Molecular electronics: getting the most out of molecular functionality?

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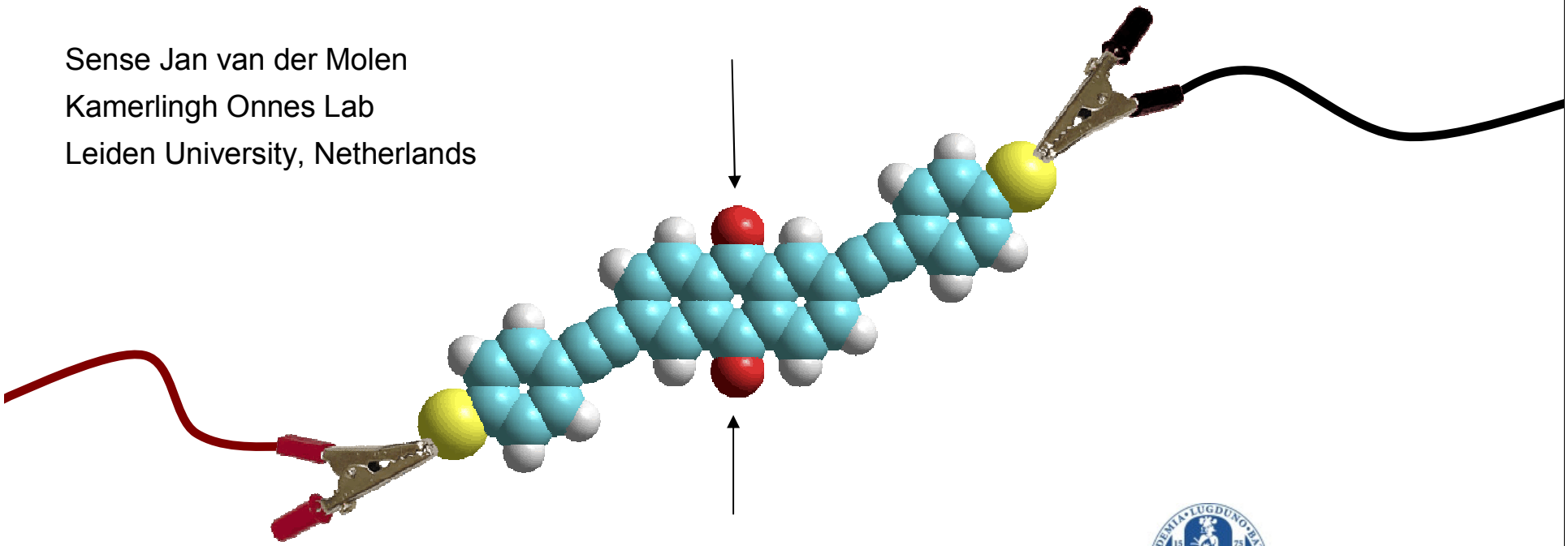


Universiteit Leiden

Overview

Intro molecular charge transport:

-Basics, techniques, results, stability?

Molecular switching:

-Functionality loss and gain!

Molecular logic

Towards practical devices?

Outlook

Molecular charge transport

Motivation

a) Curiosity: -quantum system (e-phonon, Kondo, …)

b) Nanodevices: -natural nanoscale

-all molecules identical

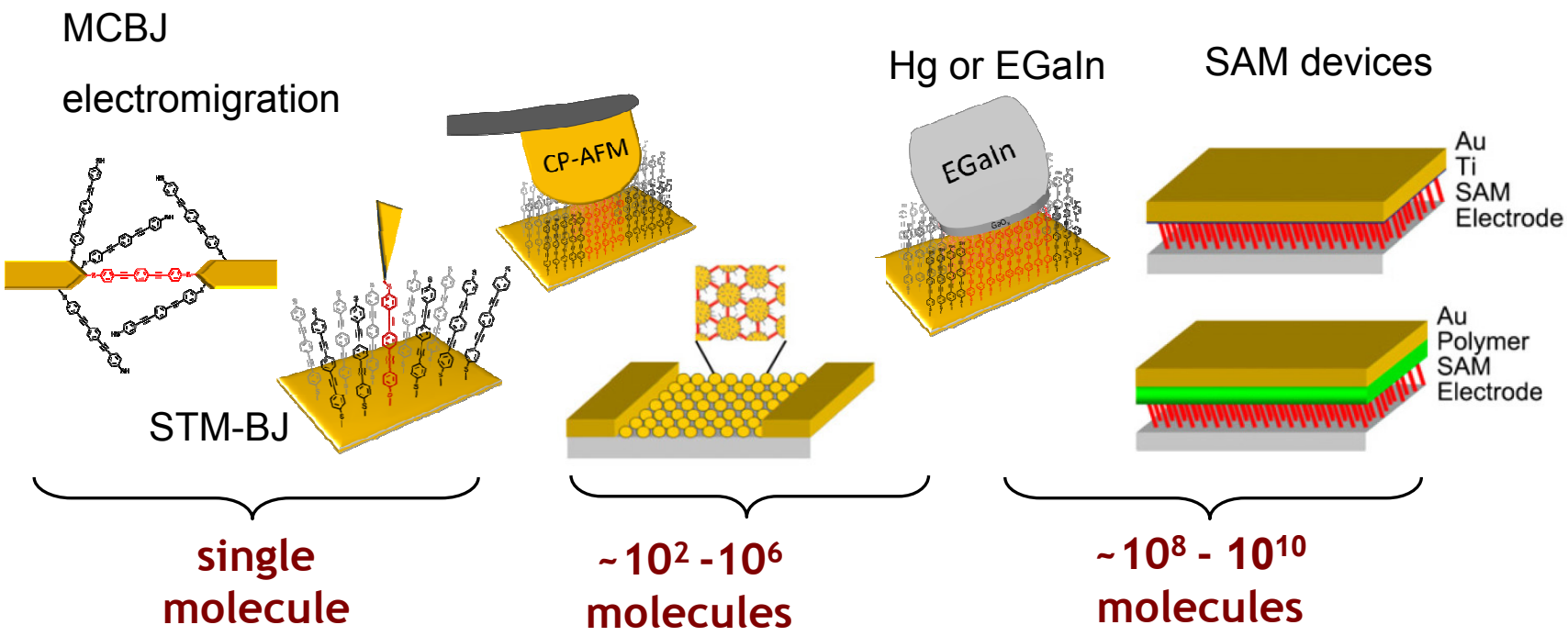
-cheap

-synthetic possibilities (!):

diodes [1,2], switches, logic gates?

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. 29, 277 (1974): starting point
[2] R. M. Metzger, J. Mater. Chem. 18, 4364 (2008): review

How to contact a molecule?

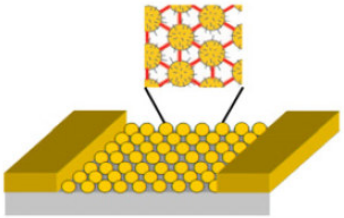


Pioneers: van Ruitenbeek, Reed, Tao, Park, Lindsay, Schönenberger, Frisbie, Whitesides, Heath, de Boer

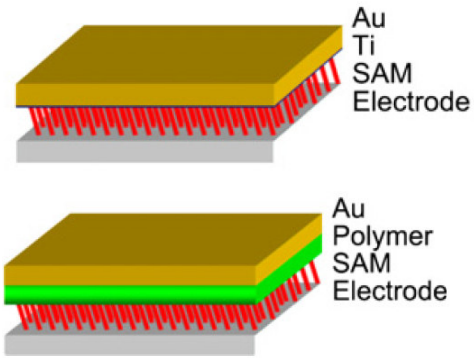
Feasible for devices: multimolecular

•addressable

•(quite) robust



SAM devices



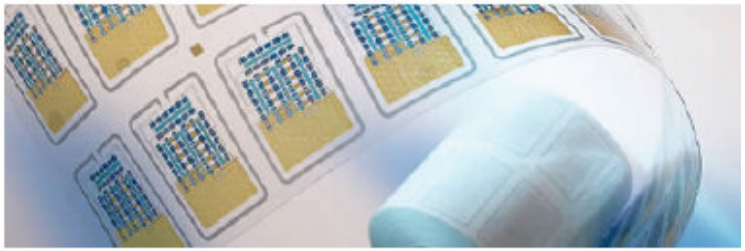
single molecule

~10^2 -10^6 molecules

~10^8 - 10^{10} molecules

Pioneers: van Ruitenbeek, Reed, Tao, Park, Lindsay, Schönenberger, Frisbie, Whitesides, Heath, de Boer

Cf. Organic (plastic) electronics



L > µm

t > few 10 nm

plastic electronics
(OLED, OFET, OPV)

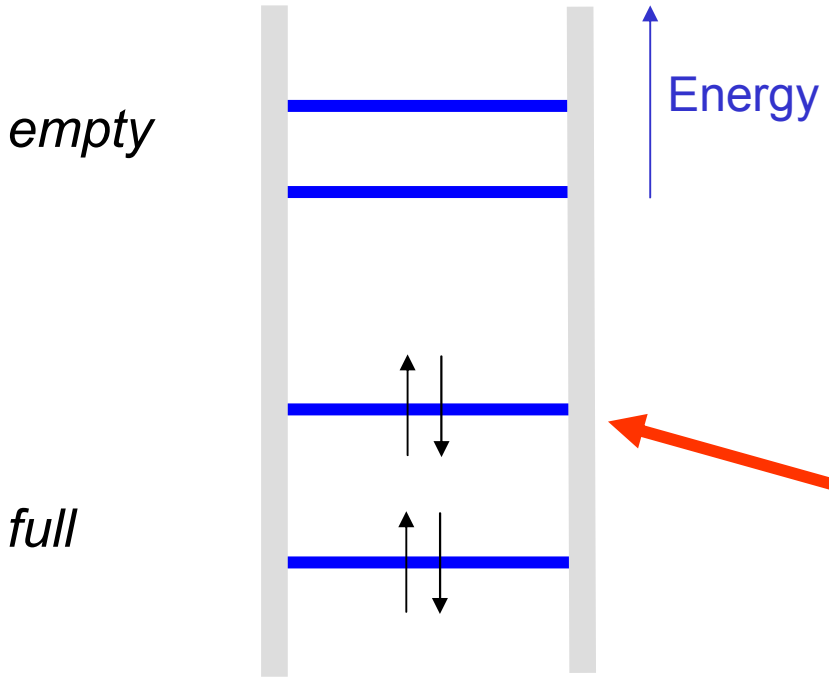
some products already
commercialized

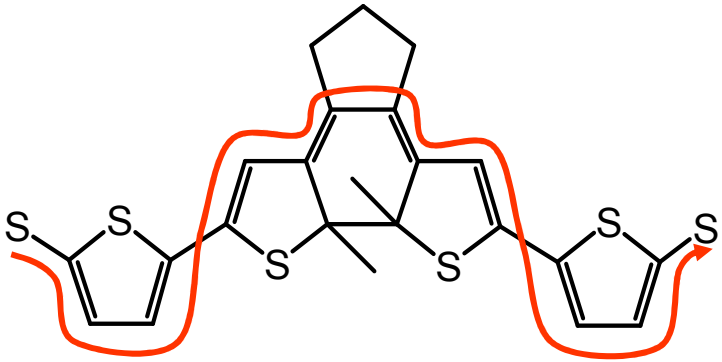
Ref. D. Vuillaume

Properties ⇔ Molecular Orbitals

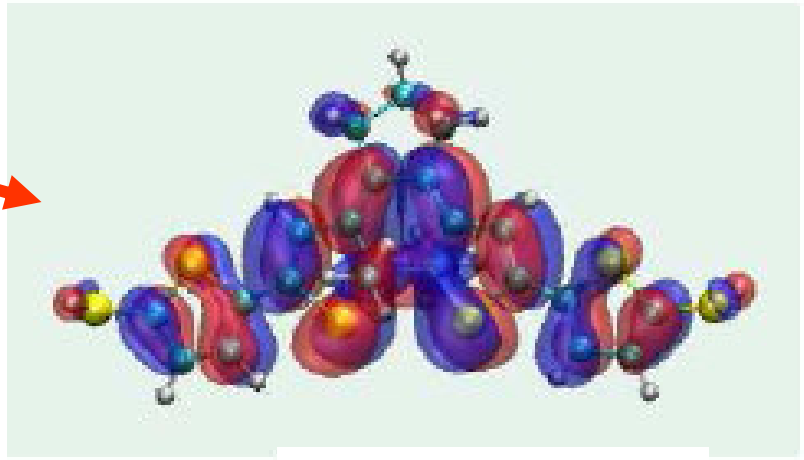
Energy levels

Conjugated molecule



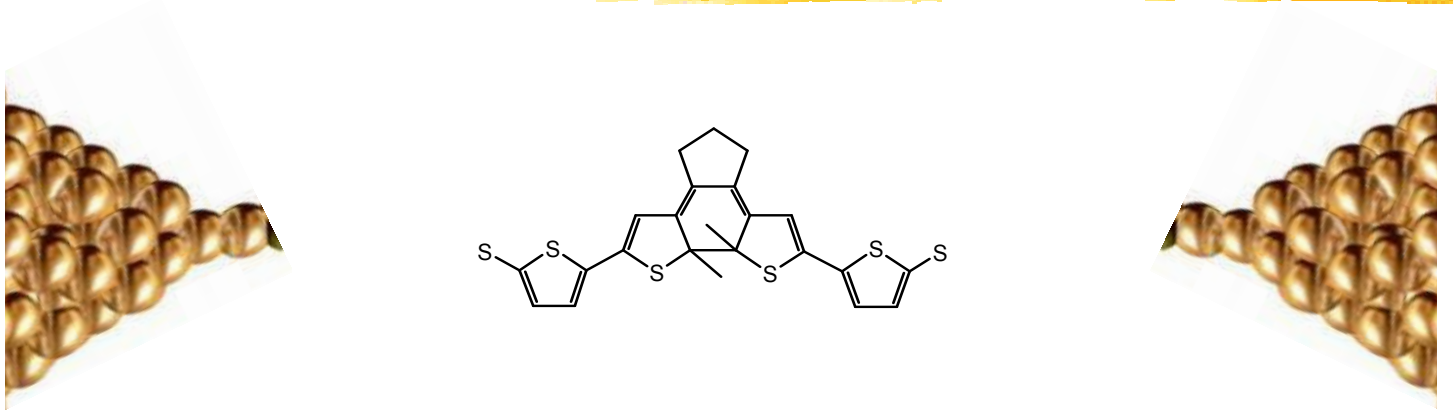


Delocalized π-electrons

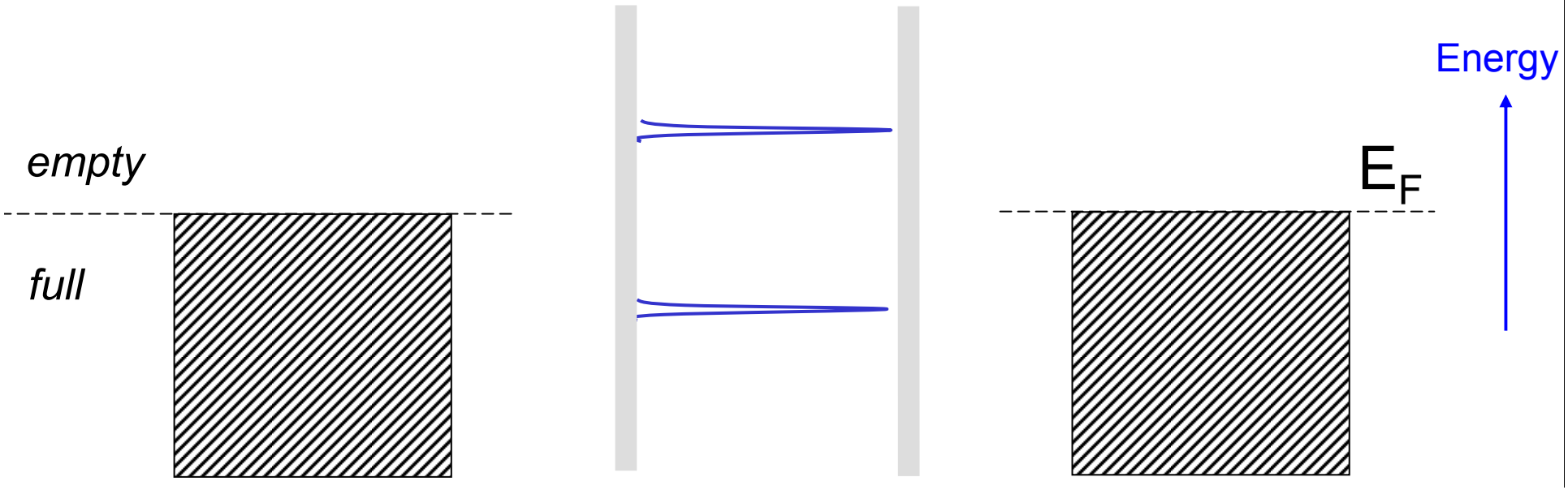


HOMO

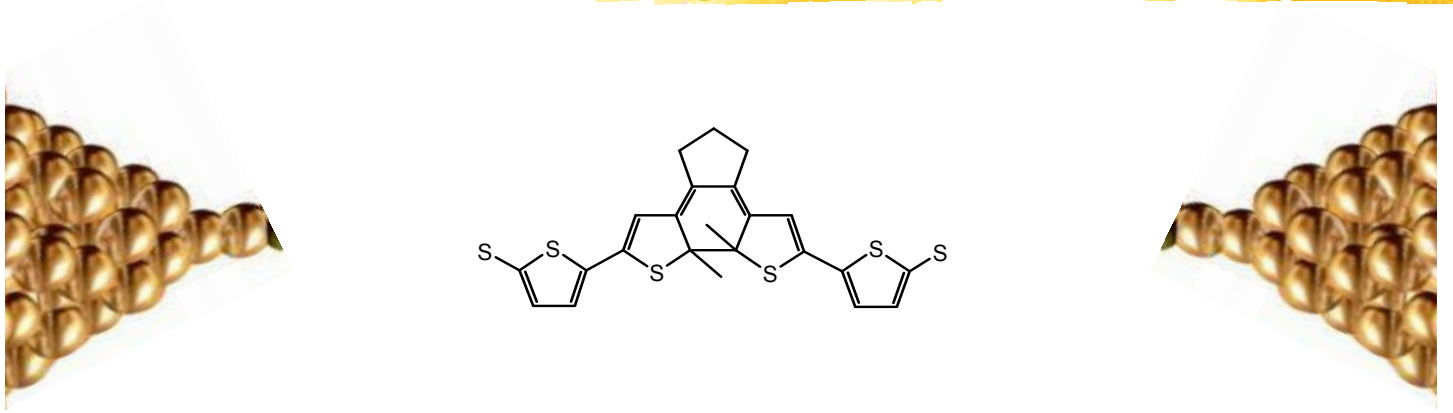
Connect to Electrodes



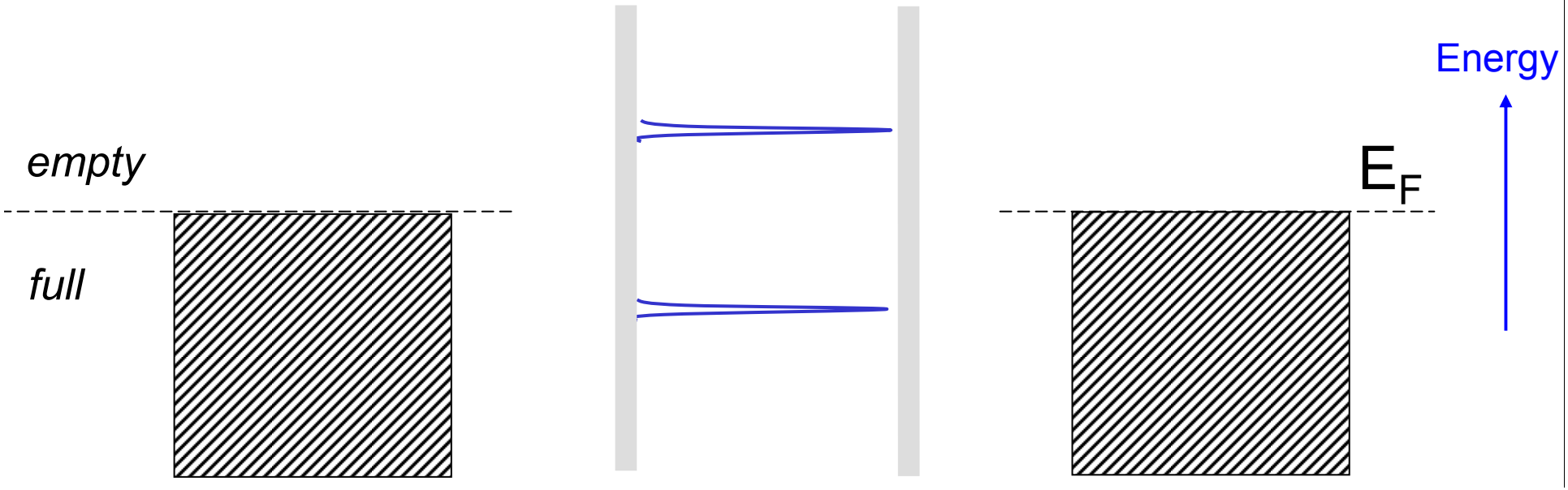
Metal: continuum of states



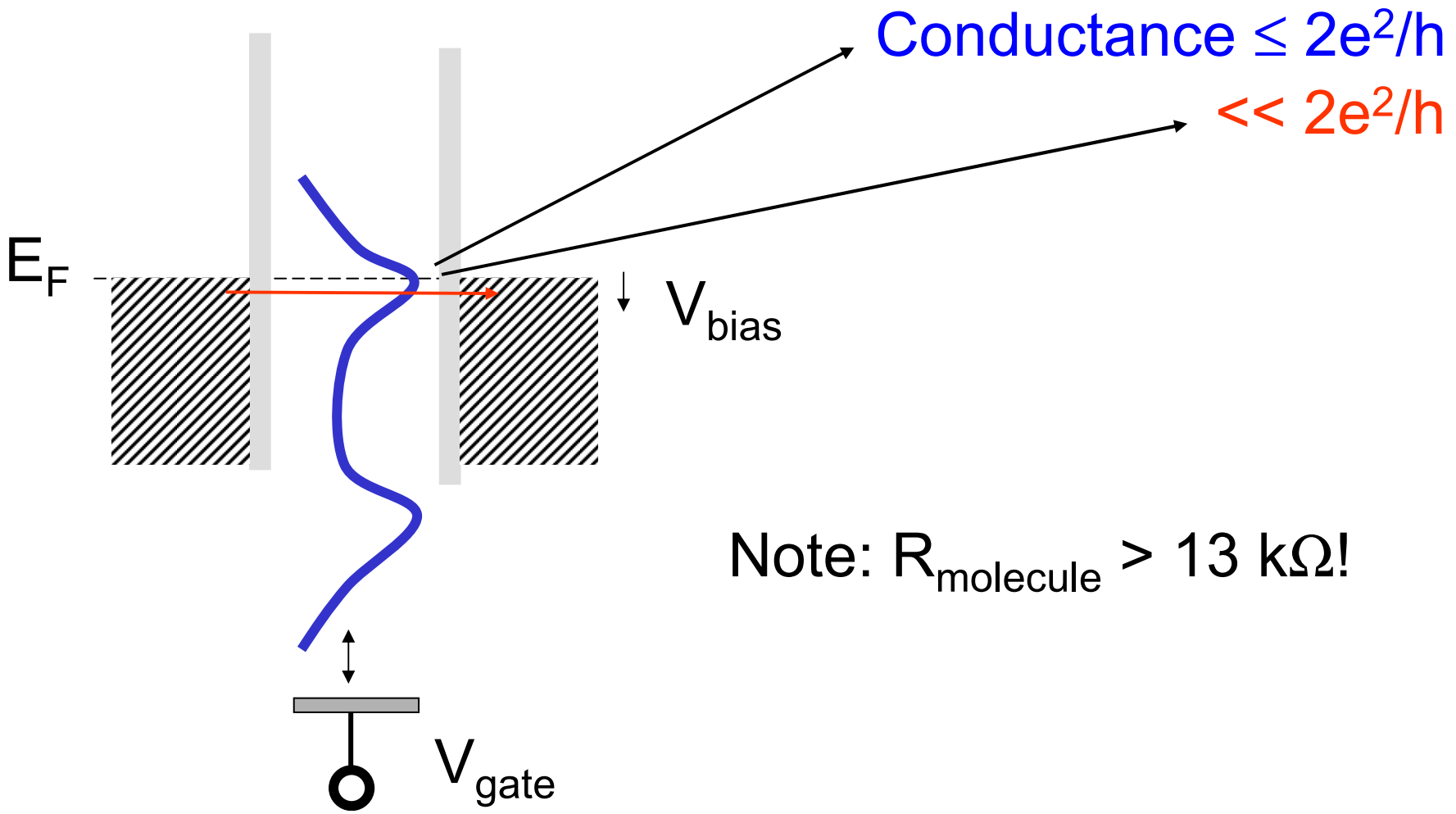
Hybridization: broadening & shift



Metal: continuum of states



Voltage V, measure I



Note: $R_{molecule} > 13\ k\Omega$!

General issues

-Stability of junction (depends on T)

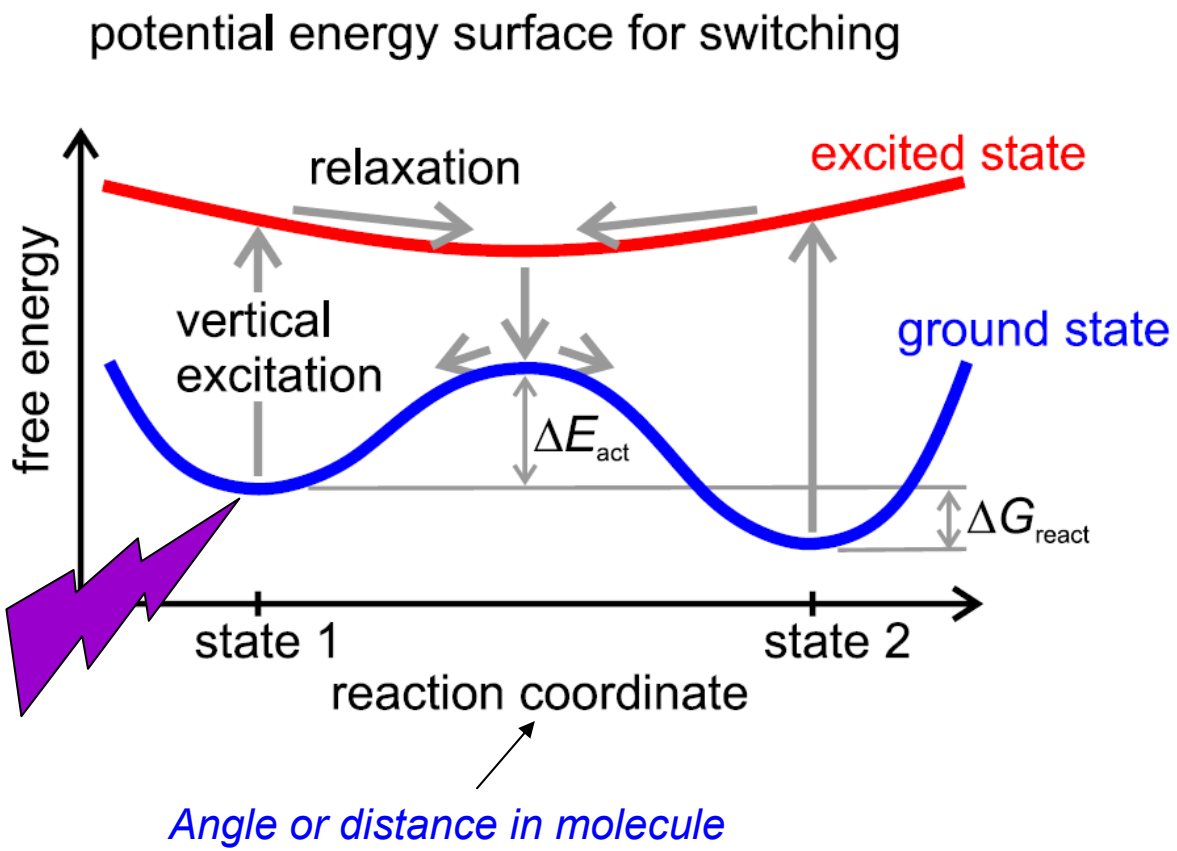
-Exact device geometry?

-How do we know it is the molecule?

Single-molecular: fundamental studies (low T)

Multi-molecular: more stable at RT: ‘devices’
niche integration w/ CMOS?

Molecular switches: principle



Stimuli:

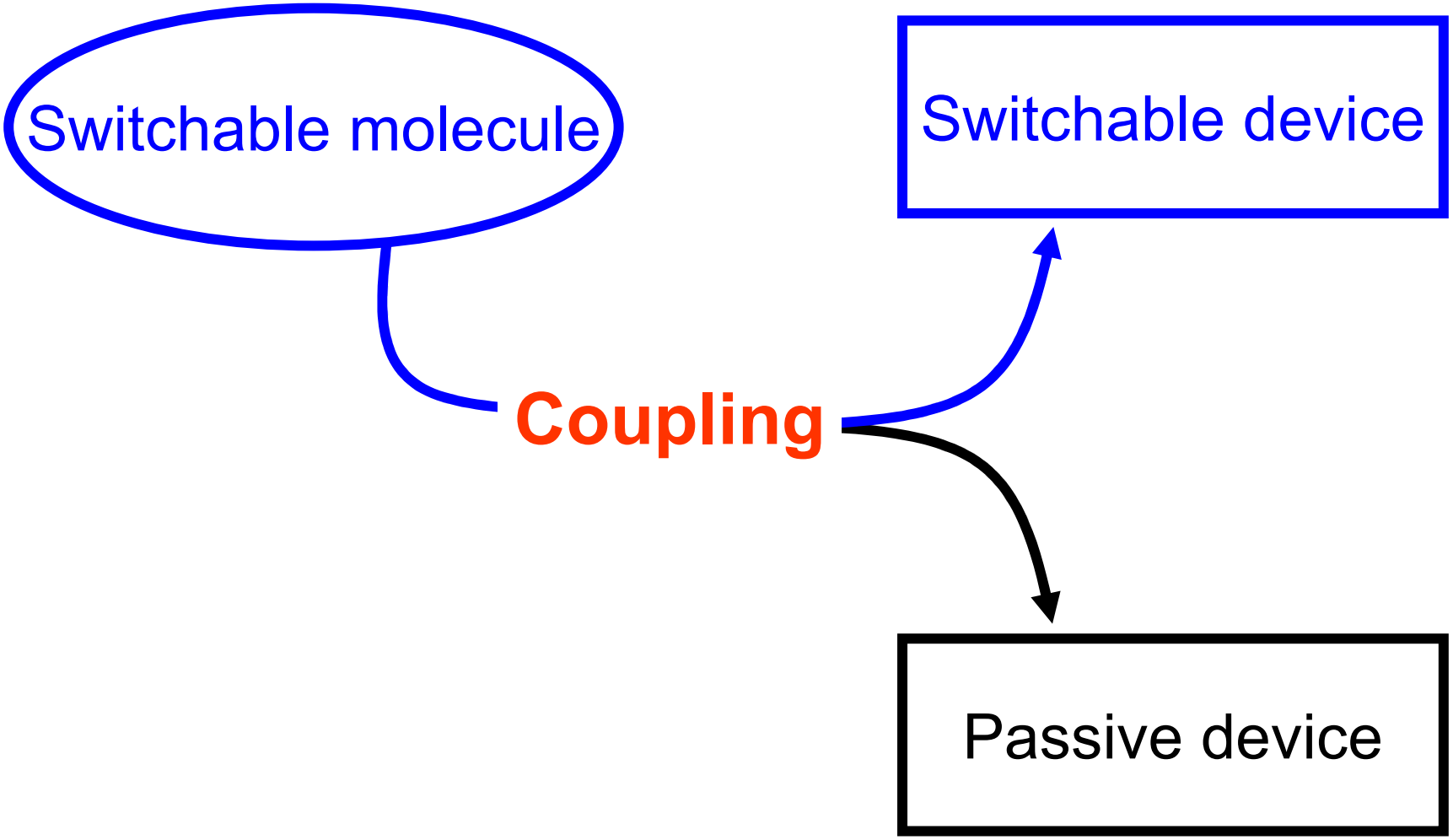
-Light

-Heat

-Current: e-phonon

-Voltage/Field

Contacting a Switch?



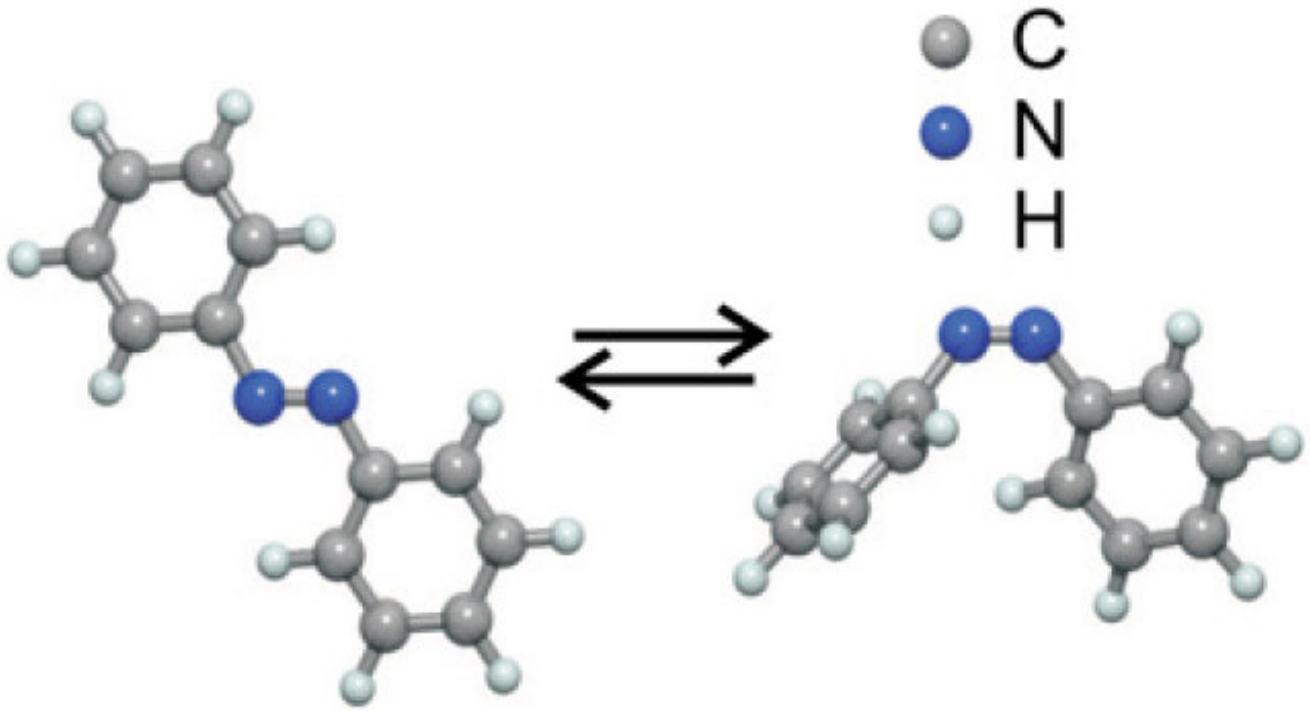
State of the Art

Essential molecular switching experiments

From single molecules to multimolecular devices

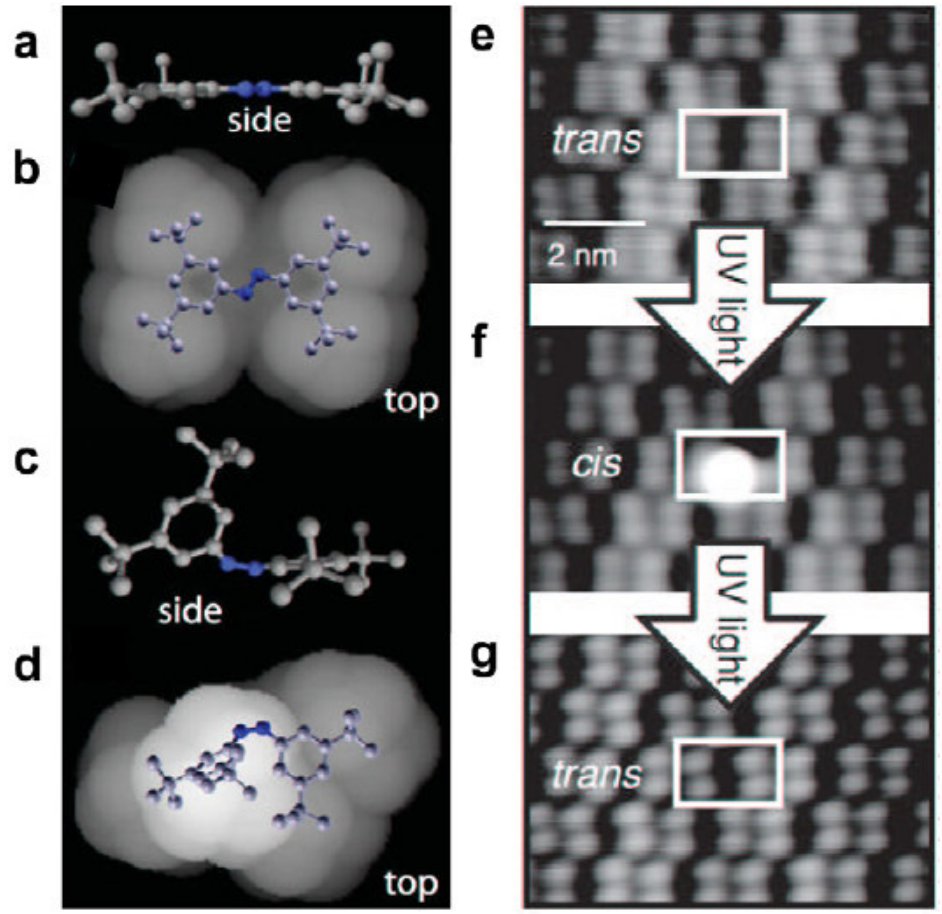
Review: SJvdM & P. Liljeroth, J. Phys. Cond. Matt. **22**, 133001 (2010)

Light-sensitive azobenzenes



- light-induced *trans* to *cis* isomerization
- change of length: ***flexible geometry needed!***

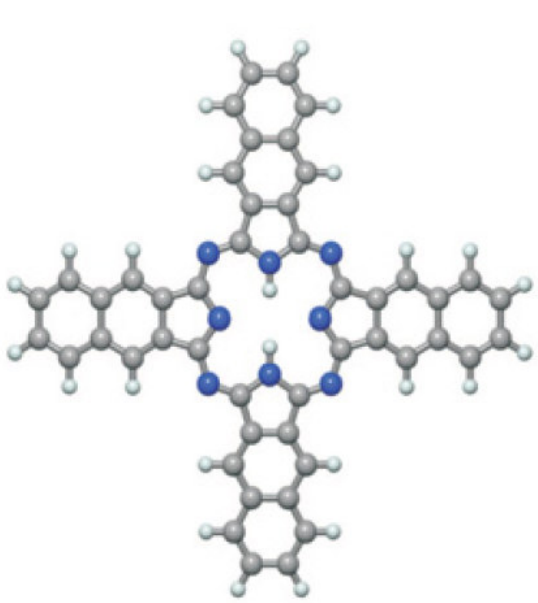
STM: azobenzene on surface

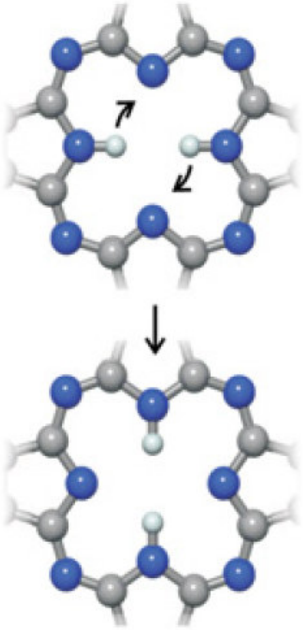


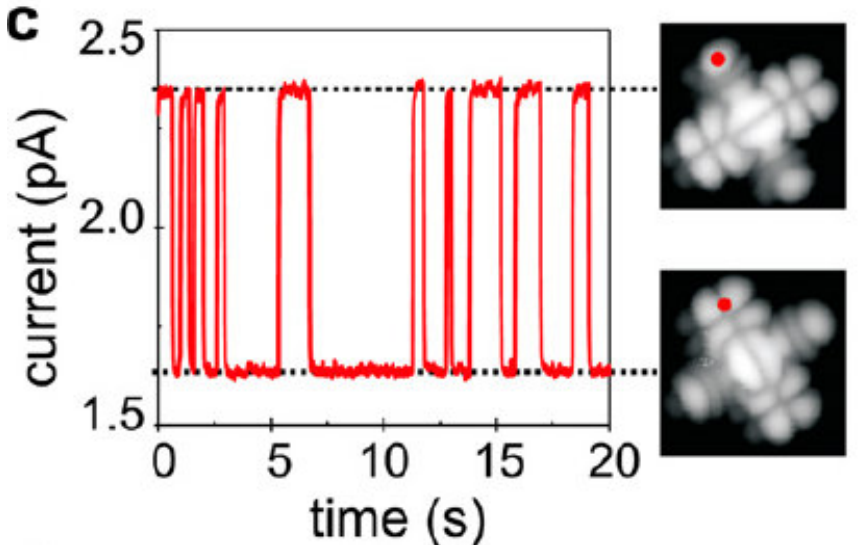
T=30 K

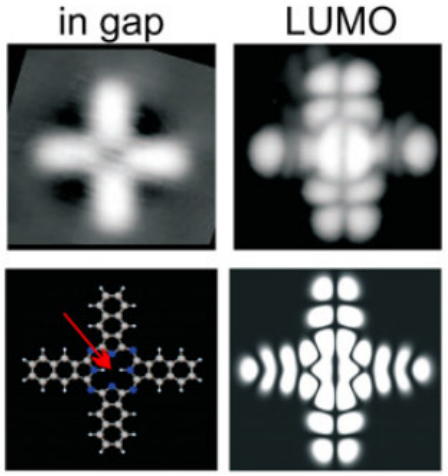
Comstock and Crommie *et al., Phys. Rev. Lett.* 99 038301 (2007)

Napthalocyanine







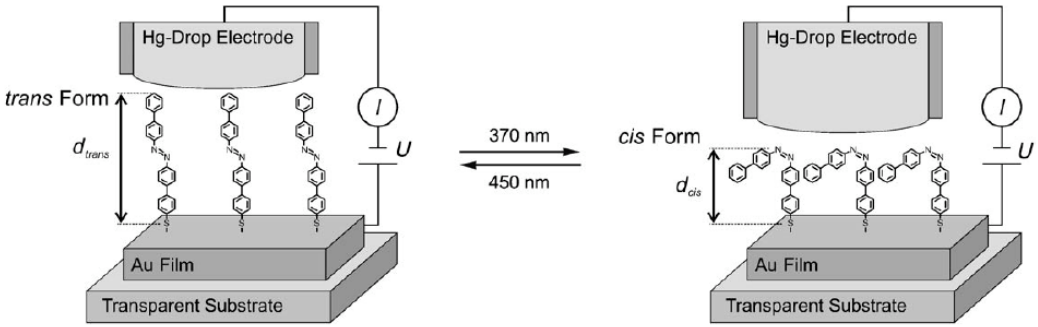


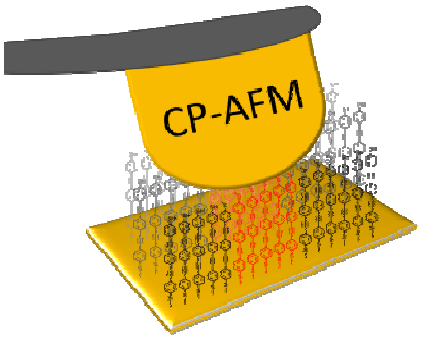
Induce H-tautomerization

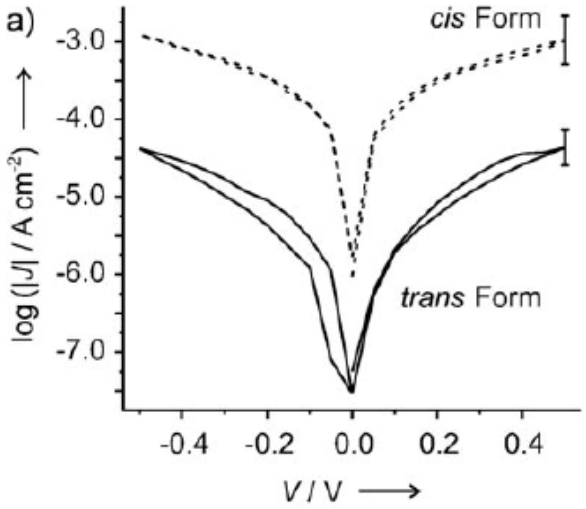
Control LUMO by H-position

Low T STM: Liljeroth, Repp, Meyer, Science (2007)

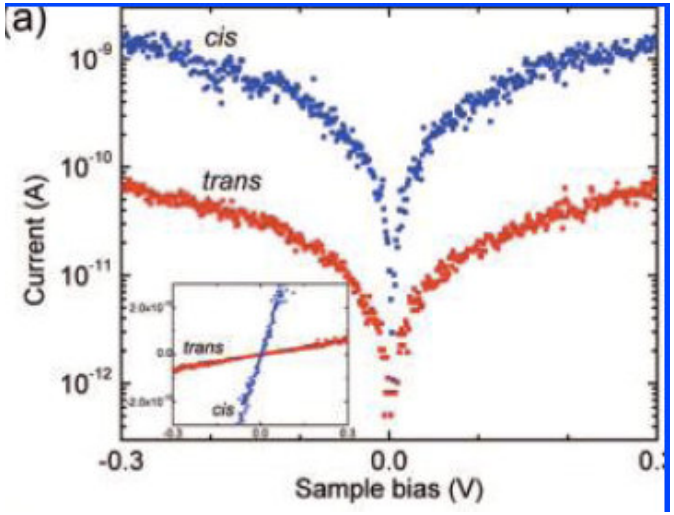
Multi-molecular devices







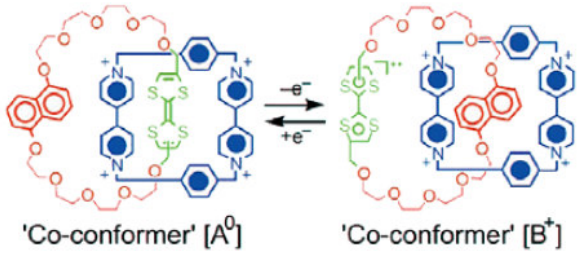
Ferri et al. , Angew. Chem. Int. Ed. 47, 3407 (2008)

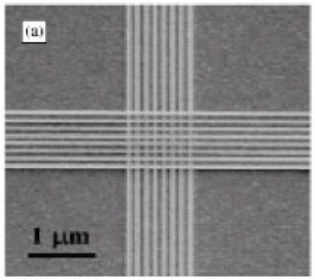


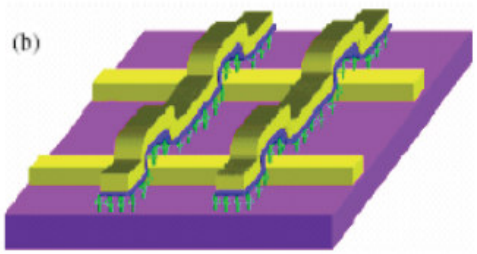
Mativetsky et al. , JACS 130, 9192 (2008)

Interlocked molecular switches

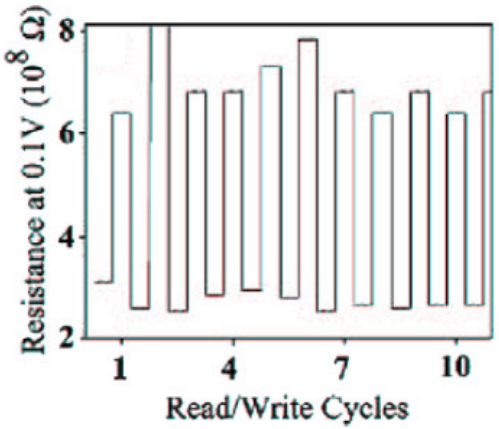
Switchable crossbars. Role of molecules unclear: extrinsic switching?

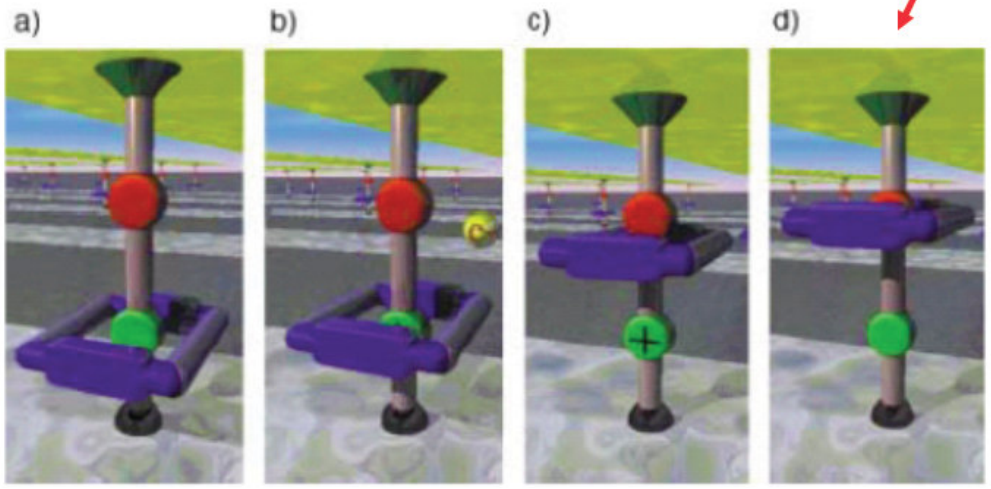






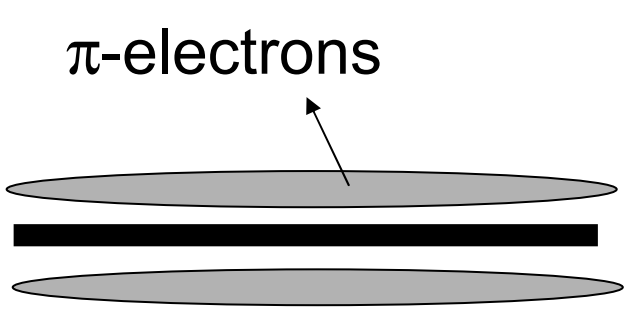
2-terminal voltage switch



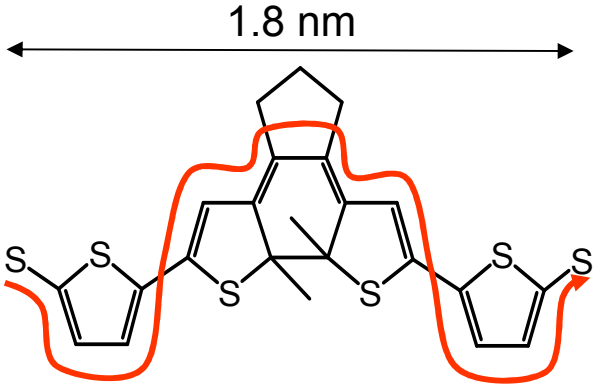


Heath, Williams, Stoddart

Switchable diarylethenes

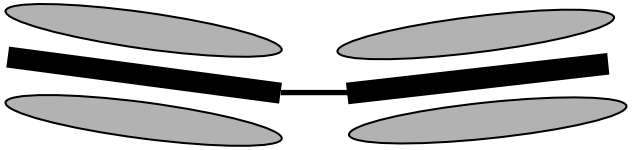


ON

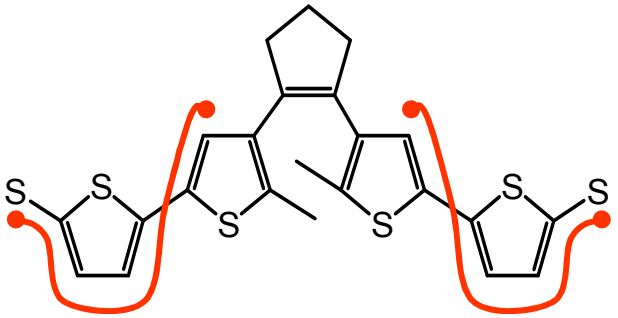


External ↓ ↑ stimulus

$\lambda_1 \approx 560$ nm ↓ ↑ $\lambda_2 \approx 330$ nm



OFF



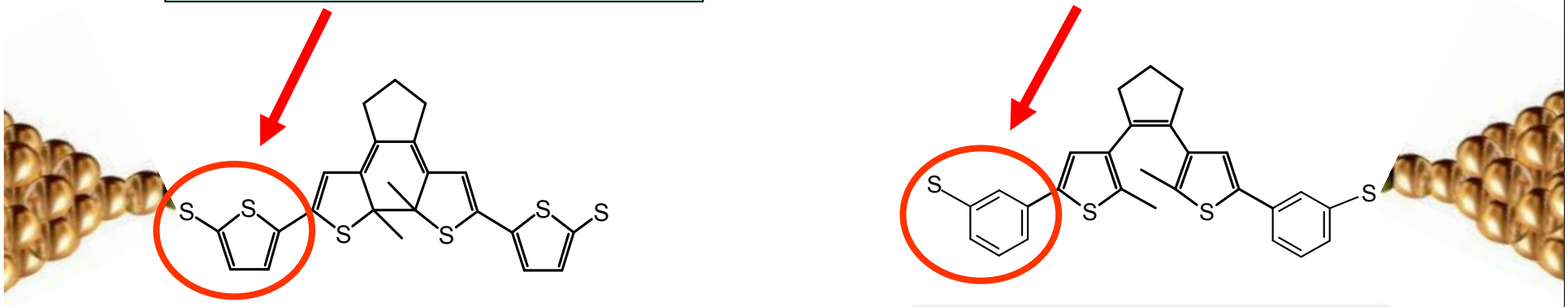
‘conjugation’ broken

M. Irie

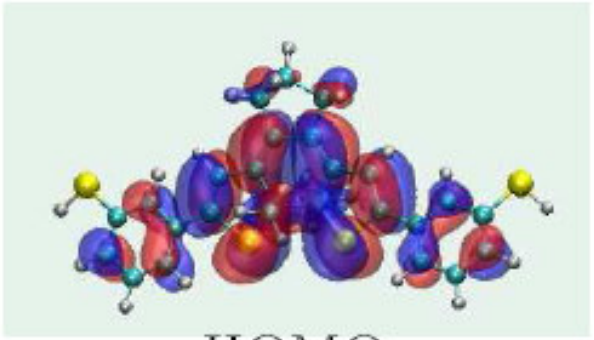
Chemical engineering: Decrease overlap

Thiophene:
Strong coupling:
hampers switching

Meta-Phenyl:
Weak coupling:
switching



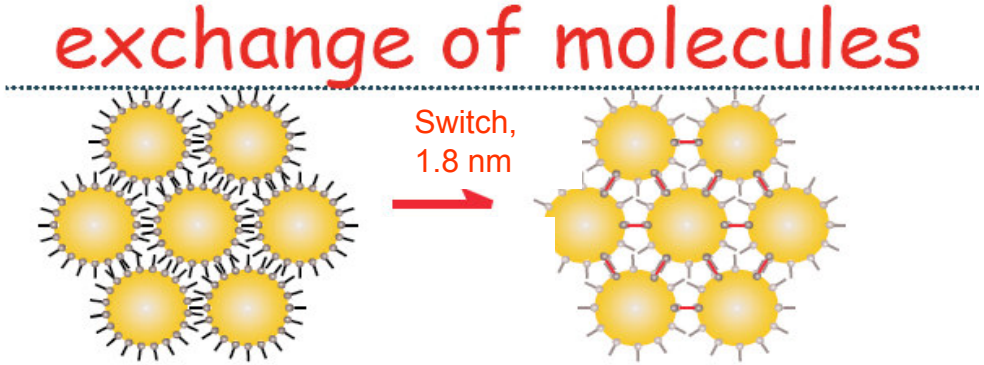
HOMO

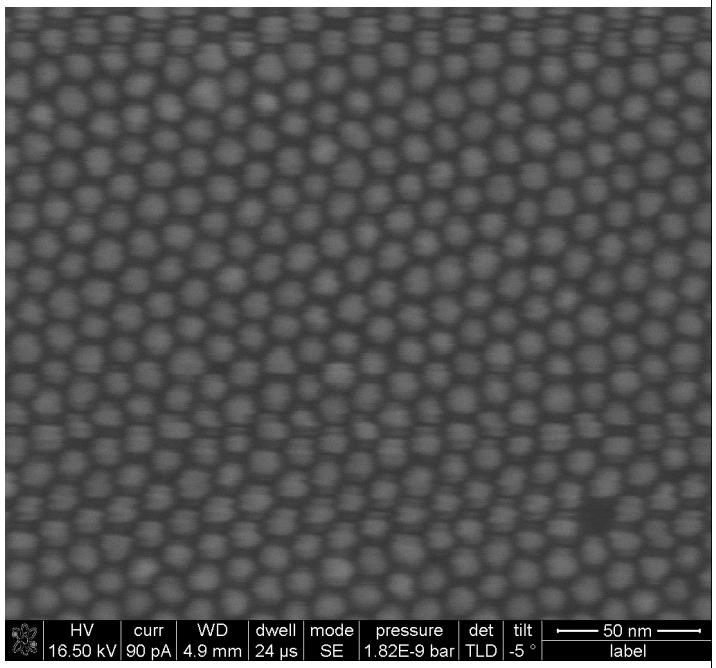


HOMO

T. Kudernac, SJvdM et al. Chem Comm (2006). Calc. by Zhuang and Ernzerhof, see Mayor *et al.* Ang. Ch. (2003)

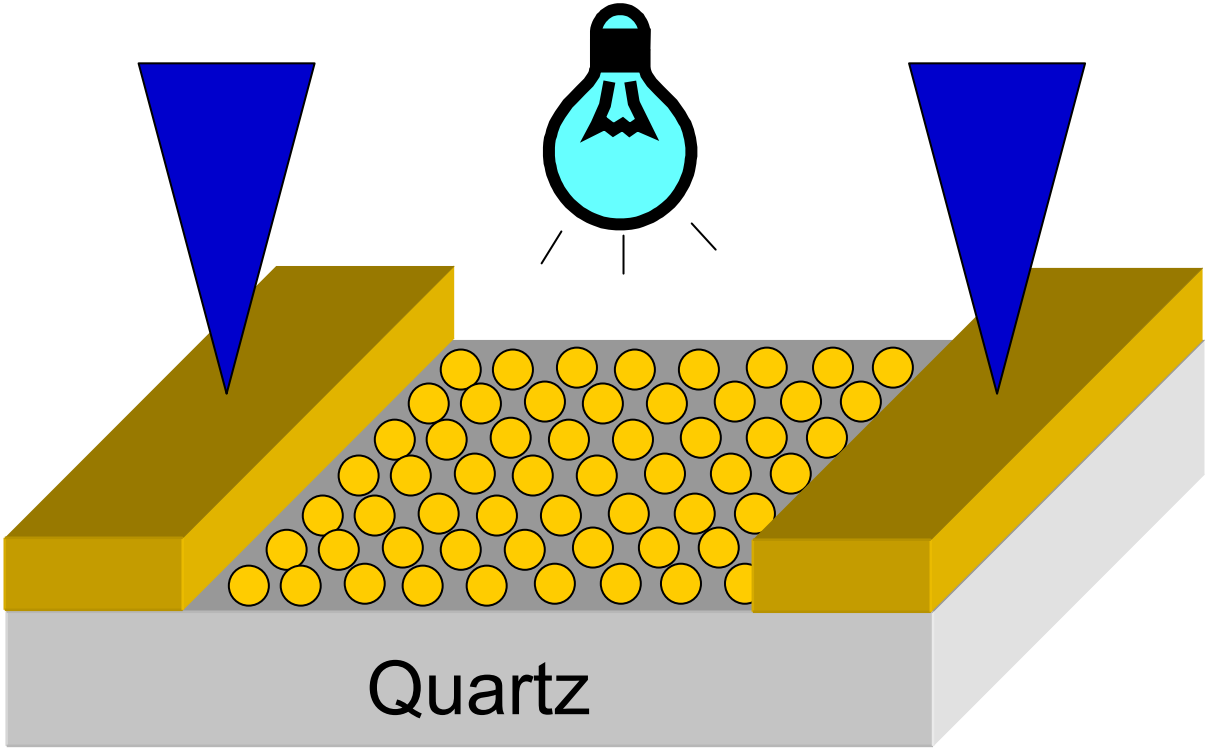
Multiple devices at RT



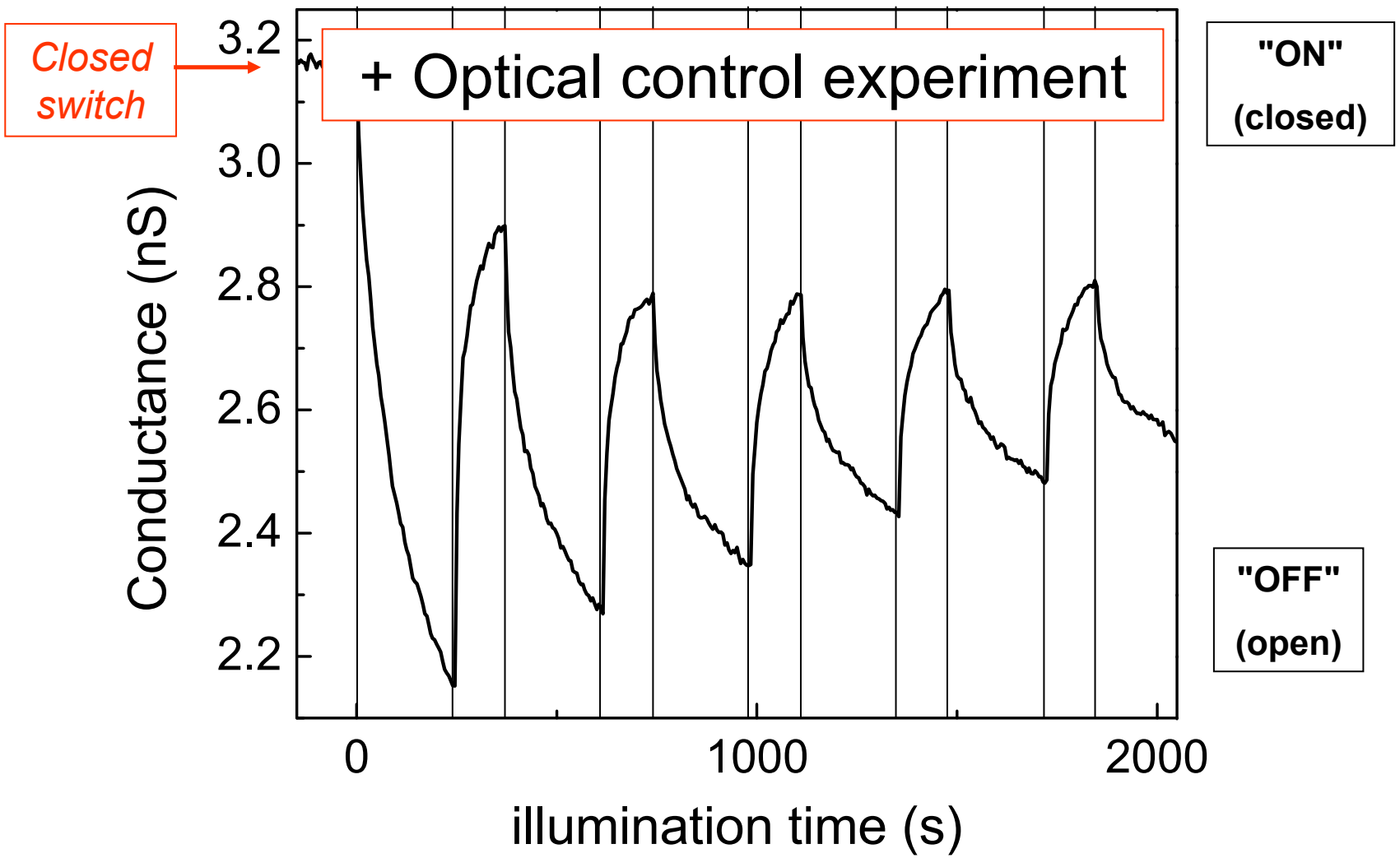


- Switch in C8-defined network
- Argon-flow cell at 293 K
- Illumination by Hg-lamp (100 W)
- Per cycle: *5 sec. Light, 25 sec. Dark*

Set-up



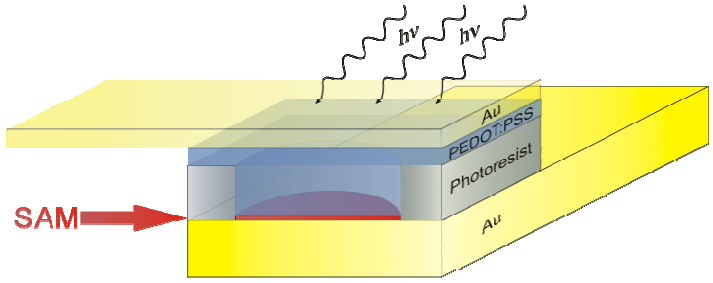
Conductance Switching at RT



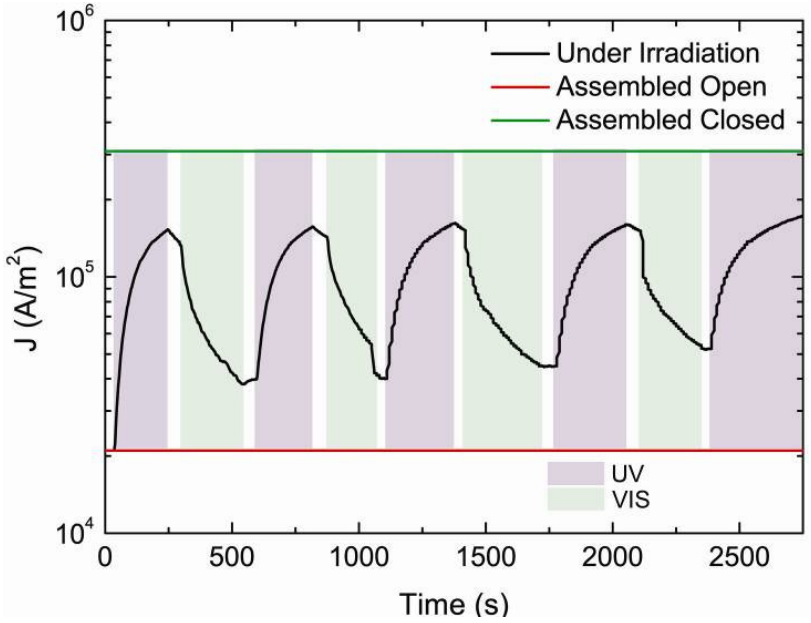
See also: He, Lindsay *et al.* Nanotech. 2005

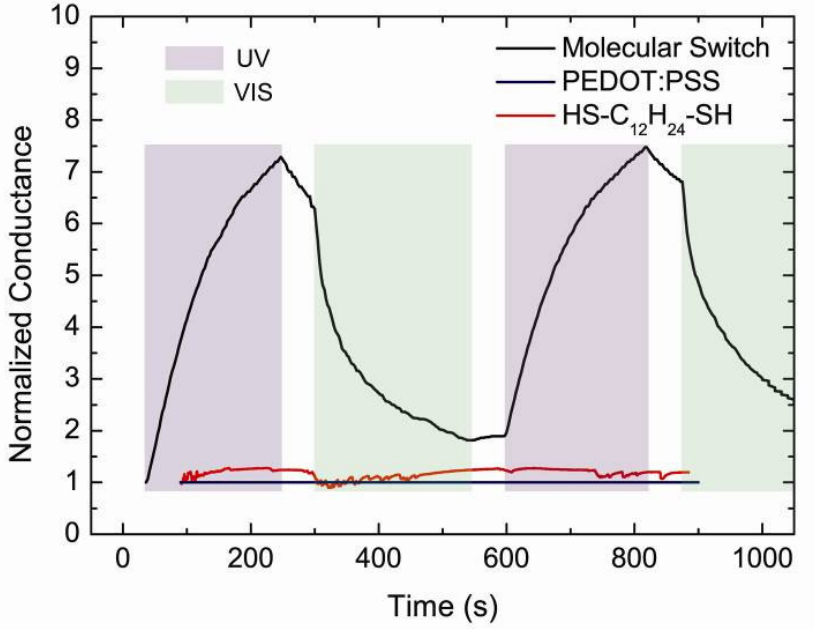
SJvdM *et al. Nano Lett.* **9**, 76 (2009)

SAM-based photochromic device



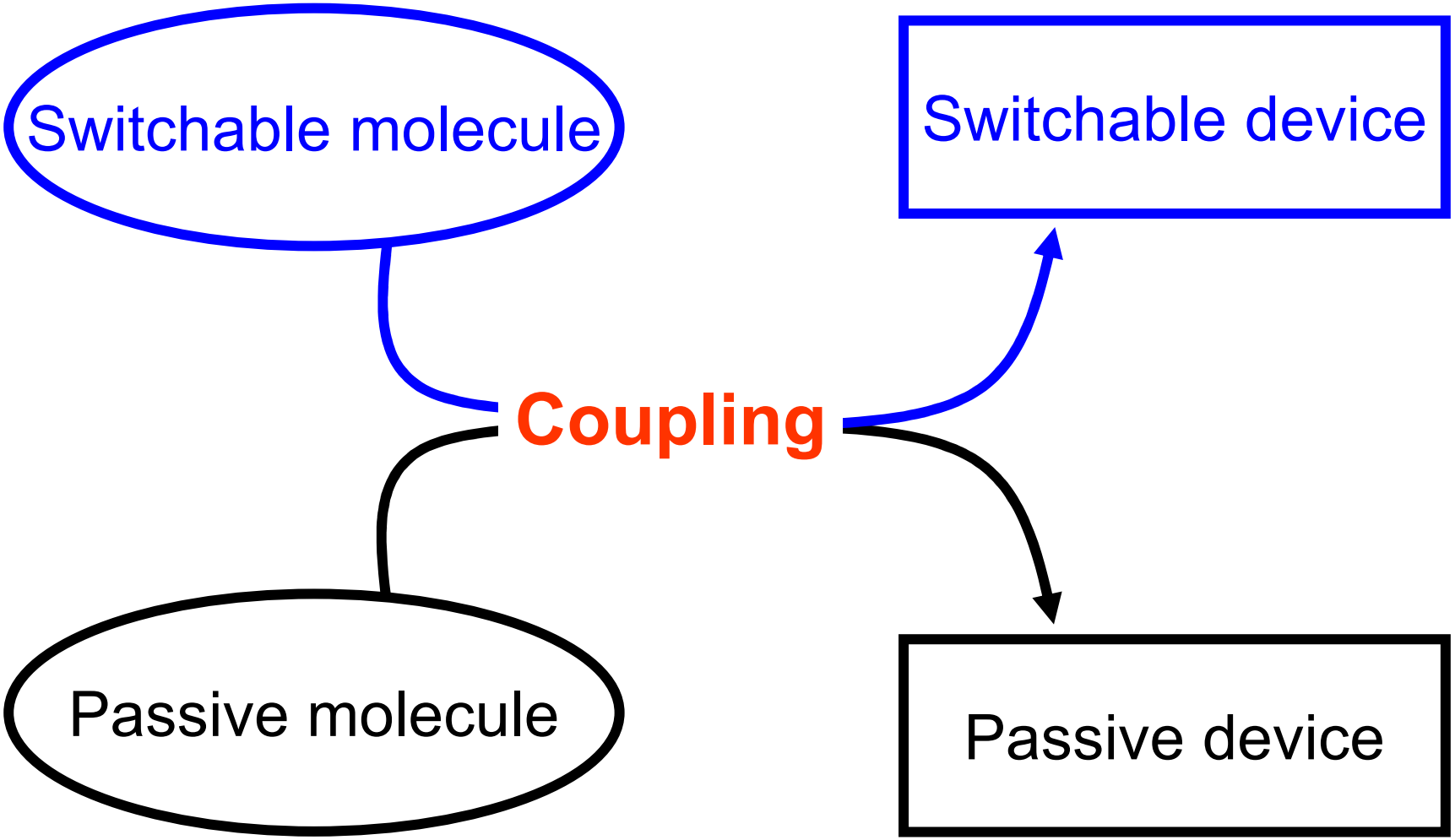
Robust at RT





A.J. Kronemeijer *et al.* Advanced Materials **20** (2008) 1467

‘Extrinsic switching’



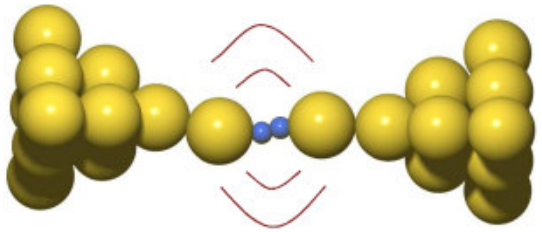
‘Extrinsic switching’

Switching becomes possible in

Metal-molecule-metal configuration

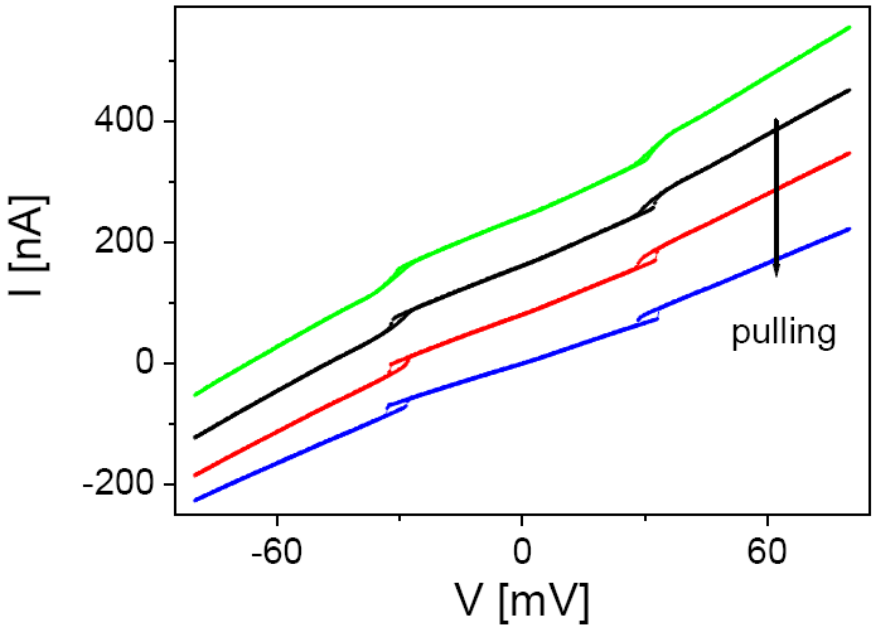
Stimuli: current, voltage or E-field

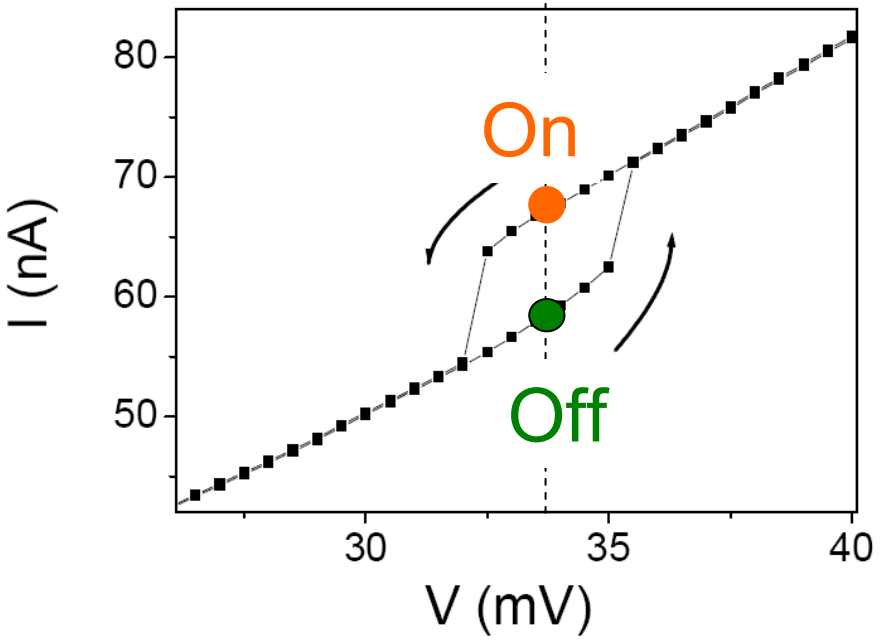
Au-H_2-Au break junction: hysteresis



T=4.2 K

Time-independent hysteresis

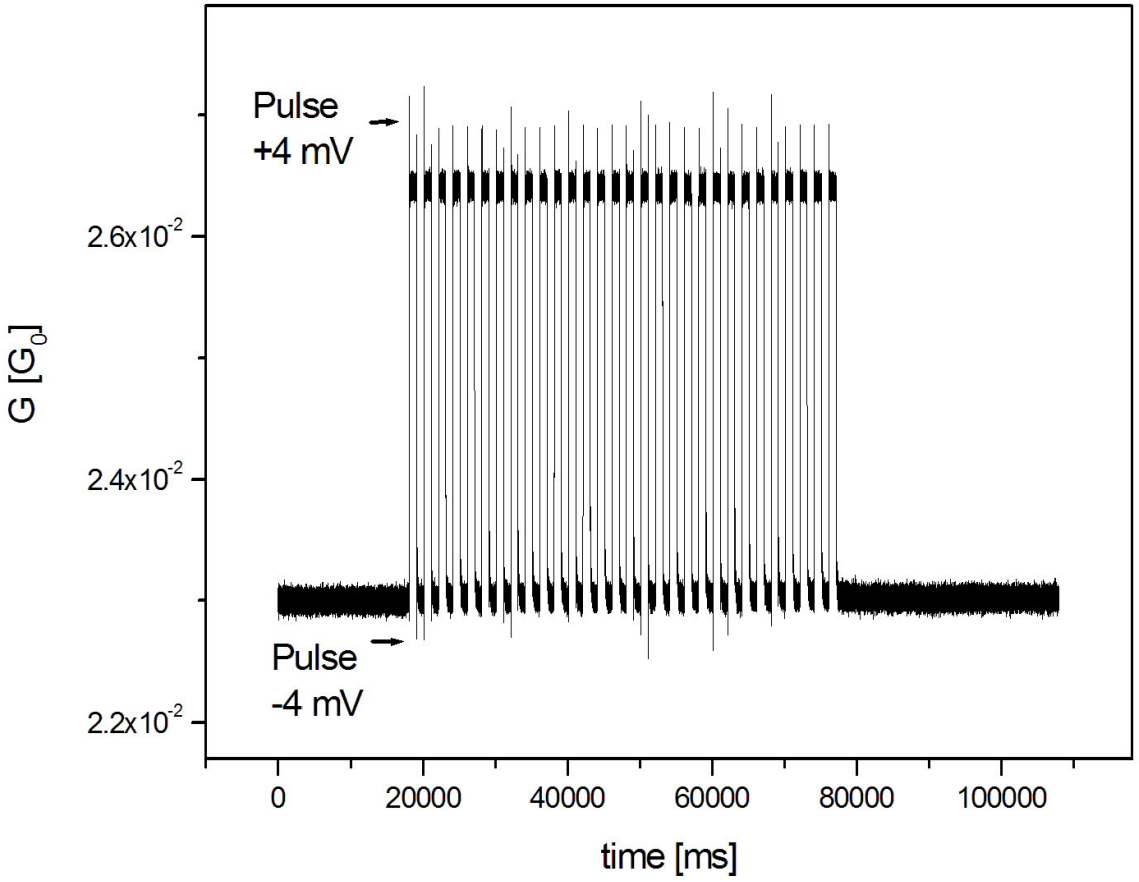


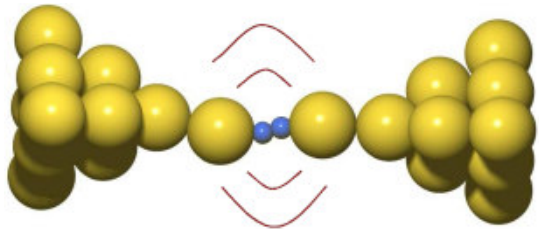


1st: Pt-H2-Pt: Smit, van Ruitenbeek *et al.* Nature (2002)

M.L. Trouwborst, SJvdM *et al. Phys. Rev. B* ***80****, 081407* (R) (2009)

Switching 5000x





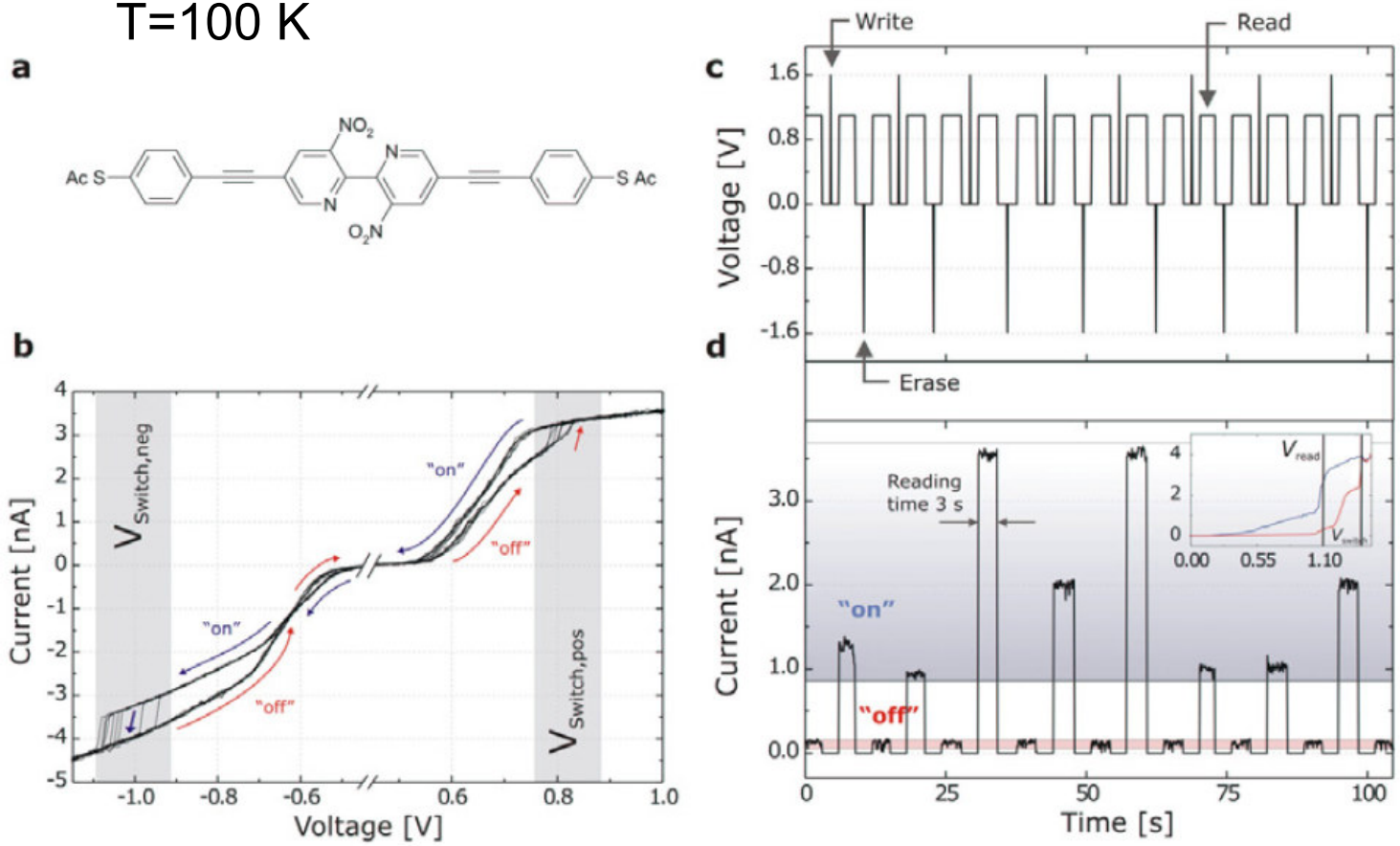
5000 x switching!

But at 4.2 K!

M.L. Trouwborst, SJvdM *et al. Phys. Rev. B* ***80****, 081407* (R) (2009)

BPDN molecule: Field-induced

T=100 K



Lörtscher et al. (IBM) *Small* **2**, 973 (2006)

SWOT for switchable molecular devices

Strengths

- programmable functionalities (vs. light, E-field, temperature)
- natural nanometer scale
- switchability is well explored
- cheap (in principle)

Weaknesses

- Low stability at room temperature
- Low conductance per molecule
- Electrodes define true dimensions

Opportunities

- Multimolecular devices (by self-assembly: SAMs, networks)
- **Sensors and specific functionalities connected to CMOS**
- Functionality enhancement by other nano-objects

Threats

- Still mostly basic research
- a niche technology at most (specific sensing functions)

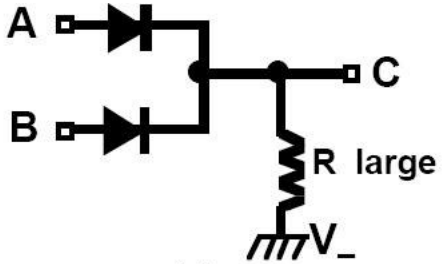
Molecular Logic: Paper and Practice

Main issue:

things look great on paper,

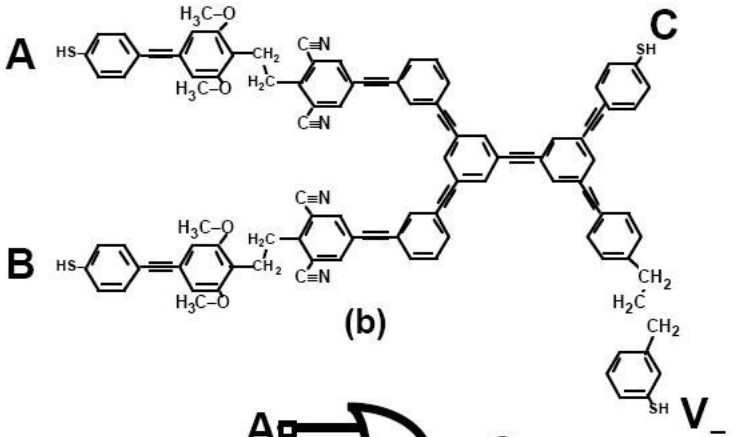
but are difficult in reality…

Pioneering ideas



(a)

Ellenbogen and Love: Proc. IEEE (2000)

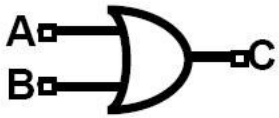


(b)

-synthesis difficult

-very low transport

-four contacts needed



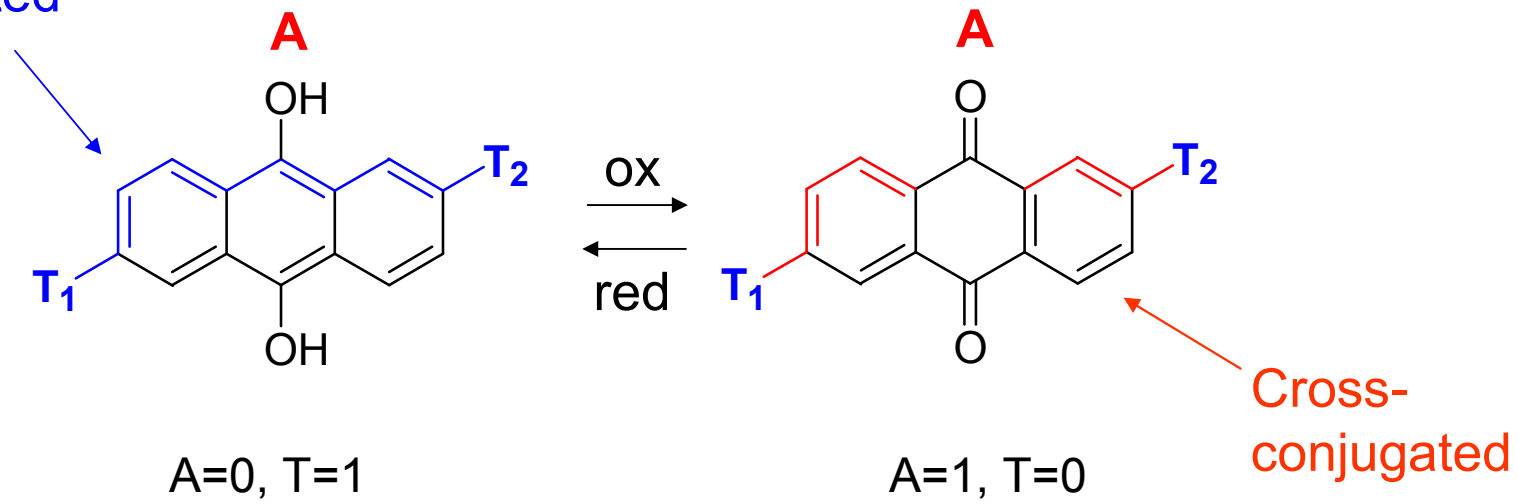
(c)

A	B	C
0	0	0
1	0	1
0	1	1
1	1	1

Can you do logic with smaller molecules?

Quinone switch

(Linearly) conjugated

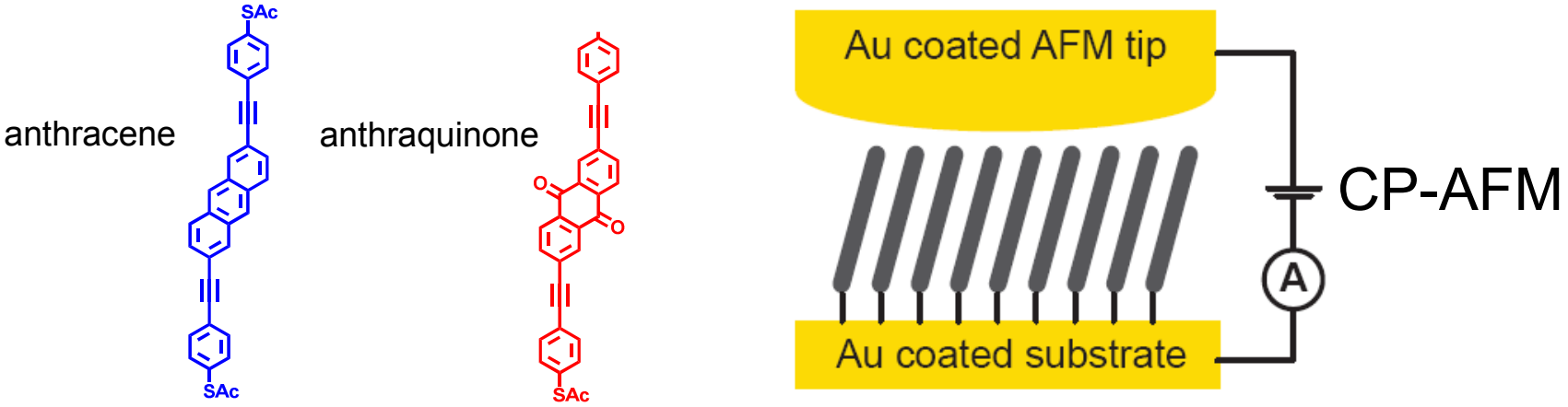


A=0, T=1 A=1, T=0

Advantage: virtually no length change

E. H. van Dijk (= H. Valkenier), D. J. T. Myles, M. H. van der Veen, J. C. Hummelen, Org. Lett. 2006, 8, 2333

Can the principle work?

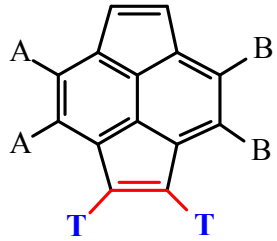


The principle works via quantum interference!

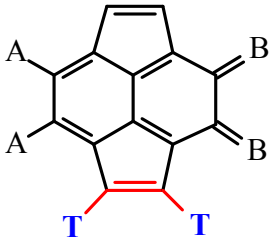
Ref. Guédon, SJvdM et al. Nature Nano (2012)

π-logic: very academic

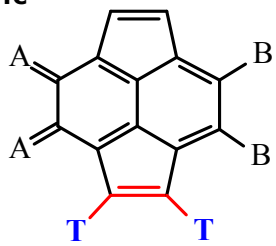
4a



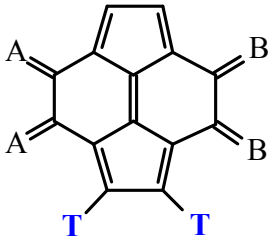
4b



4c



4d



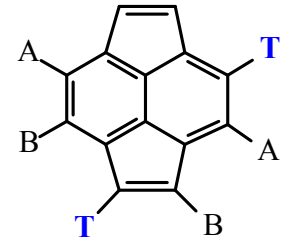
	A	B	T4
a	0	0	1
b	0	1	1
c	1	0	1
d	1	1	0

NAND

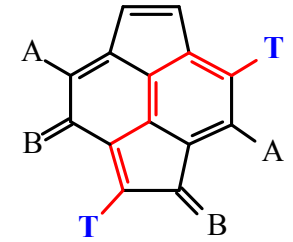
- channels A & B act cooperatively
- change the terminals changes the π-logic

M.H. van der Veen, J. C. Hummelen

8a



8b



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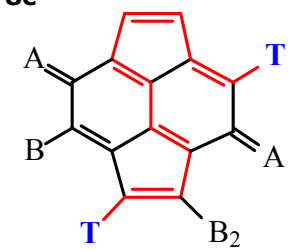

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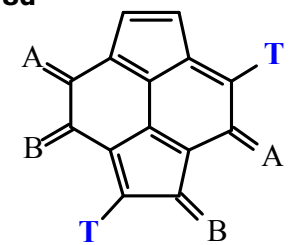
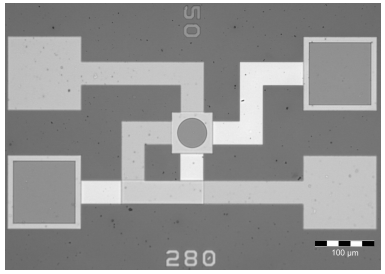


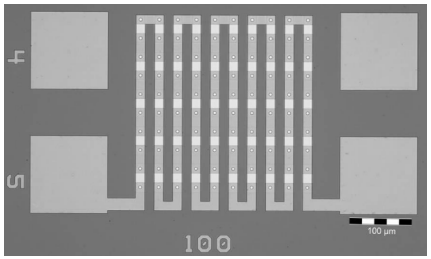
Multidevice logic

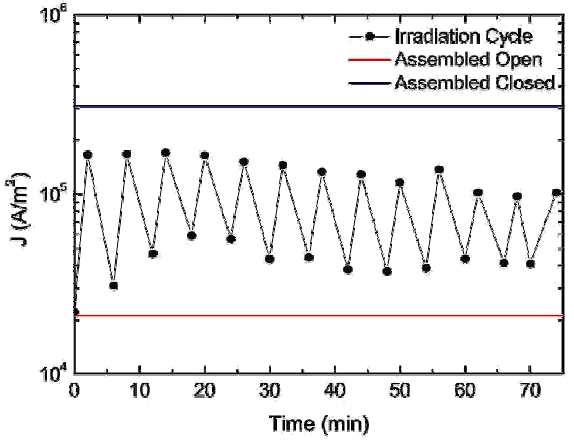
A first step is set (interesting physics!)

but single molecular logic is very far away.

Way out: Multi device logic?



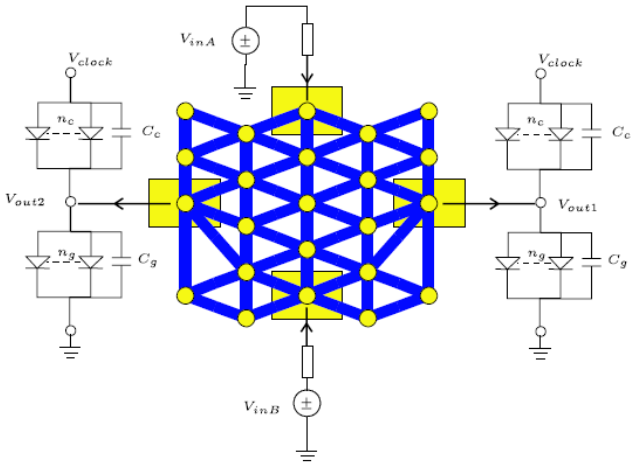


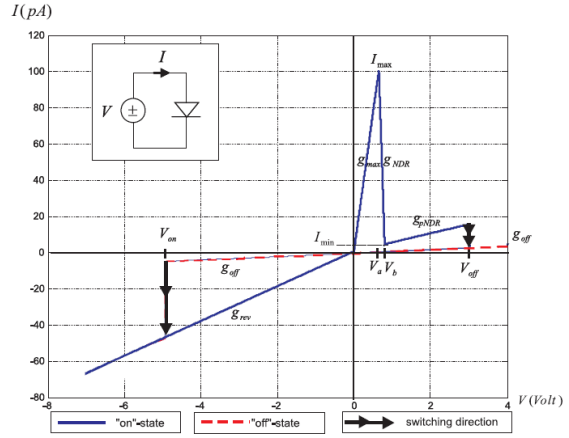


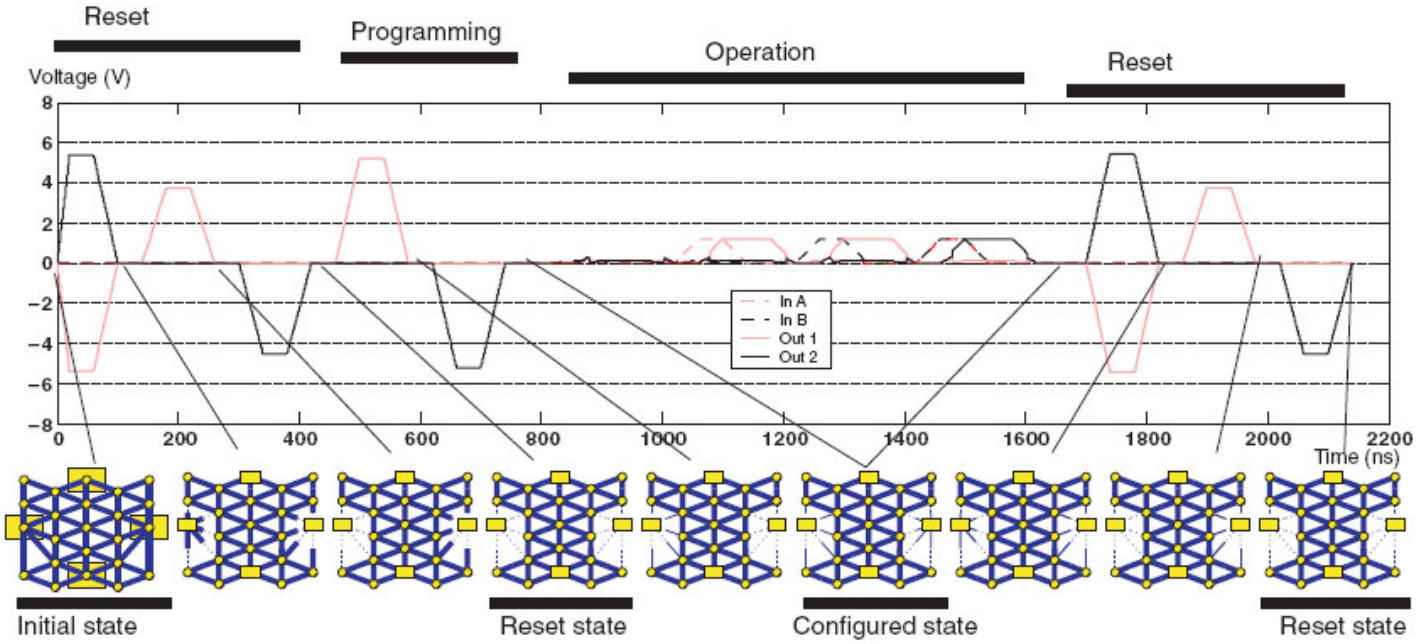
Integration of many switchable devices in series

A.J. Kronemeijer *et al.* See also J. Heath, T. Lee, et al.

Sköldberg & Wendin approach







SWOT for molecular logic

Strengths

- programmable functionalities (vs. light, E-field, temperature)
- natural nanometer scale
- cheap (in principle)

Weaknesses

- Low stability at room temperature
- Low conductance per molecule
- **Definition of electrodes**

Opportunities

- Multiple devices (by self-assembly: SAMs, networks)

Threats

- Even basic research is still in infancy.

General: Opportunities

*Single molecular research for basic understanding

(connect to plastic electronics)

*Niche applications: multimolecular sensors, connected to CMOS

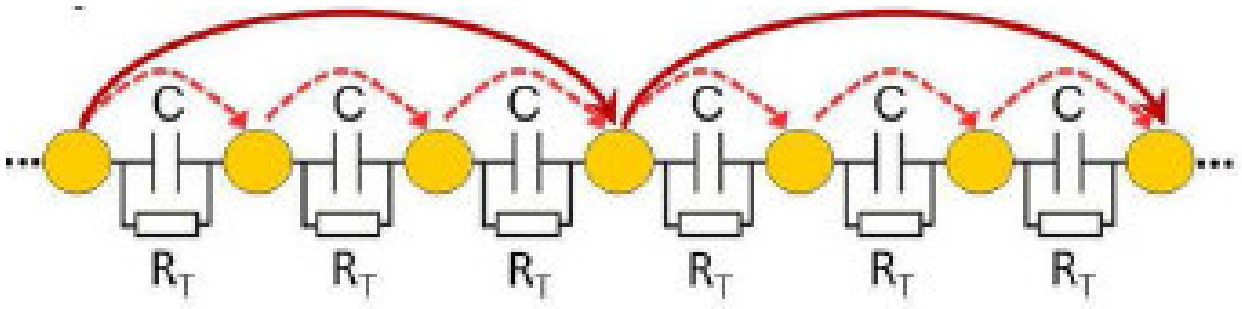
either SAMs or open-access nanoparticle networks.

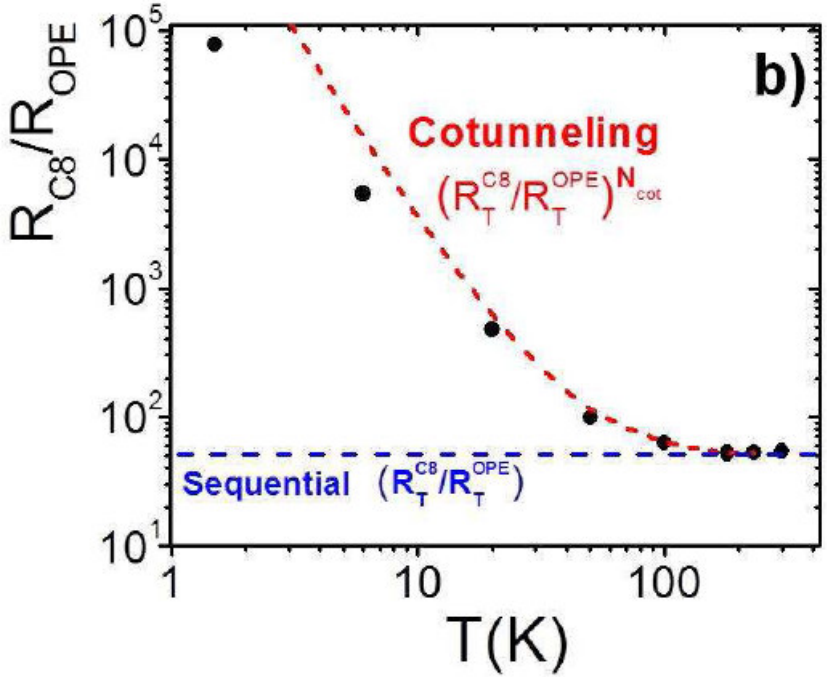
*Use nano-objects (nanowires and nanoparticles) to:

-Bridge size gap between molecules and electrodes (stability)

-Improve device functionality

Example for nanoparticles





Co-tunneling =>

(on-off ratio) ^{n}

Molecular electronics for devices

Strengths

- Making use of quantum effects at room temperature
- natural nanometer scale
- programmable functionalities (vs. light, E-field, temperature)
- cheap (in principle)

Weaknesses

- Low stability at room temperature
- Low conductance per molecule
- Electrodes define true dimensions
- Will not replace CMOS

Opportunities

- Multimolecular devices (by self-assembly: SAMs, networks)
- **Sensors and specific functionalities connected to CMOS**
- Functionality enhancement by other nano-objects
- Control of quantum interference

Threats

- Mostly basic research
- A niche technology at most

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FOM

NWO Netherlands Organisation for Scientific Research

Vidi

nanoscience Europe