Electronique moléculaire: état de l'art & perspectives

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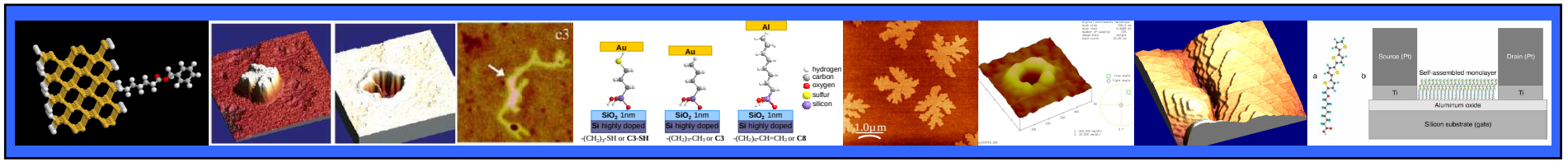
Institute for Electronics, Microelectronics & Nanotechnology – CNRS, Lille

"Molecular Nanostructures & Devices" group



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Recherche Formation Transfert
U.M.R. C.N.R.S. 9929

CNRS
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Plan

- Définition, quelques repères historiques
- Principes de base, structure et transport électronique dans une jonction moléculaire
- Exemples de composants à l'échelle moléculaire

Definition, introduction, foundations of the field

- “Information processing using photo-, electro-, iono-, magneto-, thermo-, mechanico or chemio-active effects at the scale of structurally and functionally organized molecular architectures”

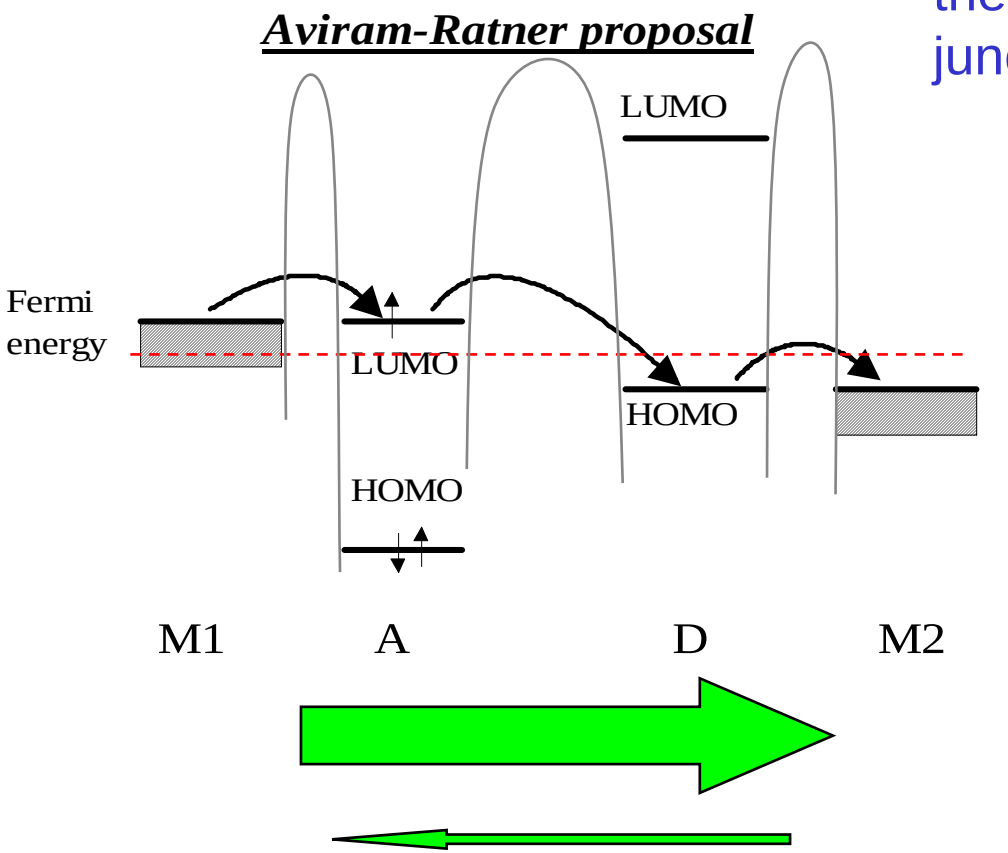
(Adapted from: J.M. Lehn, *Angew. Chem. Int. Ed.,* 1988, Noble Lecture)

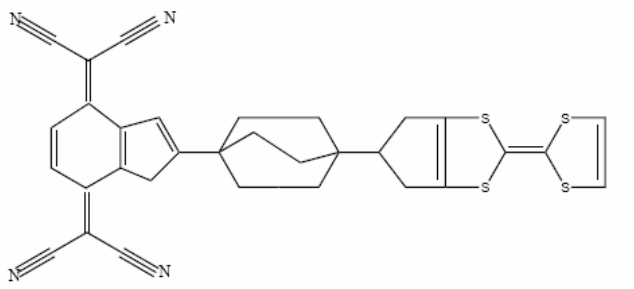
Molecular Electronics
- manipulate and control the position of one or few molecules
- tailor their electronic properties to obtain useful devices

1 molécule - 1 monocouche

Pioneer results

Theoretical suggestion of a molecular analog of the p-n junction: the donor-bridge-acceptor molecular junction.

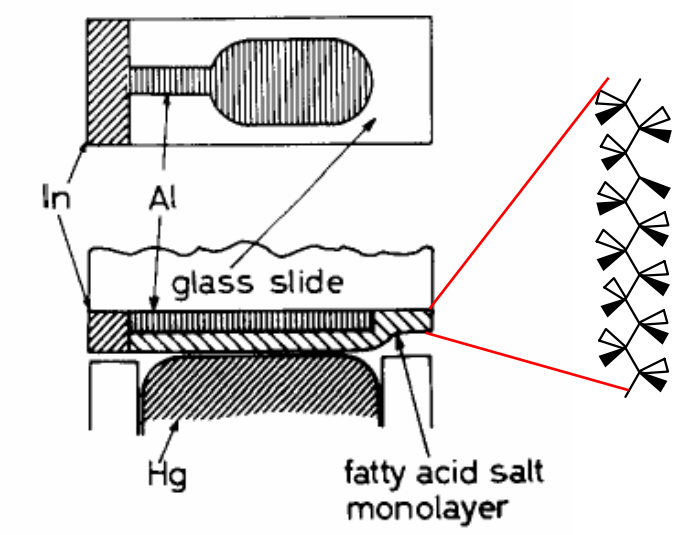


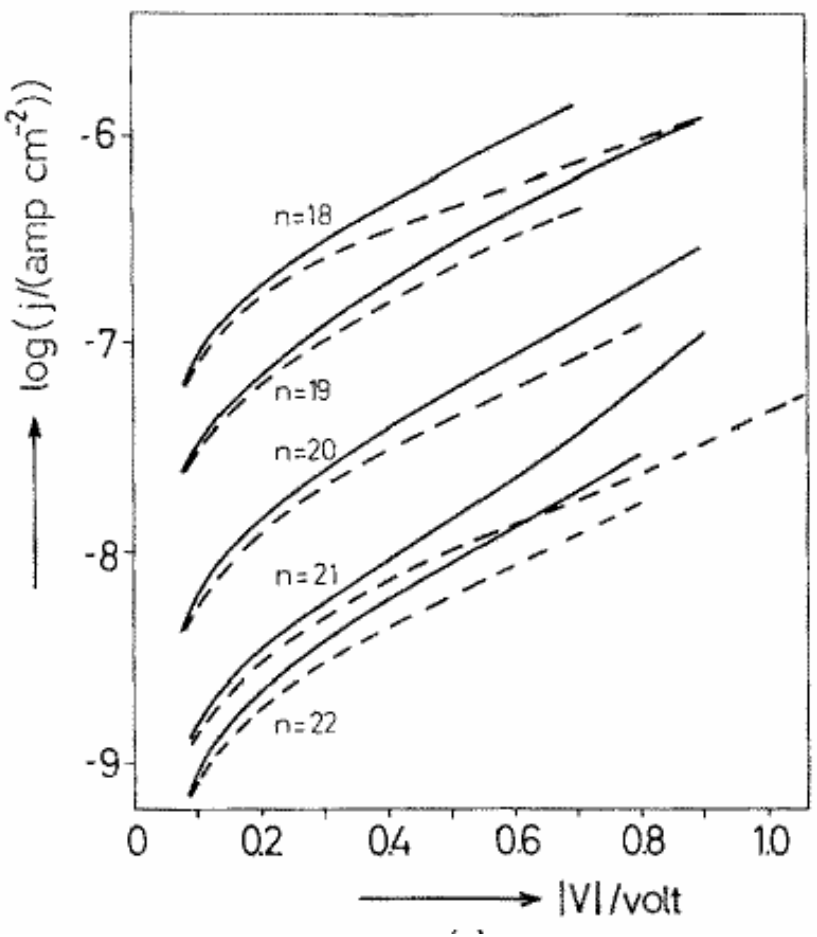


A - σ - D

Aviram & Ratner, Chem Phys Lett (1974)
IBM, New York U.

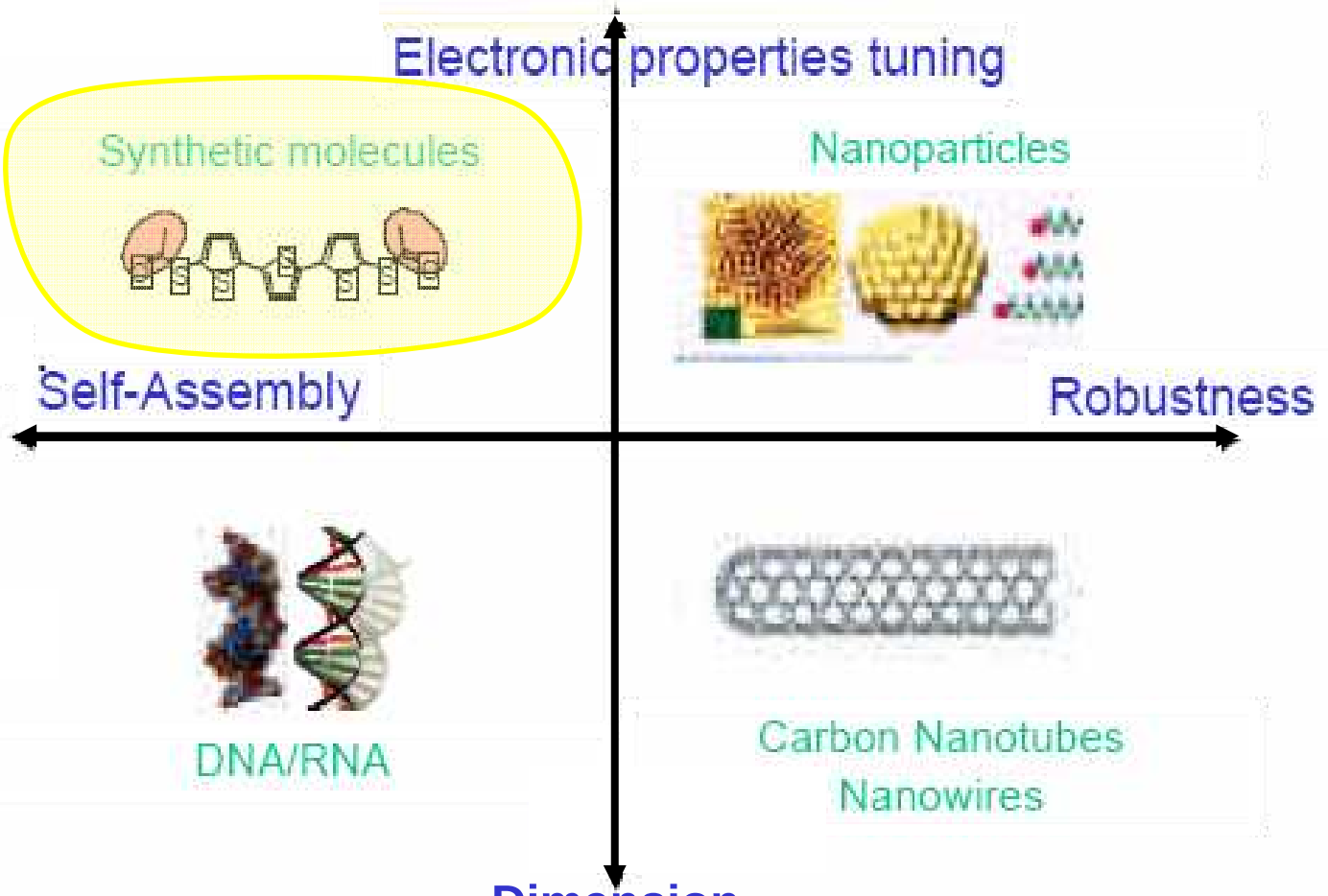
1rst evidence of tunneling through a fatty acid LB monolayer sandwiched between metal electrodes





Mann & Kuhn, JAP (1971)

MPI



tailorable by (bio) chemistry

prone to bottom-up (self-assembly)

providing functions

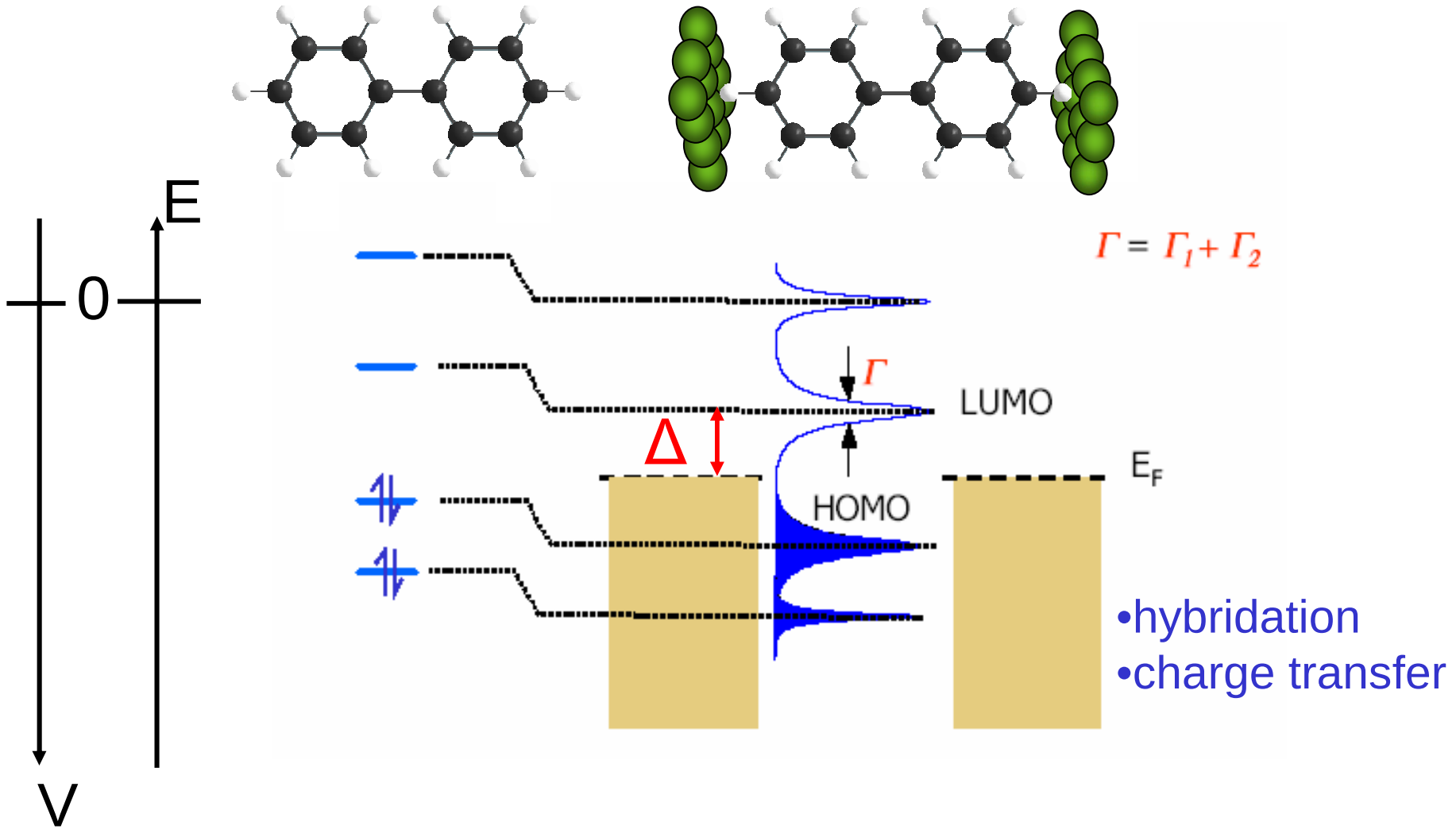
Intrinsically quantum objects

not bound to Von Neuman architecture

Courtesy of J.P. Bourgoin (LEM-CEA)

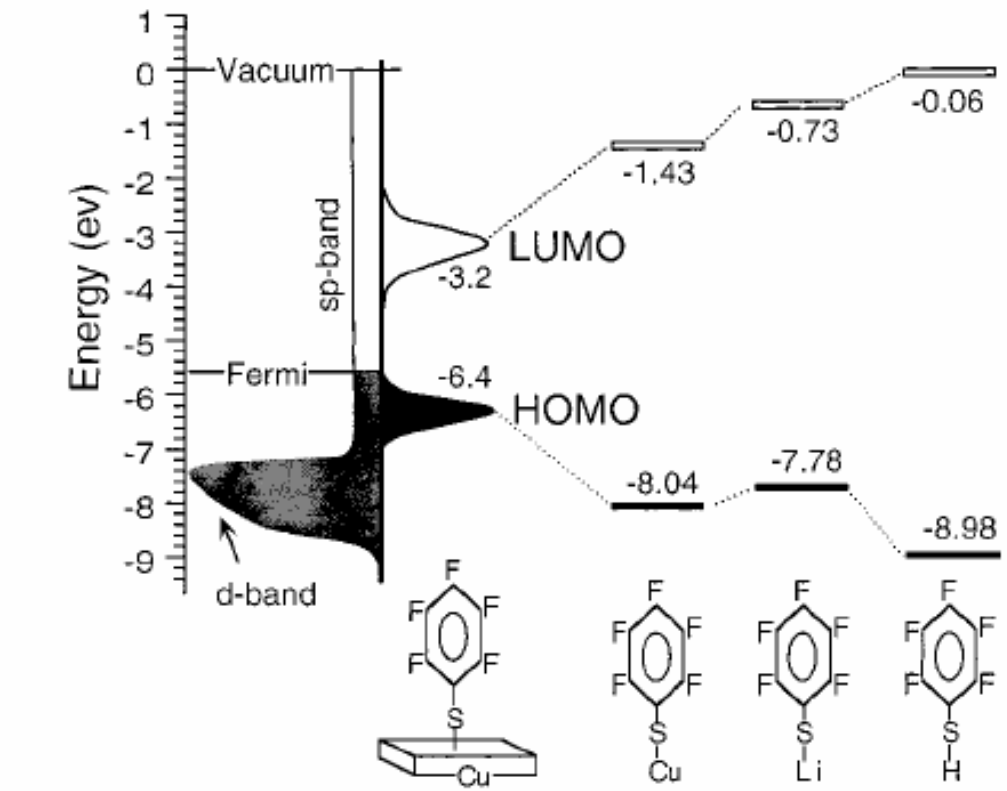
Basic problems : electronic structure, basic devices and electronic transport

Molecule vs.
Metal-Molecule-Metal junction



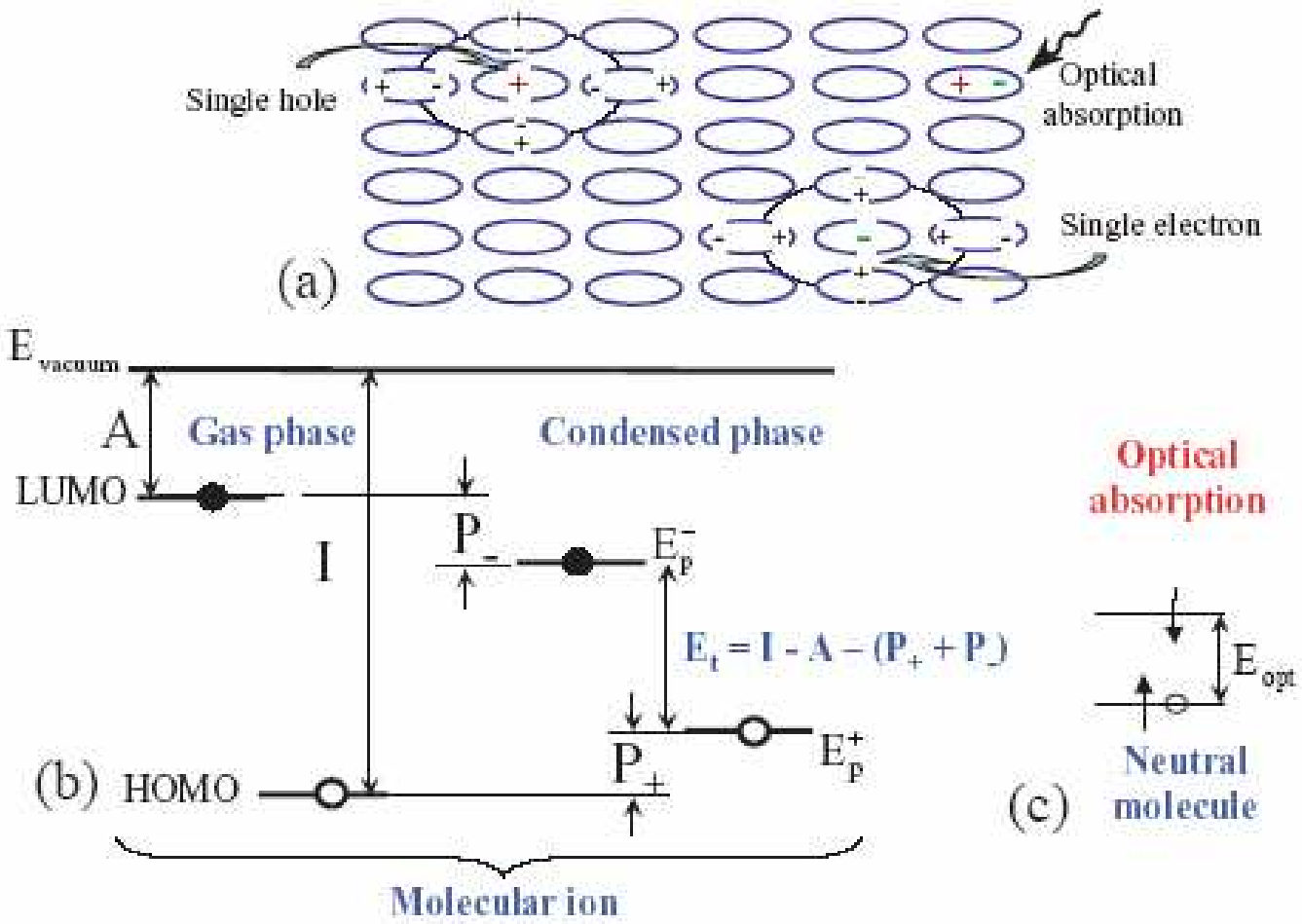
- hybridation
- charge transfer

« L'électronique moléculaire », J.P. Bourgoin, D. Vuillaume, M. Goffman & A. Filoramo.
In "Les nanosciences, nanotechnologies et nanophysique", eds. M. Lahmani, C. Dupas P. Houdy (Belin, Paris, 2004), pp.400-449



Vondrak et al., J. Phys. Chem B (1999)

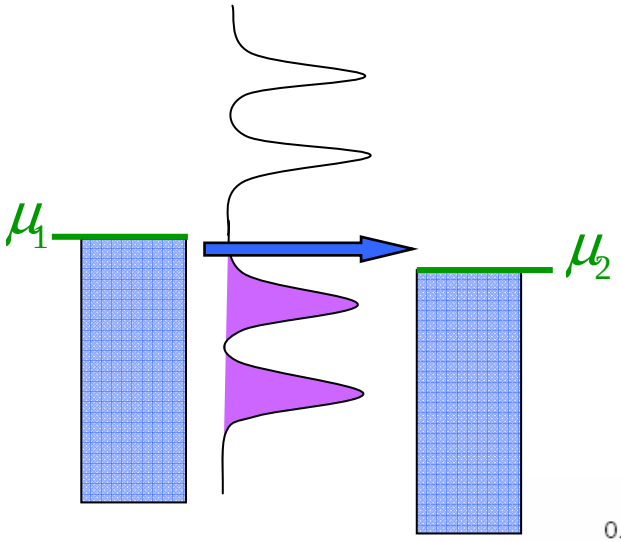
single molecule → ensemble of molecules

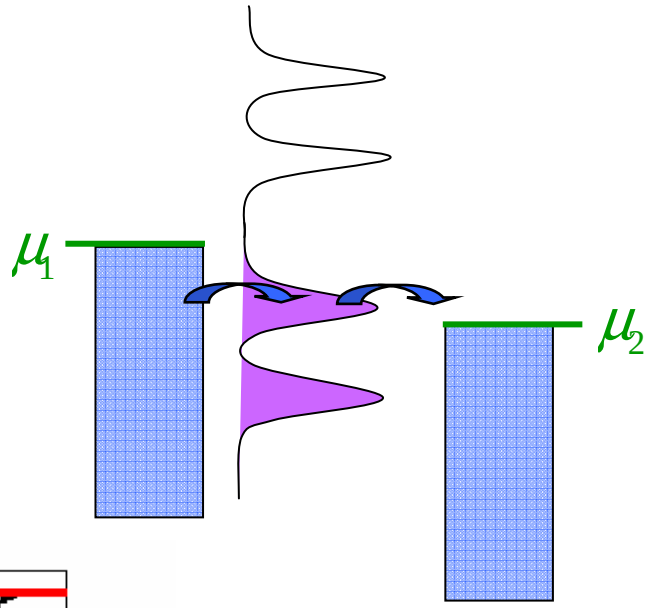


Charge transport, current-voltage

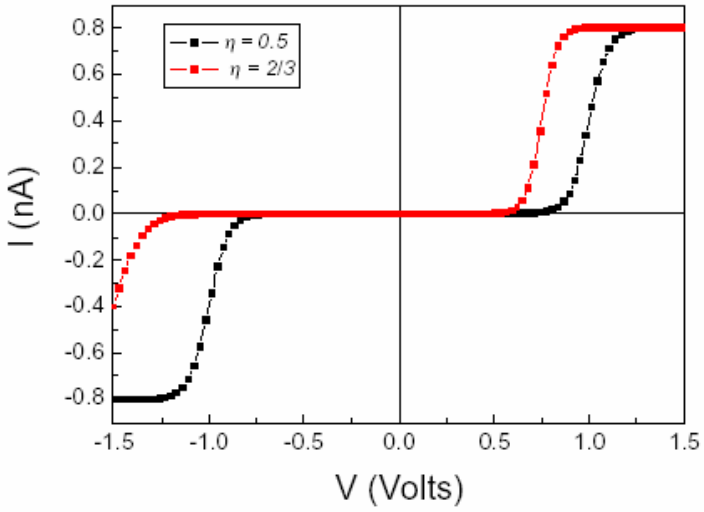
low coupling

$$\mu_1 - \mu_2 = |e|V_g$$

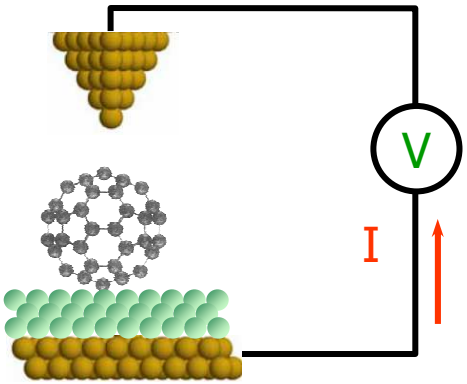


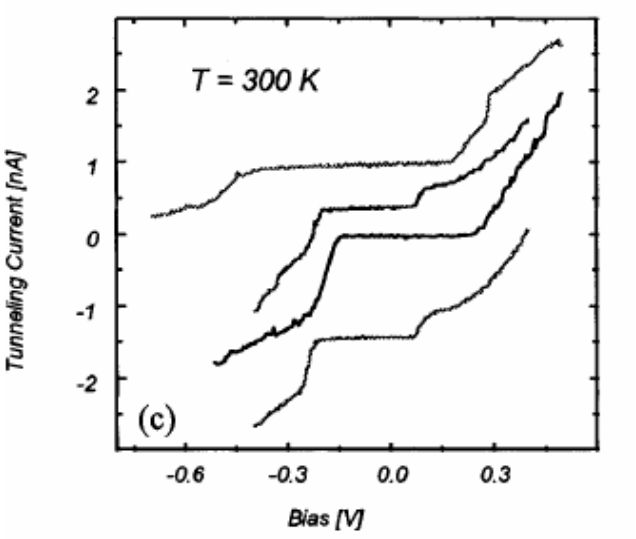


Low bias:
tunnel effect

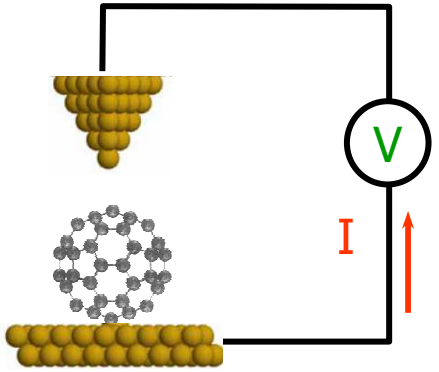


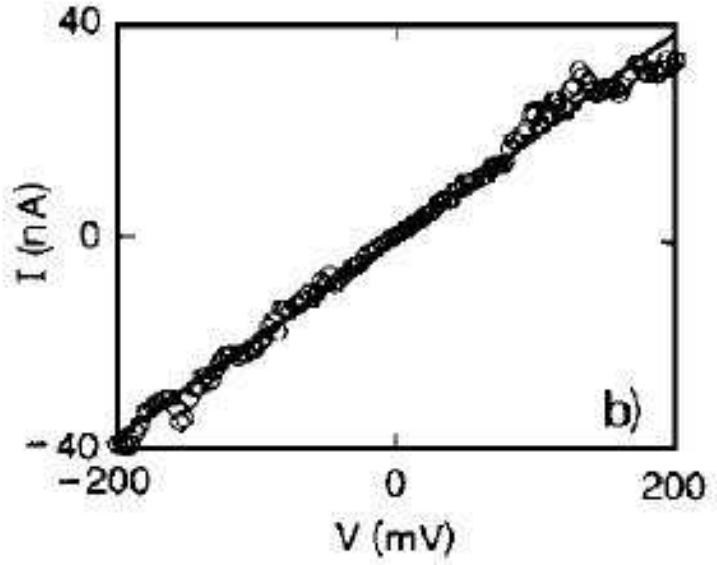
Higher bias:
resonance
through MO





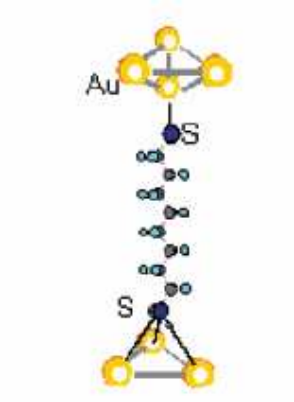
D. Porath et al.
J. Appl. Phys. **81**, 2241 (1997)
Phys. Rev. B **56**, 9829 (1997)





C. Joachim et al.
Phys. Rev. Lett. **74**, 2102 (1995)
Europhys. Lett. **30**, 409 (1995)

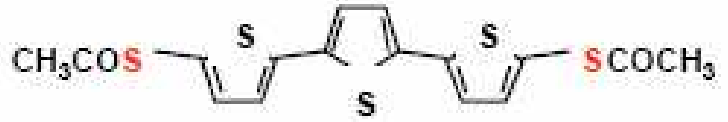
control of the electrode-molecule interface is crucial



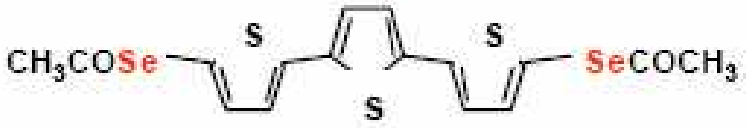
$2.5x10^{-4}G_0$

$0.5x10^{-4}G_0$

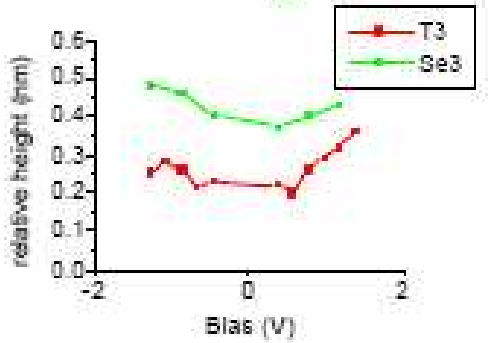
Li et al., JACS (2006)
Arizona U.



T_3



Se_3



Patrone et al PRL 91(2003) 096802

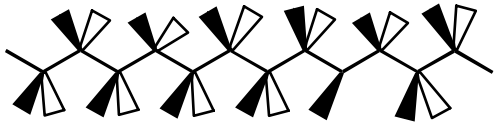
Se vs S
conductance x 25

Patrone et al., Chem Phys (2002)
LEM-CEA

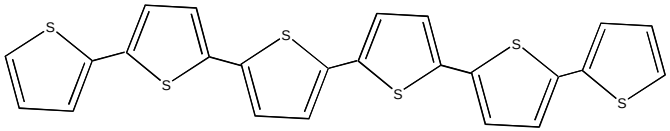
What can we do with molecules ?
Which types of electronic devices?

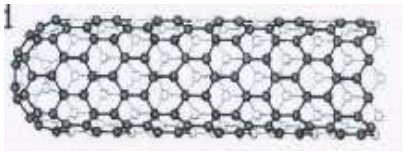
electronic function in molecules

insulator

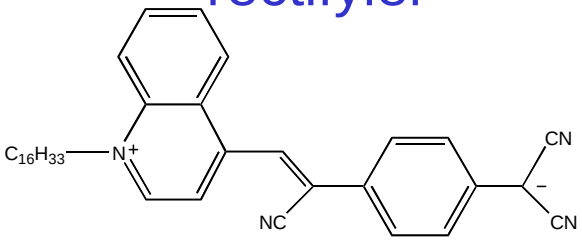


semiconductor/metal

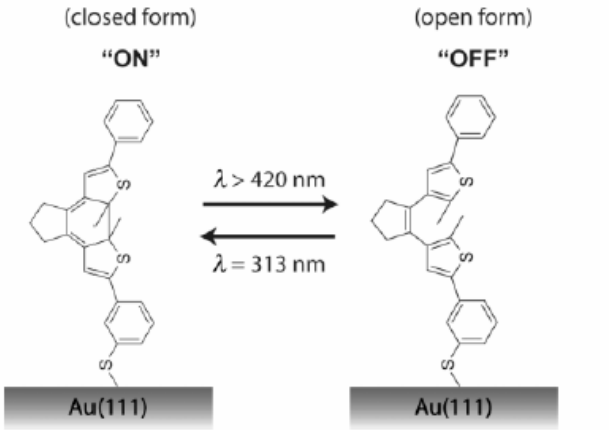




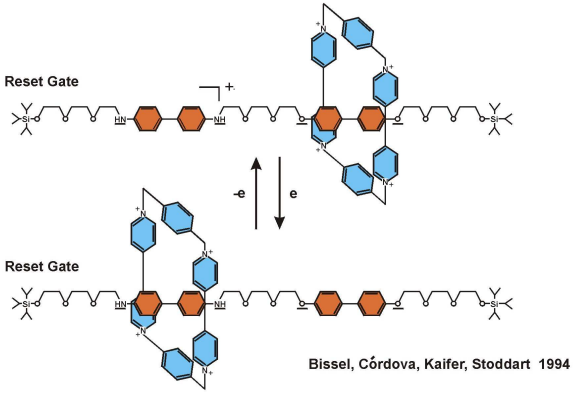
rectifyier



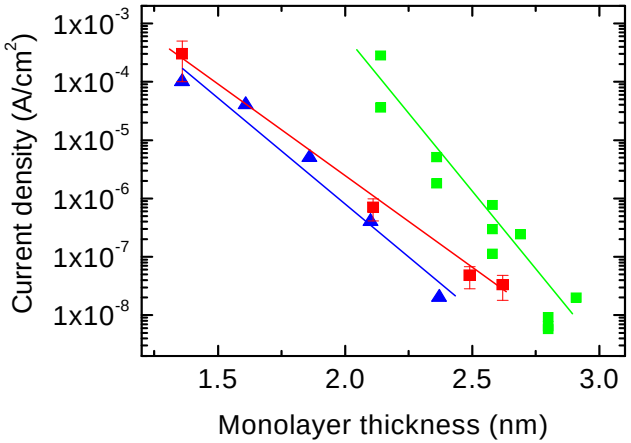
switch



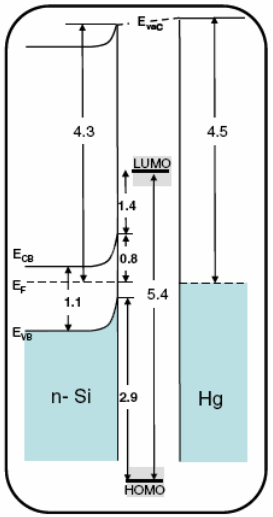
bistable, memory

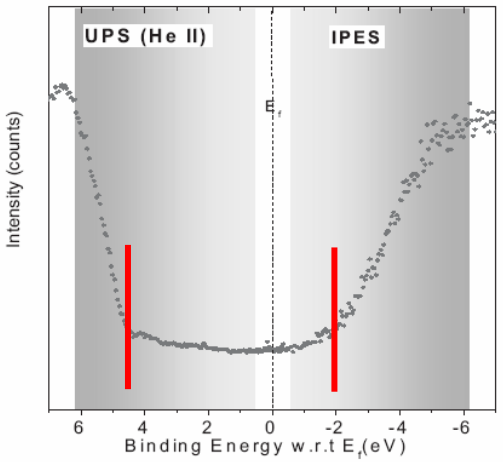


tunnel barrier

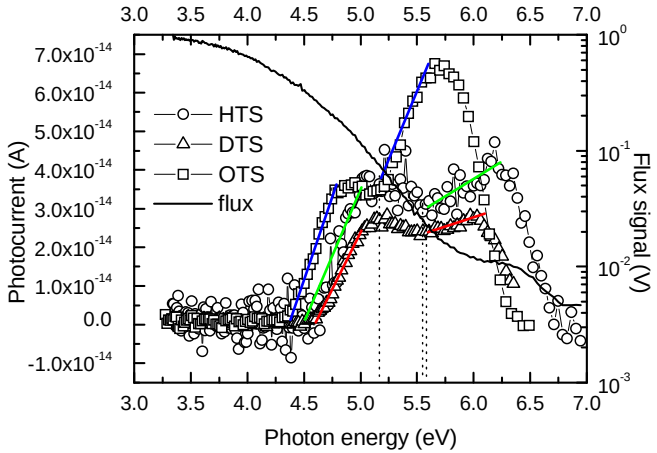


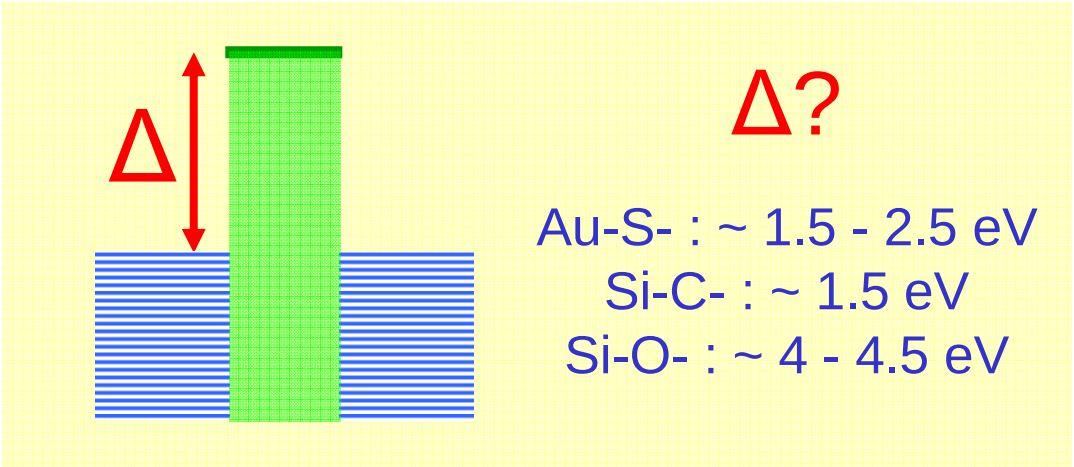
- E.E. Polymeropoulos et J. Sagiv, *J. Chem. Phys.* (1978)
- C. Boulas et al., *Phys. Rev. Lett.* (1996)
- J. Holmlin et al., *J. Am. Chem. Soc.* (2001)
- D.J. Wold et al., *J. Am. Chem. Soc.* (2000,2001)
- X.D. Cui et al., *J. Phys. Chem. B* (2002)





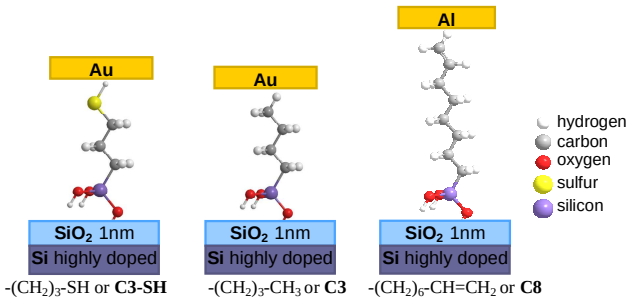
A. Salomon et al., *PRL* (2005); *Adv Mater* (2007)

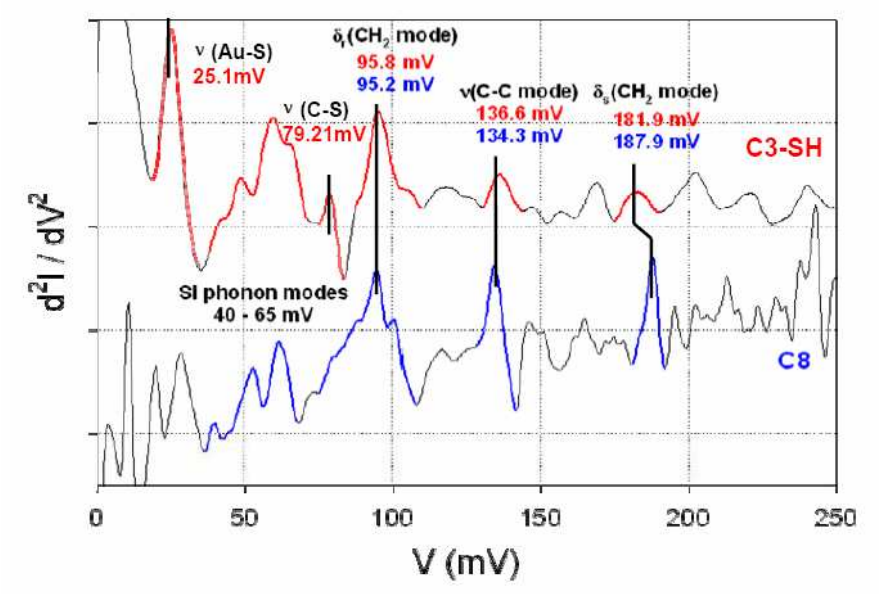




D. Vuillaume et al., *Phys. Rev. B* (1998), *Phys Rev. Lett.* (1996)

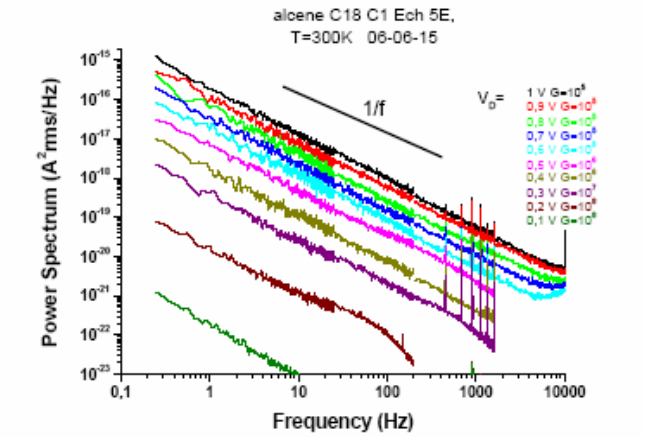
Couplage electron-vibration moléculaire IETS

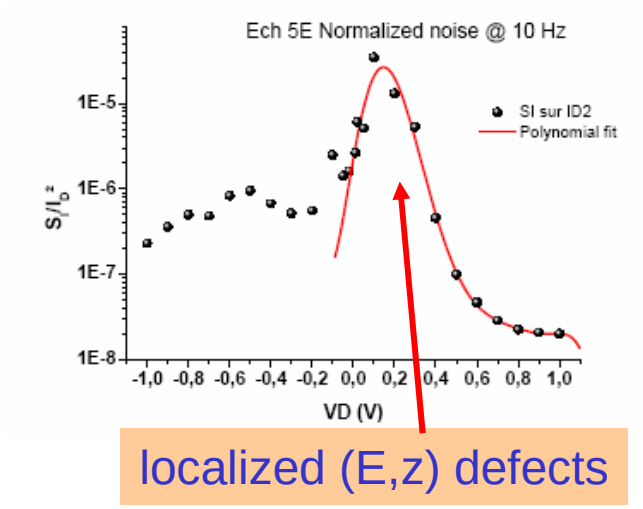




S. Lenfant et al. *Phys. Stat. Sol. a* (2006), **IEMN-CNRS**
Kushmerick et al. *Nano Lett.* (2004), **NIST**
Wang et al. *Nano Lett?* (2004), **Yale**

fluctuations, bruit



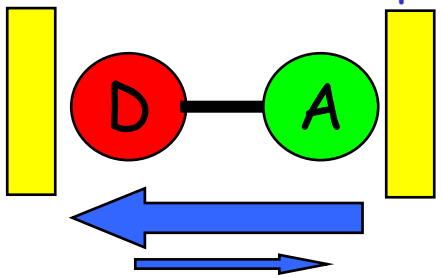


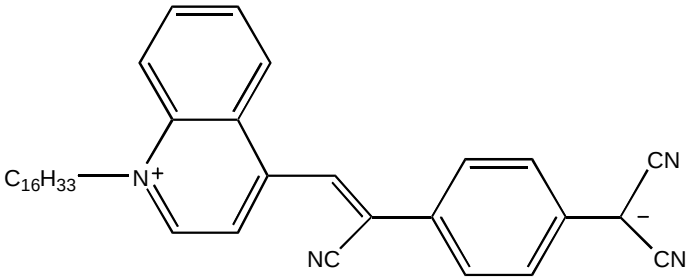
localized (E,z) defects

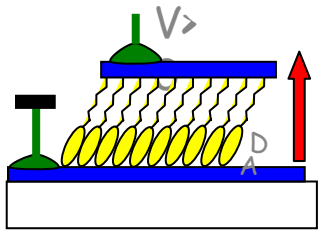
N. Clement et al., *PRL* (soumis)
IEMN-CNRS & Weizmann

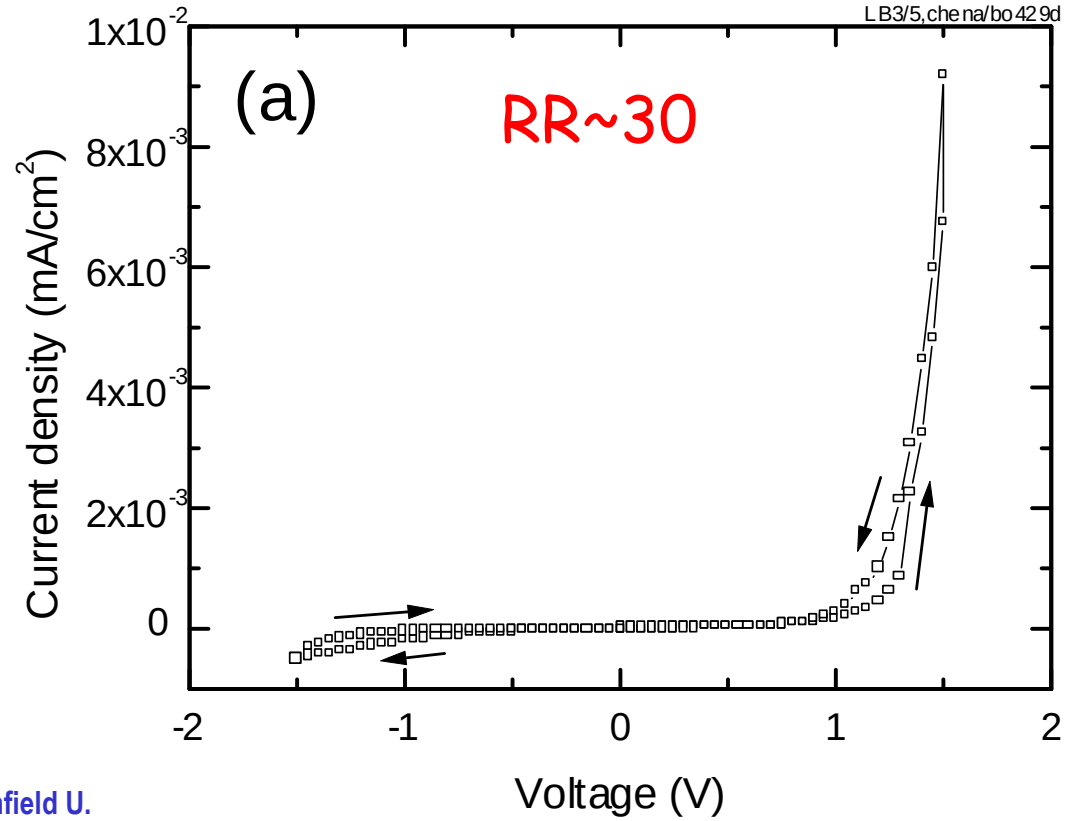
molecular rectifying diode

Aviram & Ratner concept (1974)



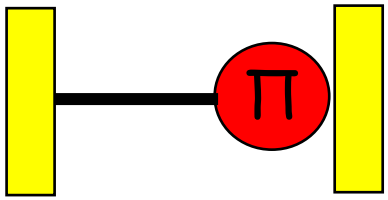


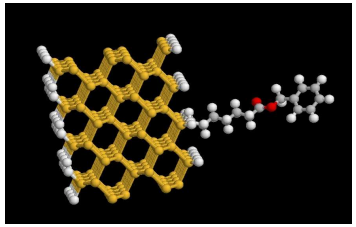


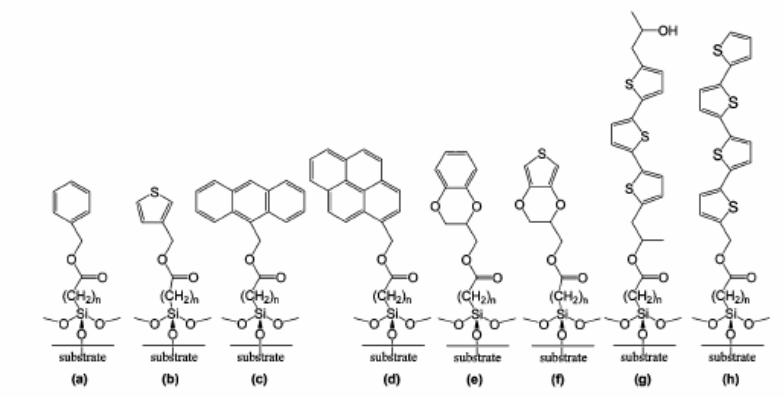


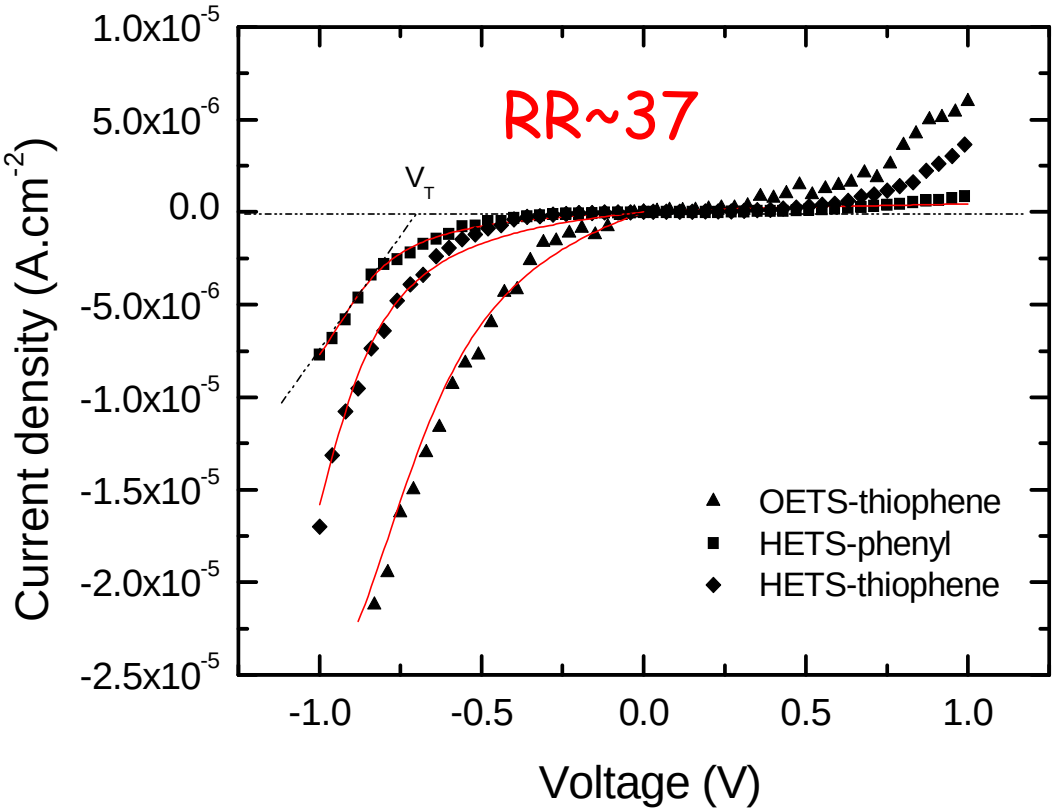
A.S. Martin et al., *Phys. Rev. Lett.* (1993), **Cranfield U.**
R.M. Metzger et al., *J. Am. Chem. Soc.* (1997), **Alabama U.**
D. Vuillaume et al., *Langmuir* (1999), **IEMN-CNRS**

simplified concept



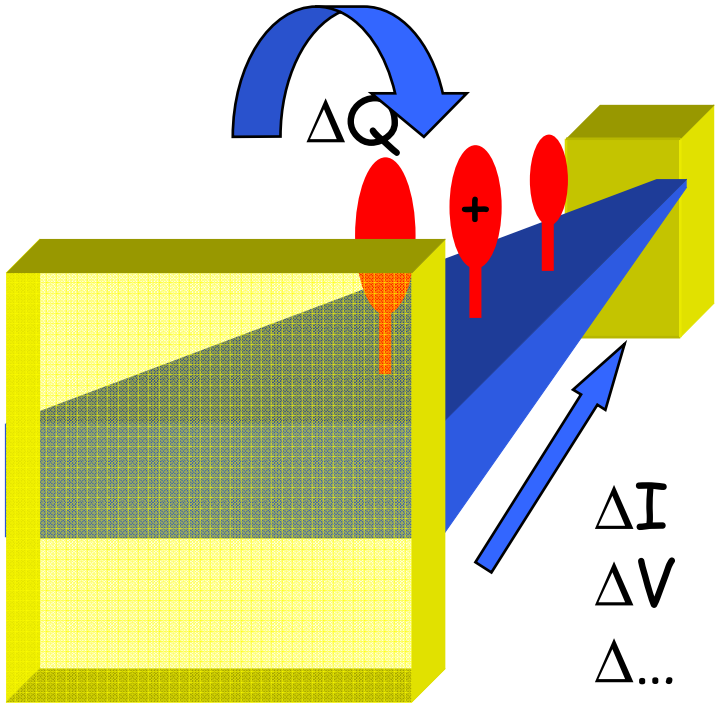


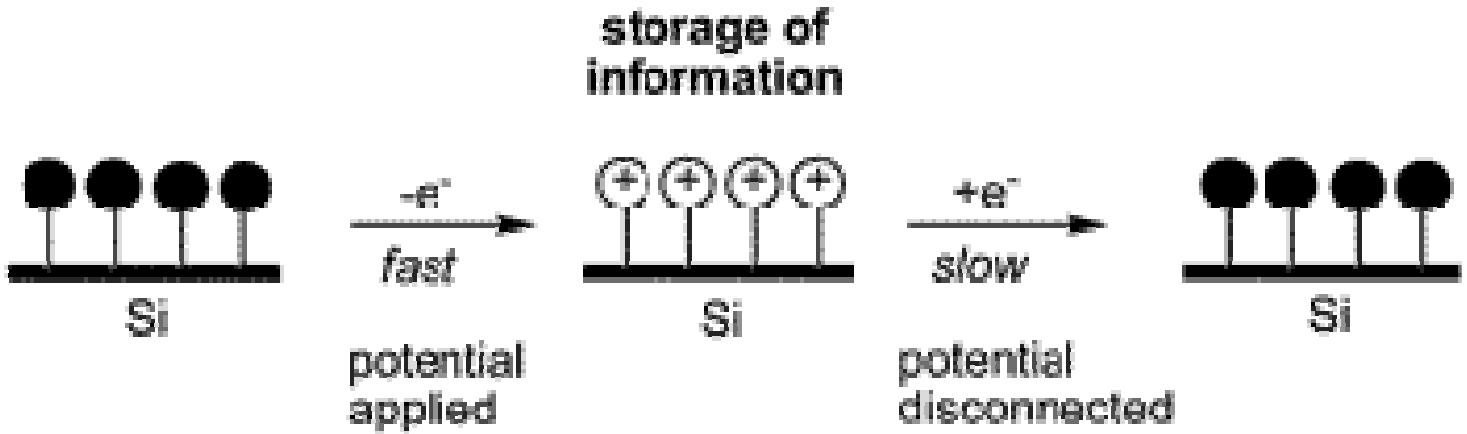




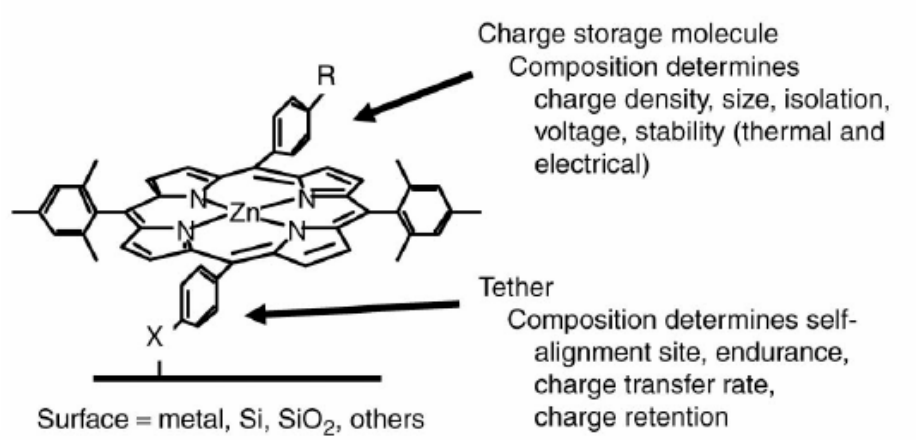
S. Lenfant et al., *Nano Letters* (2003)
D. Vuillaume, *J. Nanosci. Nanotechnol. (*2002)
S. Lenfant et al., *J. Phys. Chem. B* (2006)
IEMN-CNRS

capacitive molecular memory

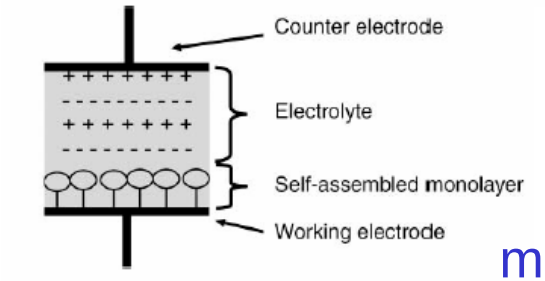




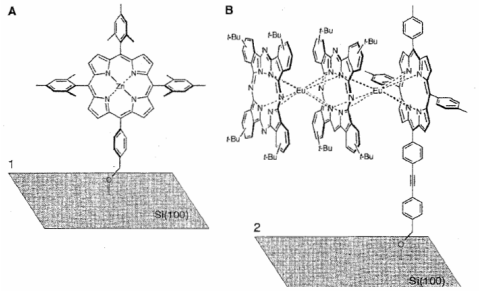
Porphyrin-based SAM on Si-H surfaces

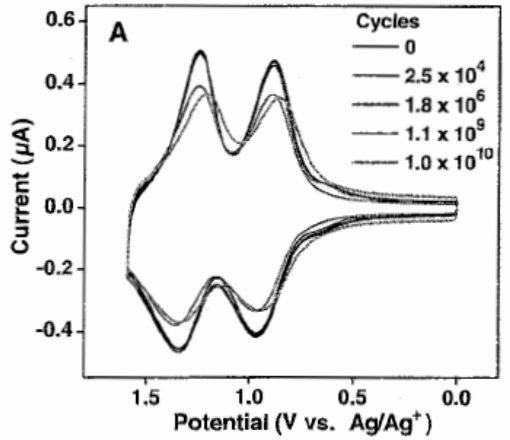


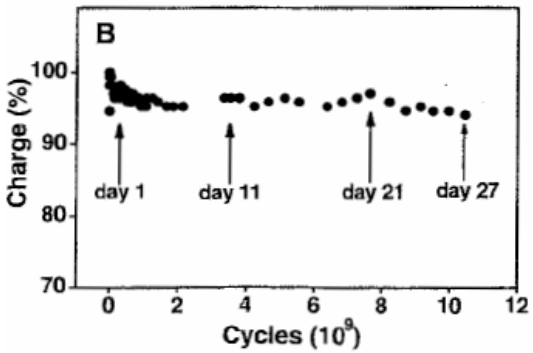
Kuhr et al., MRS Bul (2004)



multi-redox = multi-valued
write ~ 10^{-3} - 10^{-5} s
rentention ~ 100-200 s
r/w cycle : 10^{12}
stable : 400℃ (30min, inert atm)
charge density ~16 μC/cm^2



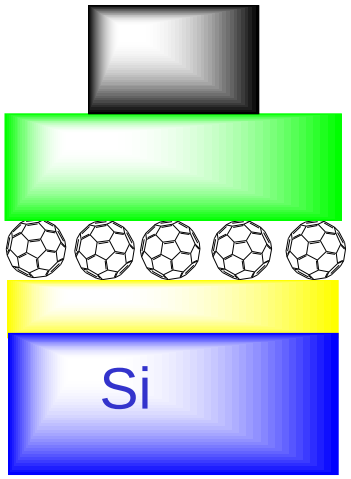




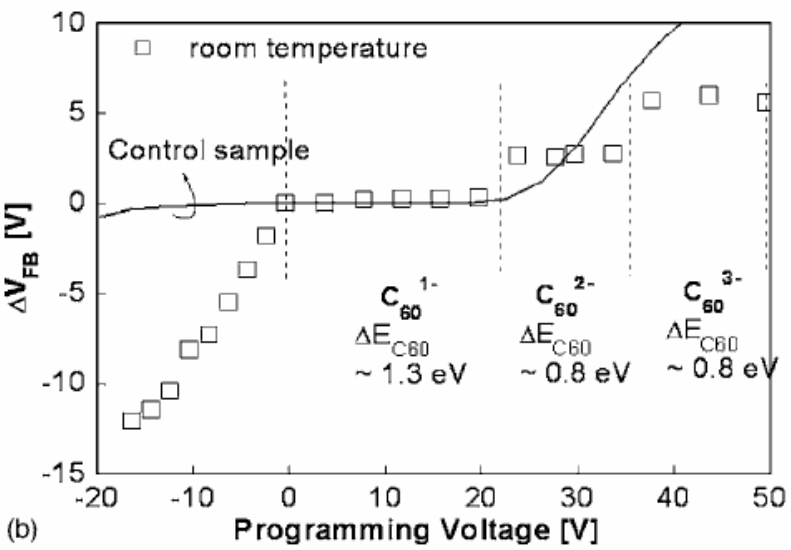
Liu et al., science (2003)

U. California Riverside, North Carolina & ZettaCore Inc (2002)

Mémoire moléculaire capacitive

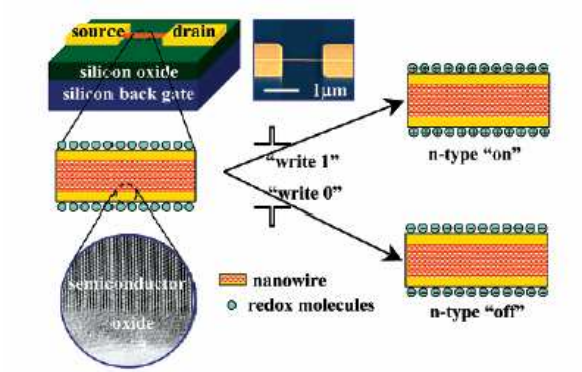


Al_2O_3 (ALD), 30 nm
SiO_2 (PECVD), 26 nm
C60, 1ML
SiO_2, 2 nm

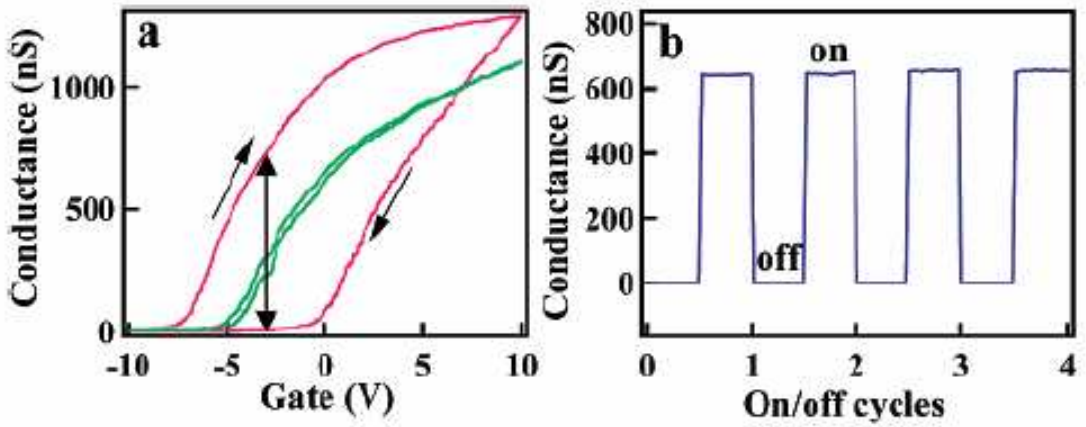


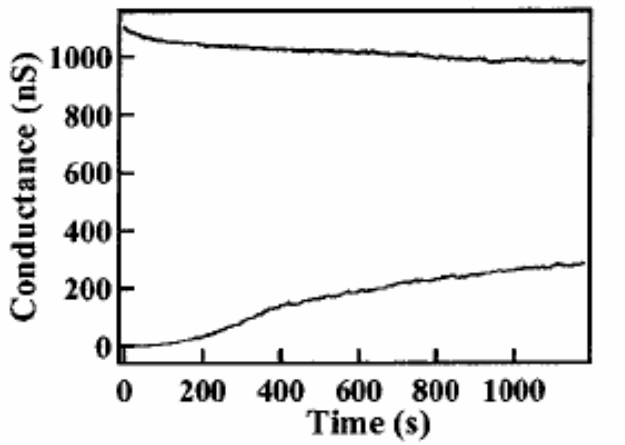
Hou et al., *APL* (2006)
Cornell

functionalized NW memory



InP (10-30 nm) + Co phthalocyanine

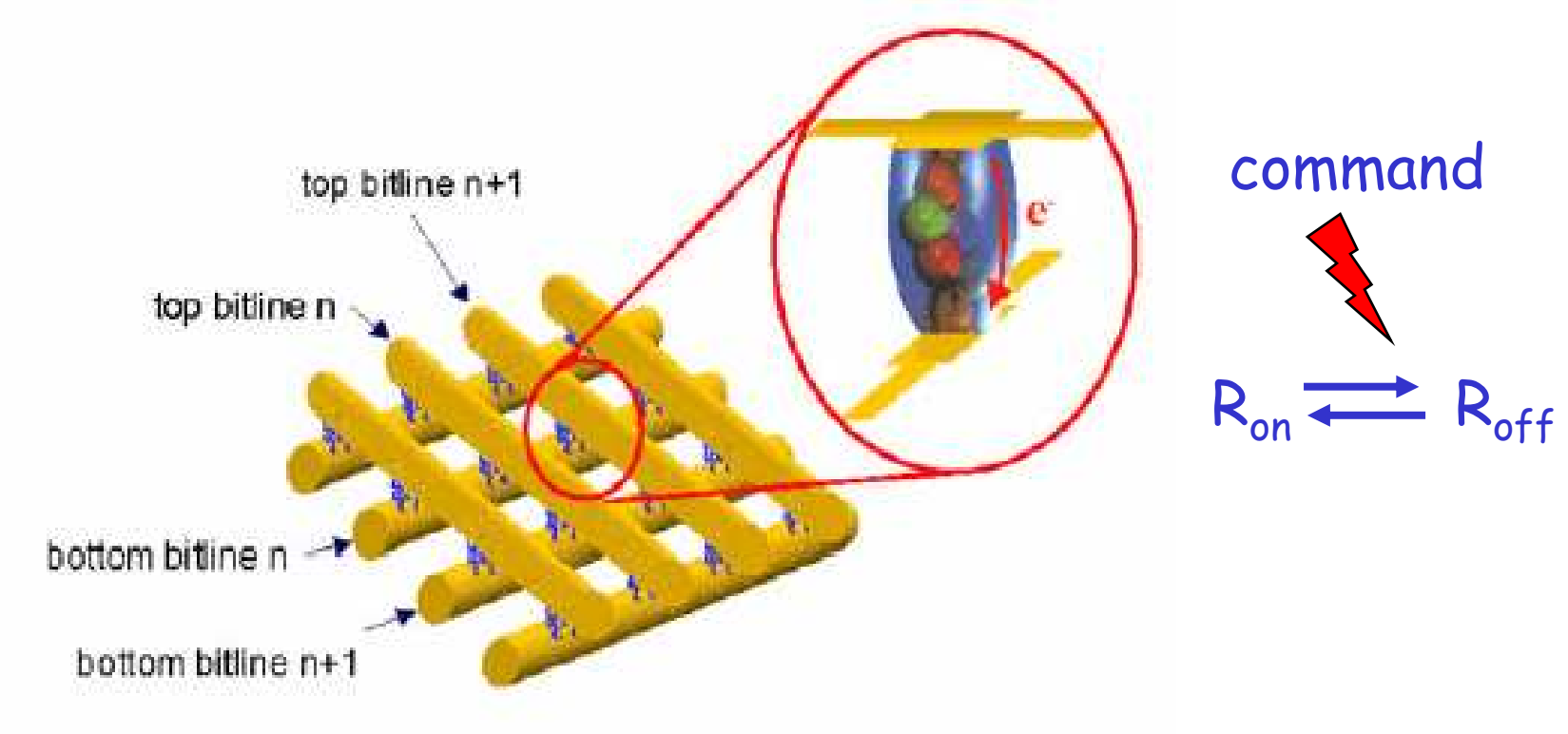


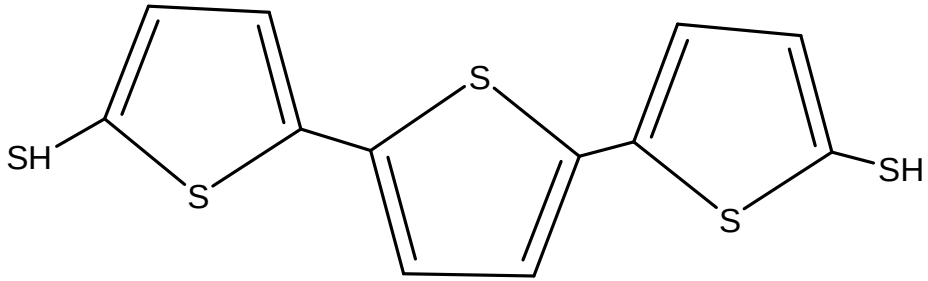


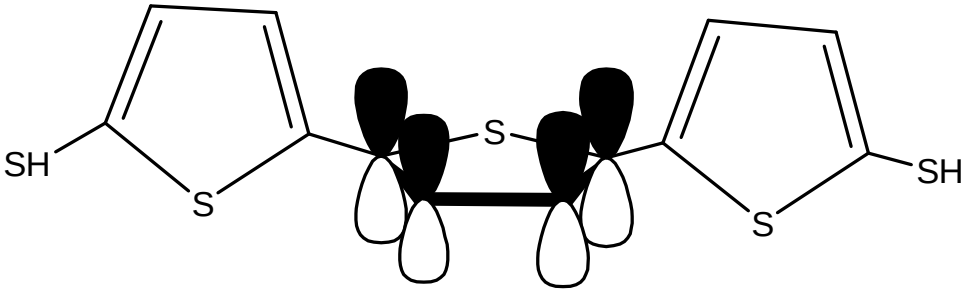
on/off ~10^4
write ~ ?? s
rentention ~ 20min - 600h
r/w cycle : ??
stable : ??

Duan et al., Nano Letters (2002)
Harvard Univ

resistive molecular memory

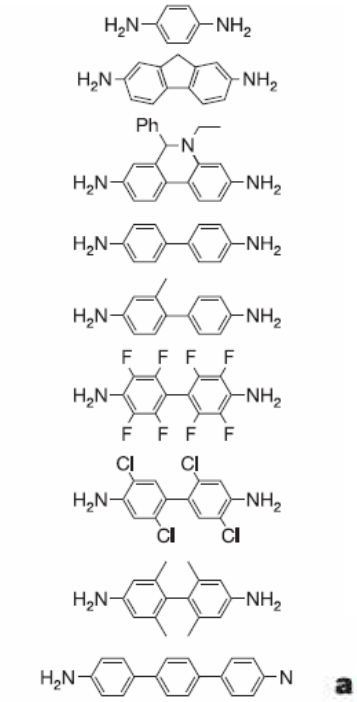


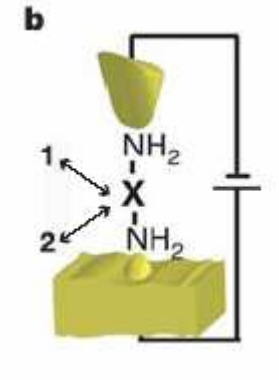


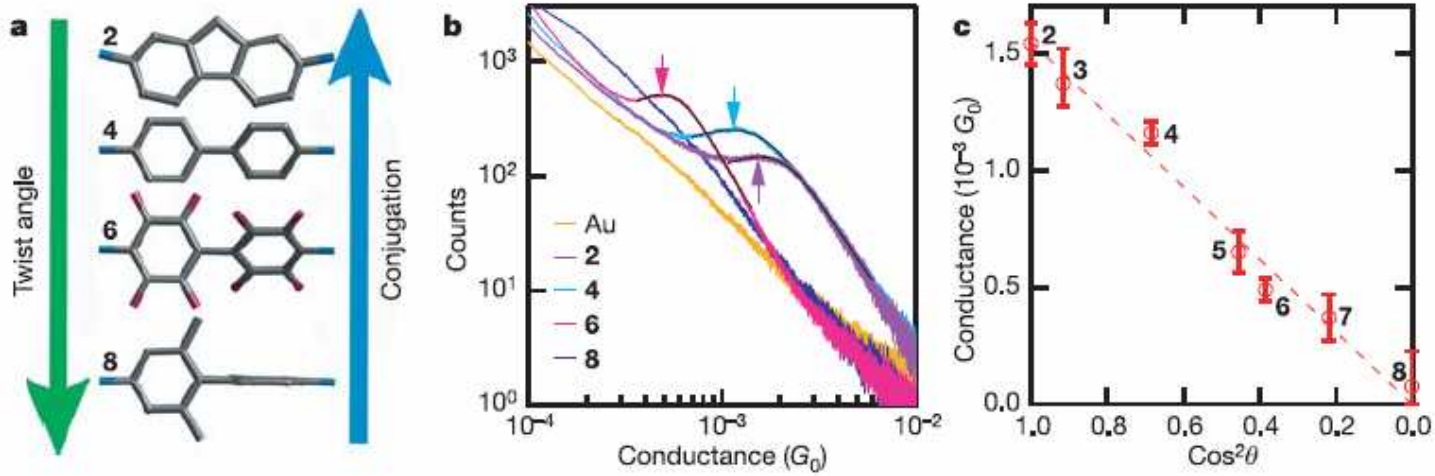


$$G_{plane} > G_{twisté}$$

$$G \sim G_0 \cos^2\theta$$

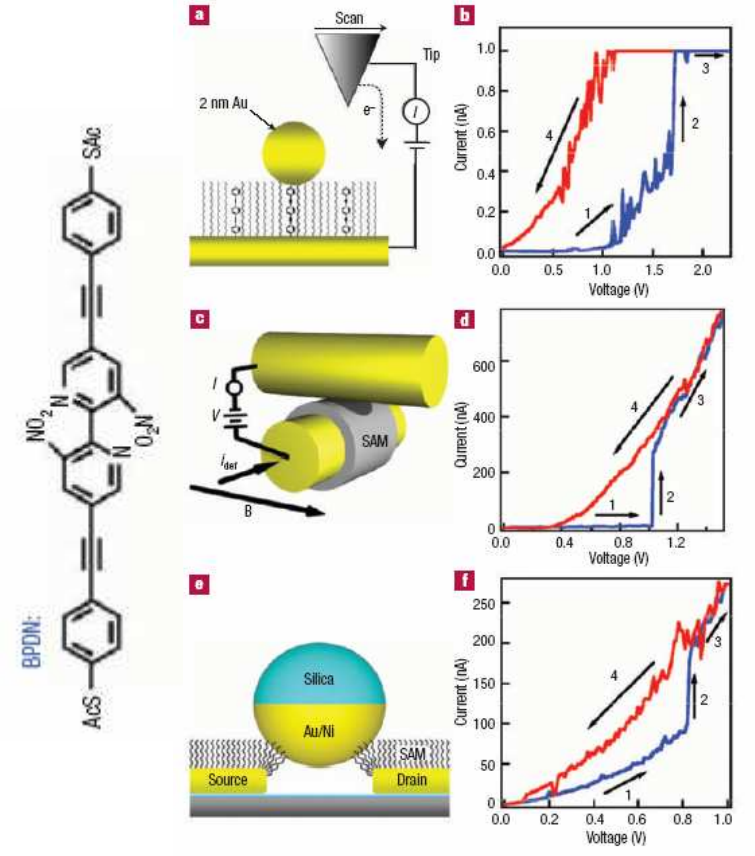






Vankataraman et al., Nature (2006)
Columbia

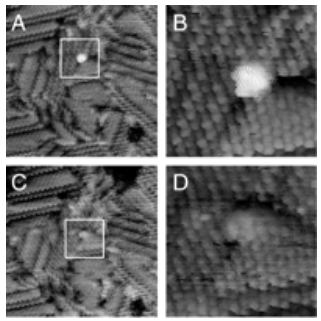
several attempts…

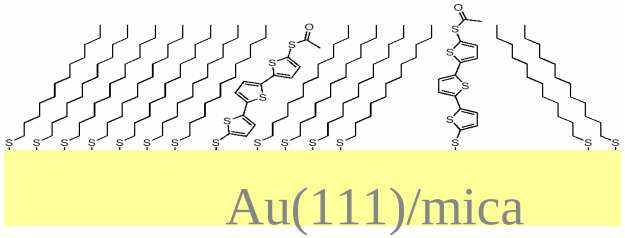


Clear demonstration of bias induced switching again with significant statistical fluctuations

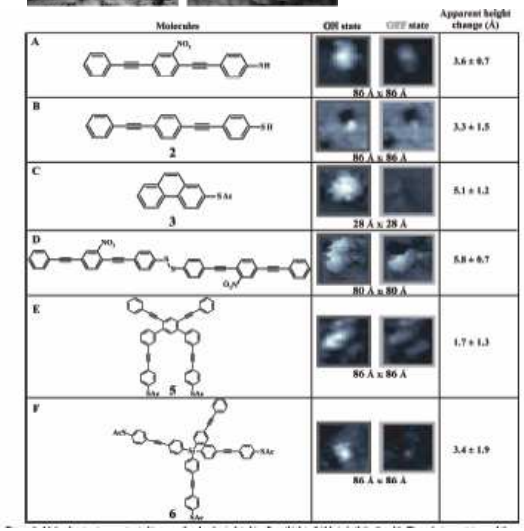
A. Szuchmacher Blum et al.,
Nature Mater. (2005)
NRL, Rice, Geo-Centers

Stochastic Switching:
Conformation change?
Weiss et al Science 2003
Or thiol bond
breaking/reforming ?
Lindsay et al Science 2003





Donhauser et al., Science (2001)
Penn State & Rice U.

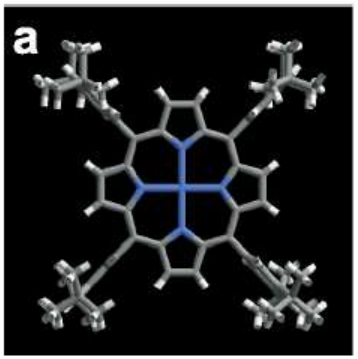


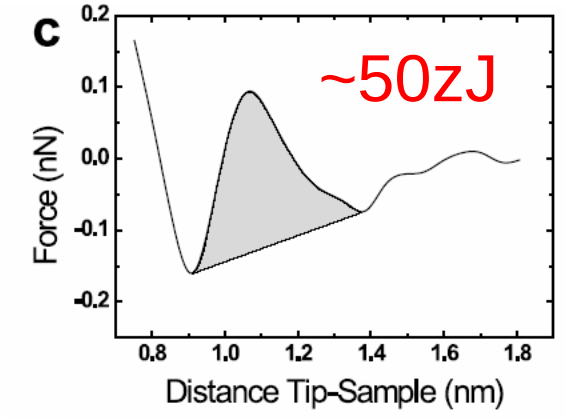
Moore et al.
JACS (2006)
Penn State & Rice U.

avoid thiol on gold !

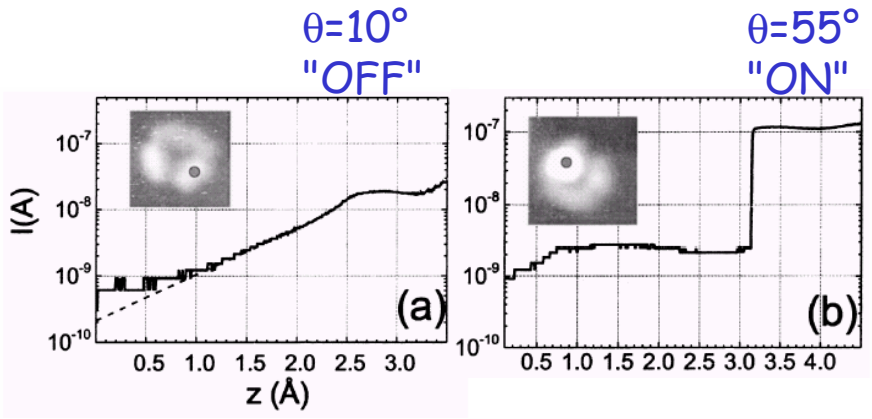
Au-S	~180kJ/mol	~1.8eV
Si-Si	~326kJ/mol	~3.3eV
Si-C	~451kJ/mol	~4.7eV
Si-O	~800kJ/mol	~8.3eV
NH_2/Au	less sensitive to local structure coupling through N lone pair	

Very low energy





Loppacher et al., PRL (2003)
U. Basel, IBM & CEMES-CNRS



F. Moresco et al., Phys. Rev. Lett. (2001)
U. Berlin & CEMES-CNRS

- CMOS FET : 0.1-1 fJ
- mol switch : 50 zJ
- kTLn2=2.8 zJ (@300K)

~ x10^4

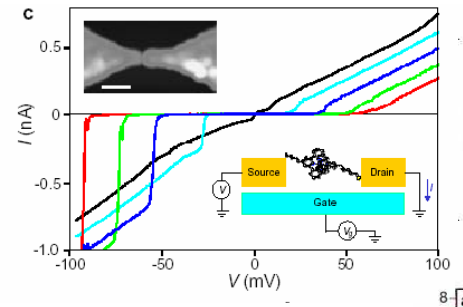
~ x20

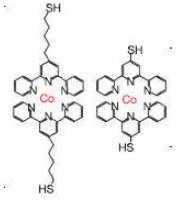
10^{12} "devices" at 1 GHz = 47 W

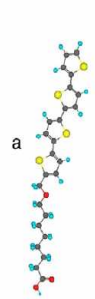
molecular transistor

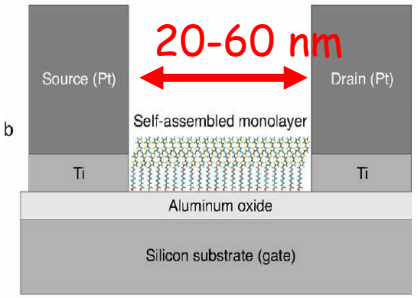
Coulomb blokade
Kondo effect

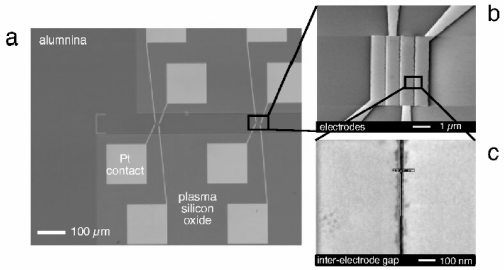
field effect

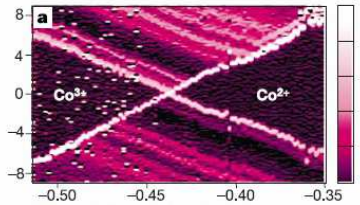


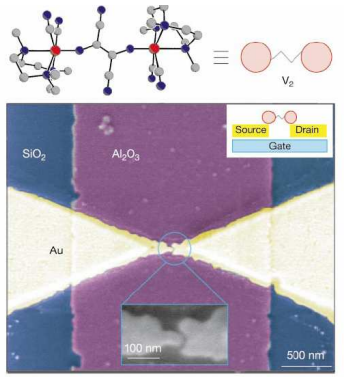


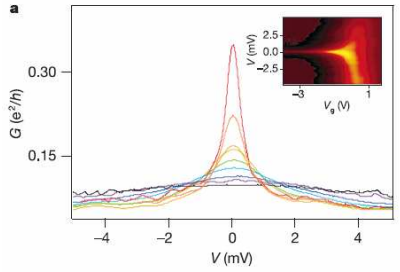


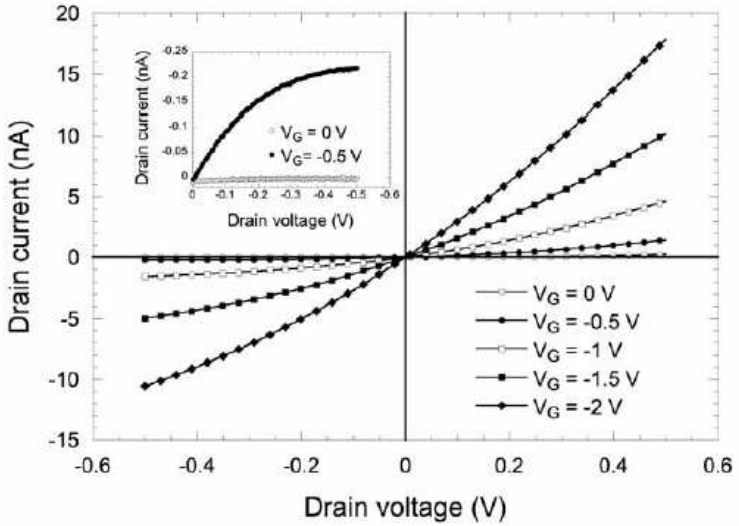












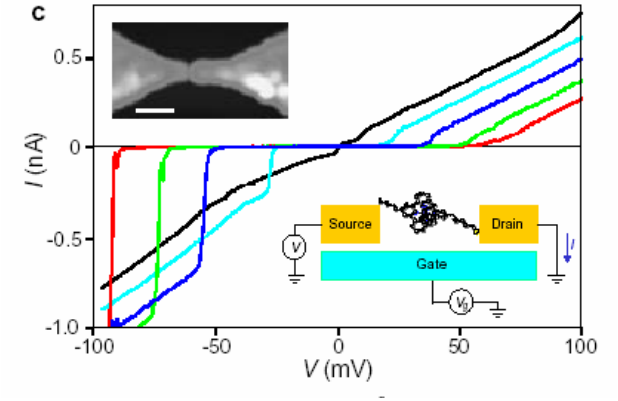
McEuen & Ralph et al. *Nature* 2002
Cornell

Park et al, *Nature* 2002
Harvard

Mottaghi et al. *Adv Func Mater.* **(**2007)
ITODYS, IEMN-CNRS

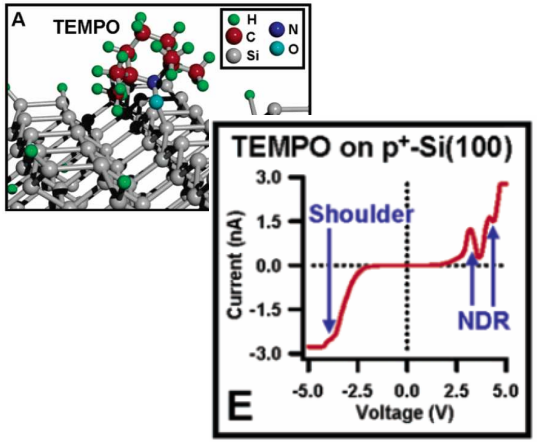
other molecular devices

Molecular transistor



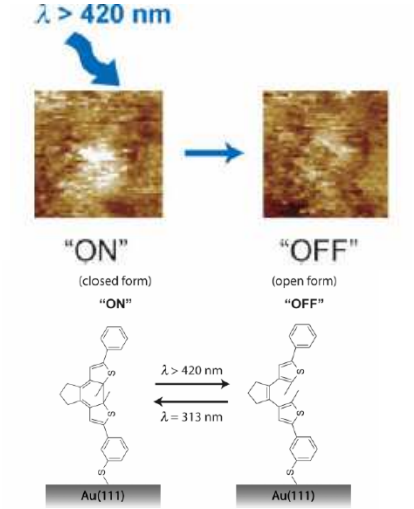
McEuen & Ralph et al. Nature 2002
Park et al, Nature 2002

NDR diode



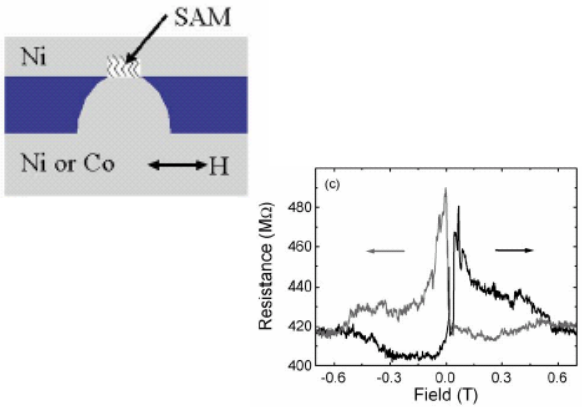
N. P. Guisinger *et al,* Nanoletters 4, 55 (2004)

Optical switch



Feringa et al., Adv. Mater. (2006)
Univ. Groningen

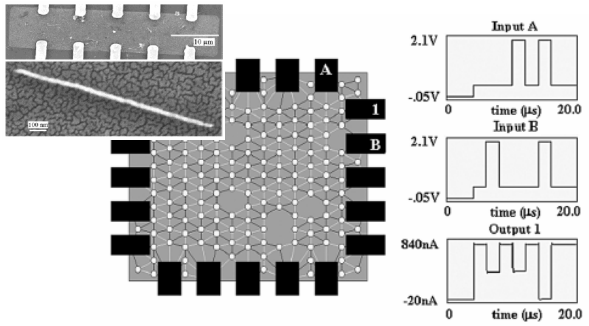
Molecular spin-valve



Ralph et al., Phys Rev Lett (2004)

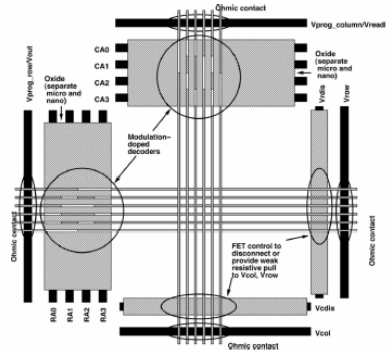
molecular-based circuits

"NANOCELL"



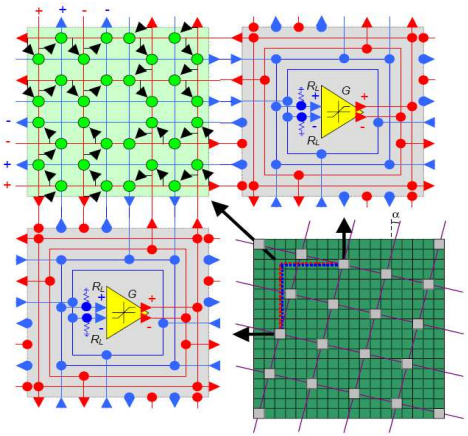
J.M. Tour et al., *IEEE Trans Nanotechnol.* (2002)
J.M. Tour et al., *J. Am. Chem. Soc.* (2003)

"Connecting nano to micro"



A. Dehon et al., *IEEE Trans Nanotechnol.* (2003)

Crossnets Synaptic plaquette



Lykharev (2004)

NanoBlocks and NanoFabrics

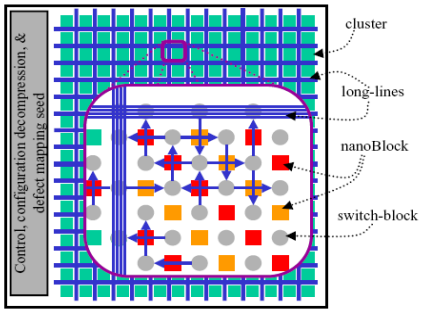


Figure 2. *The layout of the nanoFabric with a partial blowup of a single cluster and some of the adjacent long-lines.*

Goldstein (2001)

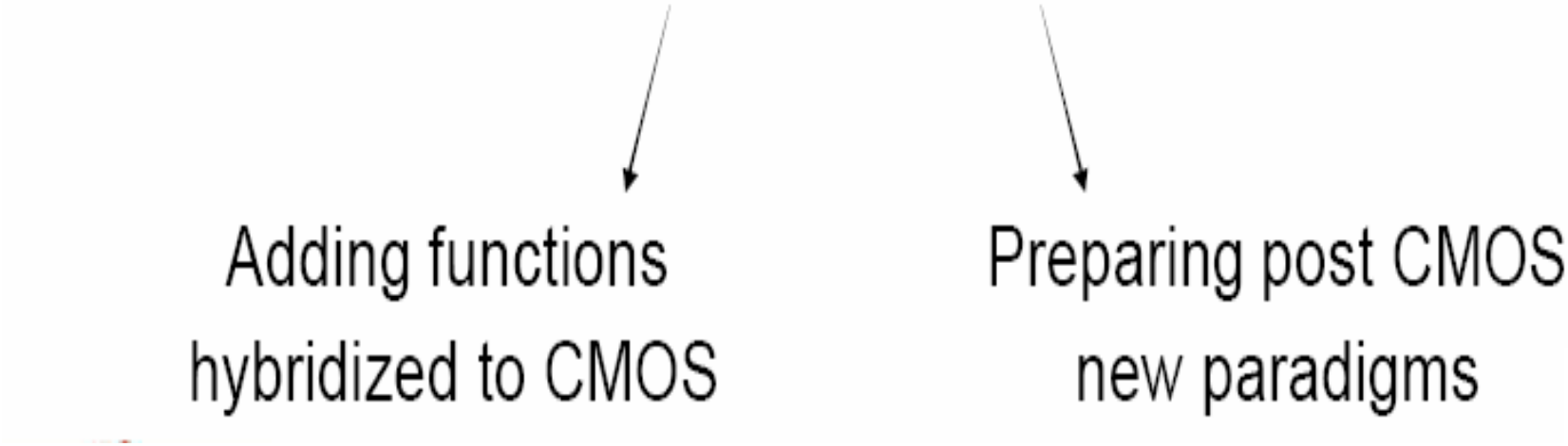
Conclusions and perspectives

- Several functions and devices have been studied at the molecular scale : tunnel barrier, molecular wire, rectifying and NDR diodes, bistable devices and memories.
  - A better understanding and further improvements are mandatory.
  - Need to be confirmed
  - What's about a true molecular 3-terminals device?

- Molecule-electrode coupling and conformation strongly modifies the molecular-scale device properties. Molecular engineering (changing ligand atoms for example) may be used to improve or adjust the electrode-molecule coupling.
  - A better control of the interface (energetics and atomic conformation) is still compulsory.

- Towards molecular architecture and circuits: mainly the « cross-bar » architecture has been studied. Is it sufficient?
  - More new architectures must be explored (e.g. non Von Neuman, neuronal…).
  - Molecular device interconnection?
  - 3D

Unique properties compared to micro-nanoelectronics materials!



Thank you!