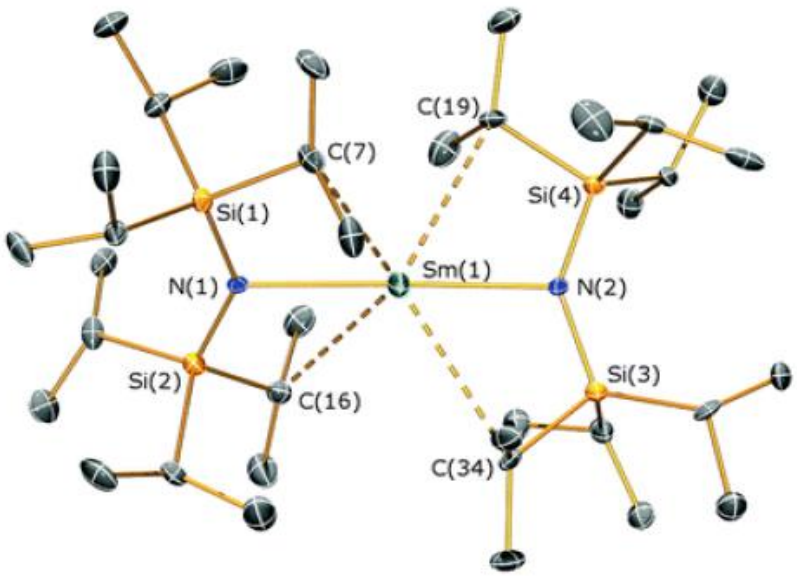
Zero Field Splitting (ZFS)

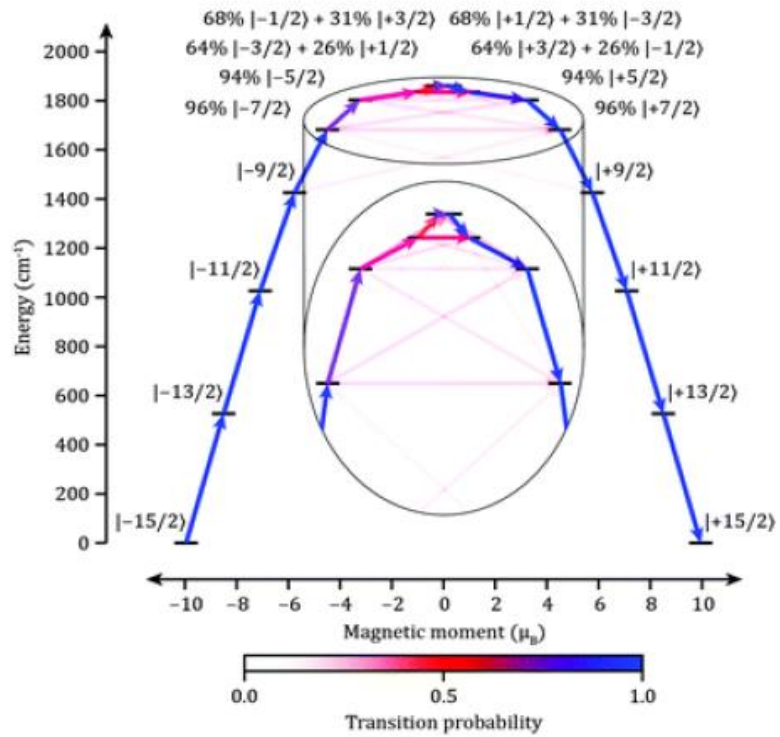
$$\hat{H} = DS^2_z + E(S^2_x - S^2_y)$$

ORCA

https://orcaforum.cec.mpg.de/

Estimation of the blocking temperature



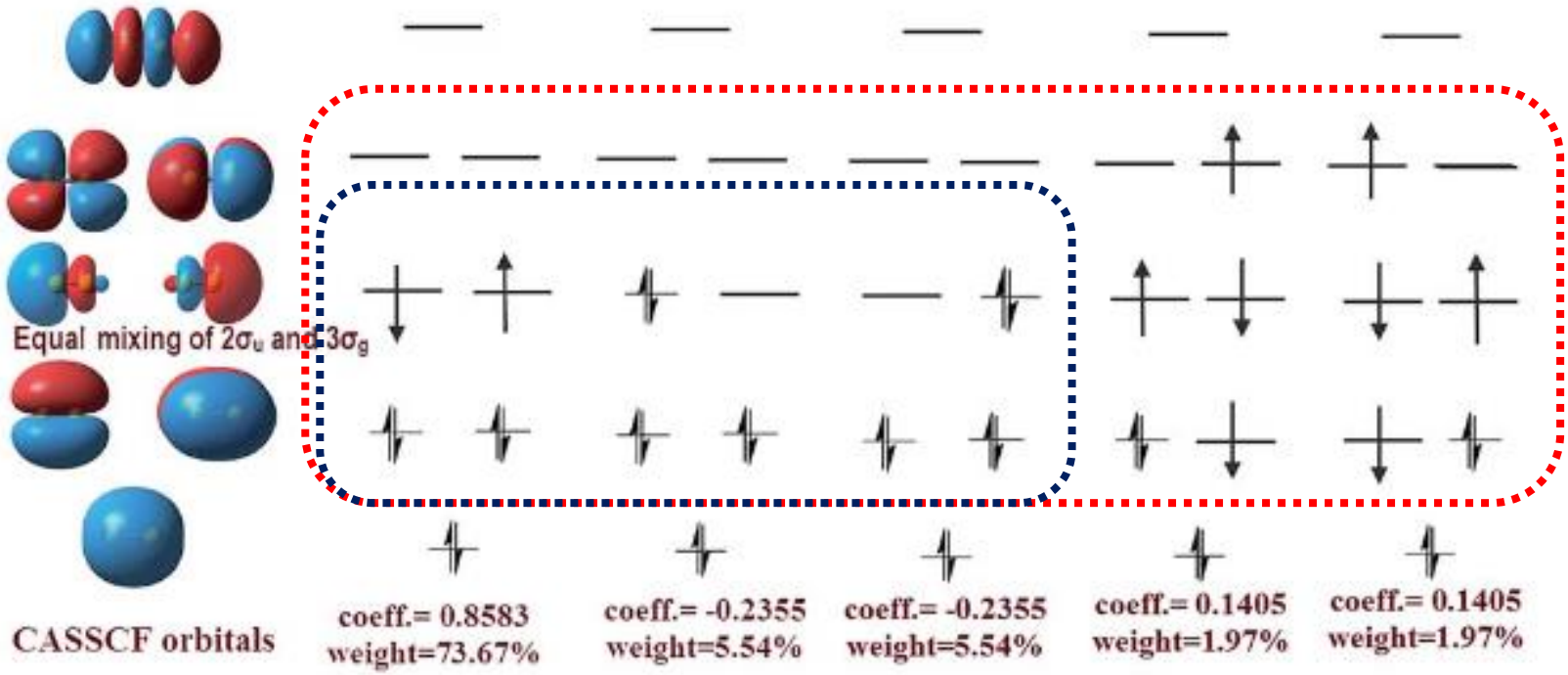


N.F. Chilton, et al. *Chem. Commn,* **51**, 103 (2015)

MOLCAS package
CASSCF/RASSI-SO module

CASSCF … complete active space scf
RASSI … restricted active space state interaction

CASSCF



Chem. Sci.,2016,7,102

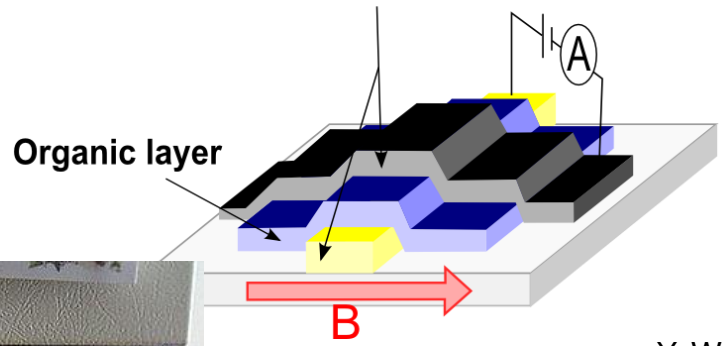
5. Organic Magnetoresistance

Organic magnetoresistance (OMAR)

Usual MR

MAGNETIC ⇐ **Electrodes** ⇒ **NON MAGNETIC**

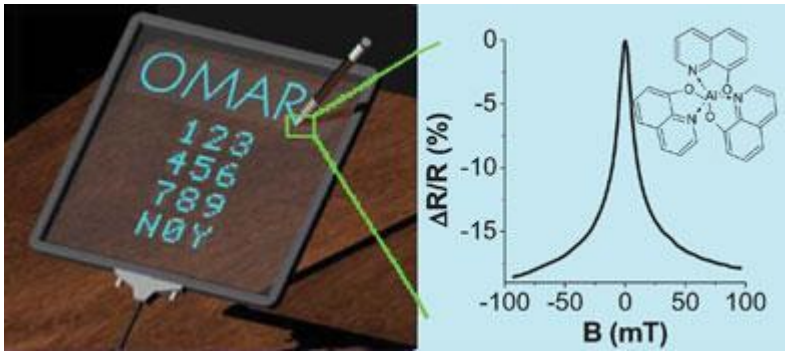
GMR, TMR
Spinvalve.



Room temperature.
Low magnetic field (mT)

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

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

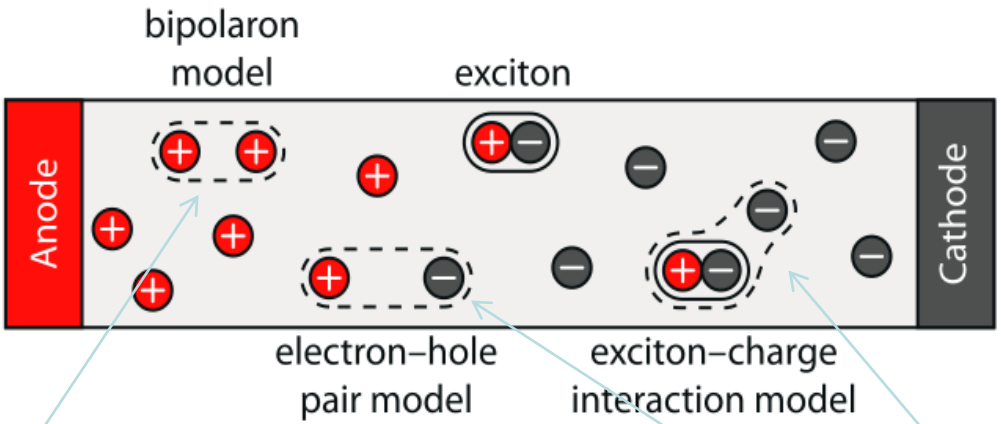


Nguyen et al. *J. Mater. Chem.* **17** (2007) 1995

MR: magnetoresistance

Theory: Single vs. Double carriers

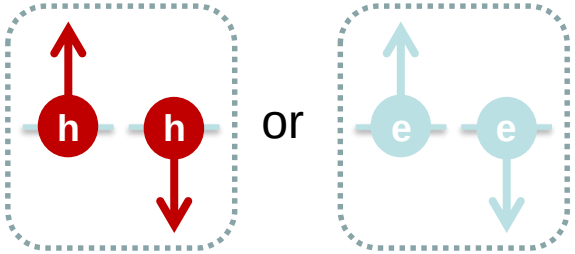
The magnetic field modifies
the ratio between SINGLET and TRIPLET



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

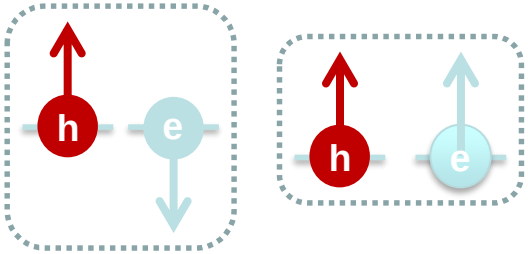
Single carriers

Only ONE type of carrier



Double carriers

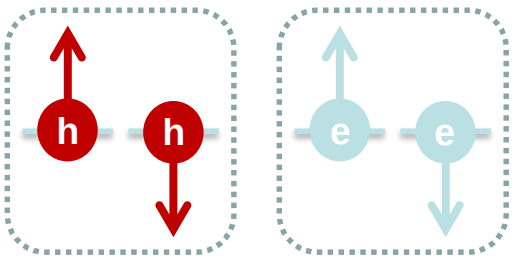
BOTH hole and electron are require



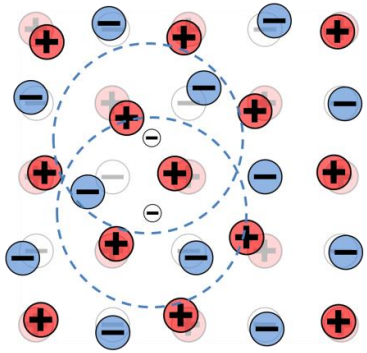
Theory: Single vs. Double carriers

The magnetic field modifies
the ratio between SINGLET and TRIPLET

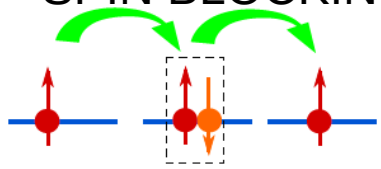
Single carriers



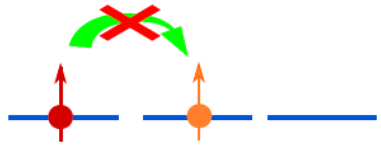
BIPOLARON



SPIN BLOCKING

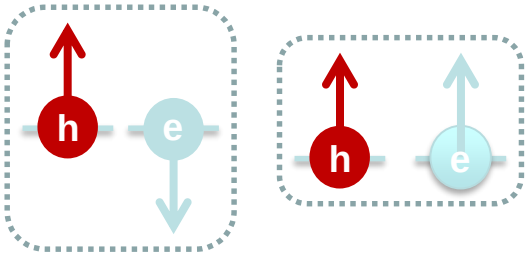


Singlet bipolaron allowed



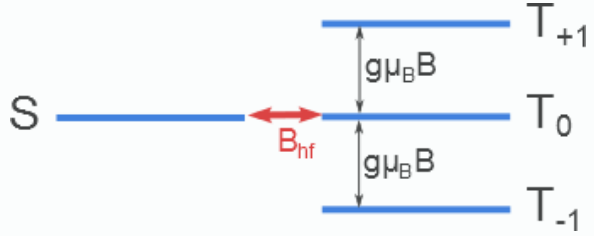
Triplet bipolaron forbidden

Double carriers



Singlet: Recombination/Dissociation

Triplet: Reaction with charge

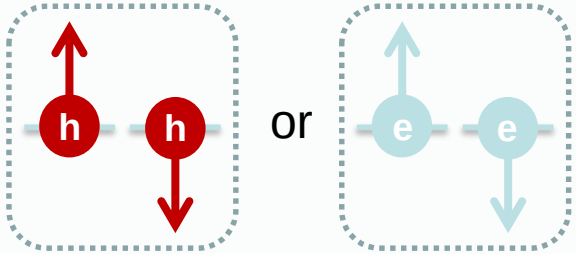


Modified **singlet to triplet ratio**

Theory: Single vs. Double carriers

Single carriers

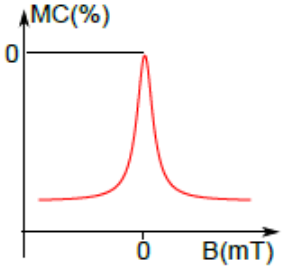
Bipolarons



B decreases the number of bipolarons

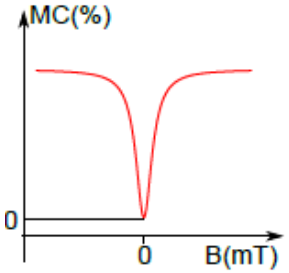
*Bipolaron **lifetime**:*

short



-MC

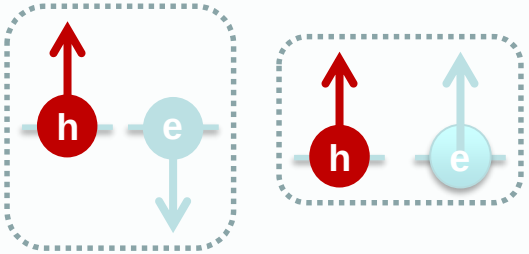
long



+MC

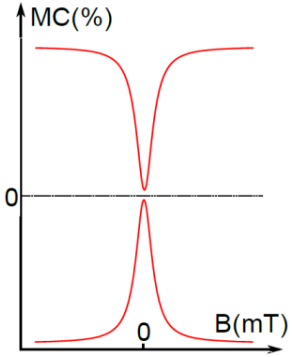
Double carriers

Excitons and e/h pairs



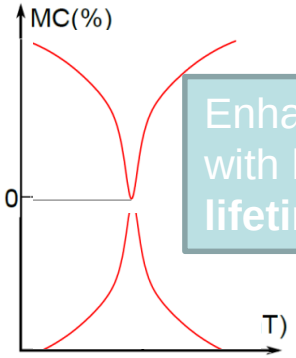
B changes the singlet/triplet ratio

Singlet:
recombination



+MC or -MC

Triplet:
Reaction with charge

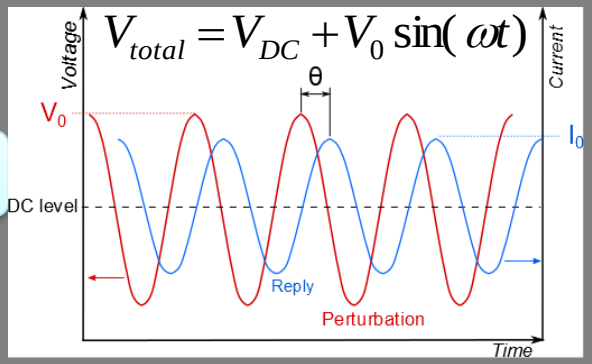


Enhanced with long **lifetime**

+MC or –MC
with HFE

Impedance spectroscopy

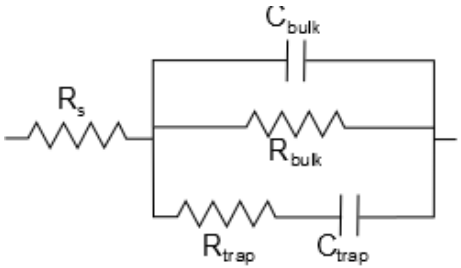
Measurement



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

Equivalent circuit

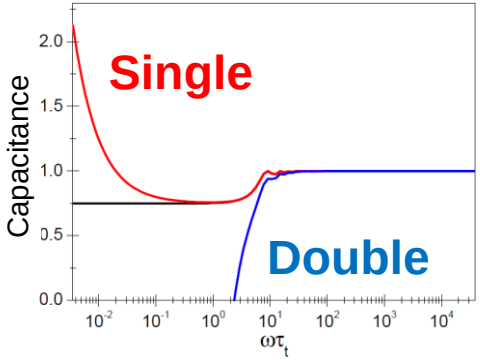
Fitting of the data



Nyquist diagram, Phase.

Give information on electronic processes

Capacitance vs frequency



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

Sign : type of injection

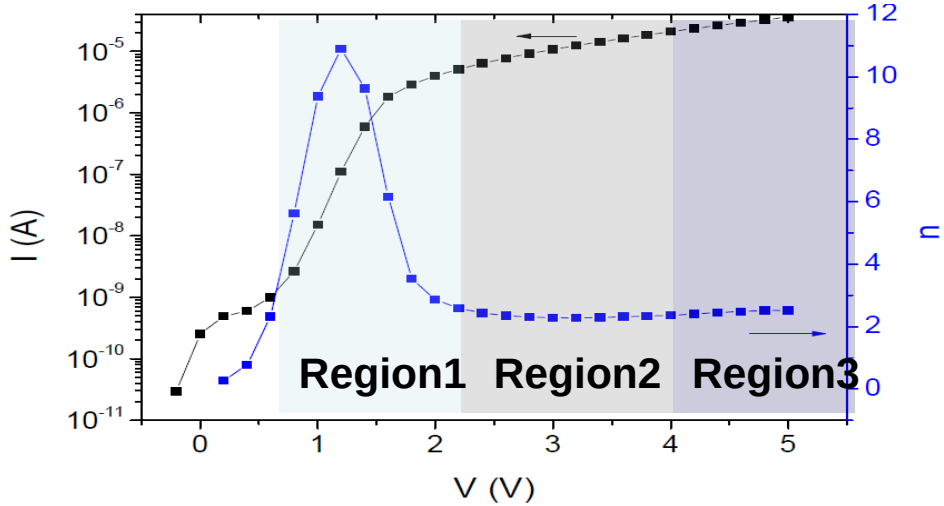
Value: traps characterization

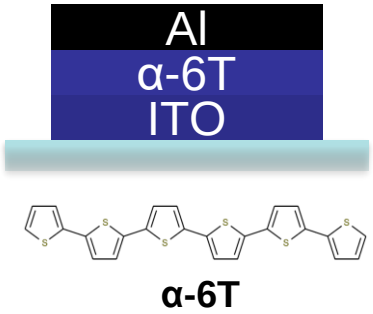
OMAR results

I-V characteristics:

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

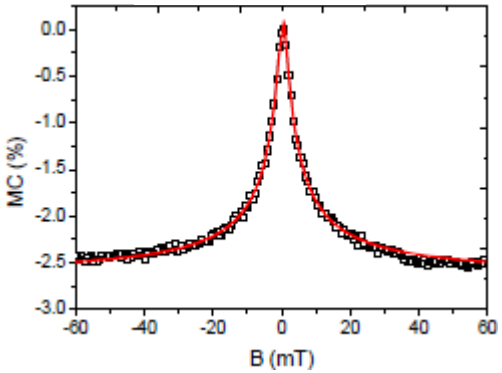
$$MC(\%) = \frac{I(B) - I(0)}{I(0)}$$





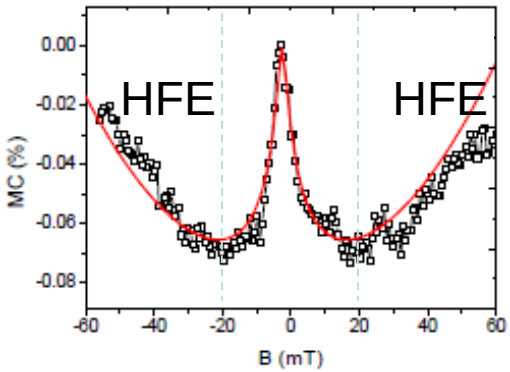
OMAR results:

Region 1



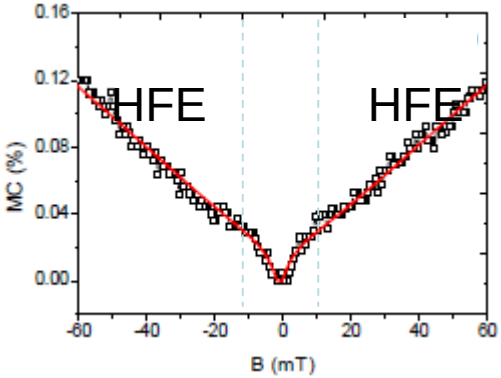
-MC

Region 2



–MC with HFE

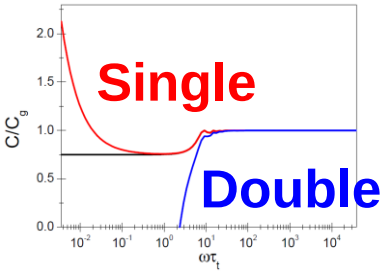
Region 3



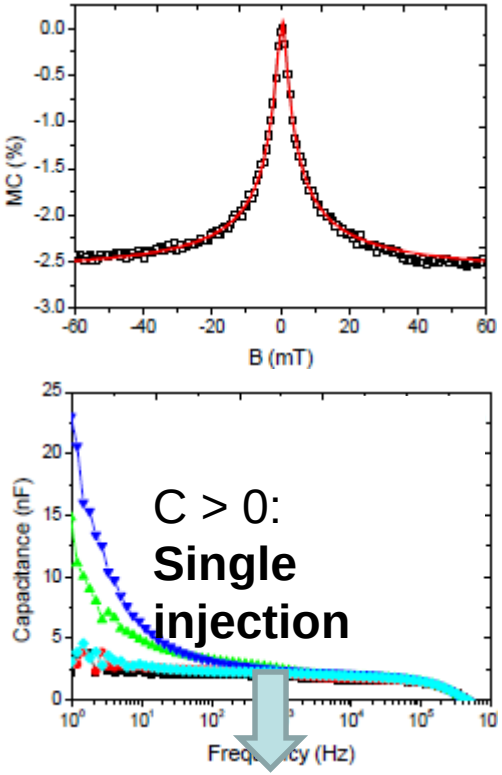
+MC with HFE

How to explain the various OMAR shapes?

Capacitance results



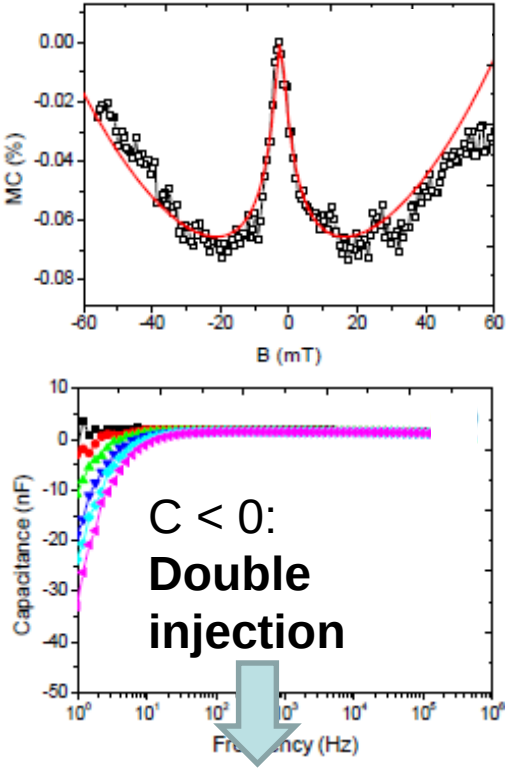
Region 1



Bipolaron OMAR

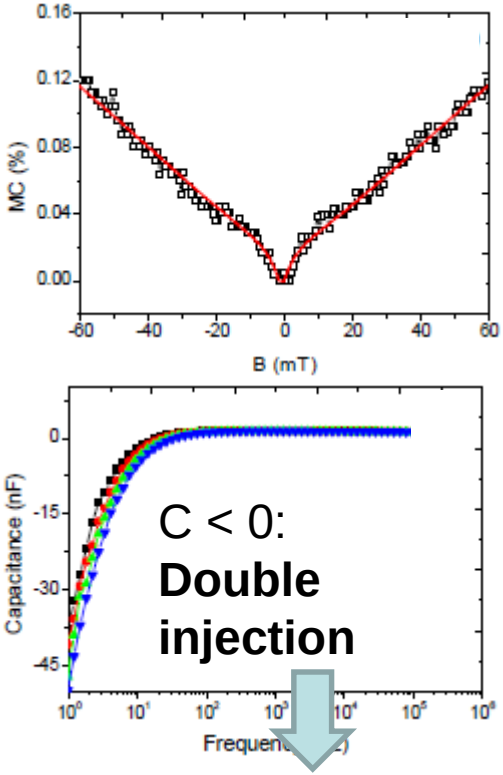
Negative OMAR

Region 2



Transition: double + single carriers OMAR mix

Region 3



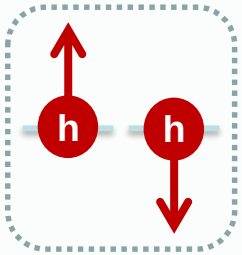
Double carriers OMAR

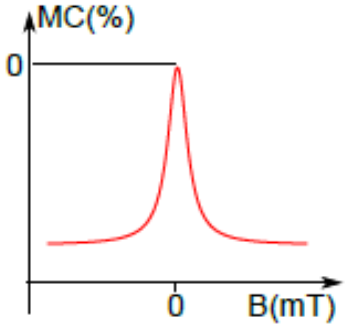
Positive OMAR

Summary

Single carriers

Bipolarons

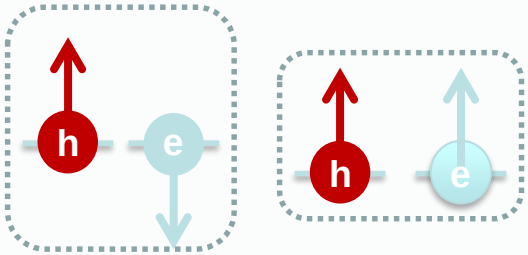


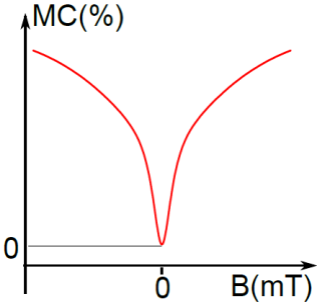


-MC

Double carriers

Excitons and e/h pairs



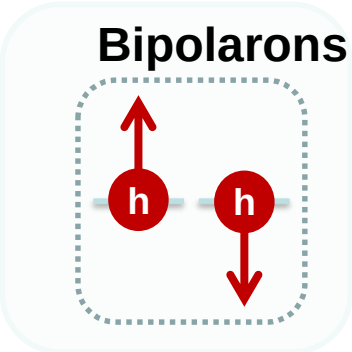


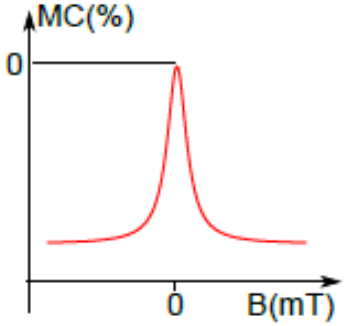
+MC with HFE

The mechanism is identified.

Perspective

Single carriers



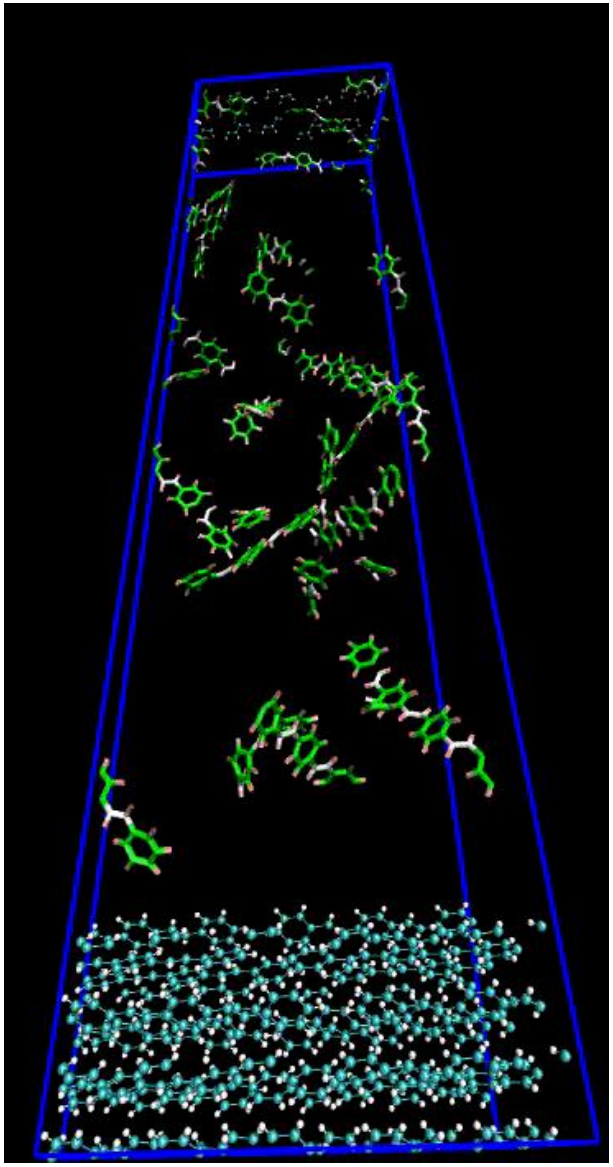


-MC

・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