Molecular and carbon-based electronic systems

Lecture 6

Single Molecule Devices &

Template structures for functional molecular junctions: nanoparticle arrays

Vorlesung Uni Basel, FS2017

Single molecule devices

"In 1952, Erwin Schrödinger wrote that we would never experiment with just one electron, atom, or molecule (1). Eight years later, Richard P. Feynman told us that there are no physical limitations to arranging atoms the way we want (2)."
Gimzewsky, Joachim, Science 1999

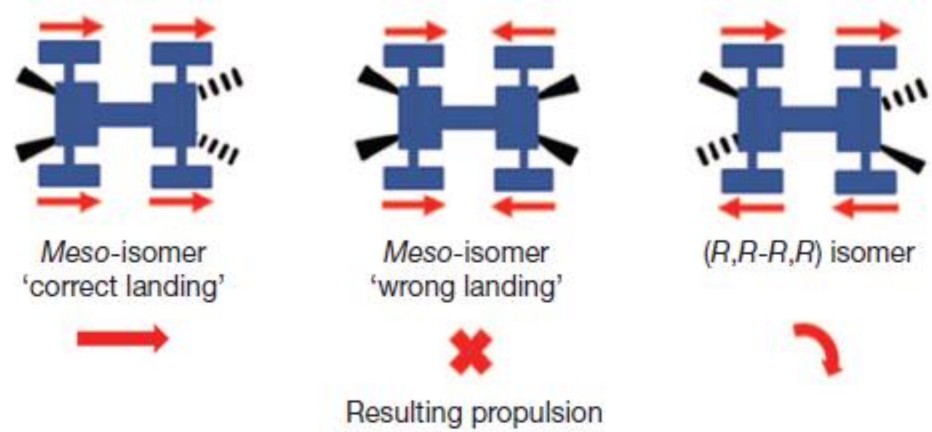
1. E. Schrödinger, *Br. J. Philos.* (1952), p. 233; **2**. R. P. Feynman, *Sci. Eng.* **23**, 22 (1960)

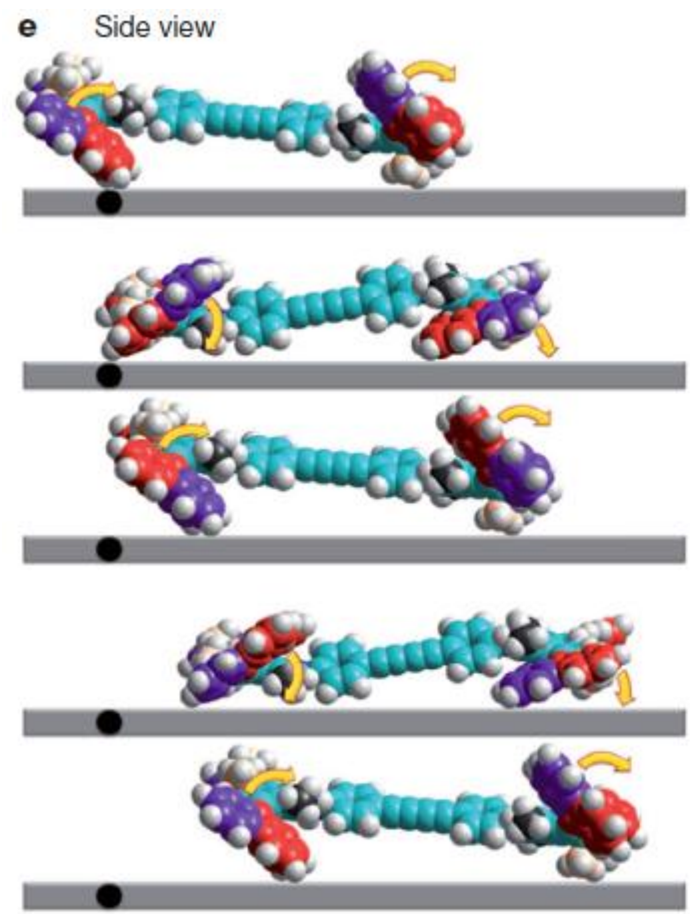
LETTER

doi:10.1038/nature10587

Electrically driven directional motion of a four-wheeled molecule on a metal surface

Tibor Kudernac[1,2]†*, Nopporn Ruangsupapichat[2]*, Manfred Parschau[3], Beatriz Maciá[1], Nathalie Katsonis[1,2]†, Syuzanna R. Harutyunyan[1], Karl-Heinz Ernst[3,4] & Ben L. Feringa[1,2]





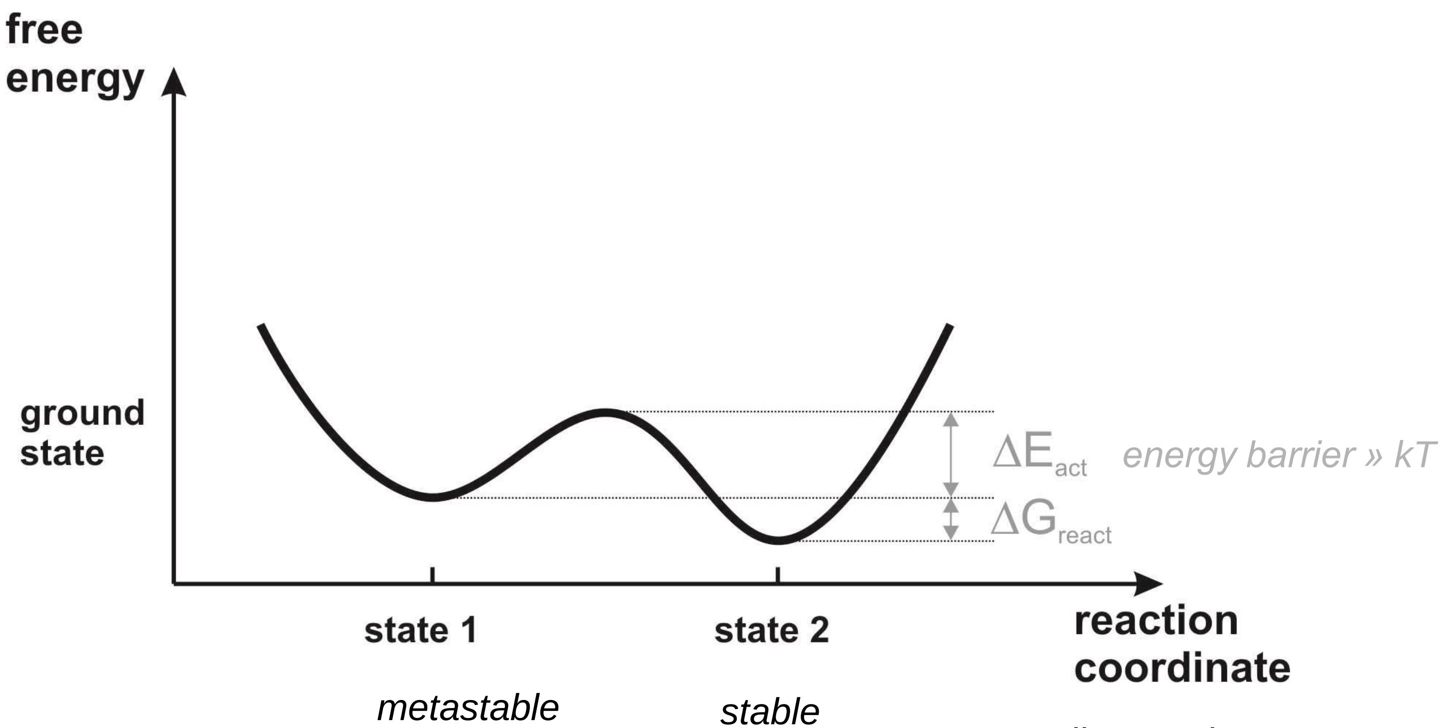
- two-state systems at the molecular scale
- families of molecular switches
- contacting strategies for upscaling

Examples

- optical switching for nanoelectronics
  from individual junctions to arrays
- and more functions

molecular switches

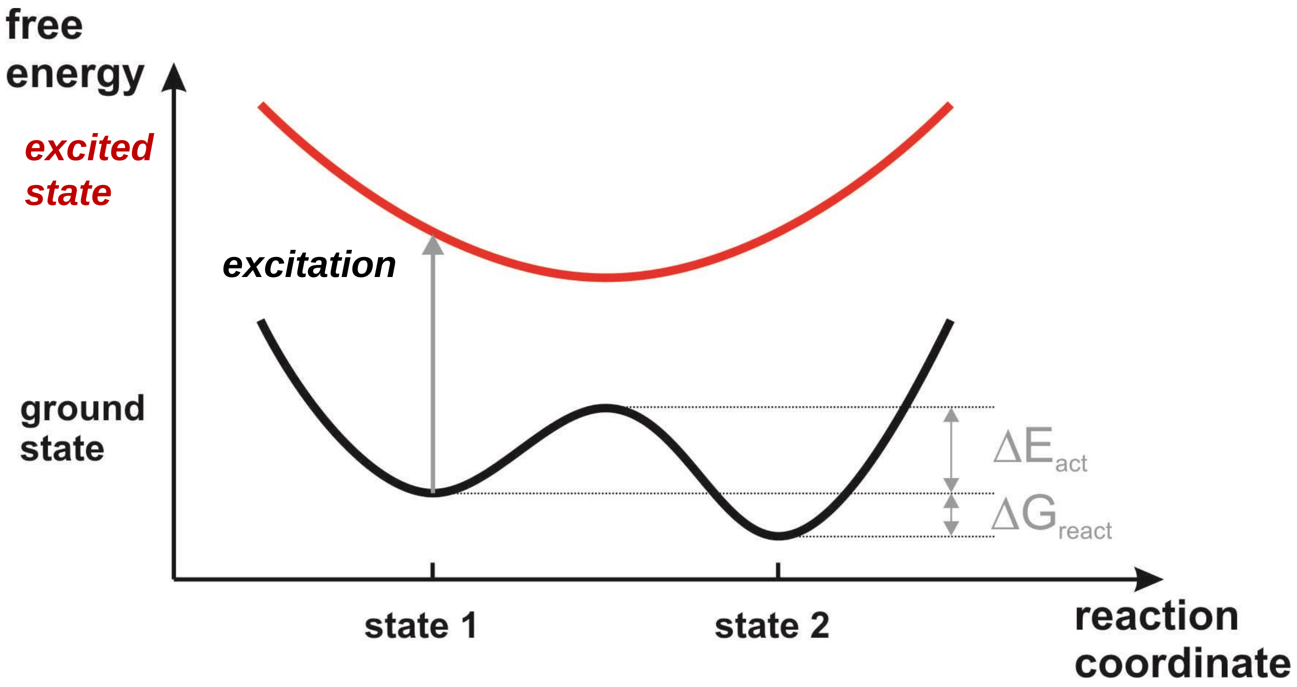
- intrinsic switches: 2-state systems



e.g.: distance between 2 atoms, torsion angle between 2 subunits

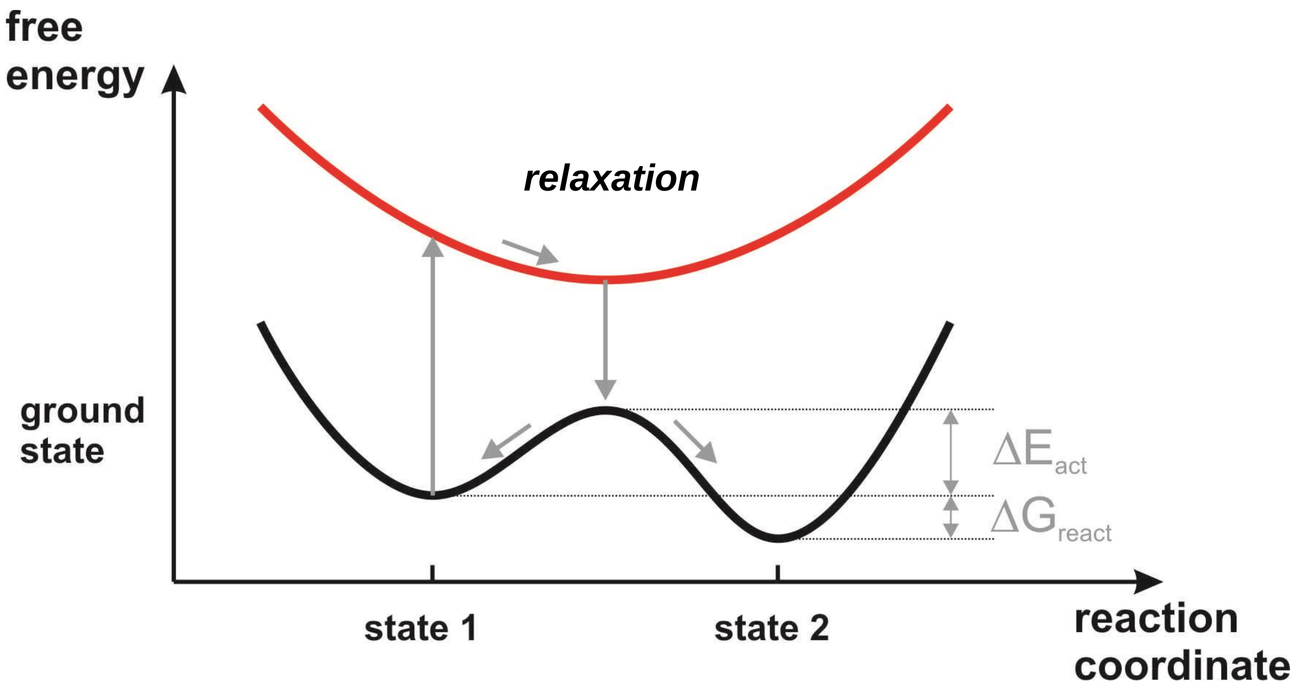
molecular switches

- intrinsic switches: 2-state systems



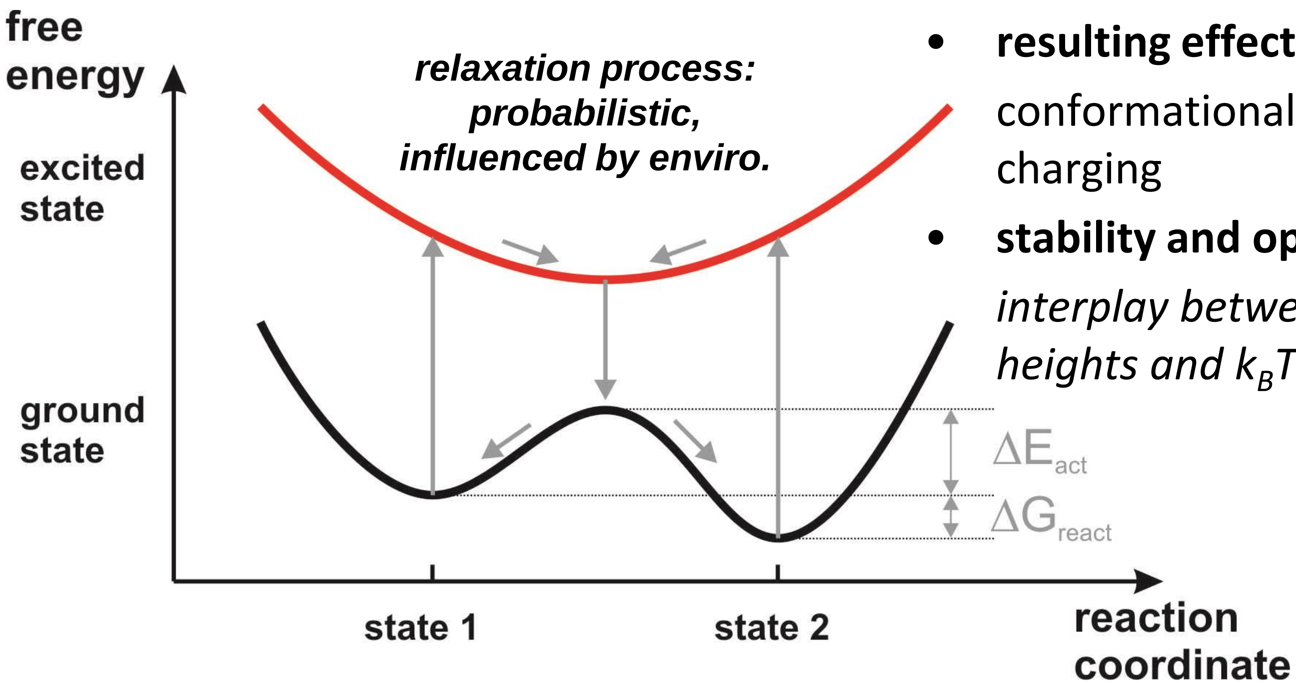
molecular switches

- intrinsic switches: 2-state systems



molecular switches

- intrinsic switches: 2-state systems



- **stimuli**

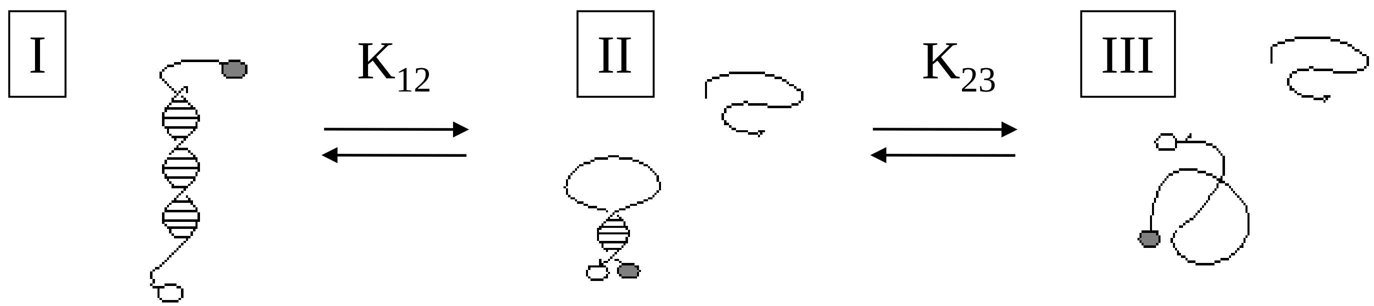
  light, electric field, current (vibronic, e-ph), temperature, (electro-) chemical reaction
- **resulting effect**

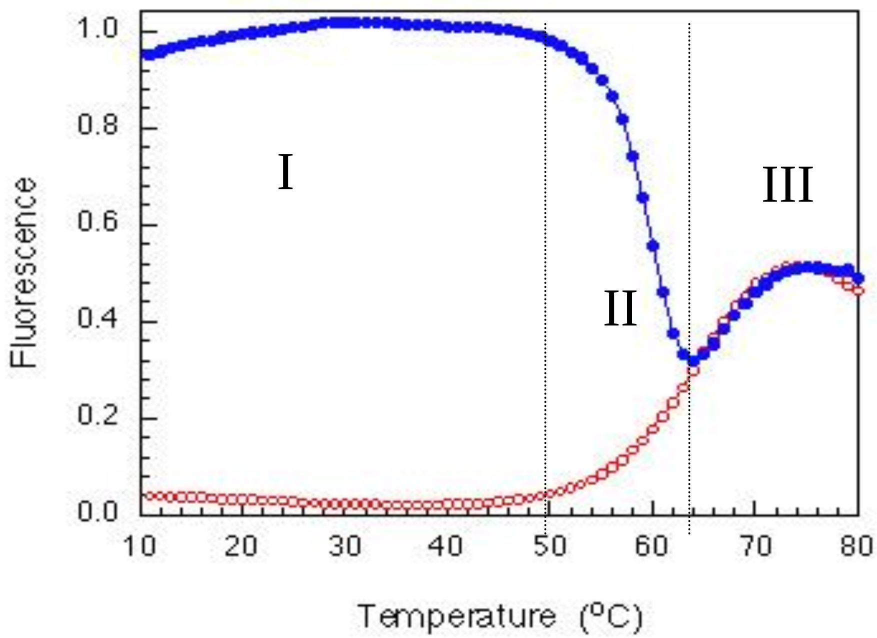
  conformational change, charging
- **stability and operability**

  interplay between barrier heights and $k_B T$

⇨ **memory elements, rectification, transistor, multiple states …?**

example: a biomolecular switch ...





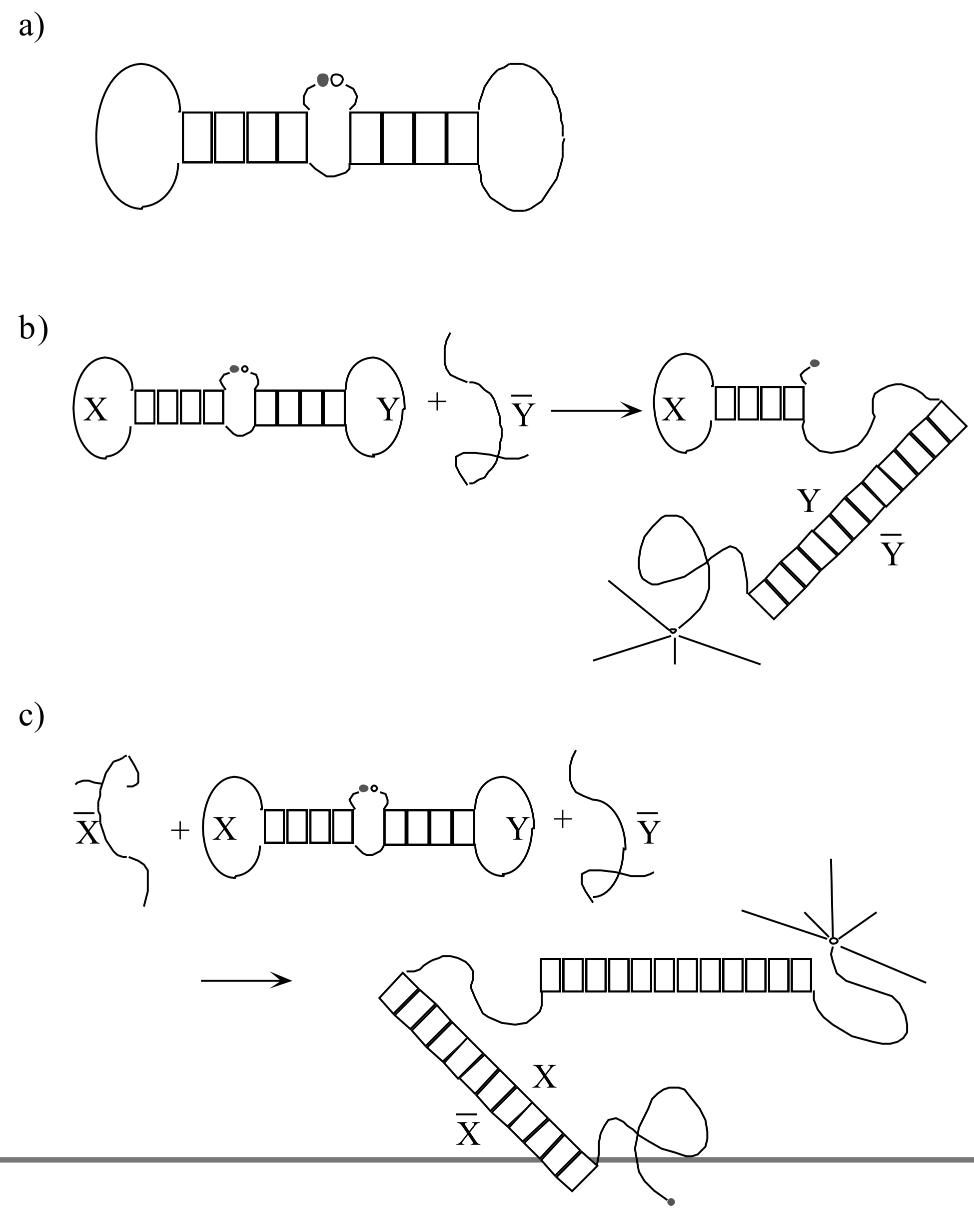
beacons + targets

beacons alone

F. Kramer, S. Tiagi; G. Bonnet et al., PNAS 1999

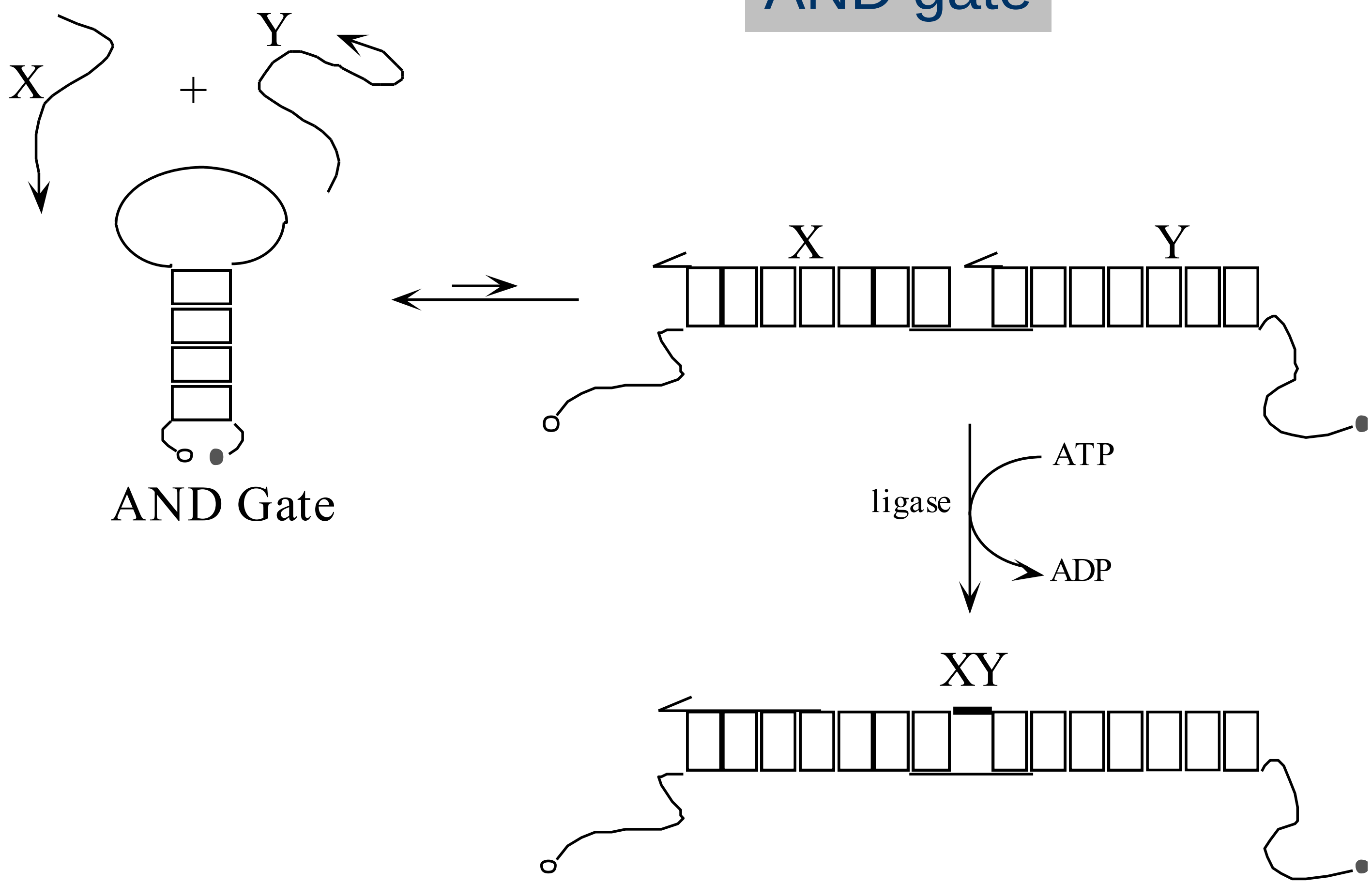
a biomolecular switch ... for logical operations

OR gate



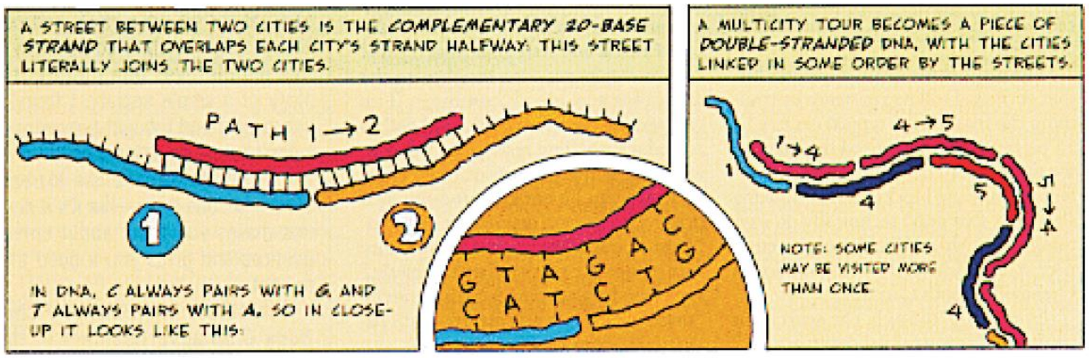
a biomolecular switch ... for logical operations

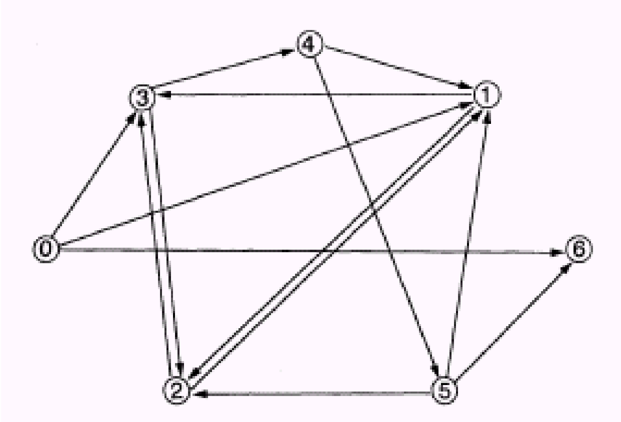
AND gate

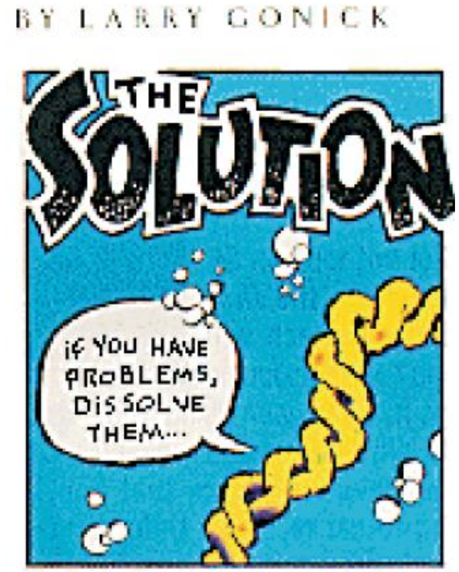


DNA computing

L. Adleman, Molecular computation of solutions to combinatorial problems.
Science 266, 1021 (1994).







- **molecular recognition**

  computing with molecules – in solution - is highly parallel

  different aspects to molecular computing:

  electronic, chemical and biochemical

  see e.g. Libermann, Cell as a molecular computer, 1972

- two-state systems at the molecular scale

- families of molecular switches

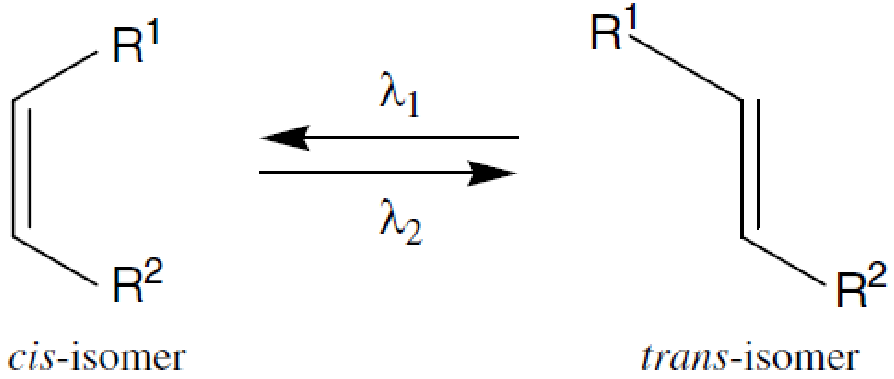
- contacting strategies for upscaling

Examples

- optical switching

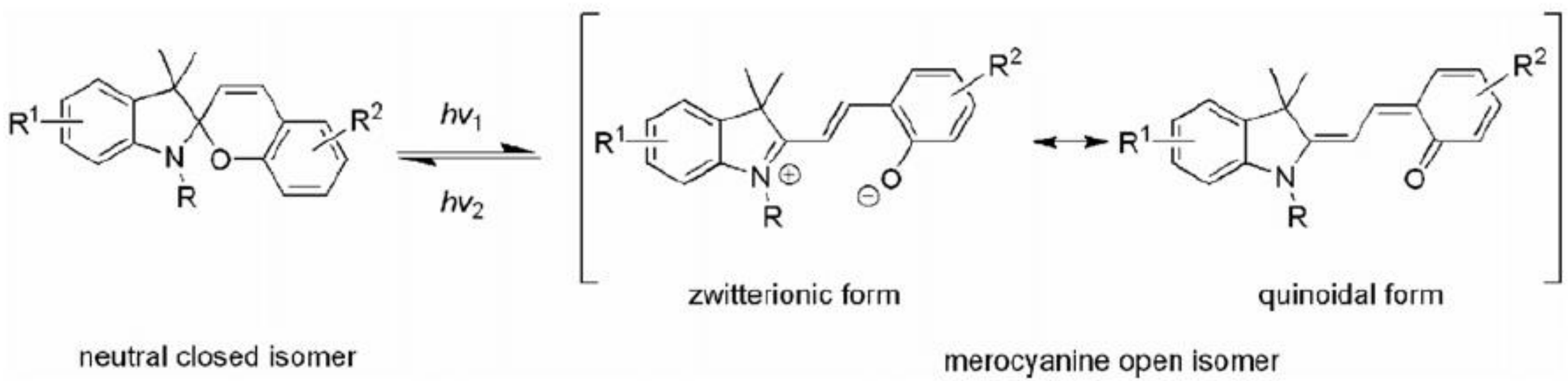
- and more functions

alkenes



photochemical interconversion between the cis and trans configurations

spiropyrans

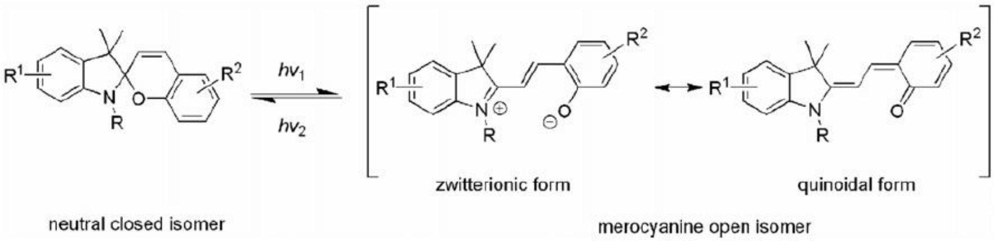


reversible photoisomerization of spiropyran moieties

Katsonis et al., Prog. Surf. Sci. 2007

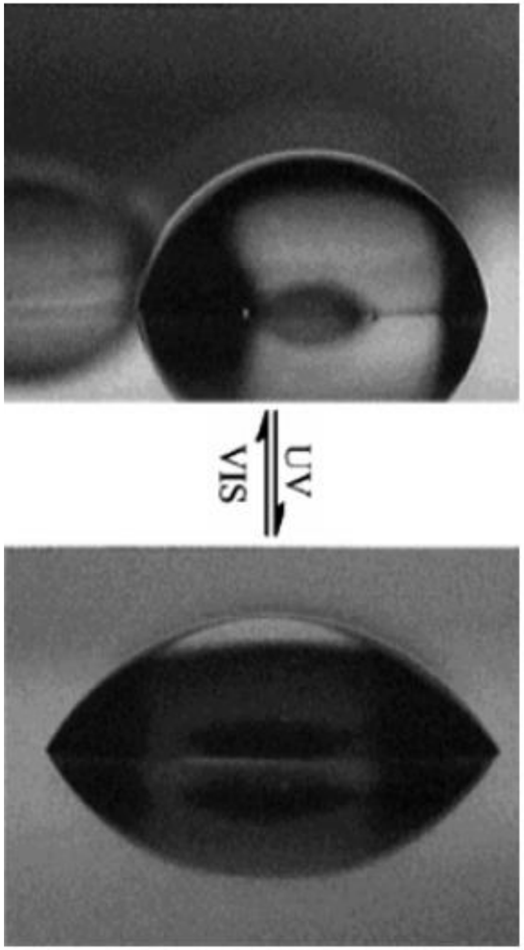
example of spiropyrans implementation

- functional surfaces



hydrophobic

hydrophilic
highly polar, zwitterionic isomer
(large dipole moment)

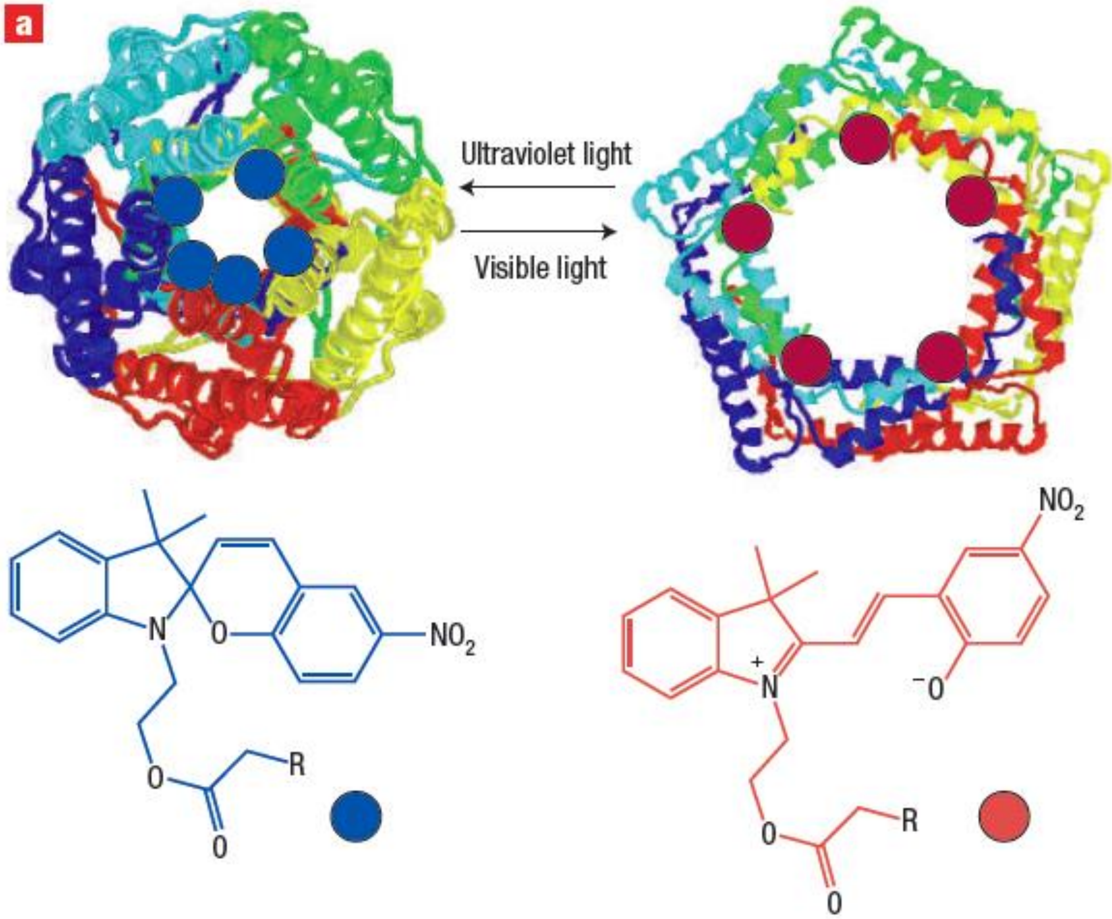


water drops deposited on spiropyran functionalized surfaces

Katsonis et al., Prog. Surf. Sci. 2007

example of spiropyrans implementation

light-actuated nanovalve
mechano-sensitive channel protein modified with spiropyran photoswitches



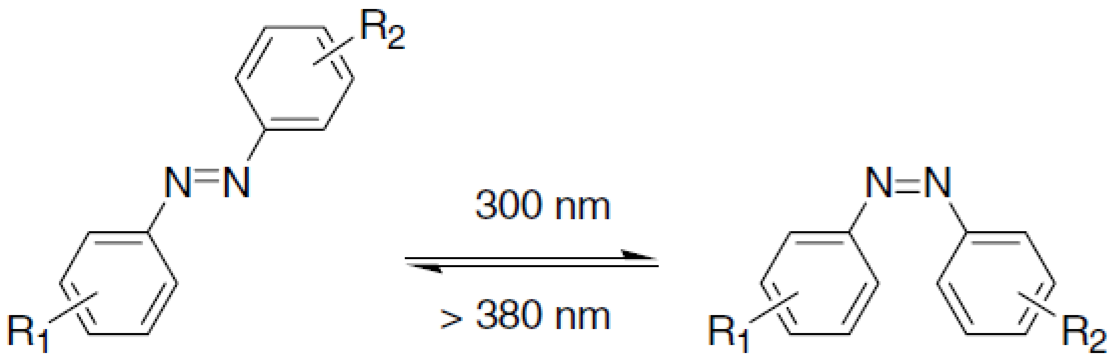
hydrophobic ***hydrophilic***

Ferringa et al., Nat. Nano 2006

azobenzenes

trans

cis

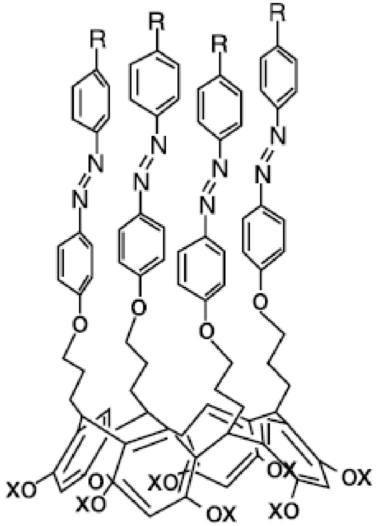


Katsonis et al., Prog. Surf. Sci. 2007

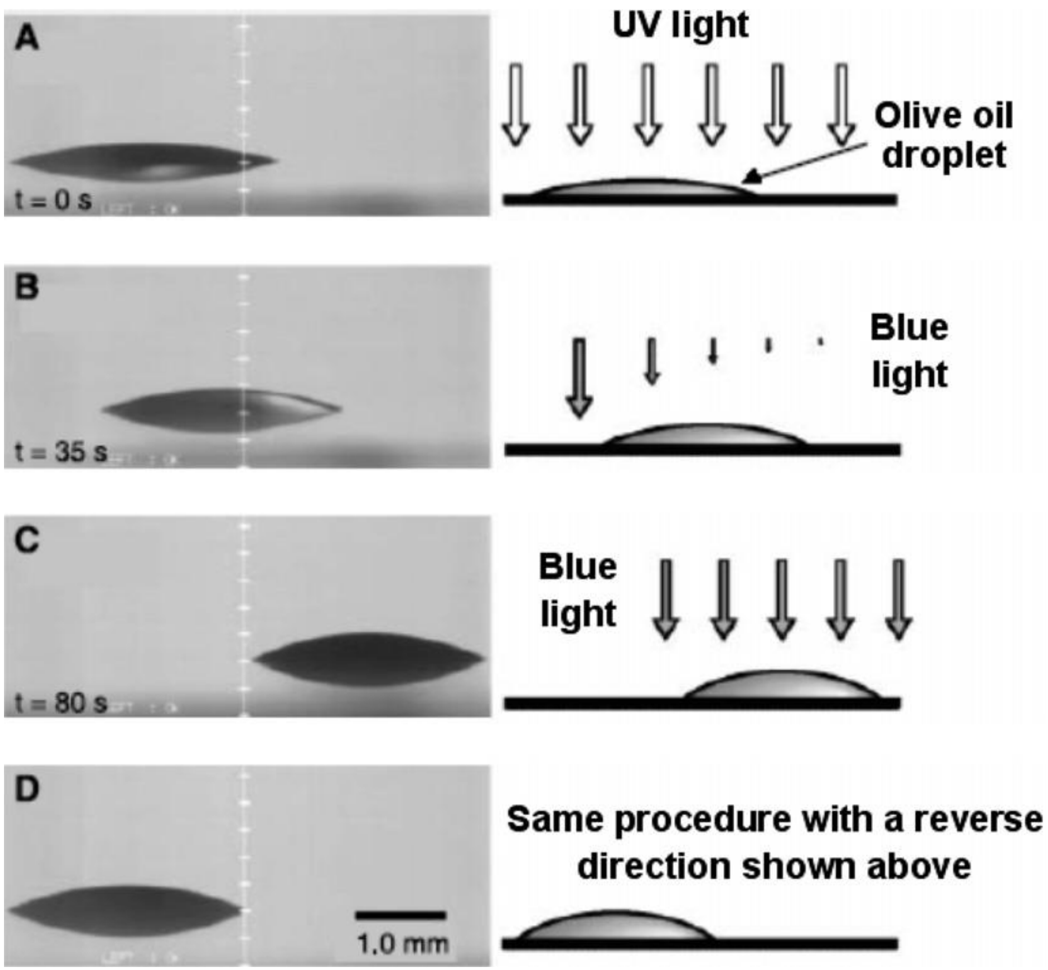
example of azobenzene implementation

functional surface: light-driven motion
olive oil droplet on a silica plate modified with an azobenzene derivative

asymmetrical irradiation (436 nm)
⇔control of motion



X = $-CH_2COOH$
R = $-(CH_2)_7CH_3$



Ichimura et al., Science. 2000

example of azobenzene implementation

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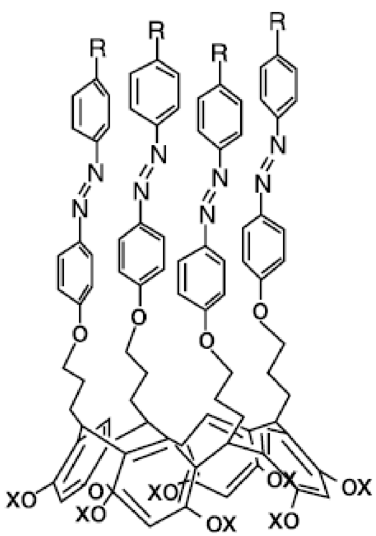

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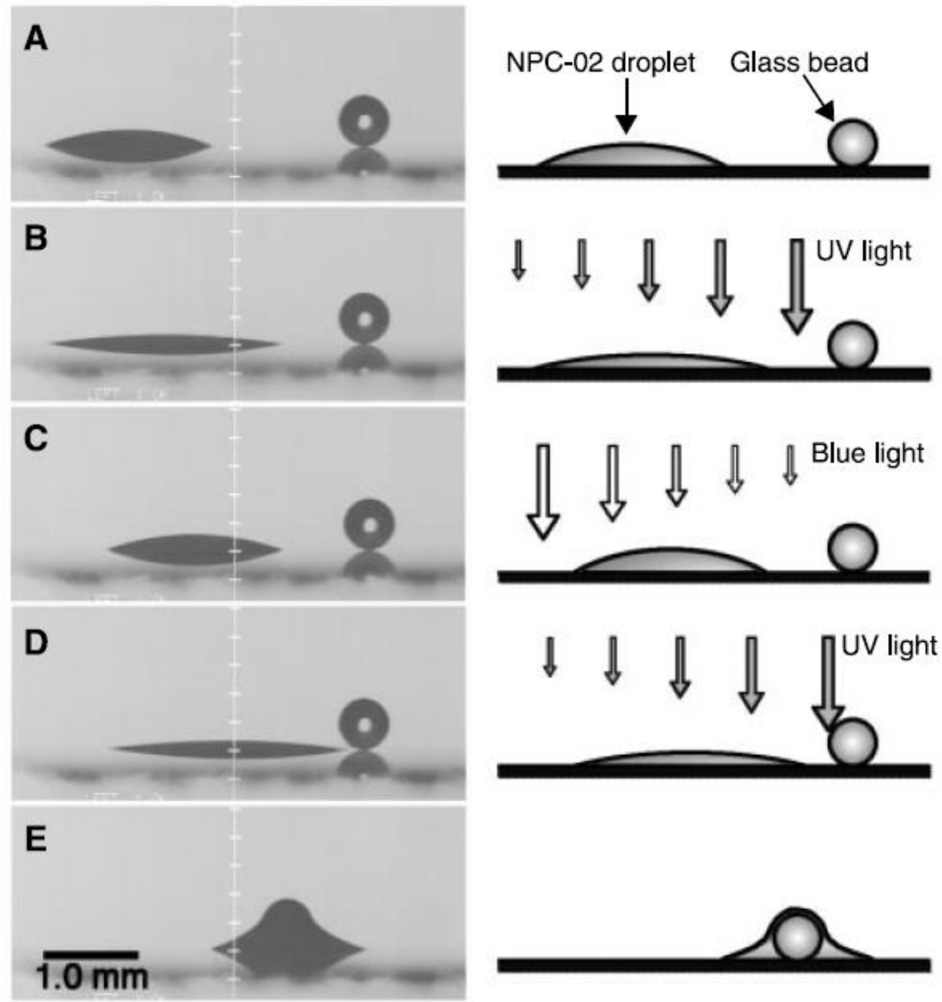
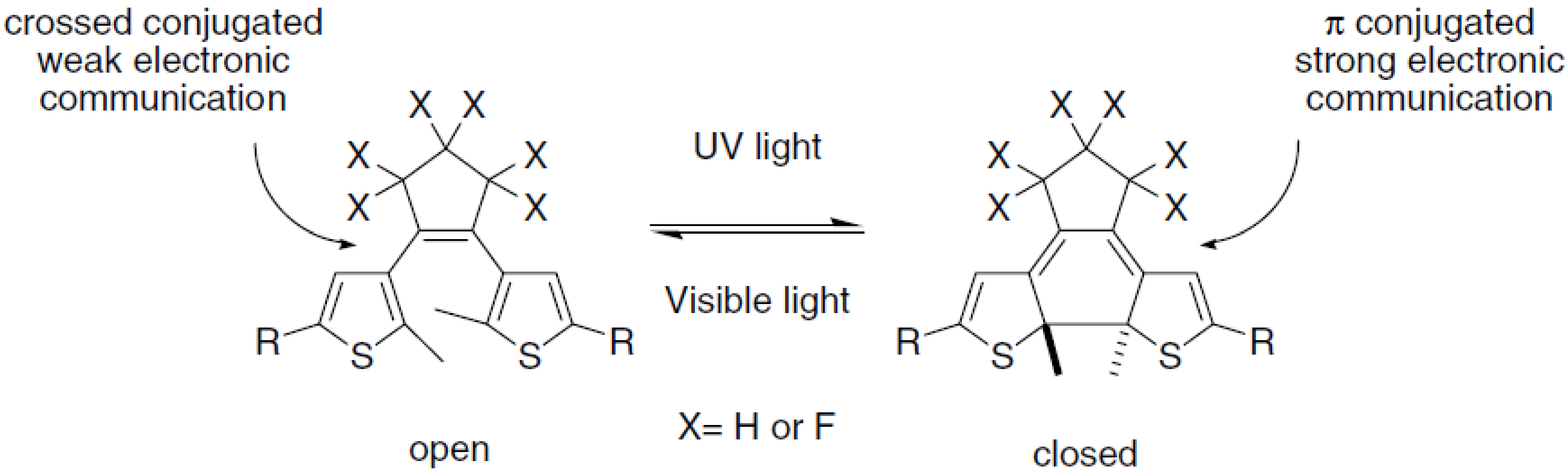


Ichimura et al., Science. 2000

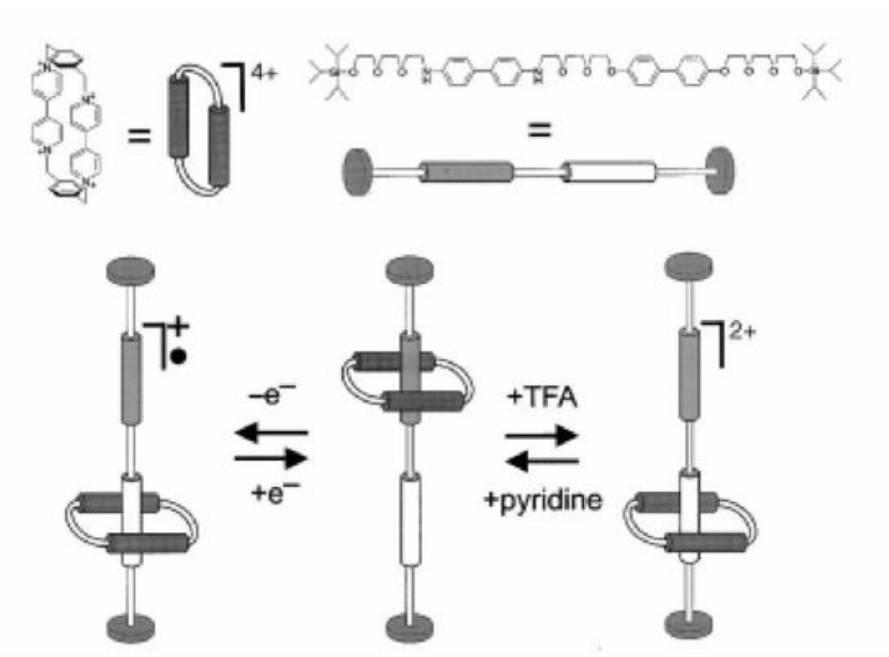
diarylethenes, dithienylethenes



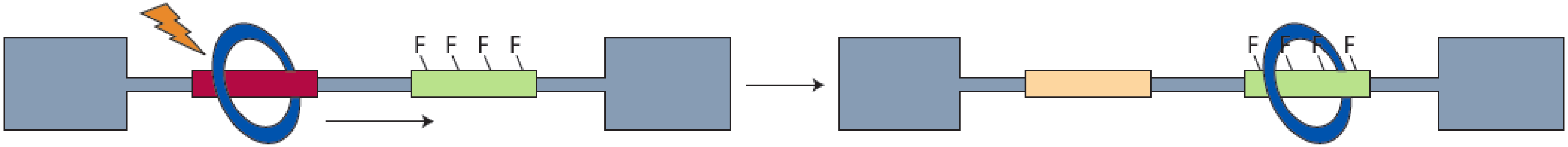
Reversible photocyclisation of 1,2-dithienylethene moieties
upon UV–Vis light irradiation

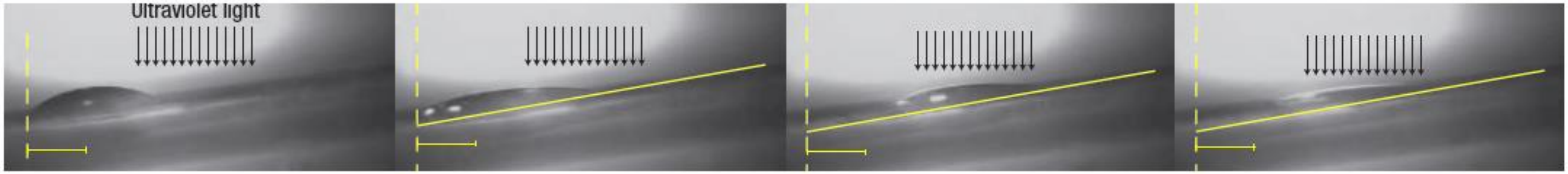
Katsonis et al., Prog. Surf. Sci. 2007

rotaxanes and examples of implementation



Stoddart et al.

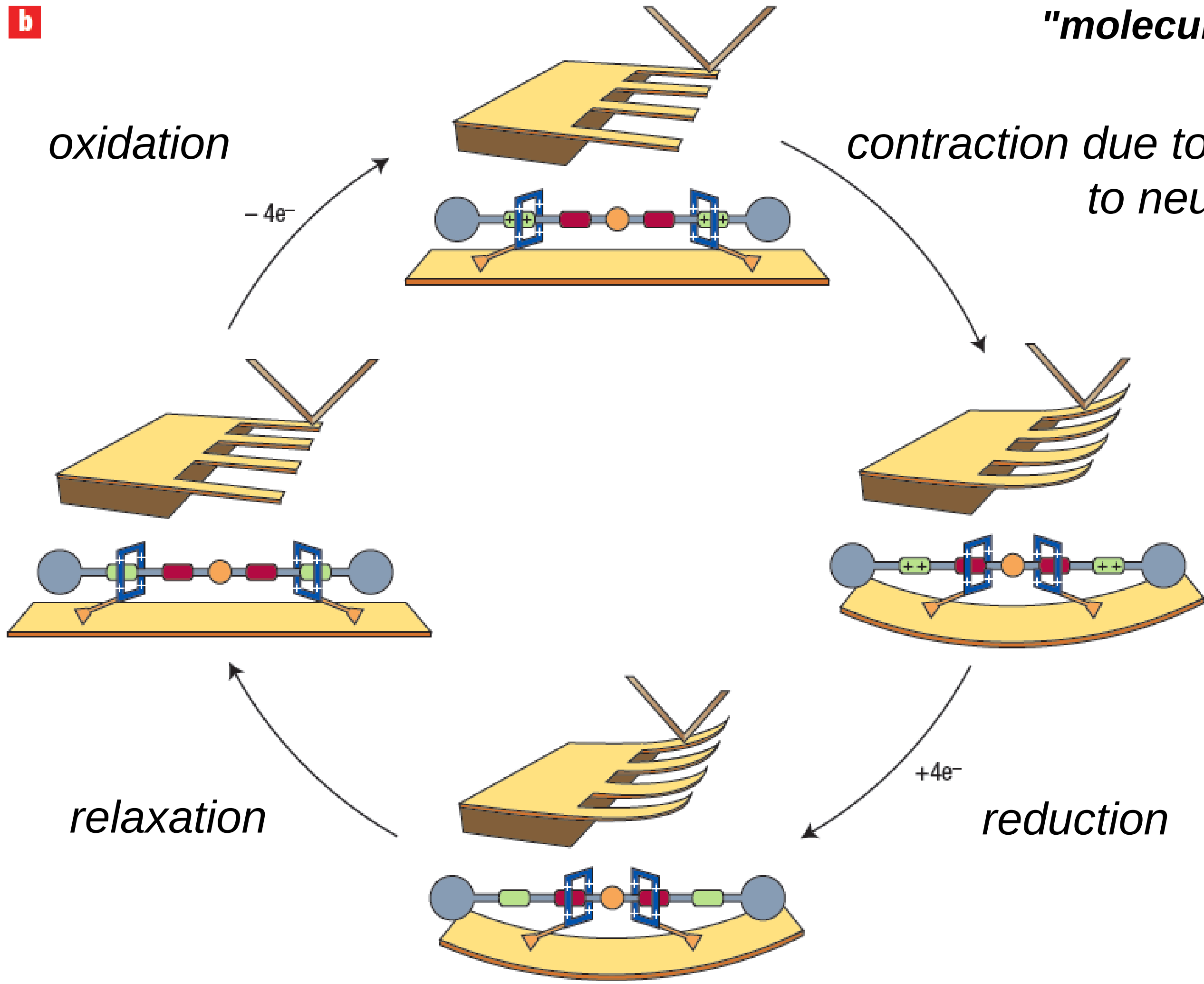




Stoddart et al.; Ferringa et al., Nat. Nano 2006

rotaxanes and examples of implementation

"molecular muscle"



start

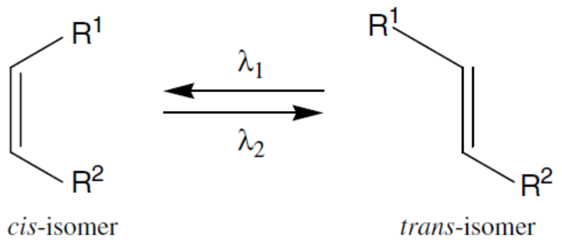
oxidation

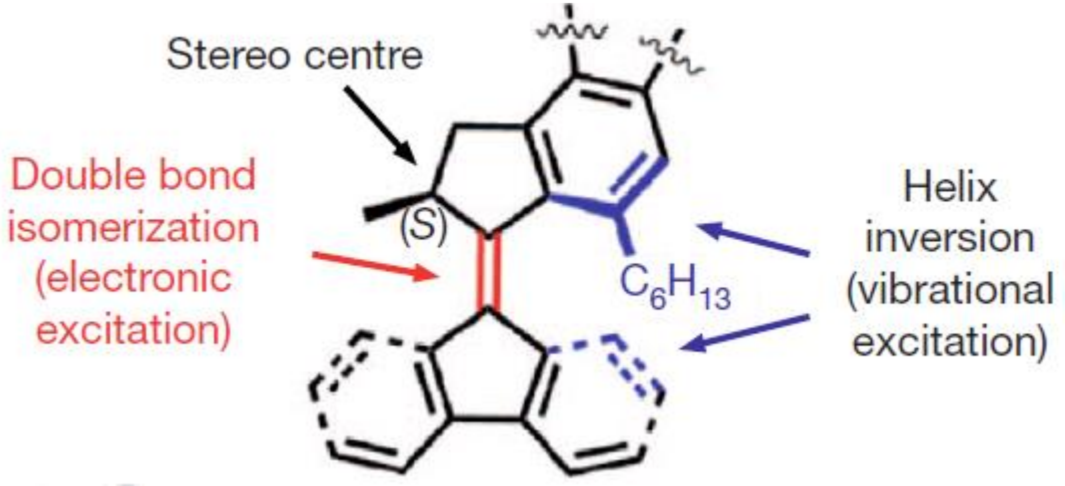
contraction due to ring motion to neutral stations

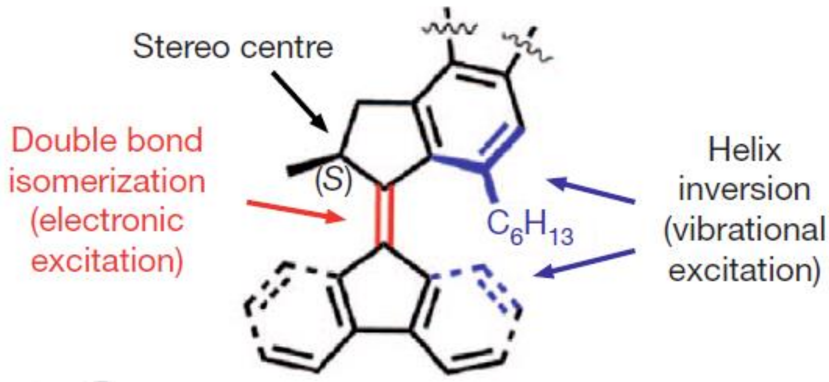
reduction

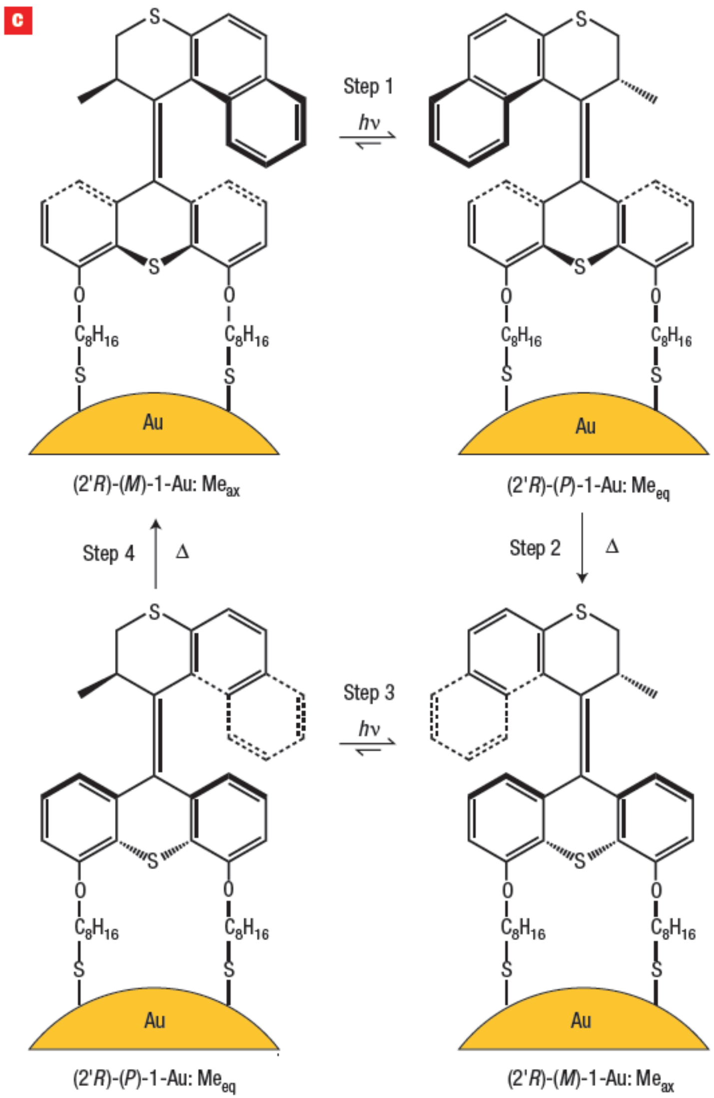
relaxation

Stoddart et al., Ferringa et al., Nat. Nano 2006


R1
R2
λ1
λ2
R1
R2
cis-isomer
trans-isomer


Stereo centre
Double bond isomerization (electronic excitation)
(S)
C6H13
Helix inversion (vibrational excitation)

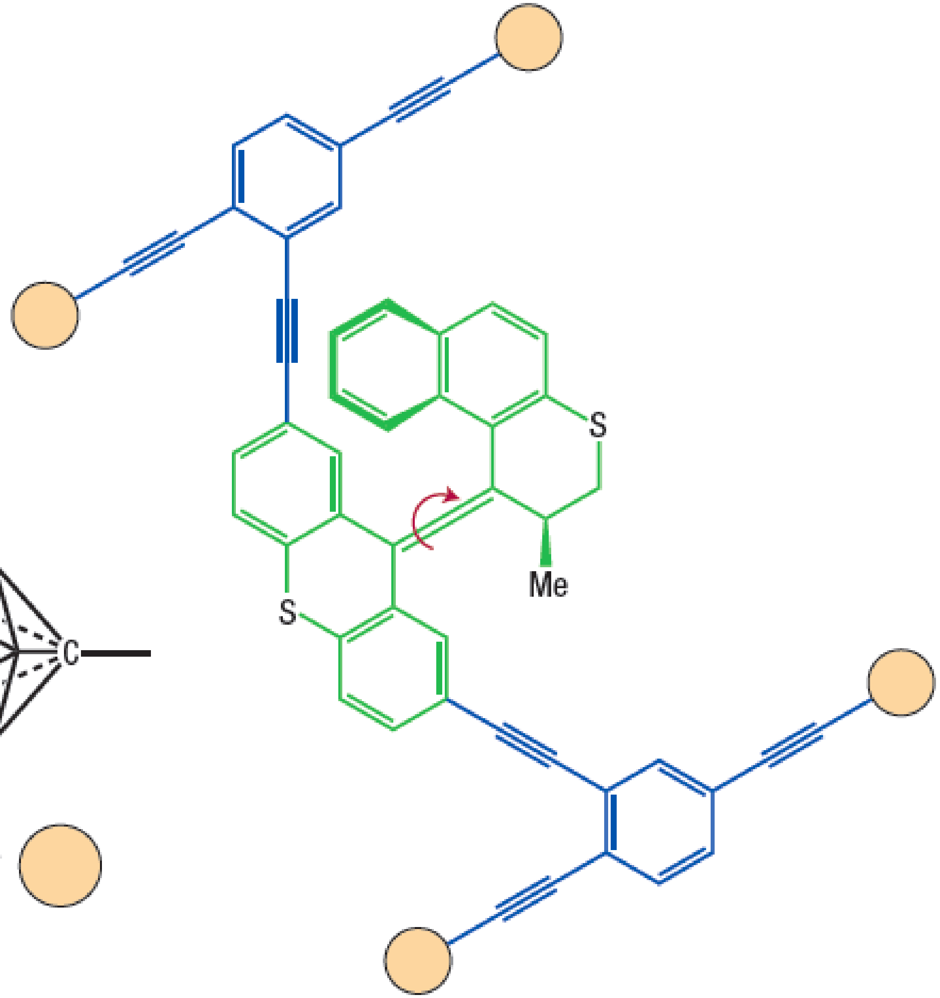


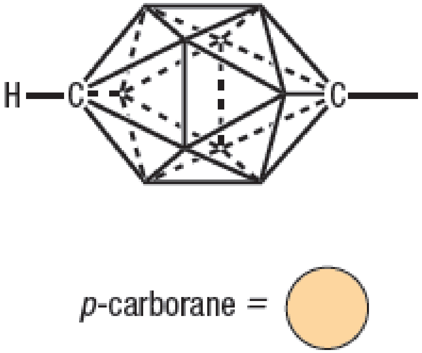


Ferringa et al., Nat. Nano 2006; Nature 2011

rotary motor

prototype of light-driven molecular car....?

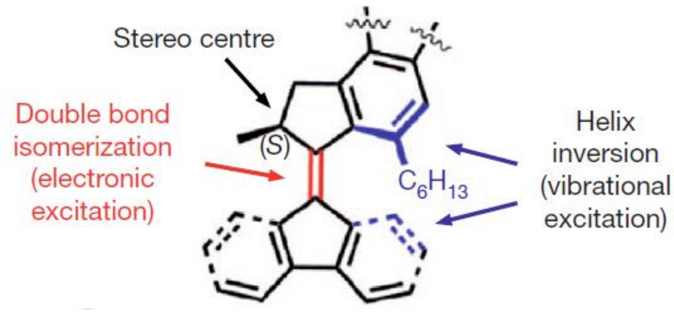


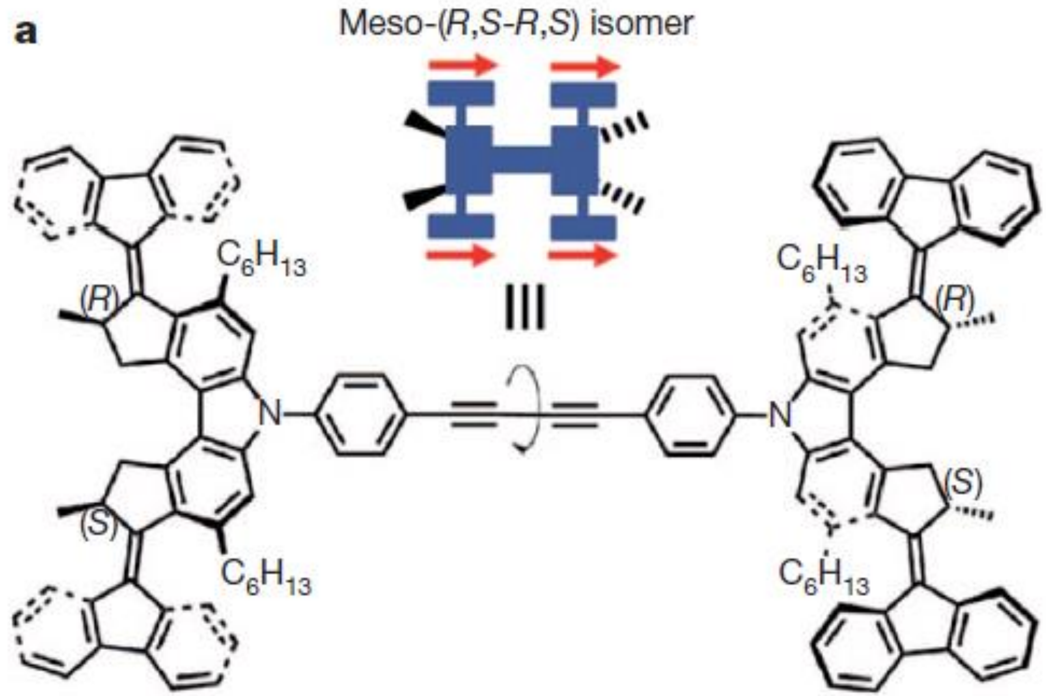


Ferringa et al., Nat. Nano 2006

rotary motor

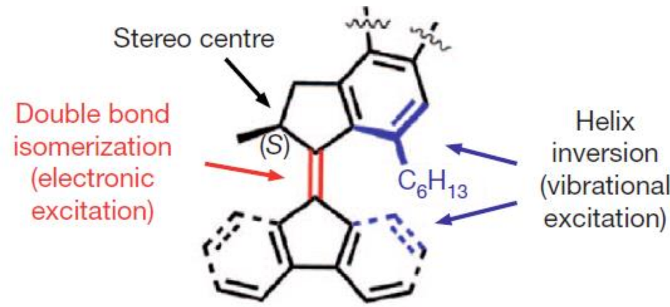
implementation of electrically driven molecular car....!

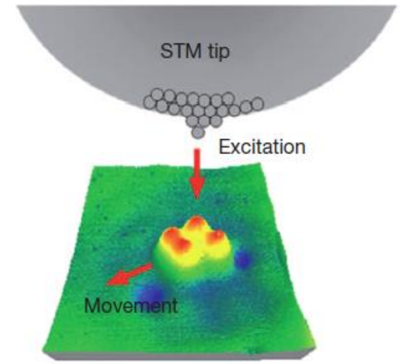


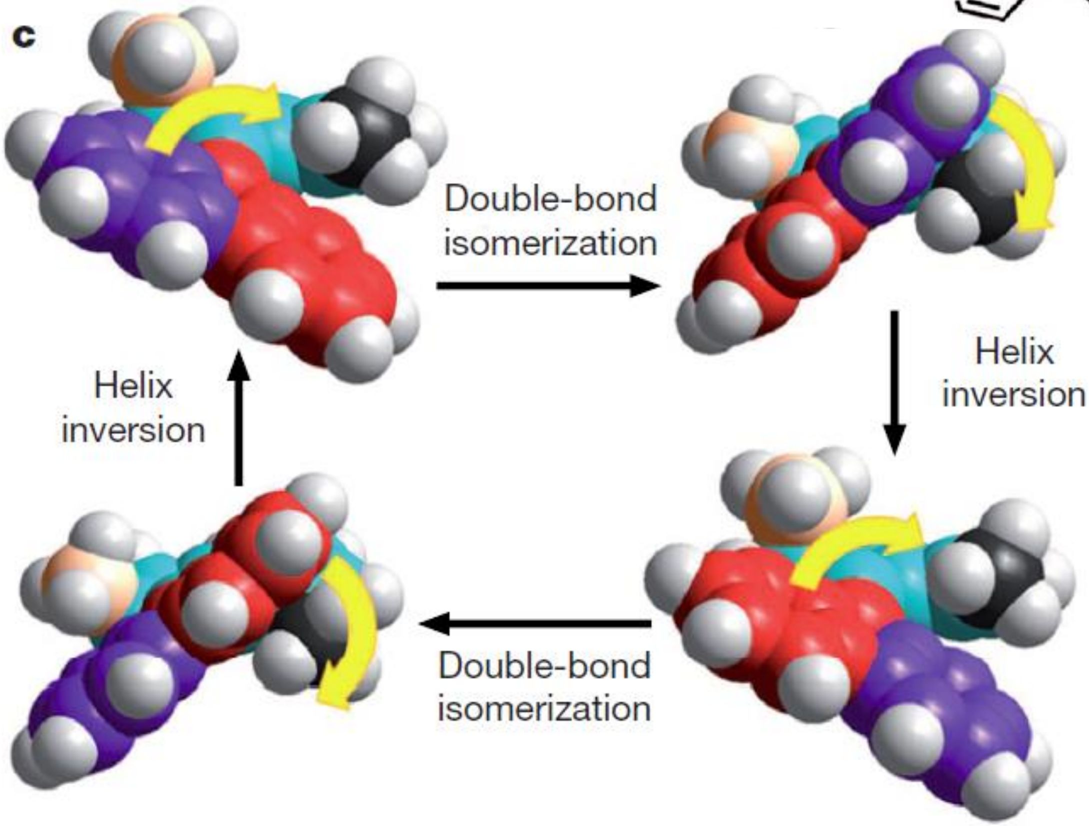


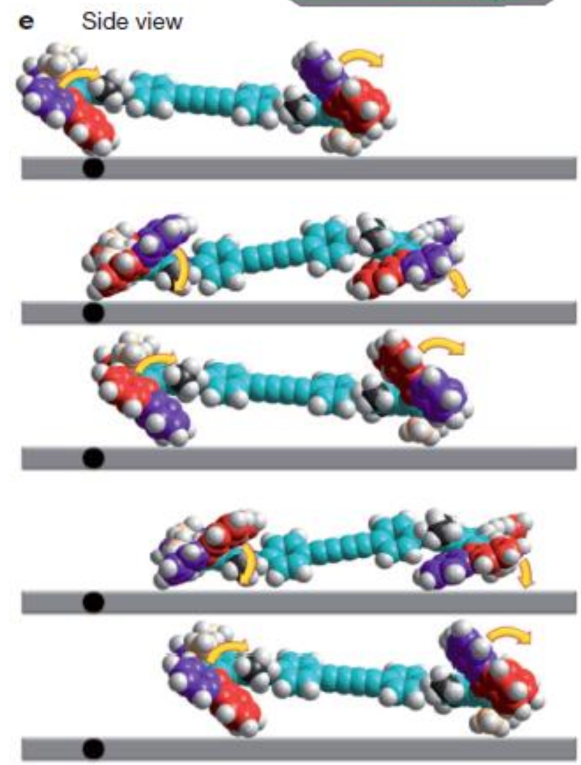
rotary motor

implementation of electrically driven molecular car....!





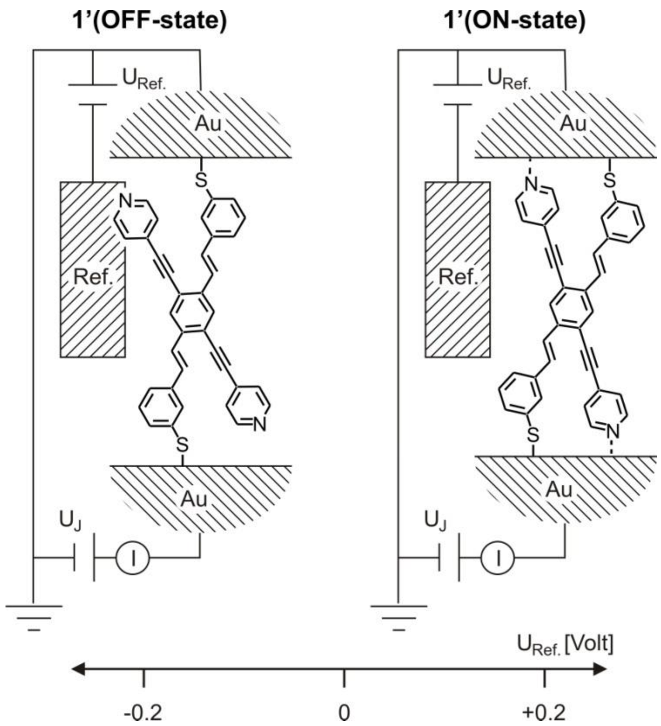


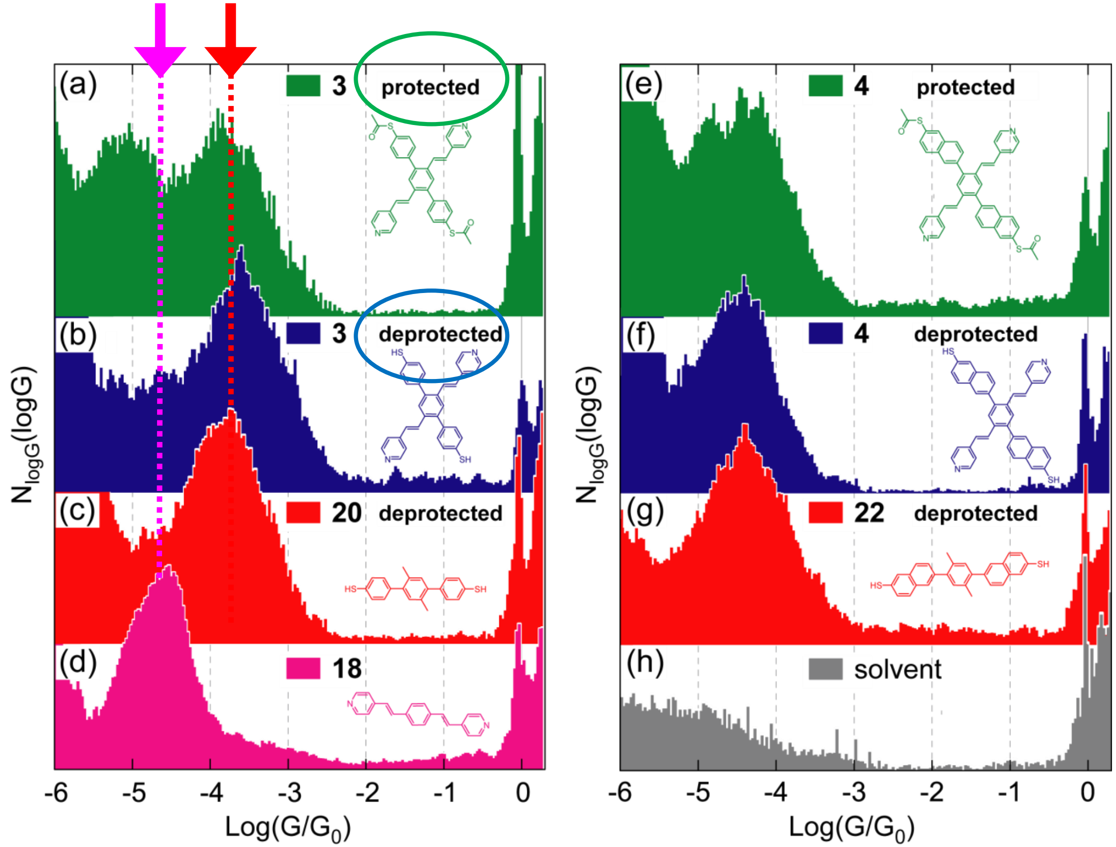


Ferringa et al., Nature 2011

electro-(mech-)chemical switch

possible implementation of coordination induced switching





S. Grunder, R. Huber et al., JOC (2007); EJOC (2009)

- two-state systems at the molecular scale
- families of molecular switches
- contacting strategies for upscaling

Examples

- optical switching
- and more functions

contacting molecules: exp. techniques

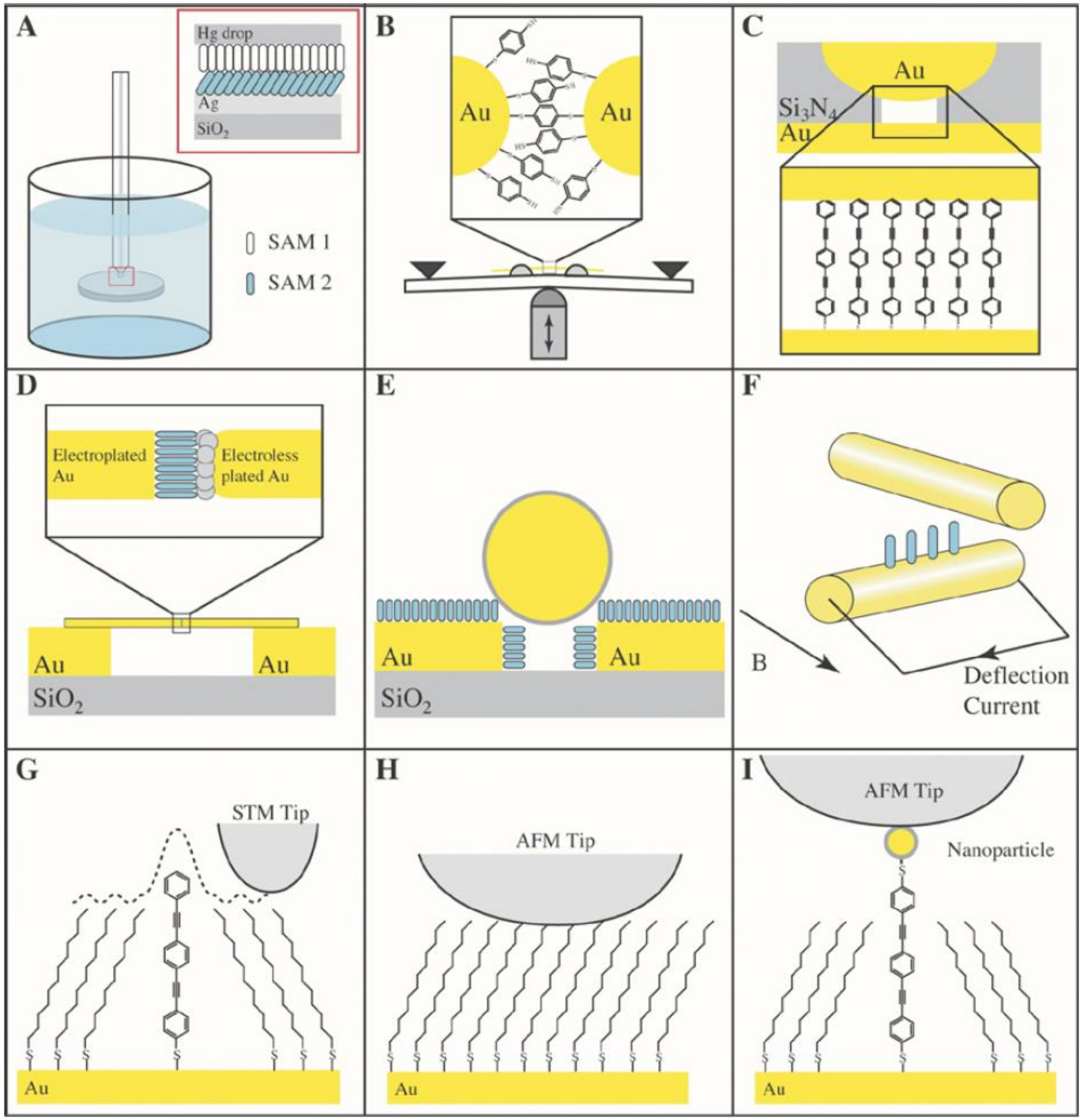
single molecule & molecular monolayer contacting

⇨ **upscaling ?**
implementation of devices at wafer scale

thin films, ultra-thin films
⇨ **monolayers at large scale**

see for instance

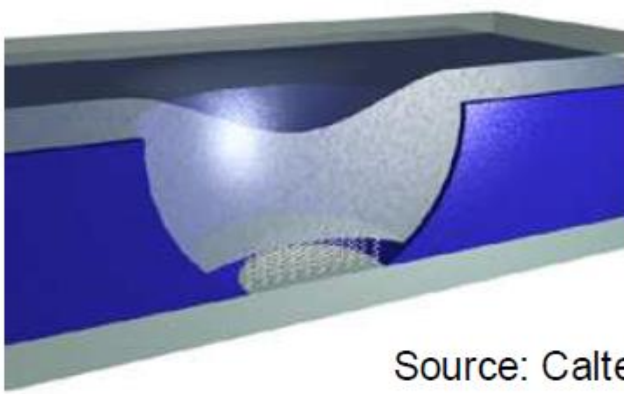
- P. Blom et al., Philips Research
- F. Wrochem et al., Sony Research
- C. Hacker at al., NIST
  Nanoelectronic device metrology



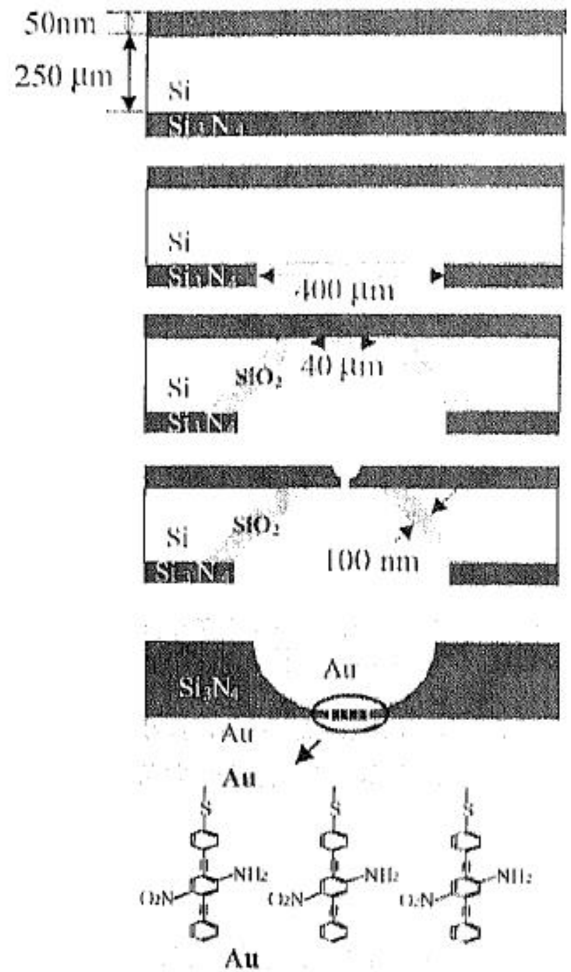
Mantooth, Weiss., Proc. IEEE, 2003

nanopore architecture

- Si_3N_4 thermally grown, boxes opened.
- KOH etching depends on orientation and stops on the Si_3N_4 (selectively etching), leaving a suspended Si_3N_4 membrane.
- Eliminates pinholes and other defects
- 1000 molecules / pore



Source: Caltech



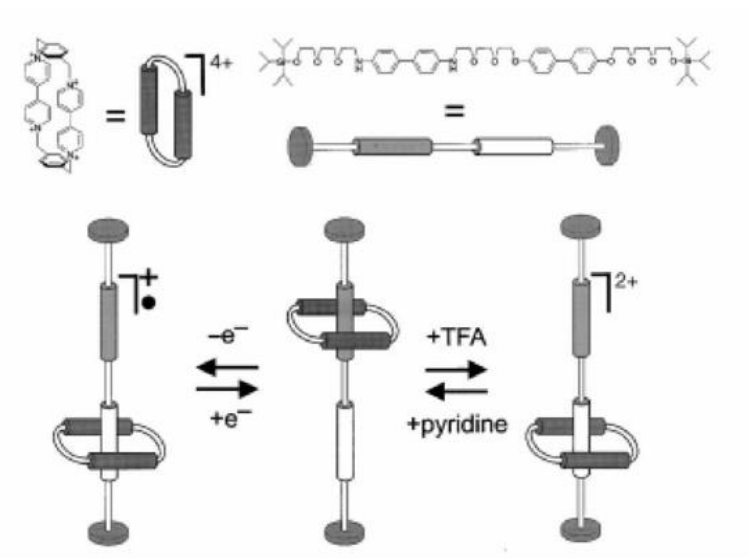
E. Lörtscher, IBM

Reed et al., Electronic Memory Effects in SAMs, Phys. E. (2003)

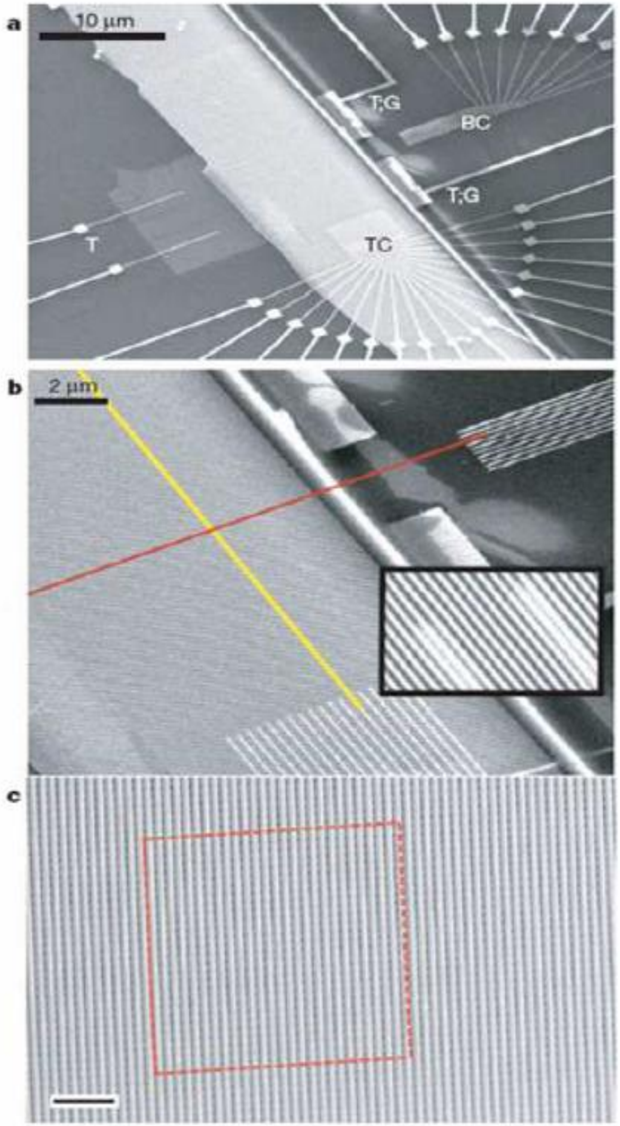
crossbar architecture

- **cross-bar memory** with 10^{11} bits per square centimeter fabricated by nanoimprint lithography
  world-record in bit density in 2007 *Heath et al., Nature (2007)*

- full logic structures and architectures based on the dynamical stereochemistry in rotaxane molecules



Stoddart et al., Science (1999)

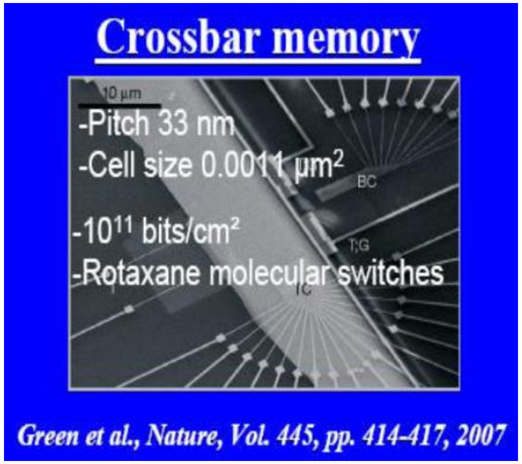


⇨ it works but is it really due to the molecules ...?

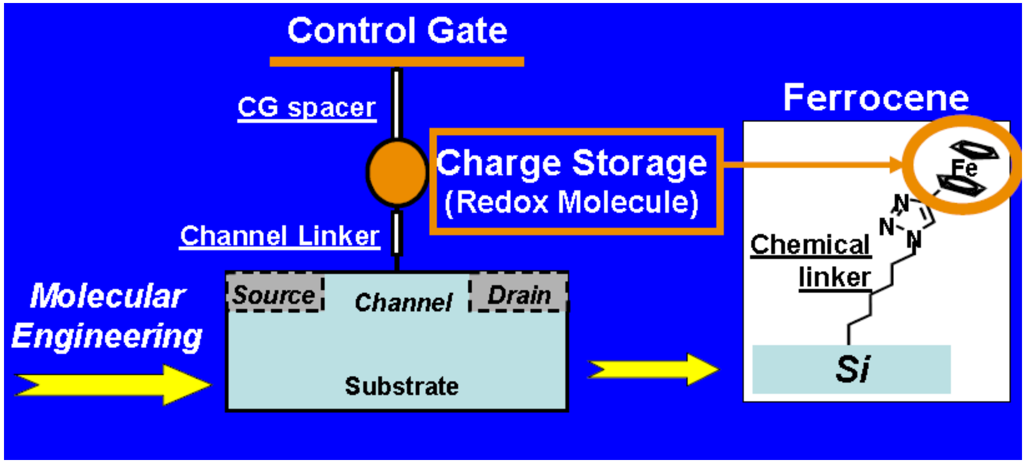
International Technology Roadmap for Semiconductors (ITRS)

Assessment of the Potential & Maturity of Selected Emerging Research Memory Technologies ITRS (2010)
- 8 identified technologies
- 3 (at least) involve an organic-inorganic interface

issues: poor or no under-standing of mechanisms



switching mechanism and role of electrodes not understood
(resistive molecular memory)



charging physics not well understood
(capacitive molecular memory)

metal filaments, electromigration, ions motion ...?

- two-state systems at the molecular scale
- families of molecular switches
- contacting strategies for upscaling

Examples

- **optical switching for nanoelectronics**
  - diaryethenes in individual junctions
  - nanoparticles arrays: a versatile platform
  - light coupling: plasmons
  - swithing in nanoparticle arrays

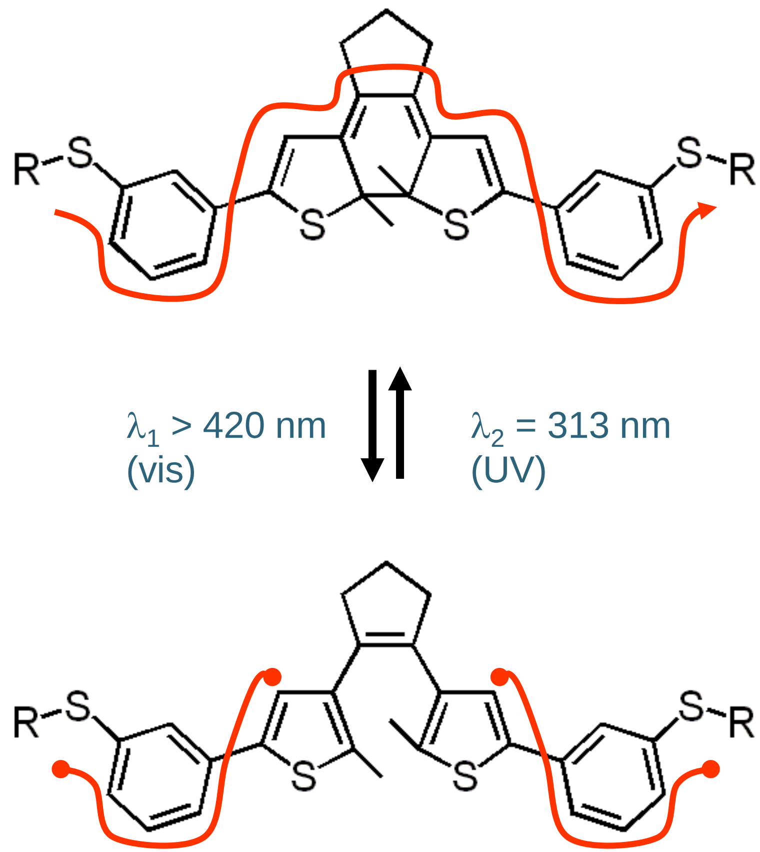
diarylethene: optical modulation of conductance?

"Irie" switch

Closed state

"ON" state

extended conjugation



Open state

"OFF" state

interrupted conjugation

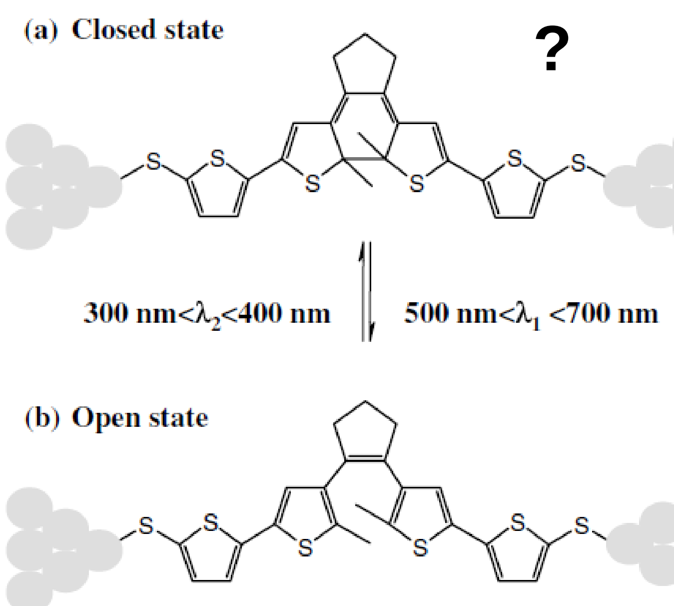
M. Irie et al., B. Ferringa et al.

in break junctions

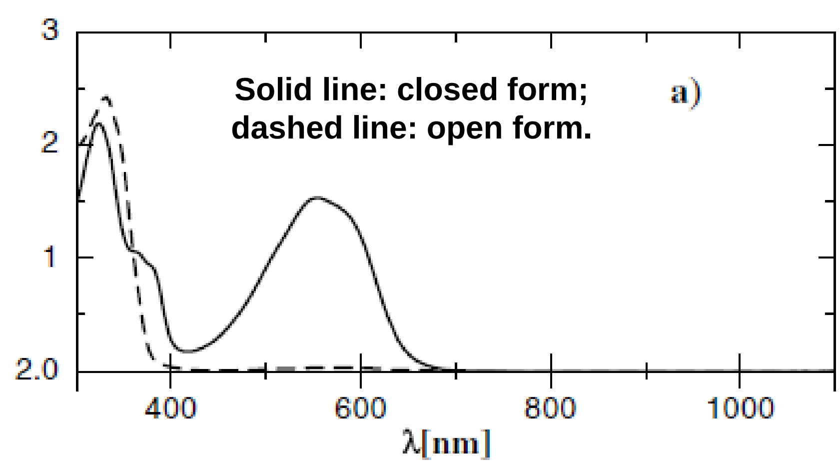
VOLUME 91, NUMBER 20 PHYSICAL REVIEW LETTERS week ending 14 NOVEMBER 2003

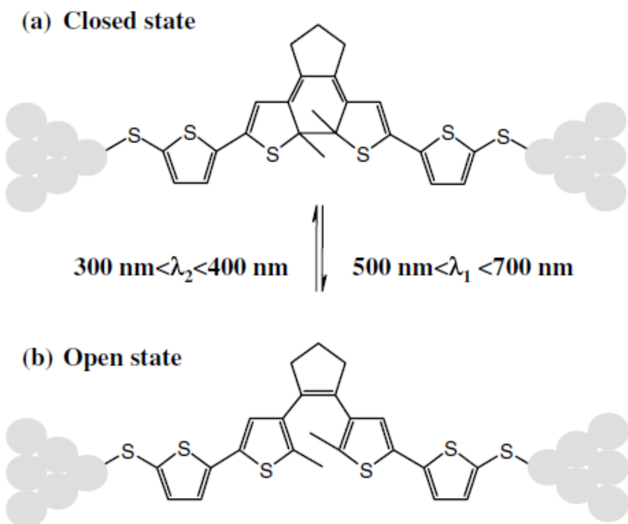
One-Way Optoelectronic Switching of Photochromic Molecules on Gold

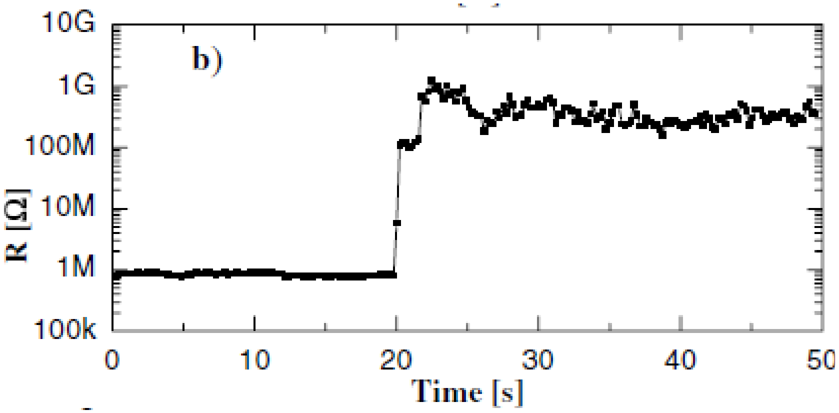
Diana Dulić,[1] S. J. van der Molen,[1] T. Kudernac,[2] H. T. Jonkman,[3] J. J. D. de Jong,[2] T. N. Bowden,[2] J. van Esch,[2] B. L. Feringa,[2] and B. J. van Wees[1]

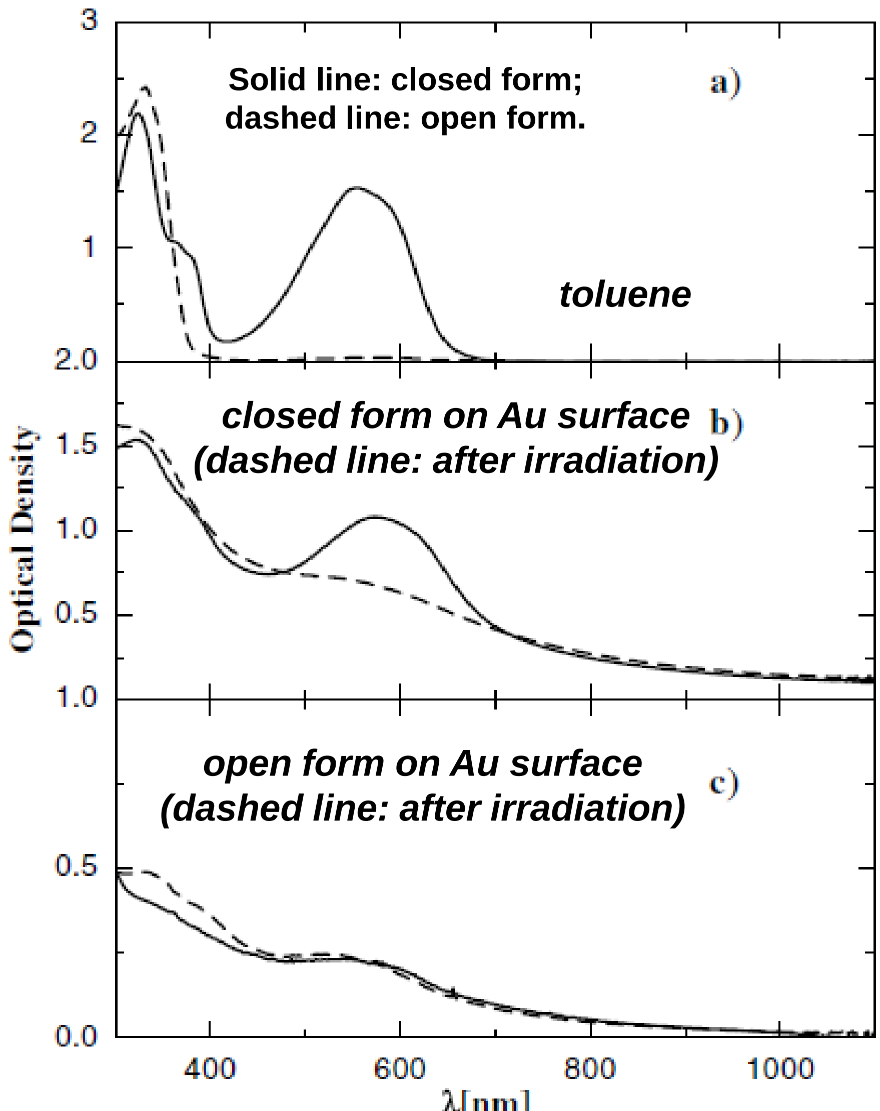


in solution *(toluene)*



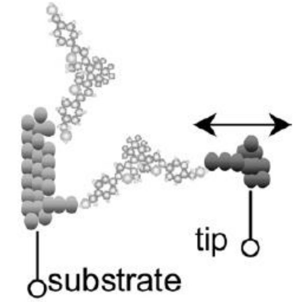






one-way switching only

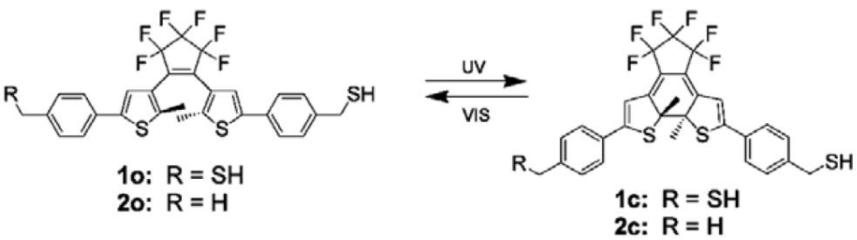
in break junctions (STM)

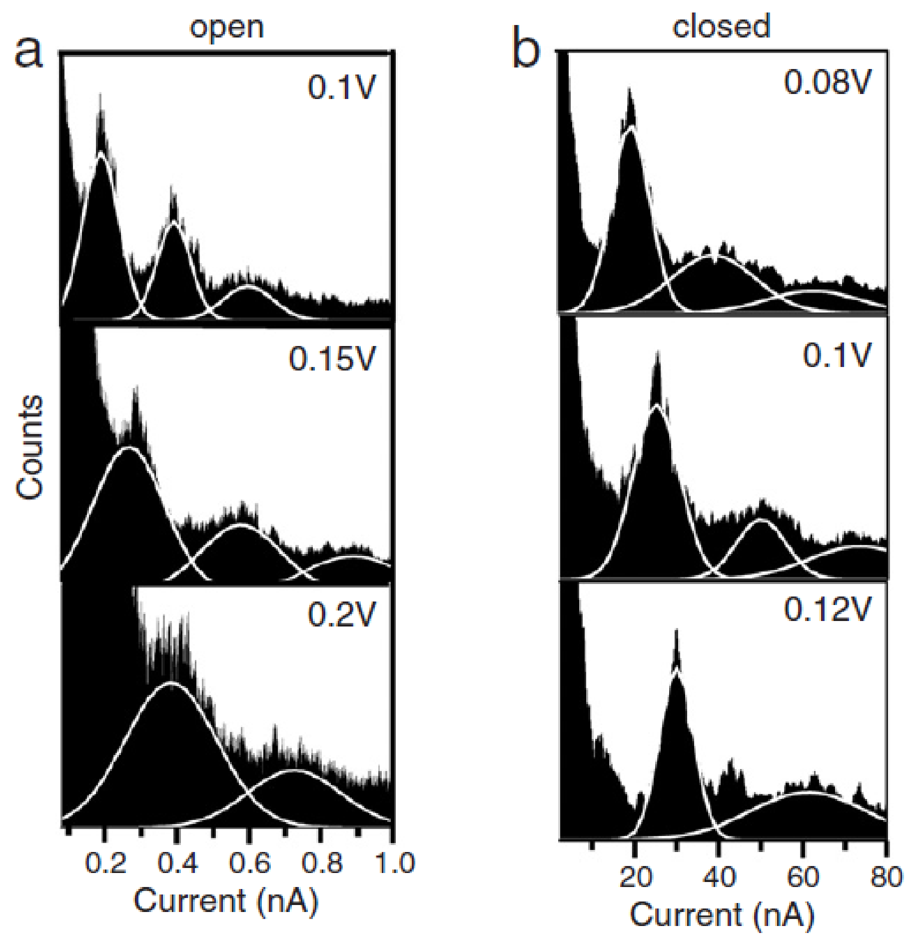


INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology 16 (2005) 695–702 doi:10.1088/0957-4484/16/6/012

Switching of a photochromic molecule on gold electrodes: single-molecule measurements

Jin He[1], Fan Chen[1], Paul A Liddell[2], Joakim Andréasson[2], Stephen D Straight[2], Devens Gust[2], Thomas A Moore[2], Ana L Moore[2], Jun Li[1], Otto F Sankey[1] and Stuart M Lindsay[1,2,3]



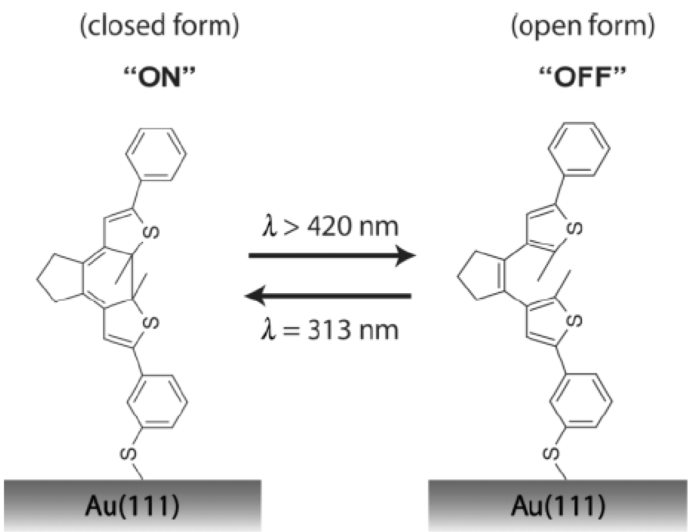


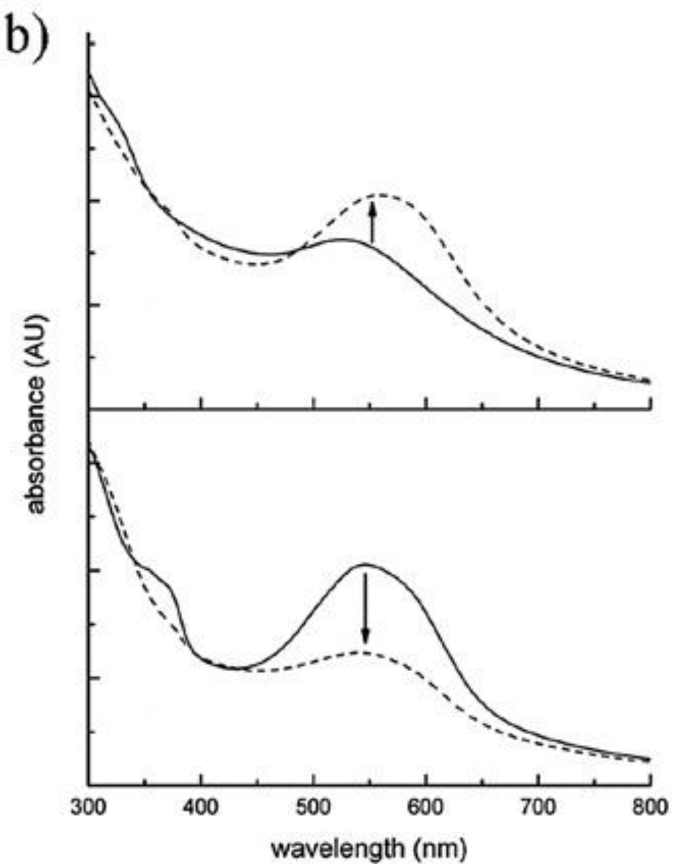
two forms of compounds measured in junction but no in situ switching

on surface

Reversible Conductance Switching of Single Diarylethenes on a Gold Surface** *Adv. Materials 2006*

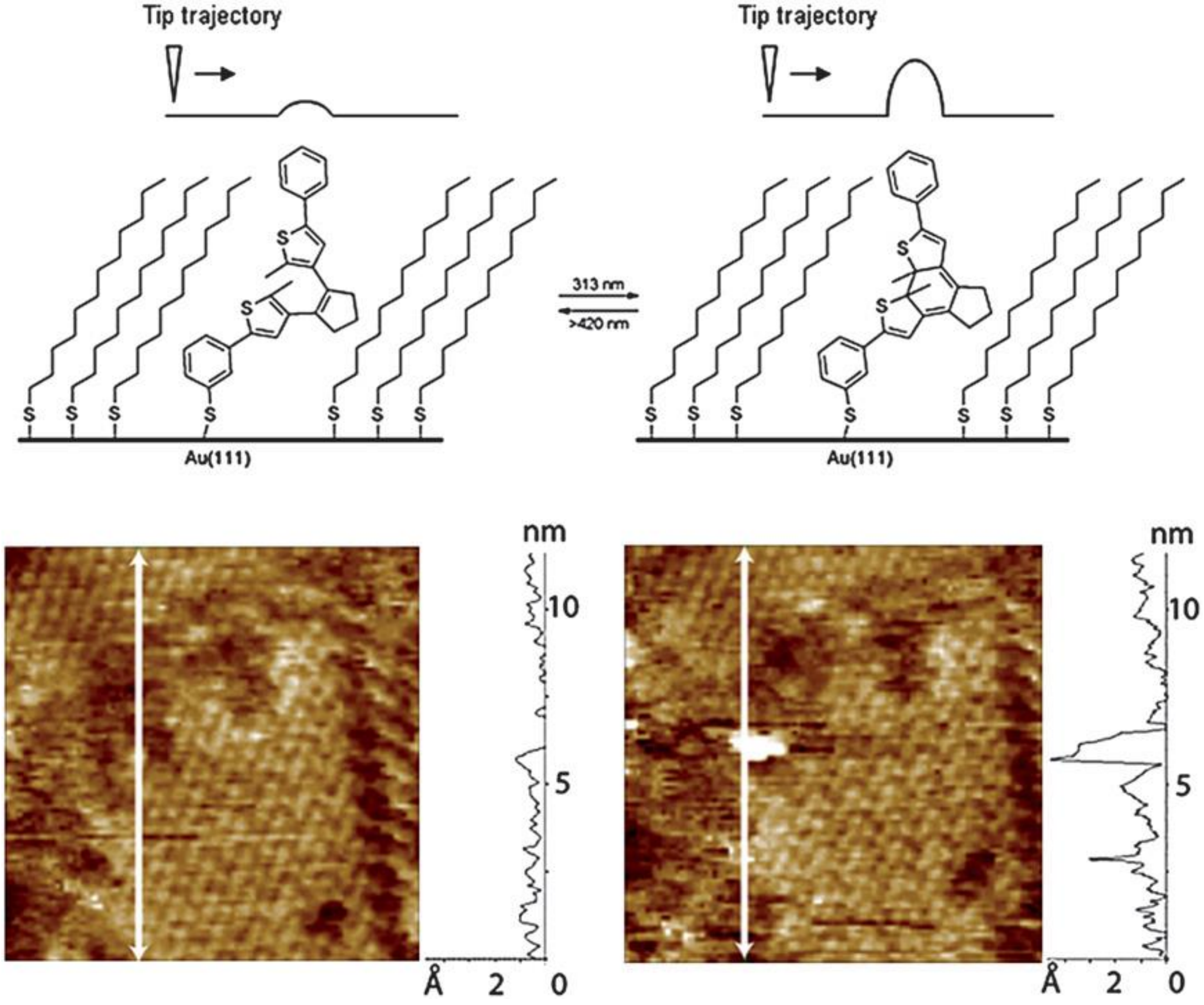
By *Nathalie Katsonis, Tibor Kudernac, Martin Wa*
*Ben L. Feringa**



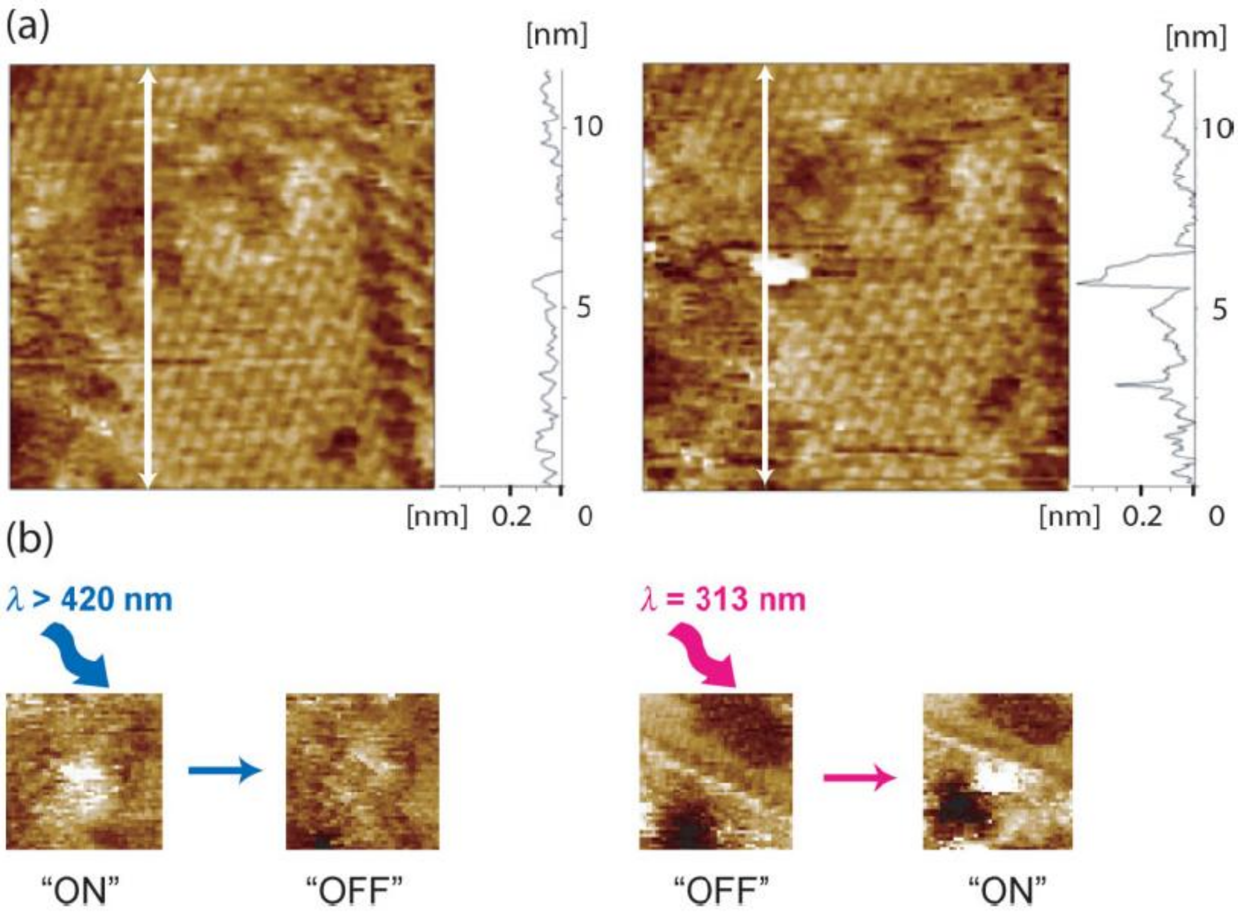


UV/Vis spectra of the open form measured in dry toluene before (—) and after (—) irradiation at 313 nm (top). UV/Vis spectra of the closed form measured in dry toluene before (—) and after (—) irradiation at >420 nm *(Chem Comm, 2006)*

on surface



Tip trajectory
Tip trajectory
313 nm
>420 nm
Au(111)
Au(111)
nm
10
5
Å
2
0
nm
10
5
Å
2
0



reversibility

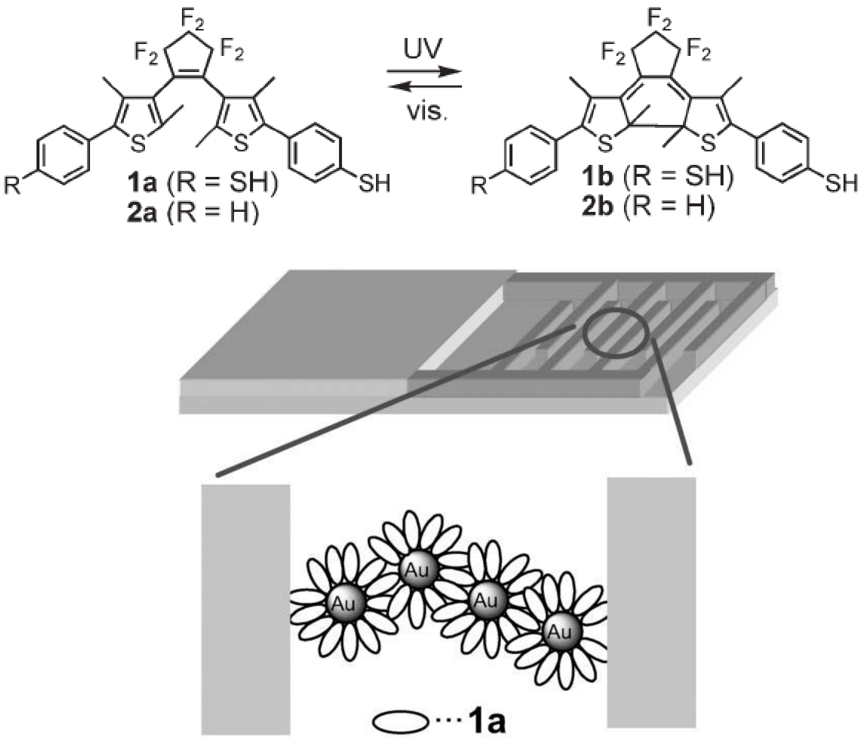
Figure 1. In situ evidence of light-controlled switching of single molecules. a) STM images registered in a time interval of approximately 3 min on the same area under UV ($\lambda = 313$ nm) irradiation. The molecular resolution of the alkanethiol lattice is evidenced by the classical $(\sqrt{3}\times\sqrt{3})R\,30°$ structure in the top-left part of the picture and the $c(4\times 2)$ superstructure in the bottom-right corner of the picture. The conductance modulation of the switches resulting from OFF to ON transition is visible (12 nm × 12 nm, $V_T = -0.853$ V, $i_T = 12$ pA). The cross sections show that the OFF form slightly protrudes from the monolayer with an apparent height of approximately 0.1 nm, whereas the ON form has an apparent height of approximately 0.5 nm. b) Extracted frames displaying single molecules (8 nm × 8 nm). The time interval between frames is 3 min. ON to OFF switching is observed during irradiation by visible light and the reverse process occurs during UV irradiation.

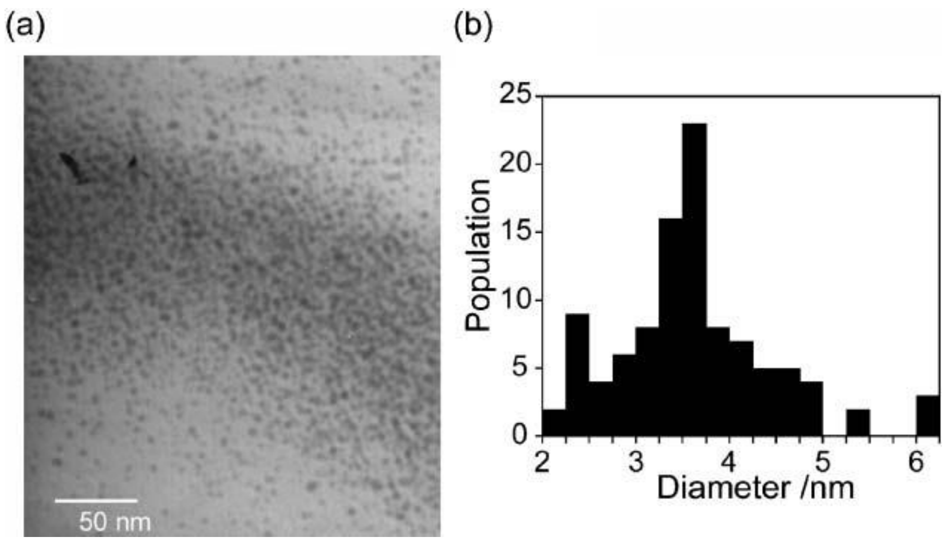
towards devices in arrays of nanoparticles

COMMUNICATION www.rsc.org/chemcomm | ChemComm

Photoswitching of conductance of diarylethene-Au nanoparticle network†

Masumi Ikeda,[a] Naoki Tanifuji,[b] Hidehiro Yamaguchi,[a] Masahiro Irie*[a] and Kenji Matsuda*[ab]





Irie et al., Chem Comm., 2007

towards devices in arrays

COMMUNICATION

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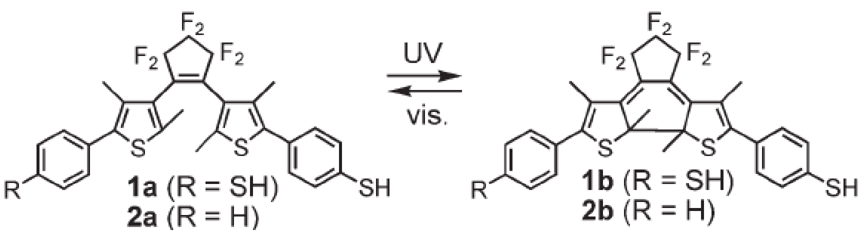
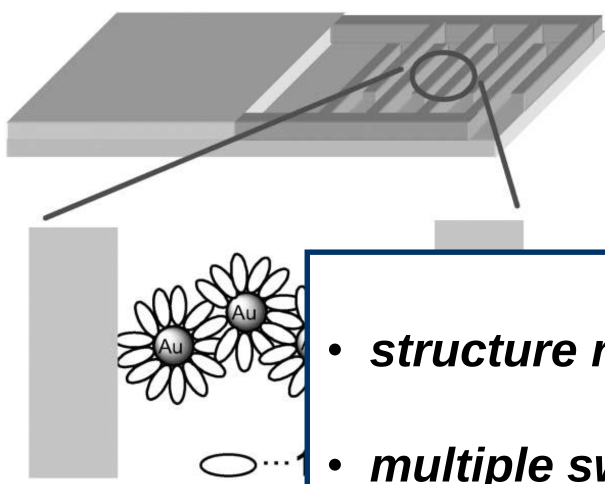
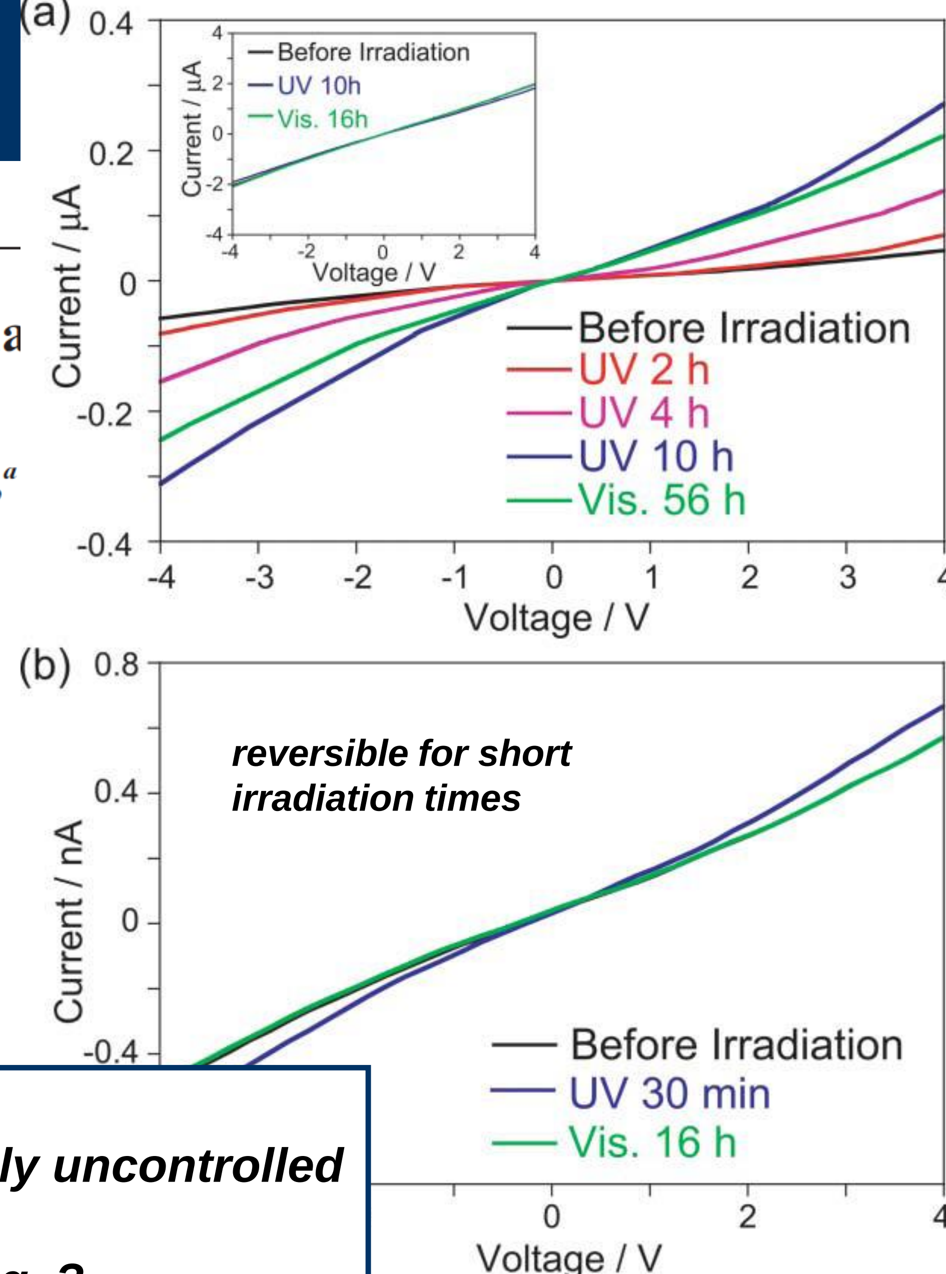
Masumi Ikeda,[a] Naoki Tanifuji,[b] Hidehiro Yamaguchi,[a]



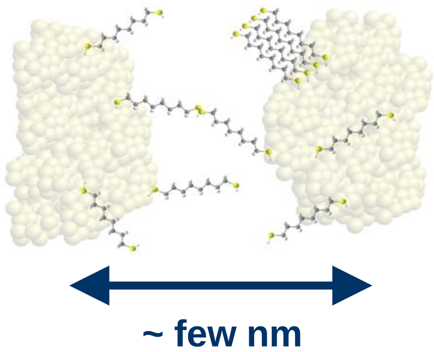


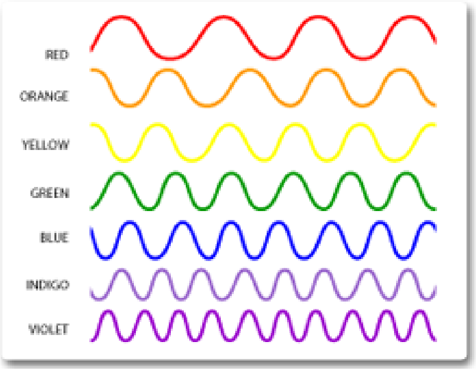


- ***structure relatively uncontrolled***
- ***multiple switching ?***

Irie et al., Chem Comm., 2007

NB: towards devices.... the problem of light coupling



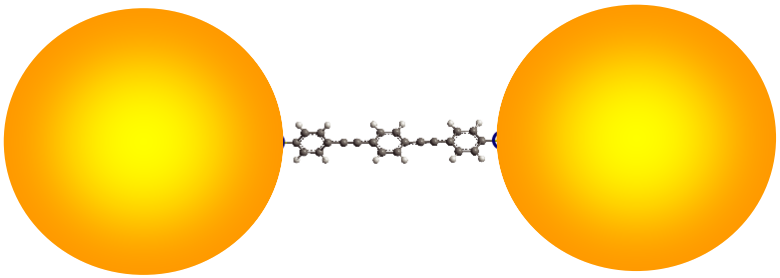


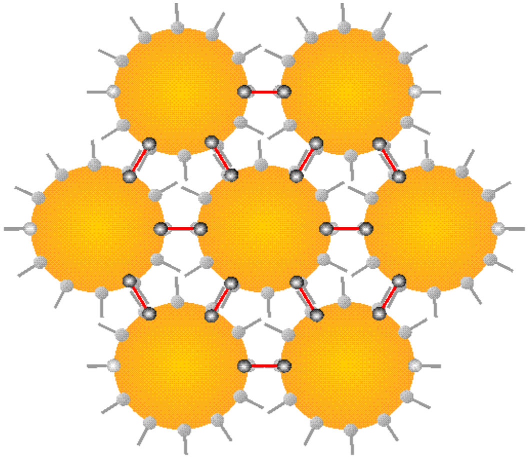
- separation of junctions « wavelength of light (400 – 700 nm)
  ⇨possible cross-talk by addressing multiple junctions
- quenching of photons in metals but also surface enhancement effects
- possible local heating

⇨ **light coupling delicate, in particular for high-density arrays in nanoelectronics**

nanoparticles as contacts

?



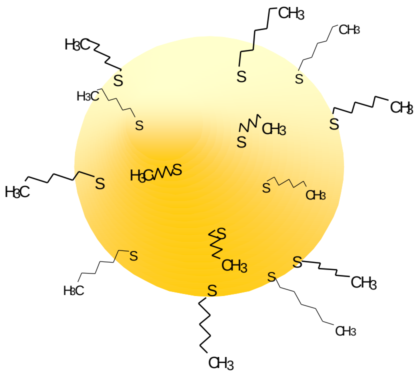


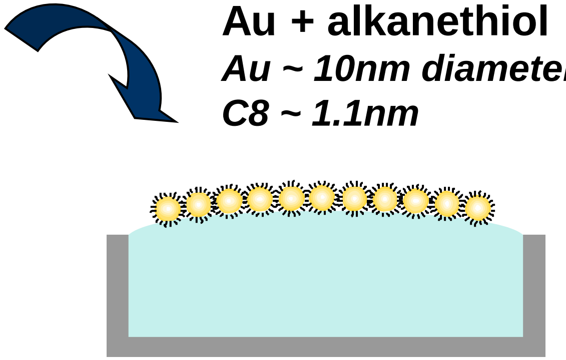
individual junctions

network of molecular junctions

how to control the structure and organisation of the nanoparticles ?

controlled arrays: self-assembly + stamping

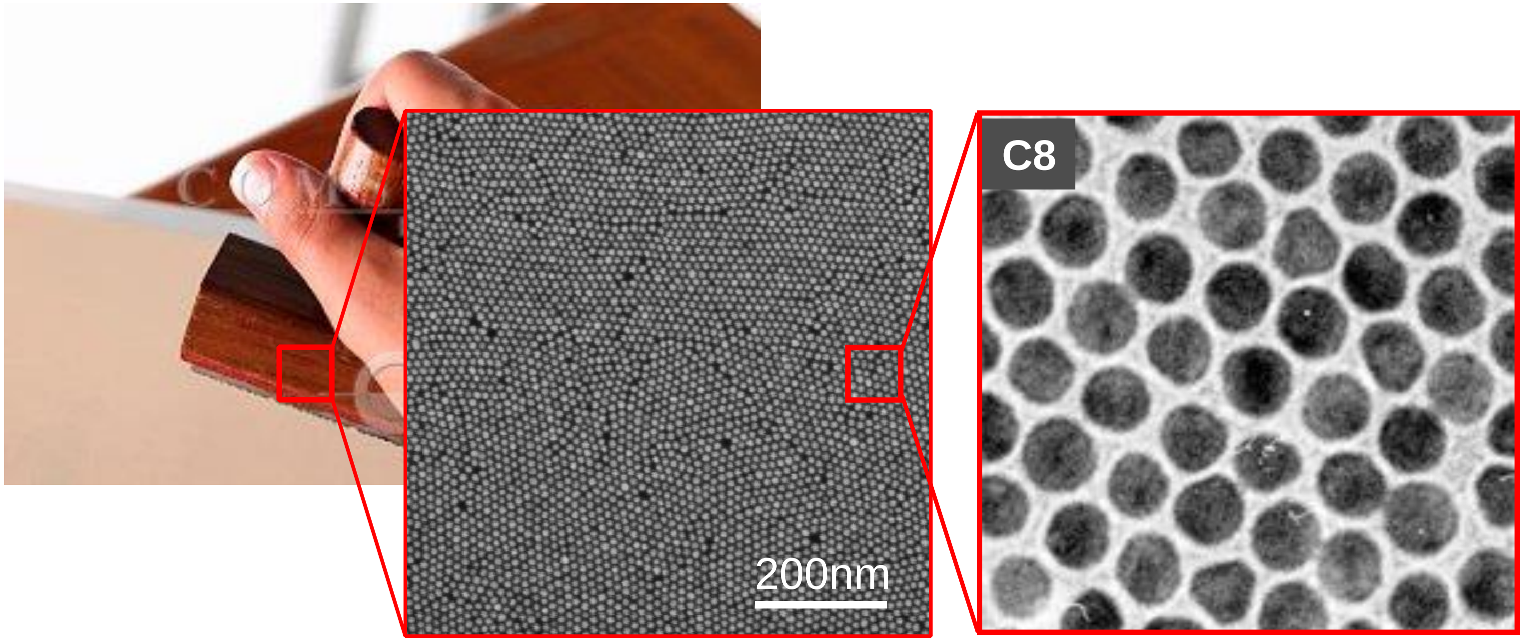




Au + alkanethiol

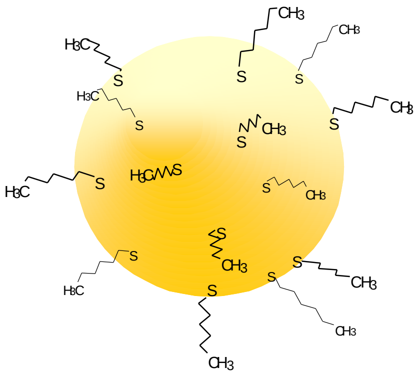
Au ~ 10nm diameter

C8 ~ 1.1nm



(TEM, 500nm x 500nm, L. Kreplak)

nanoparticles (NPs) stamping principle



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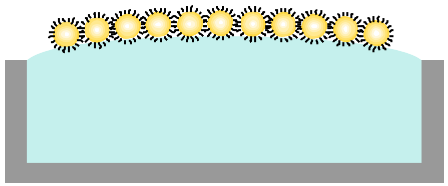
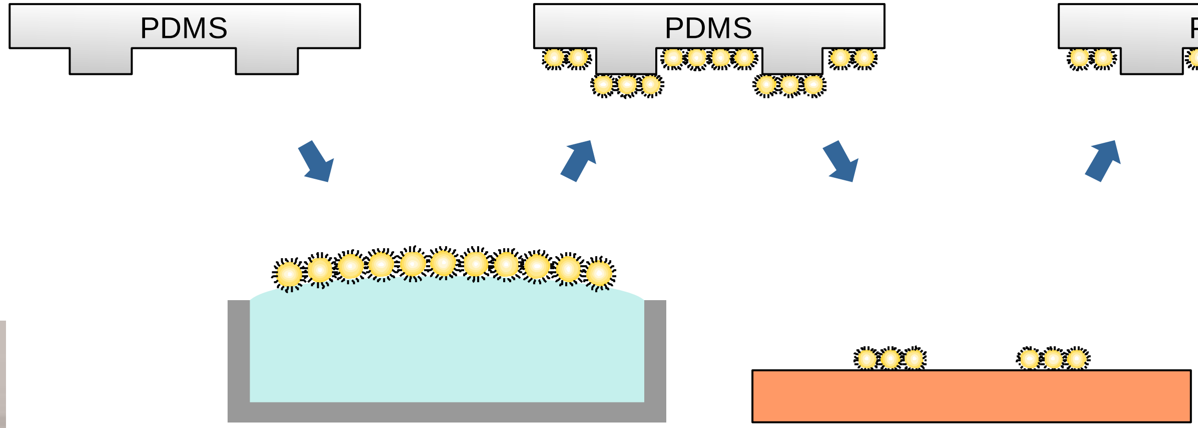
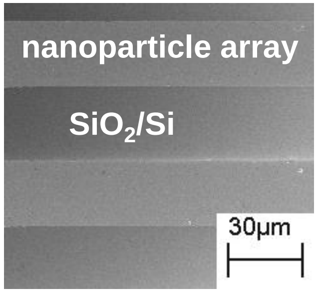


stamping



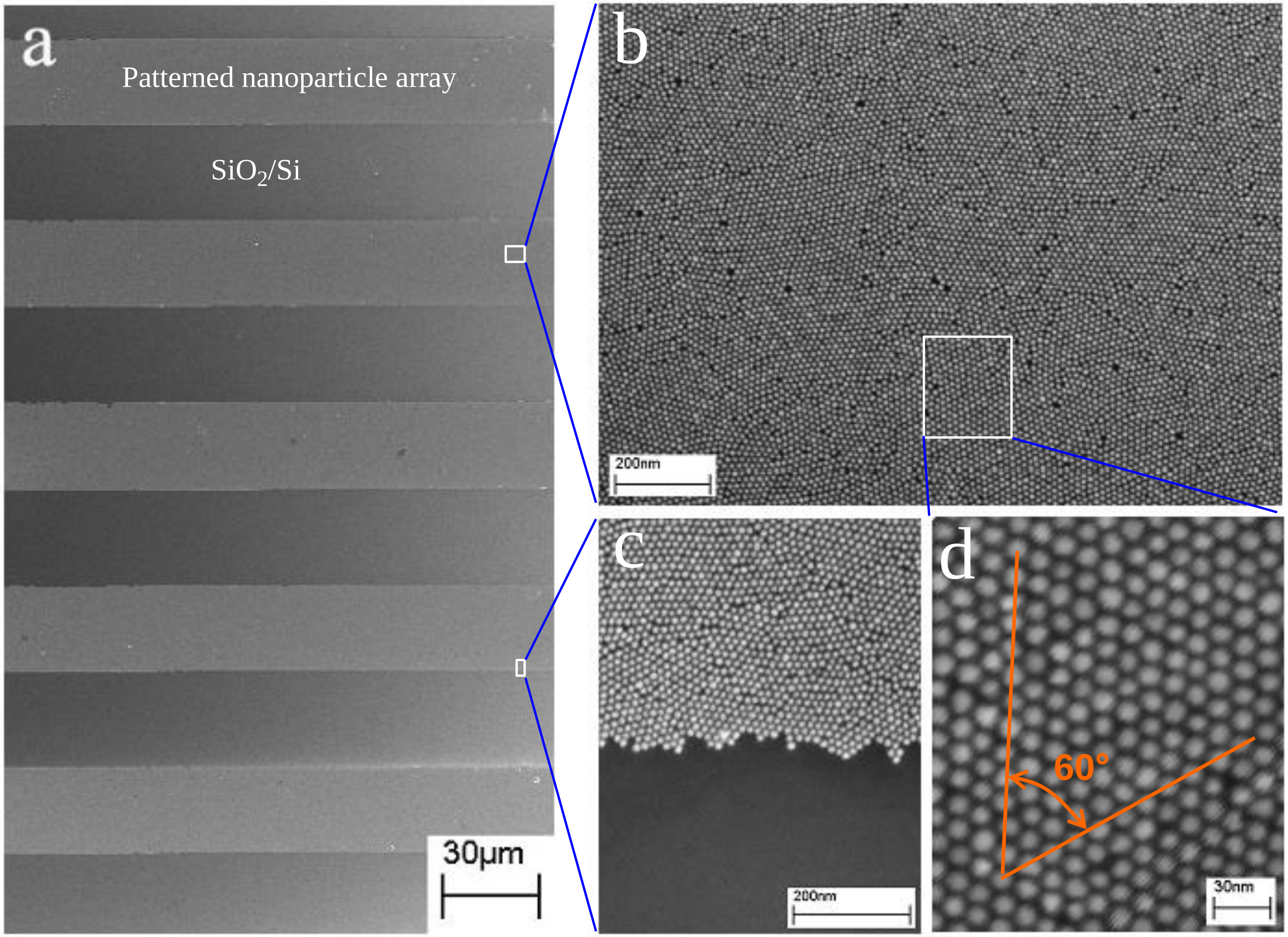


transfer of the film
to a PDMS stamp

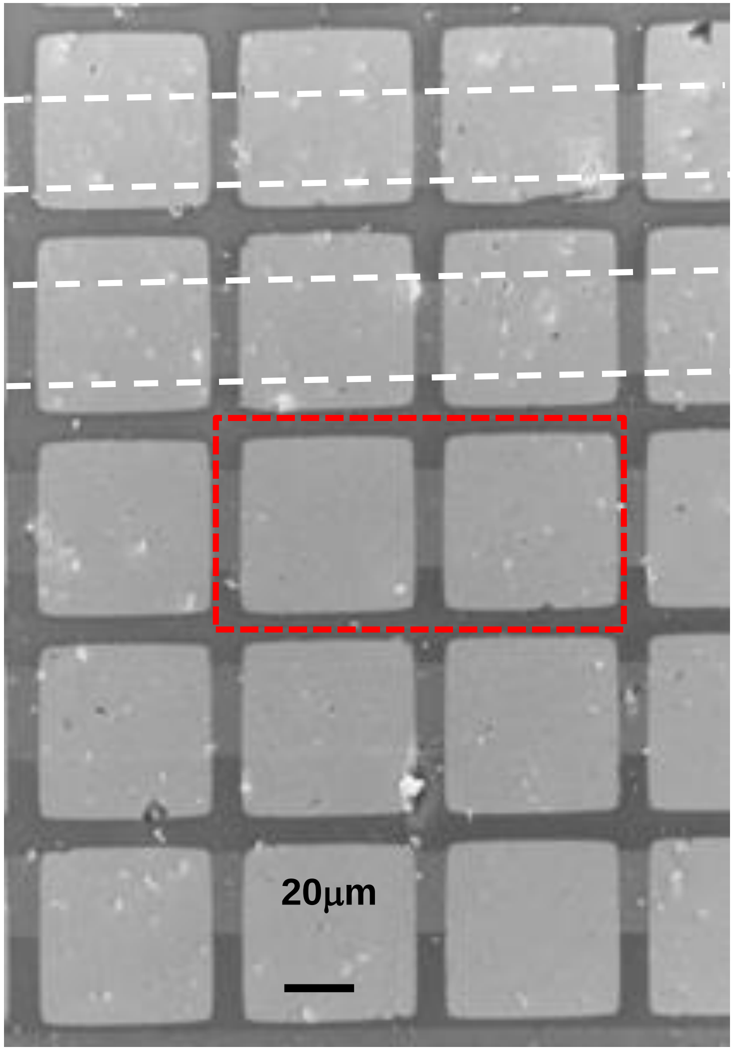
stamping on solid substrate:
patterned array

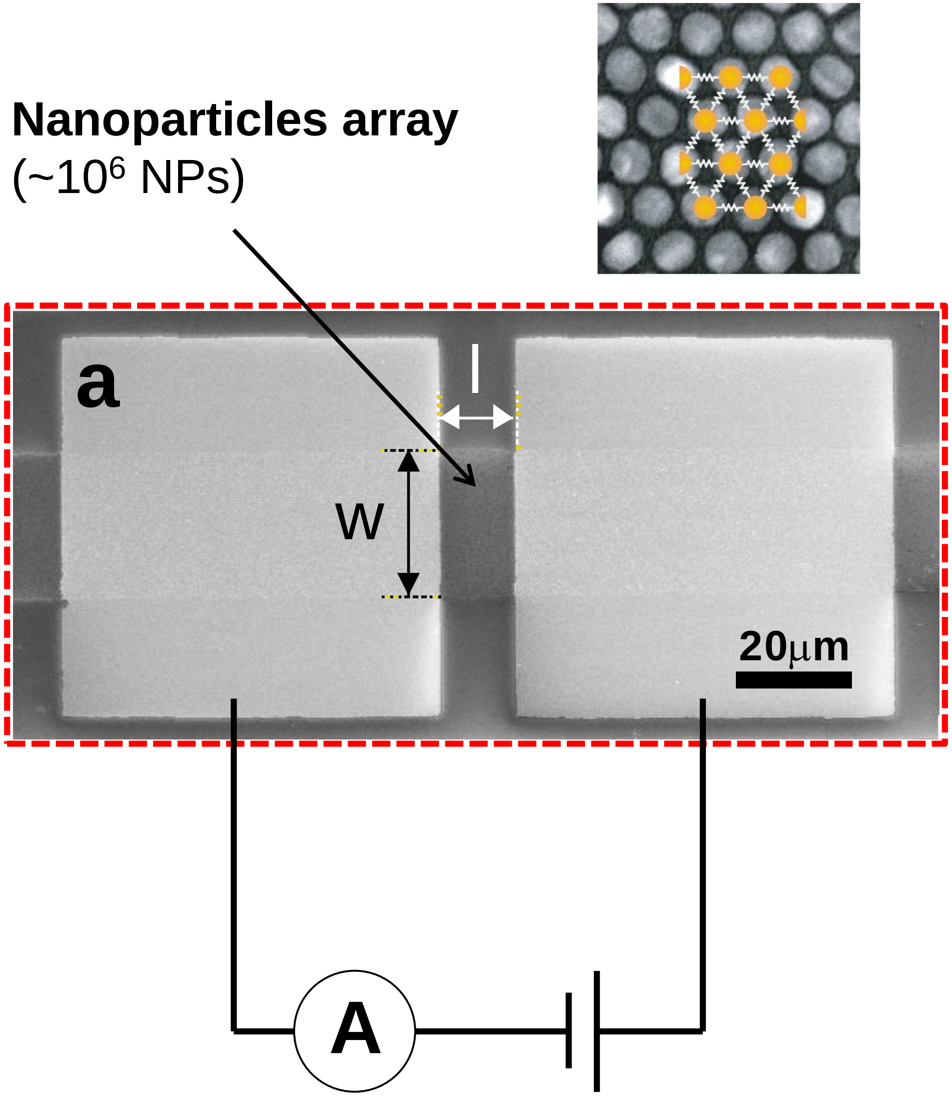
V. Santhanam and R.P. Anders, Nano Letters, 2004; *J. Liao et al Adv. Materials, 2006*

patterned colloids arrays

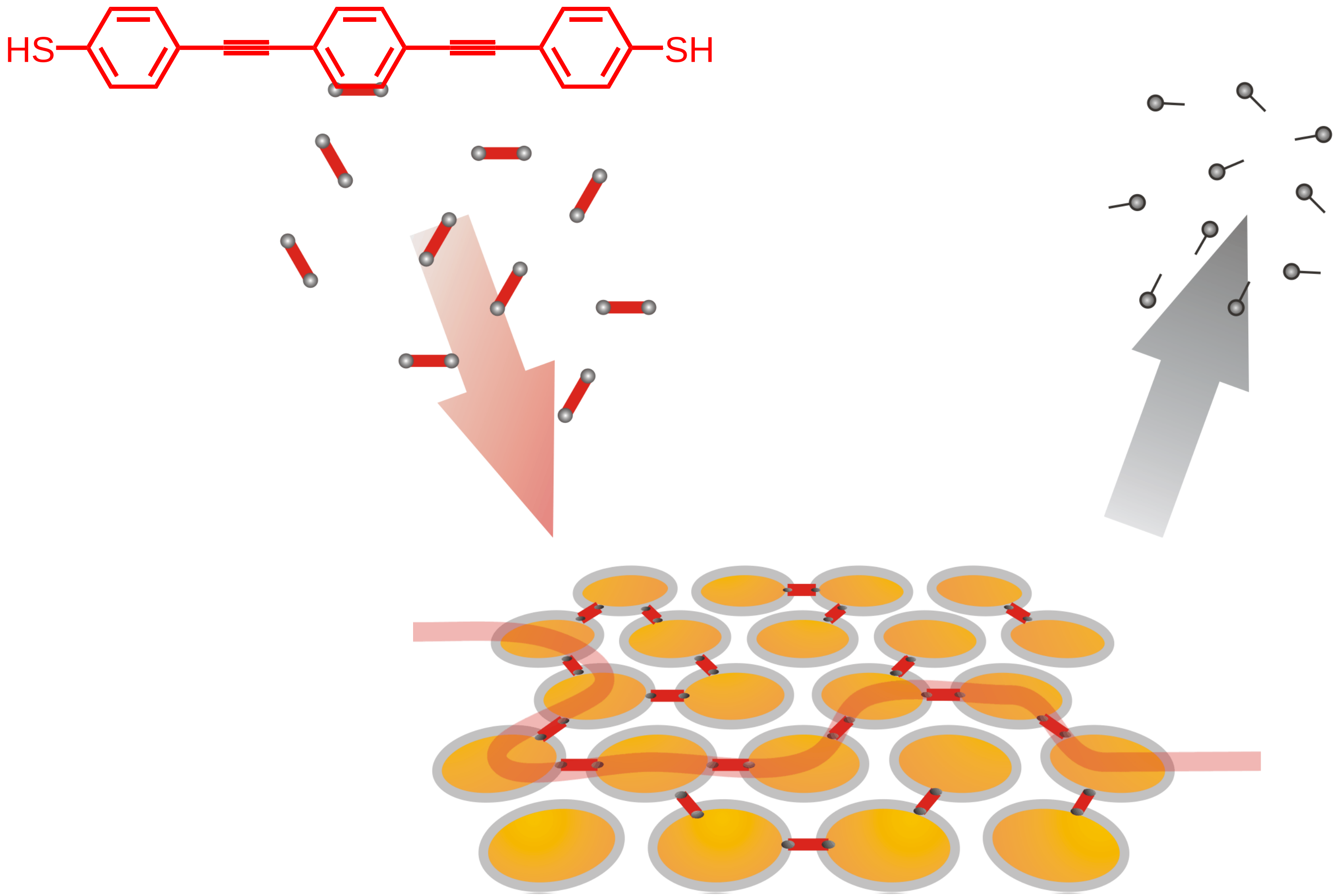


electrical contacts





molecular exchange: interlinking NPs

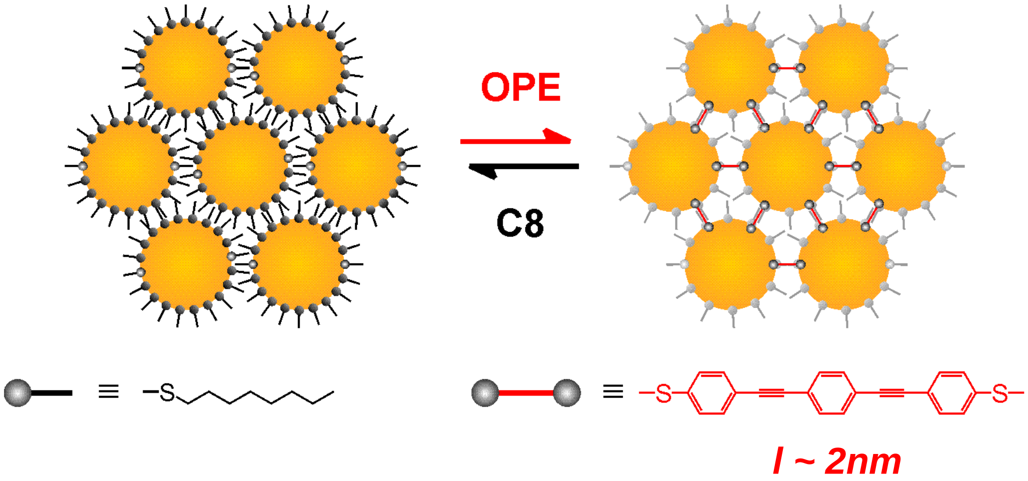


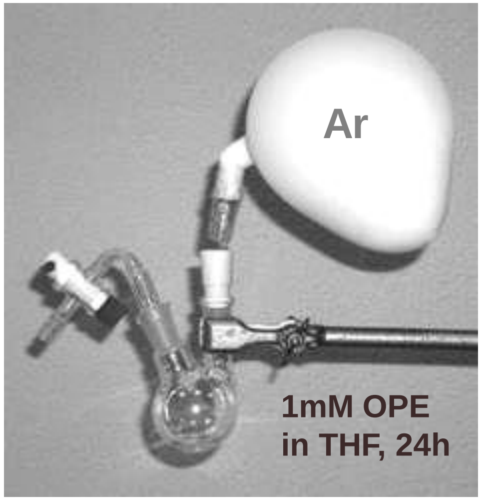
NB: transport meas. for p»p$_c$ (p$_c$ ≅ 0.35)

molecular exchange

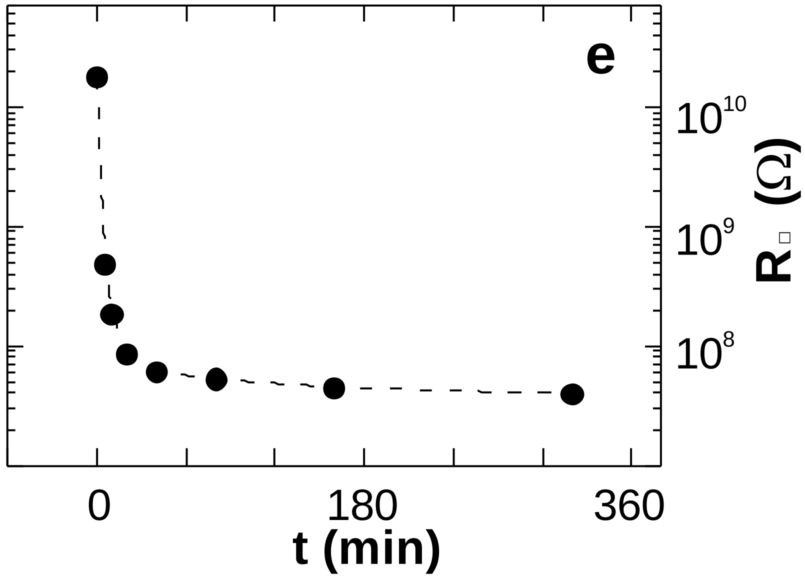
ligand place-exchange

(exchange kinetics for SAMs much slower)





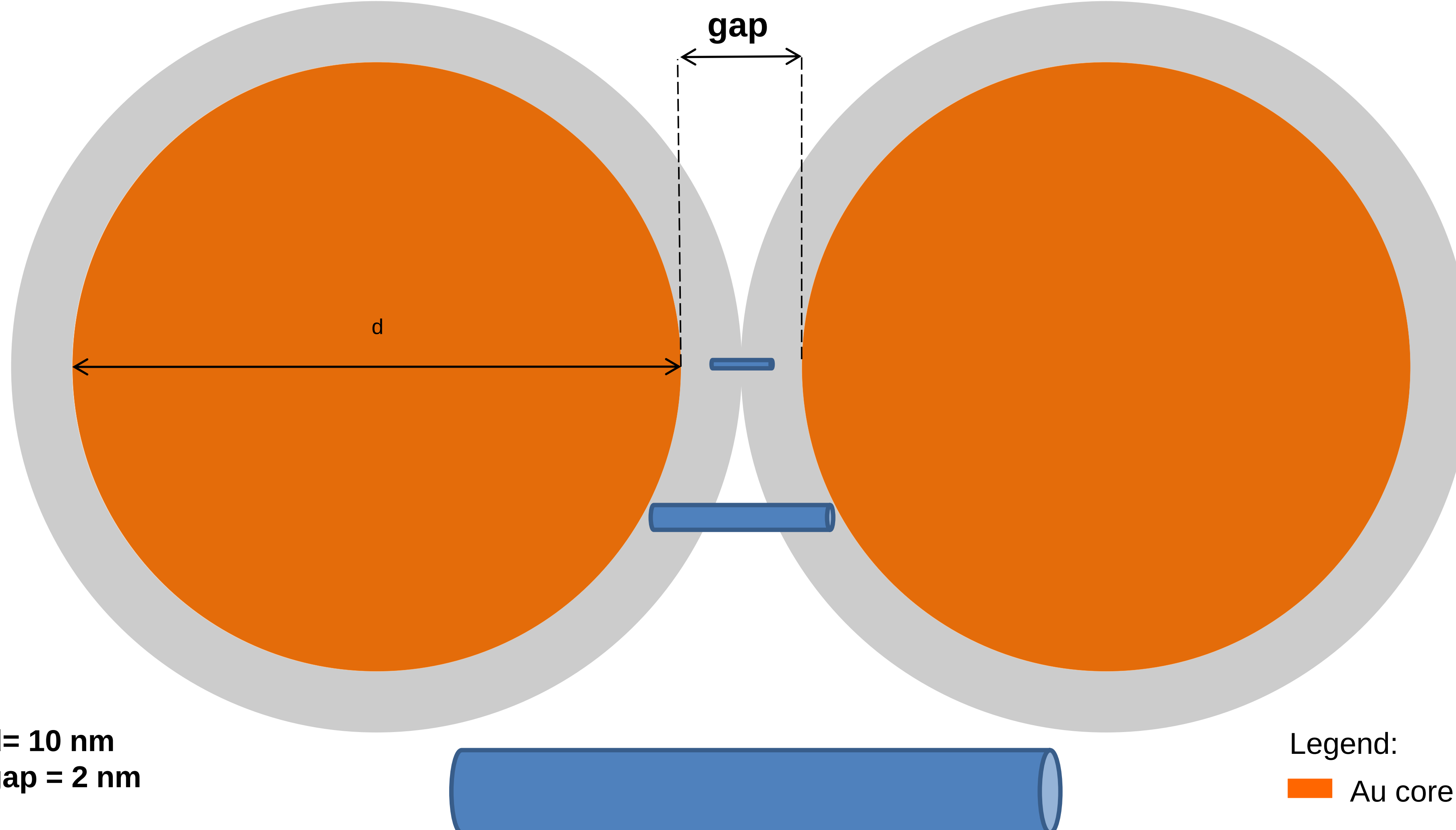
⇨ **inter-linked** network of particles by incorporation of the thiolated OPE



OPE: M. Mayor, A. Pfalz, Basel

exchange in bulk colloidal solutions:
Murray et al., Langmuir, 1999; JACS, 2002, 2003

a "more or less" to scale cartoon

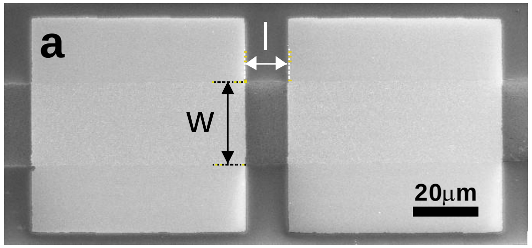


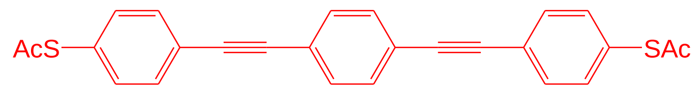
d= 10 nm
gap = 2 nm

Ligand length: 1 nm
Molecule lengths: 1, 3 & 10 nm

Legend:
Au core
Ligand
Molecule

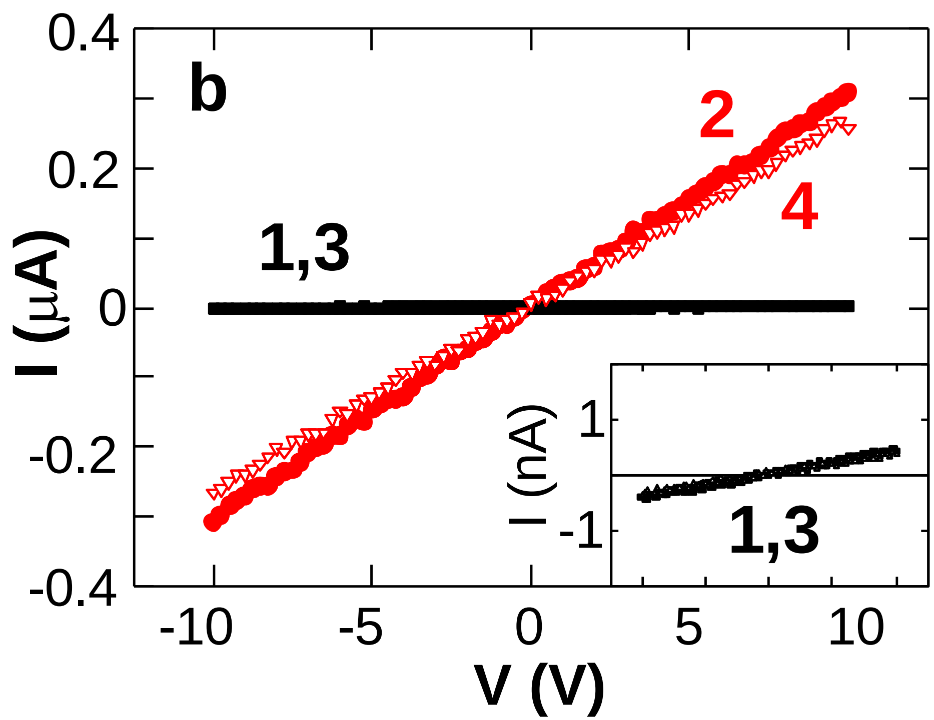
resistance of arrays (linear reponse)





sheet resistance:

$R_{\square} = R \cdot w/l$



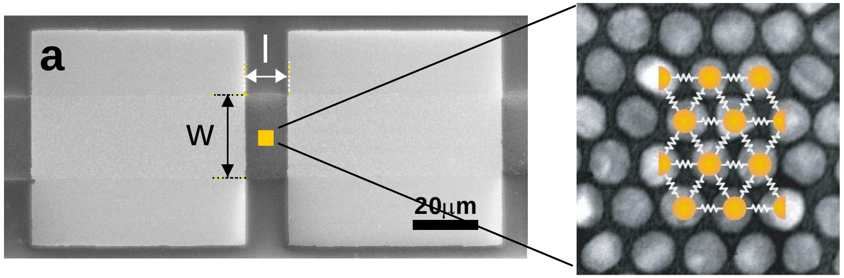
molecular exchange experiment

1. as stamped
2. after device immersion (24h) in 1mM OPE in THF
3. after device immersion in C8 solution
4. repeat 2.

⇨ $R_{\square}$ changes by 1-3 orders of mag.; **reversible process**

J. Liao et al Adv. Materials, 2006

resistance of arrays



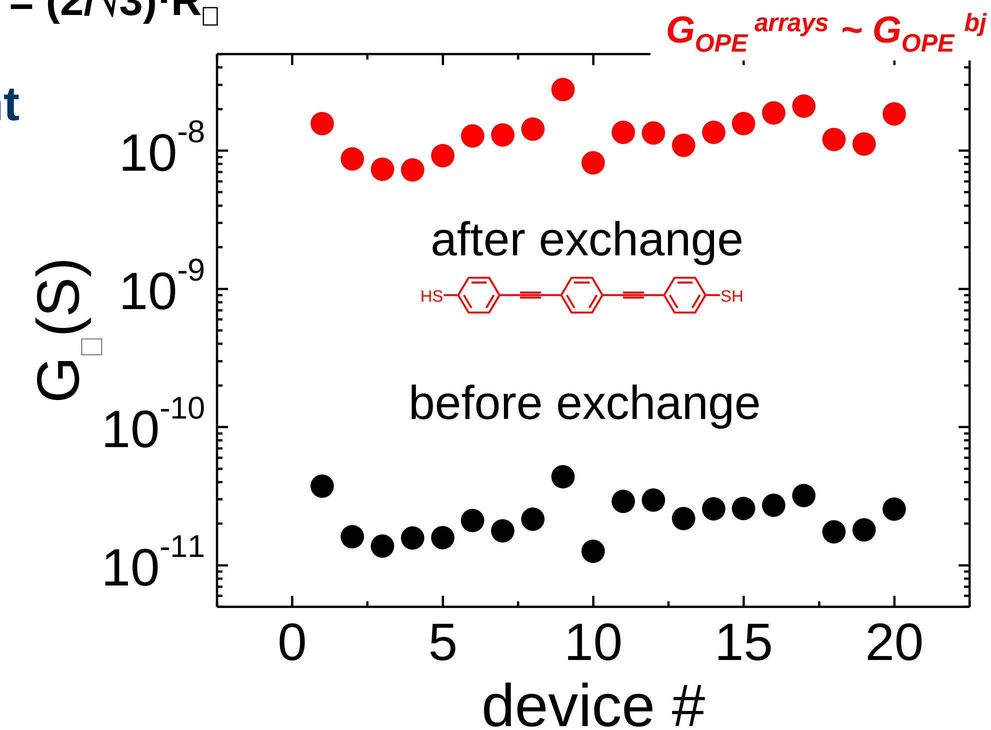
sheet resistance:
$R_{\square} = R \cdot w/l$

junction resistance
$R_J = (2/\sqrt{3}) \cdot R_{\square}$

$R_J = 1/G_J$

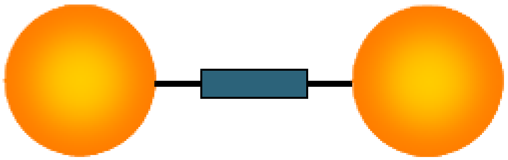
molecular exchange experiment

- ⇨ statistics: many devices in parallel
- ⇨ comparison to bj
- ⇨ exchange is **reversible**

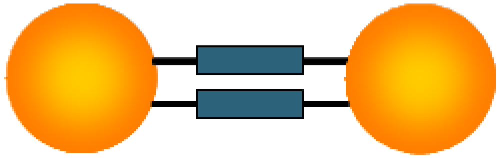


real inter-linking…?

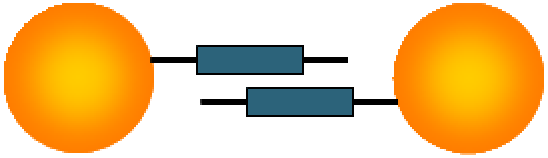
⇨ single molecule + covalent bonding ?



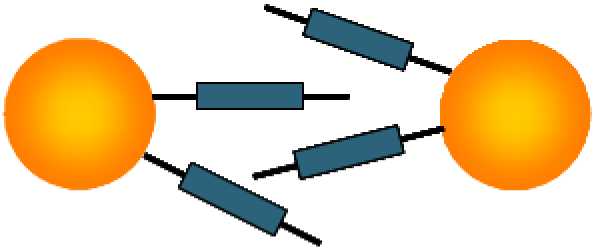
⇨ molecules in parallel?



⇨ covalent bonding + stacking ?

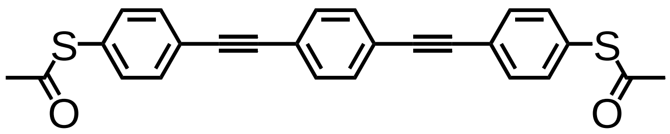


⇨ … ?

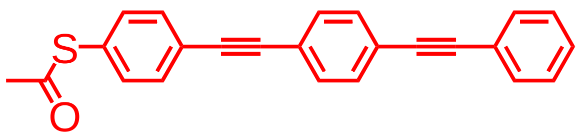


interlinking neighboring NPs in network ?

OPE-dt



OPE-mt



$G_{initial}$: conductance of C8 array

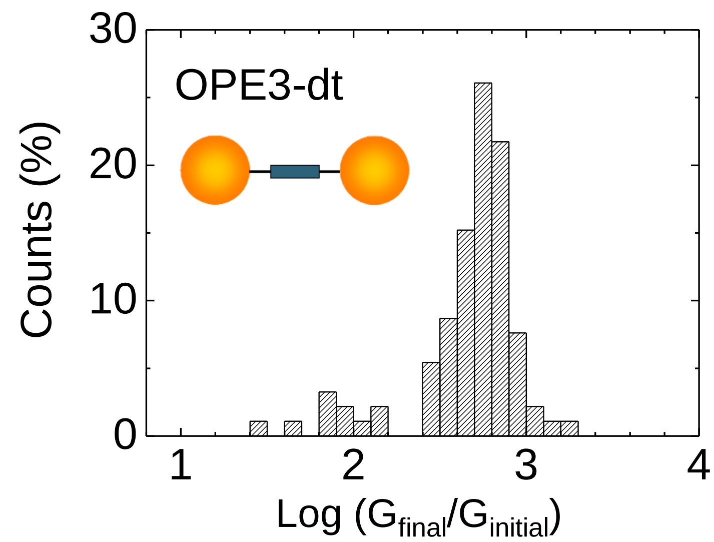
G_{final}: conductance of array after C8 exchange with OPE

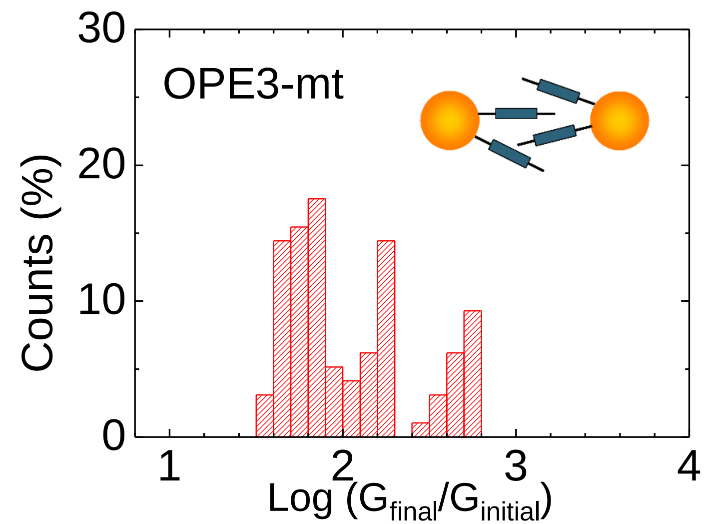
with dithiols

- larger $\langle G_f/G_i \rangle$
- better defined ratio

⇨ **supports inter-linking picture in NPs**

⇨ **interplay between stacking and covalent binding**

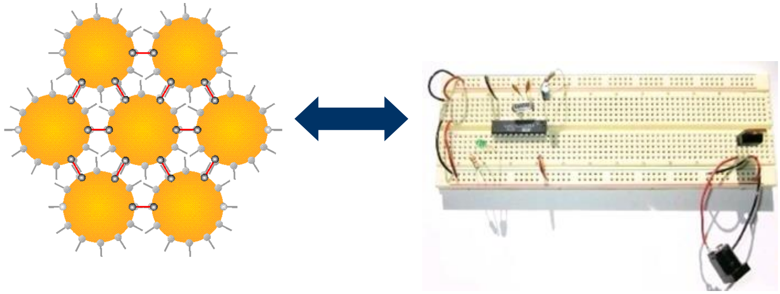


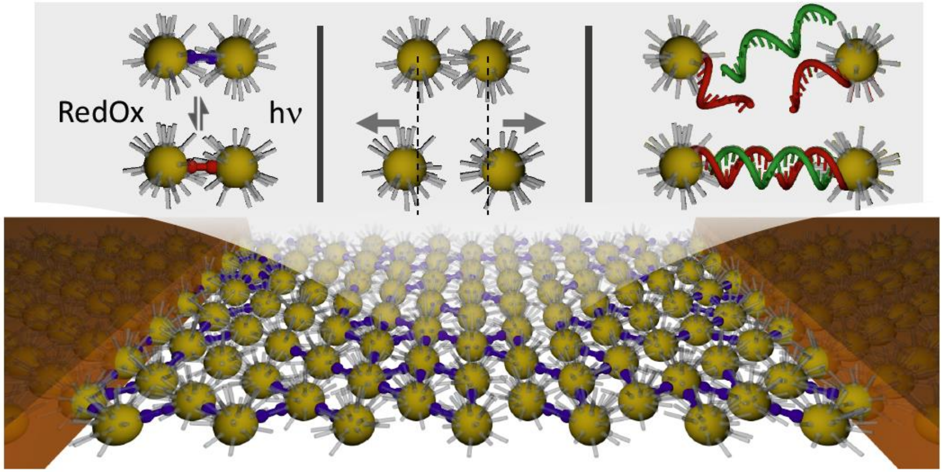


J. Liao et al., New. J. Phys. 2008

nanoparticles arrays

upscalable nanoscale structures
for functional architectures





Ordered nanoparticle arrays interconnected by molecular linkers
Chem. Soc. Rev. (**2014**)

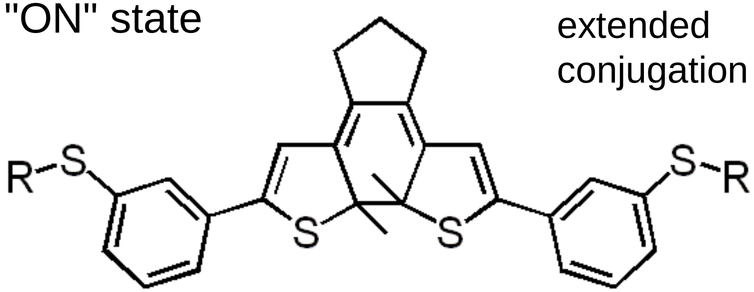
Nanoparticle arrays: structural, electrical and optoelectronic properties
to appear in ***Handbook of Nanoparticles,*** **Springer** (**2014**)

optical modulation of conductance

diarylethene light switch
(M. Irie, 2000, B. Ferringa et al.,)

"ON" state

extended
conjugation

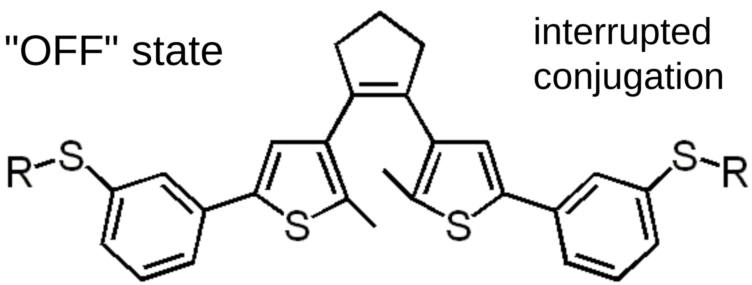


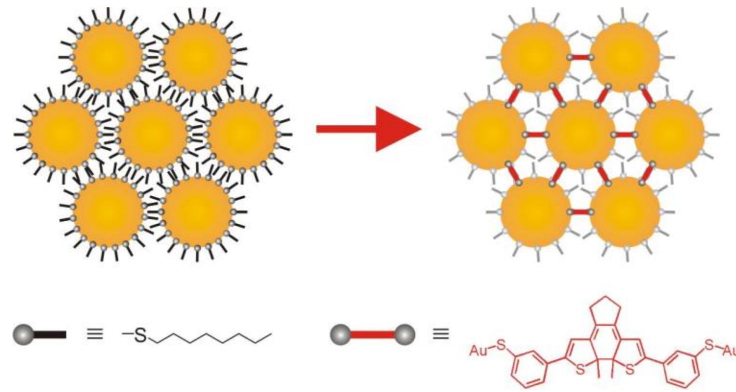
λ_1 > 420 nm
(vis)

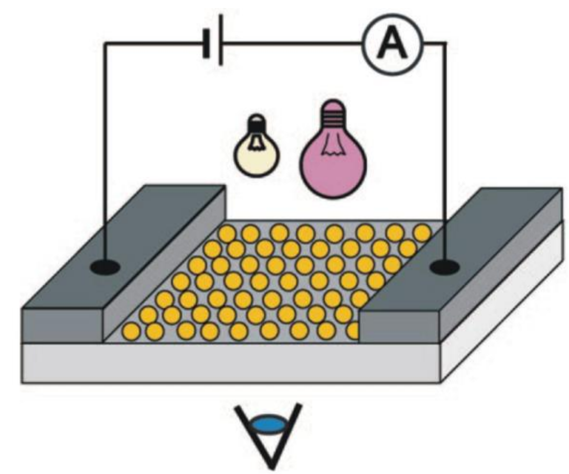
λ_2 = 313 nm
(UV)

"OFF" state

interrupted
conjugation







reversible switching on Au surface: Katsonis et al., Adv. Mat., 2006

optical modulation of conductance

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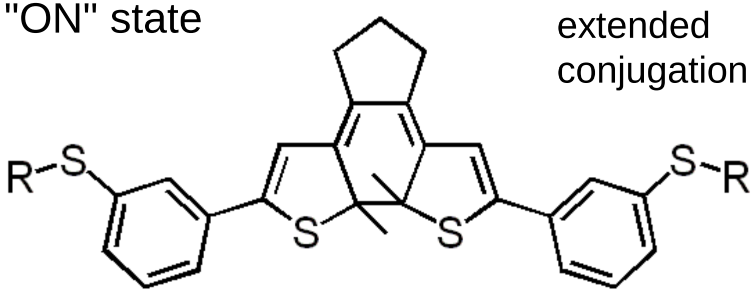
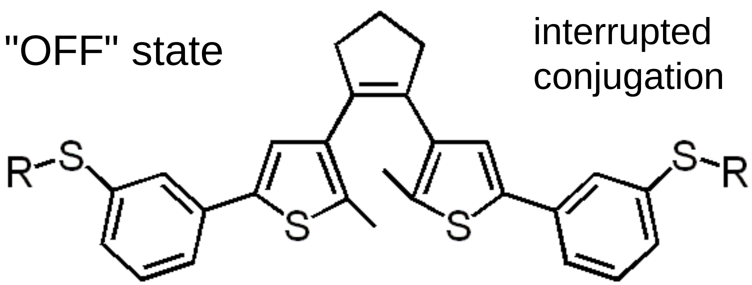


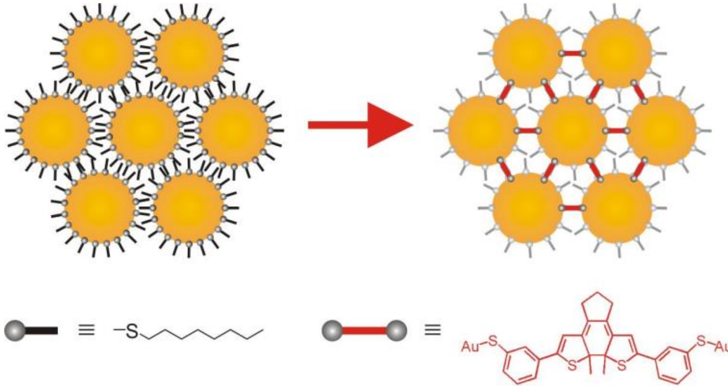
λ_1 > 420 nm
(vis)

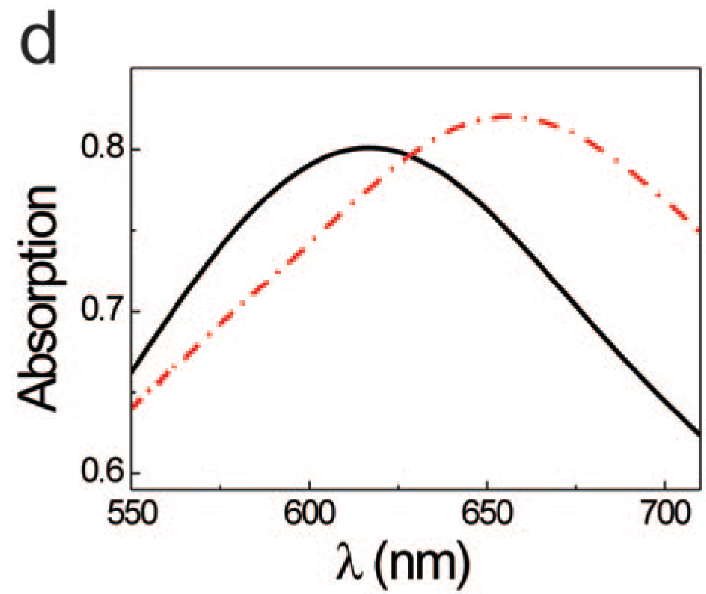
λ_2 = 313 nm
(UV)

"OFF" state

interrupted
conjugation

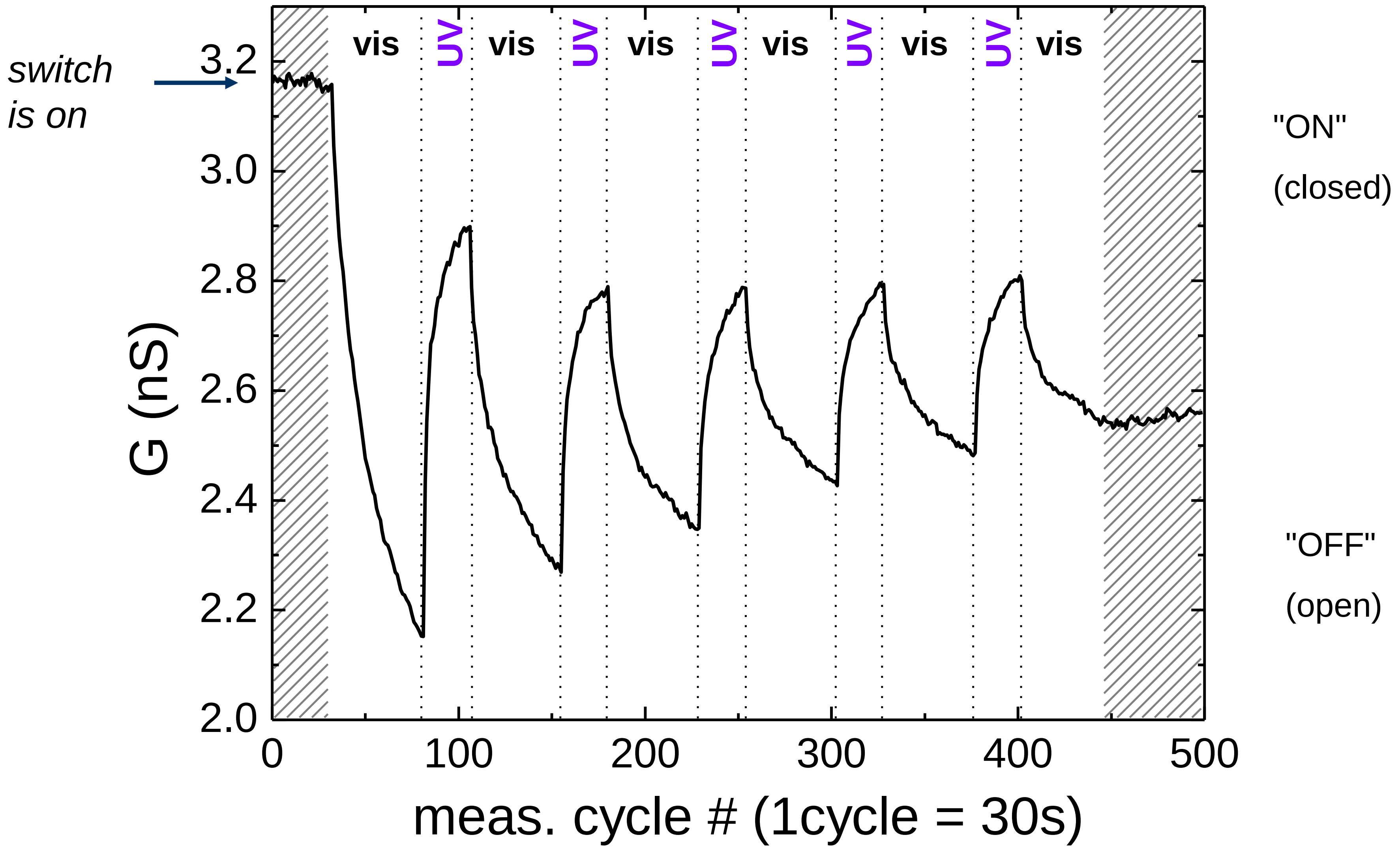






reversible switching on Au surface: Katsonis et al., Adv. Mat., 2006

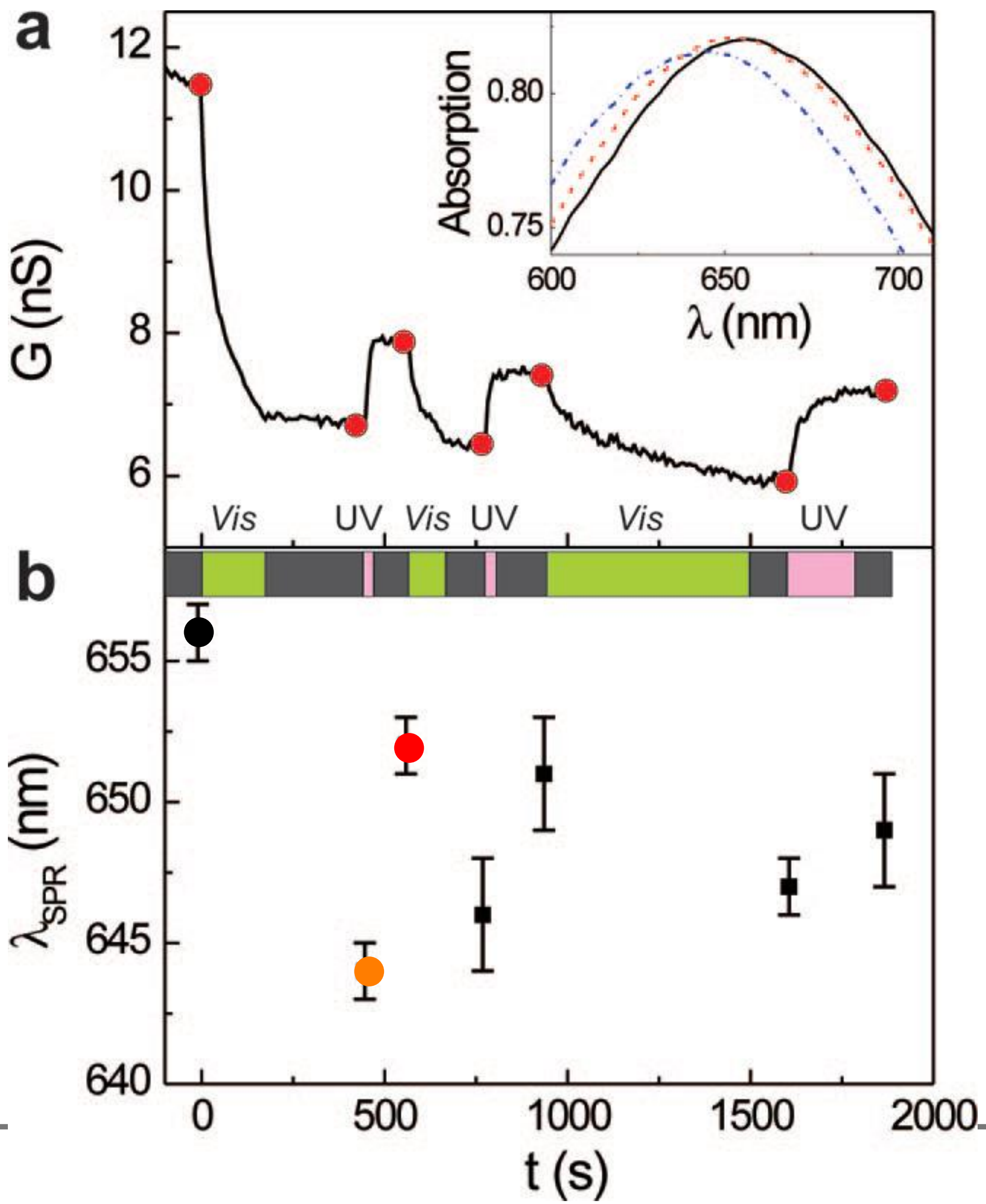
optical modulation of the conductance



S. vd Molen, J. Liao et al., Nano Letters (2008)

optical modulation of the conductance

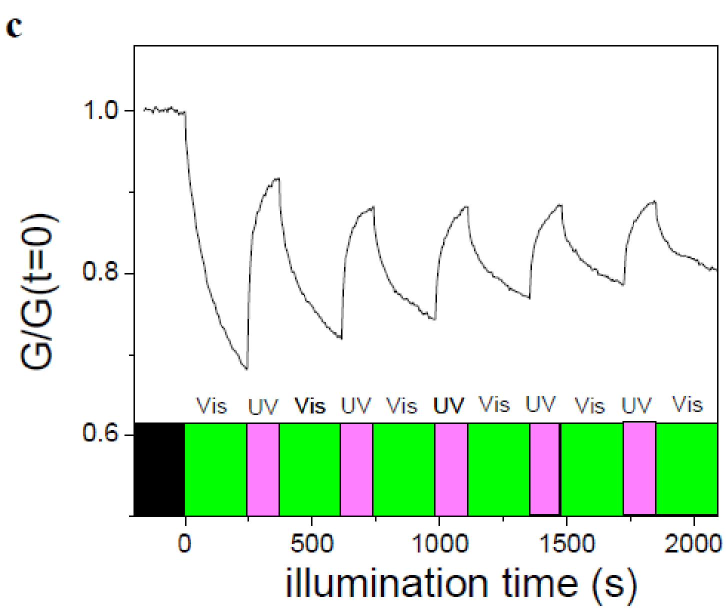
confirmation of molecular switching by optical absorption spectroscopy

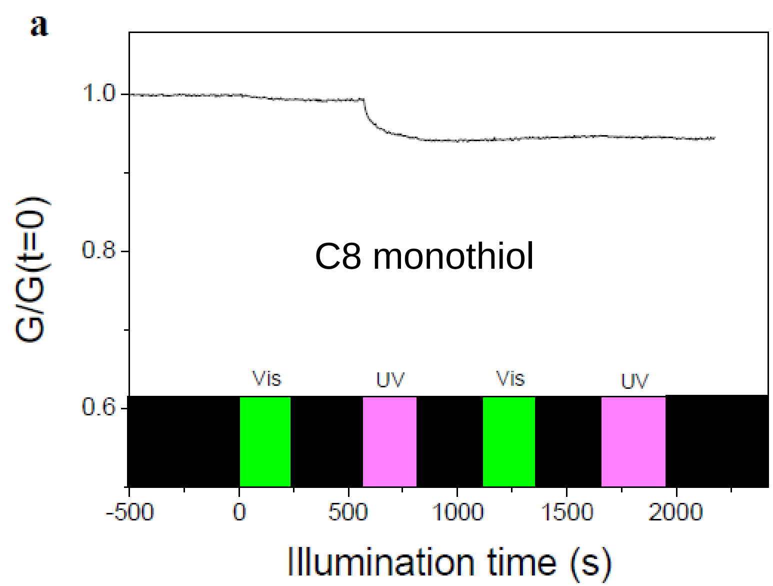


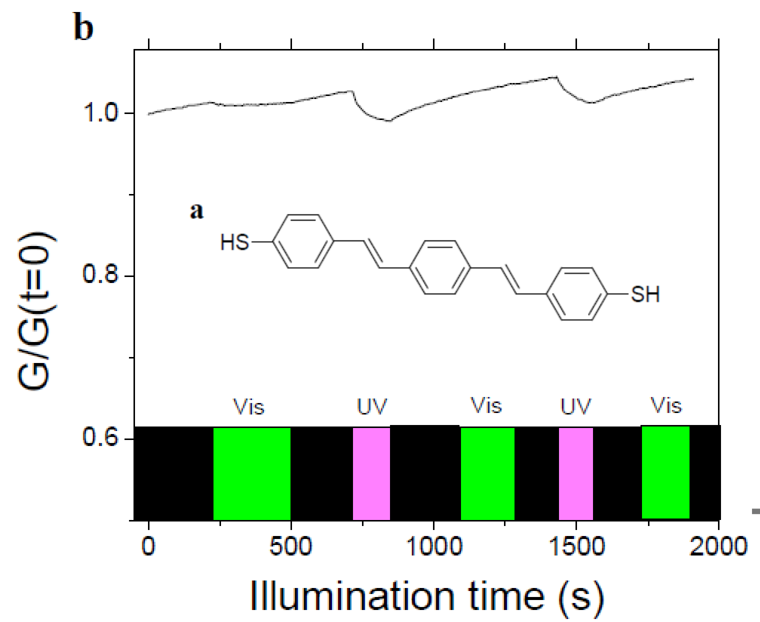
optical modulation of the conductance

controls

original data: diarylethene switch







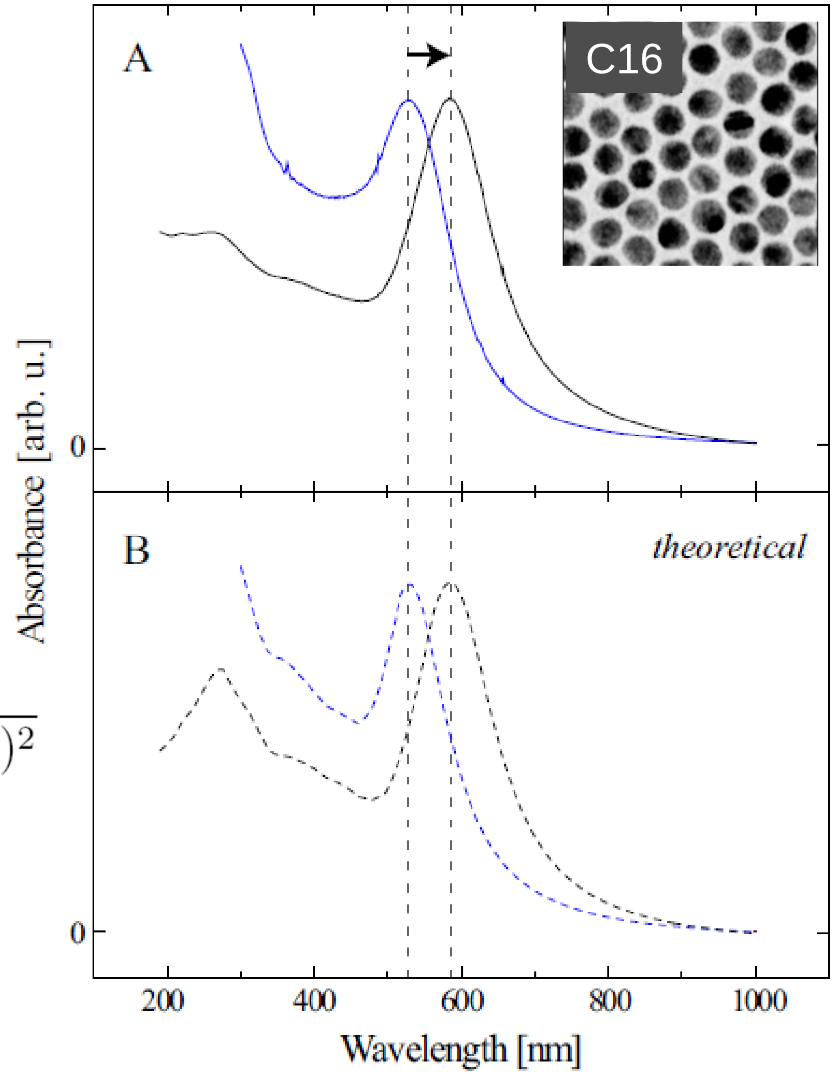
optical spectroscopy (absorption)

plasmon generated by E-field component of an irradiating EM wave

C16-capped Au nanoparticles (10nm ∅)

in solution (blue) and as an array (black)

red shift of SPR due to array



absorption cross-section: Mie

(small particles, dipolar approx.)

$$\sigma(\omega) = 12\pi\frac{\omega}{c}\varepsilon_m^{3/2}R^3\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2}$$

medium permittivity ϵ_{m}

nanoparticle $\epsilon(\omega) = \epsilon_1(\omega) + \mathrm{i}\epsilon_2(\omega)$

L. Bernard et al., JPC (2007)

characterizing plasmon resonances

absorption cross-section: Mie
(small particles, dipolar approx.)

$$\sigma(\omega) = 12\pi\frac{\omega}{c}\varepsilon_m^{3/2}R^3\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2}$$

nanoparticle permittivity: Drude-Lorentz-Sommerfeld

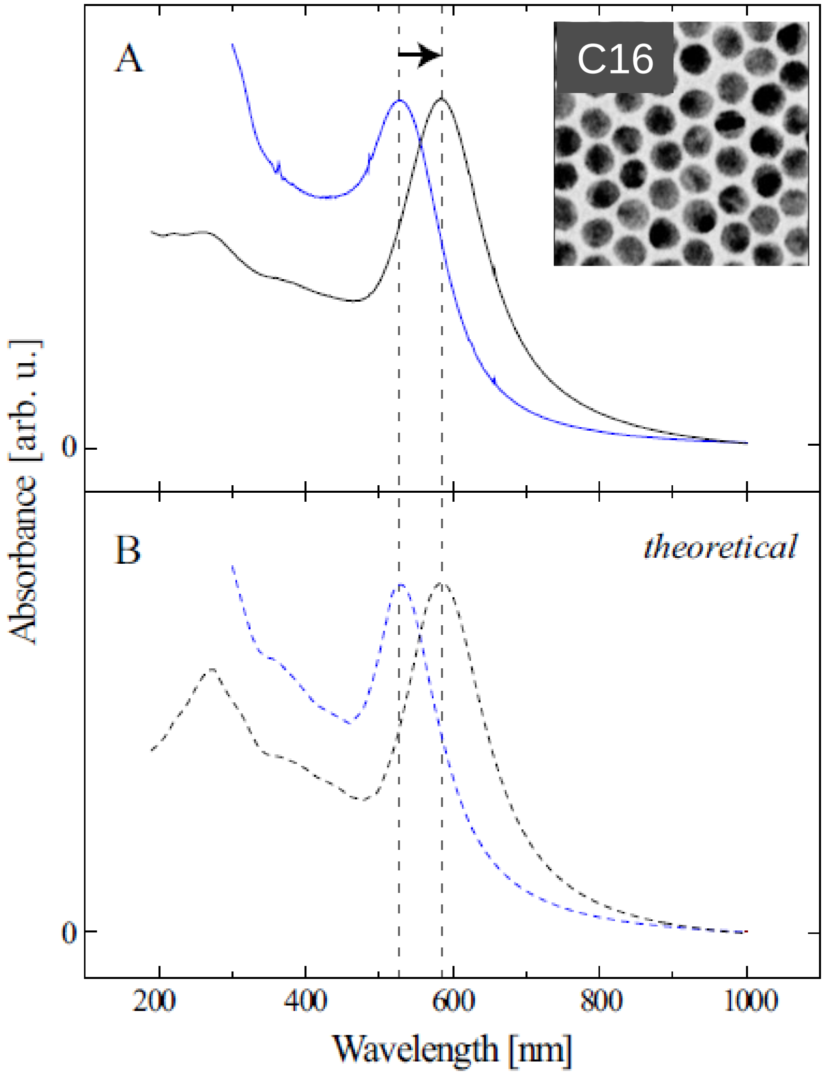
$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)} \qquad \omega_p = \sqrt{\frac{n_0 e}{\varepsilon_0 m_e}}$$

$$\epsilon_1(\omega,R) = 1 - \frac{{\omega_{\mathrm{p}}}^2}{\omega^2 + \Gamma^2(R)} + \epsilon_{1,\mathrm{core}}$$

$$\epsilon_2(\omega,R) = \frac{{\omega_{\mathrm{p}}}^2\Gamma(R)}{\omega(\omega^2 + \Gamma^2(R))} + \epsilon_{2,\mathrm{core}}$$

$$\Gamma(R) = \frac{v_{\mathrm{F}}}{l_\infty} + A\,\frac{v_{\mathrm{F}}}{R}$$

damping constant
(radius dep.)



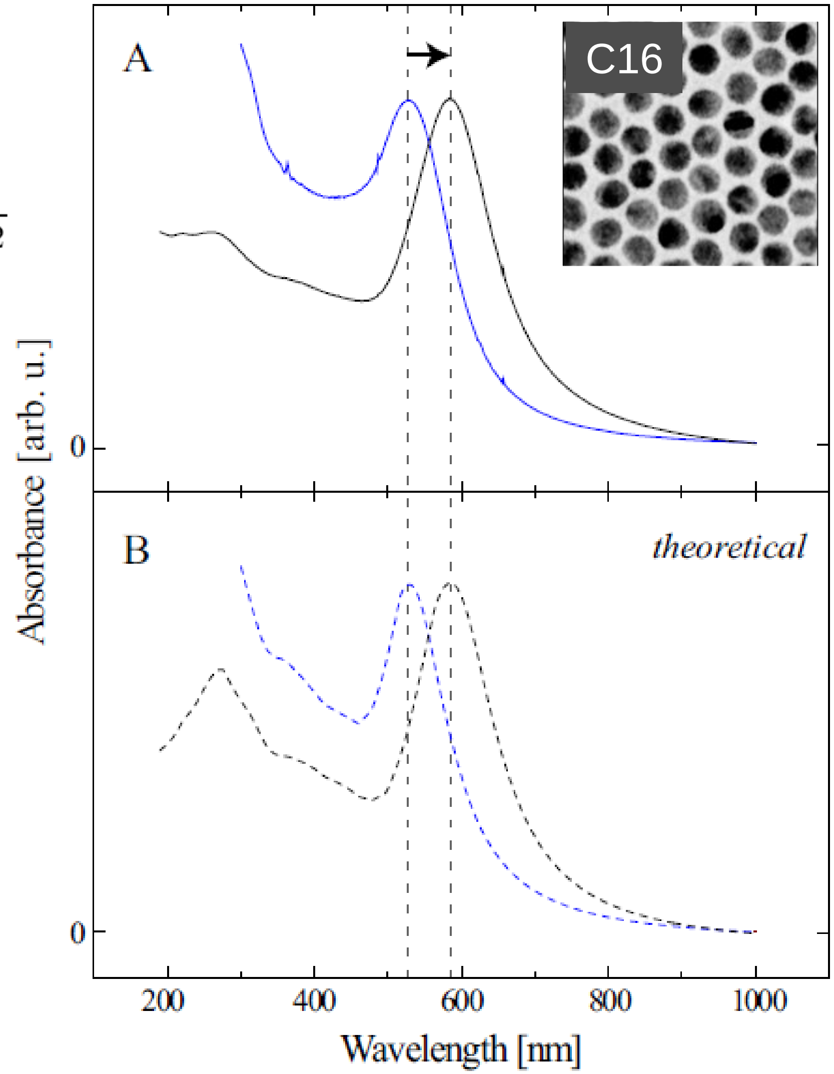
L. Bernard et al., JPC (2007)

characterizing plasmon resonances

absorption cross-section: Mie
(small particles, dipolar approx.)

$$\sigma(\omega) = 12\pi \frac{\omega}{c} \varepsilon_m^{3/2} R^3 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2}$$

$$\propto \frac{1}{(\omega - \omega_M)^2 + \left(\Gamma/2\right)^2} \qquad \omega_M = \frac{\omega_p}{(1+2\varepsilon_m)^{1/2}}$$



NB

in **solution**: dilute system, Mie ok

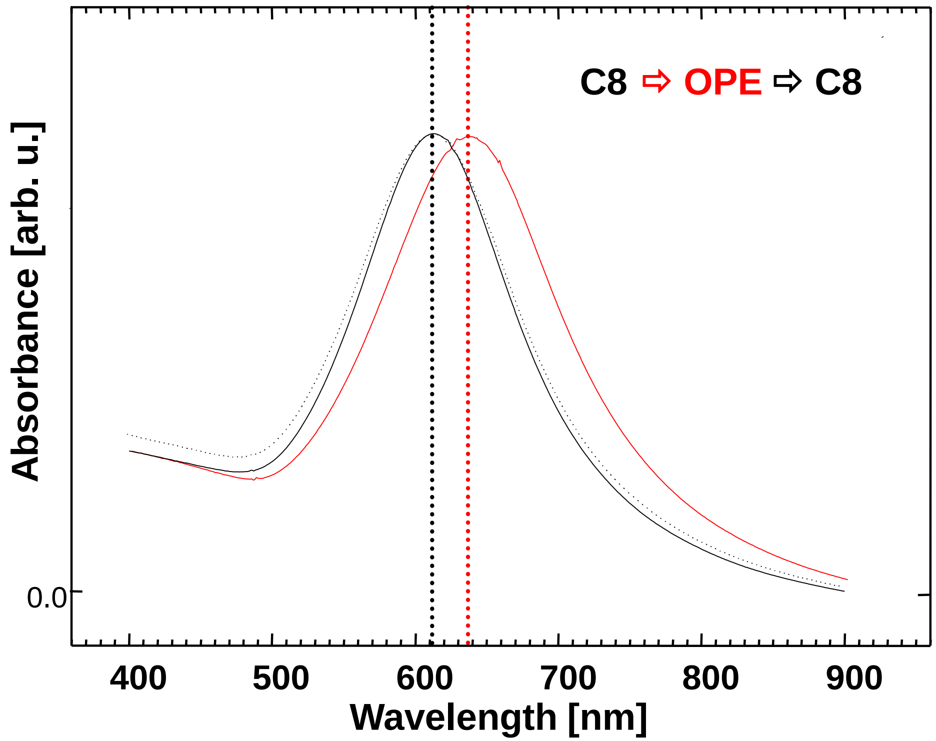
as **array** interaction between neighboring nanoparticles, red-shift

⇨ **effective medium permittivity**
Maxwell-Garnett

L. Bernard et al., JPC (2007)

optical absorption

plasmon resonance for array during exchange



Modeling: *Mie (cross-section) & Maxwell-Garnett (effective permittivity)*

$\Delta\lambda \approx$ 20nm ⬄ $\Delta\varepsilon \approx$ 0.5

ε_{C8}=1.9-2.2[(1)], ε_{OPE}=3.1-3.9[(2)]

⇨ **exchange efficiency 20% to 40%**

NB: partial exchange ensures stability of array

(1) G. Whitesides et al., , APL, 1998.
(2) J. Stapleton et al., Langmuir 2003.

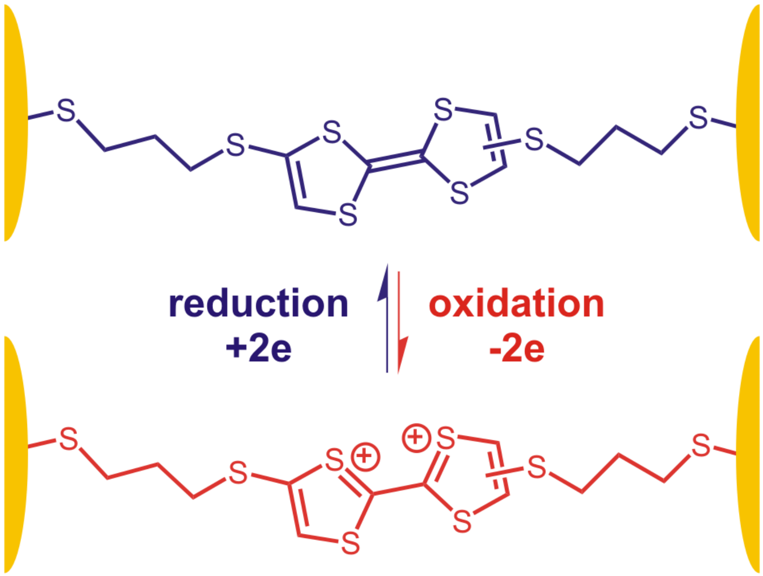
L. Bernard et al., J. Phys. Chem. C, 2007

- two-state systems at the molecular scale
- families of molecular switches
- contacting strategies for upscaling

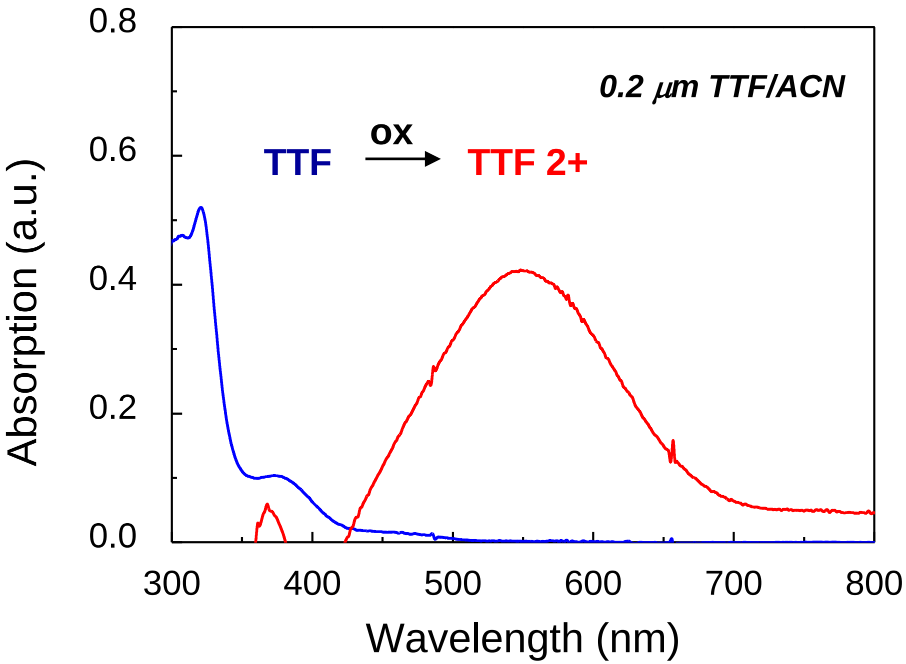
Examples

- optical switching
- and more functions

chemical modulation of the conductance in NP arrays



S. Decurtins et al.



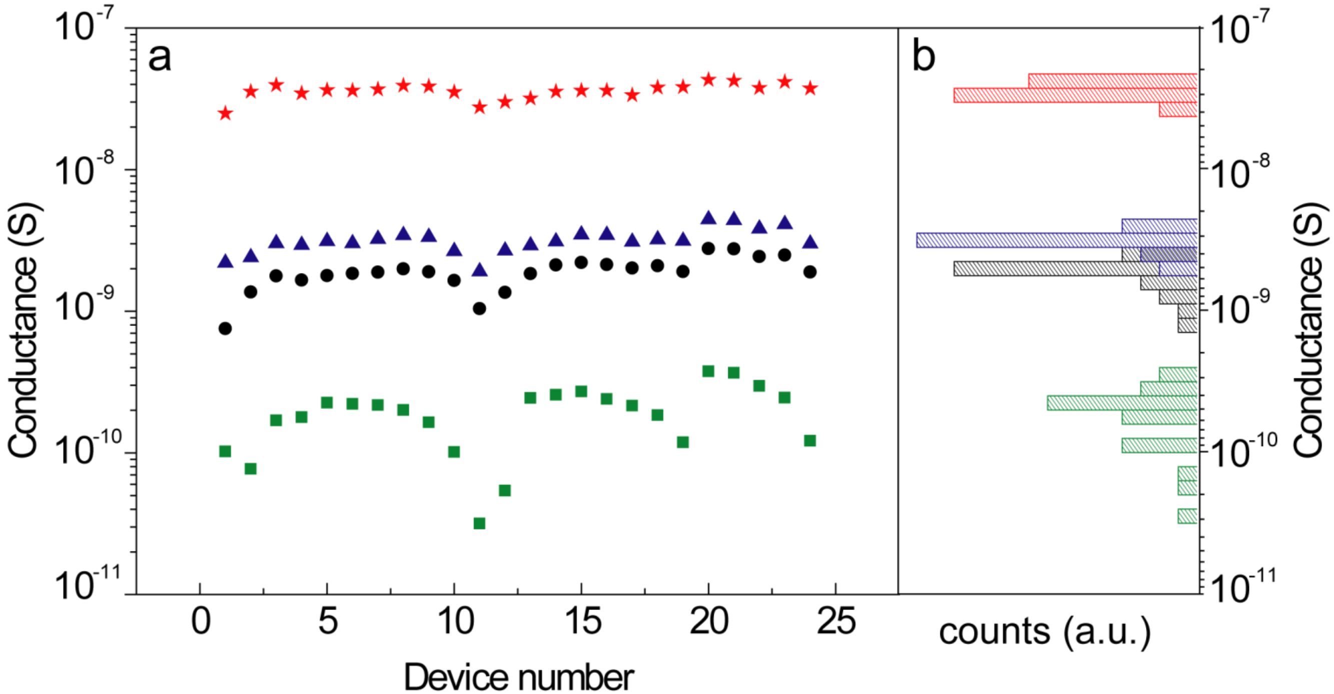
oxidation: $FeCl_3$ *(iron chloride)*

reduction: $Fe(C_2H_5)_2$ *(ferrocene)*

chemical modulation of the conductance

experiment: exchange → oxidation → reduction
(all measurements in the dry)

C8 → TTF (0)
→ TTF ox (2+)
→ TTF red (0)



chemical modulation of the conductance

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C8 → TTF (0)
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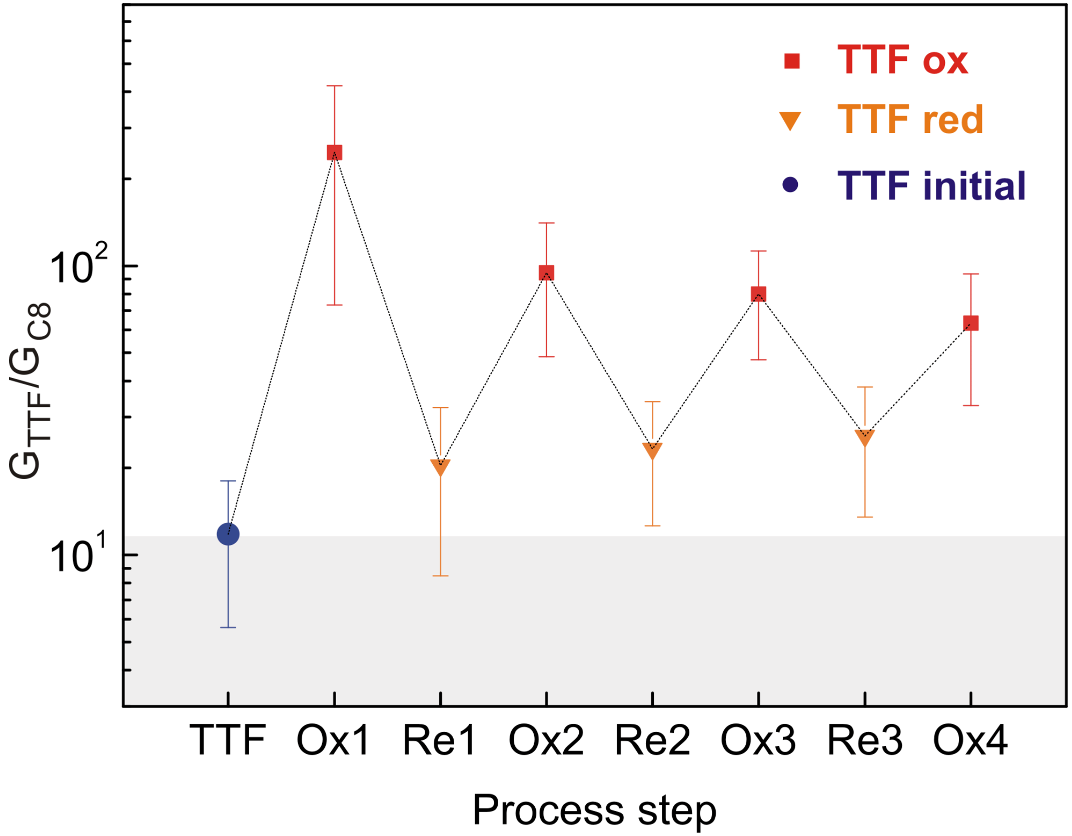


conductance change estimate
resonant tunneling

$$\frac{G}{G_0} = \frac{\Gamma_1\Gamma_2}{\varepsilon^2+(\Gamma_1+\Gamma_2)^2/4}$$

estimate
$G(2^+)/G(0) \leq 10$
measured
$G(2^+)/G(0) \sim 20$

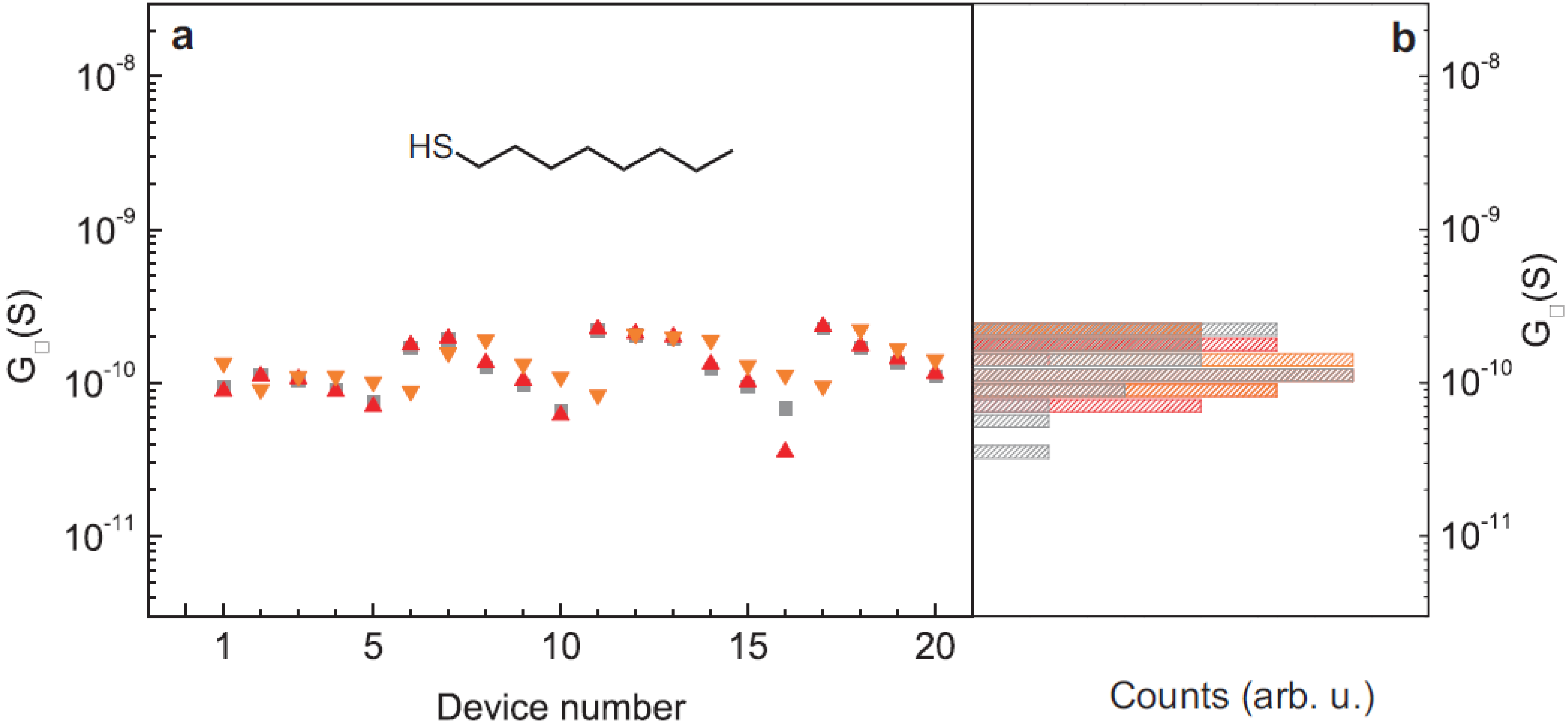
data from UV-vis for levels
$E_{HL}(0) = 3.7$ eV, $E_{HL}(2^+) = 1.8$ eV

J. Liao, J. Agustsson et al.,

chemical modulation of the conductance

controls

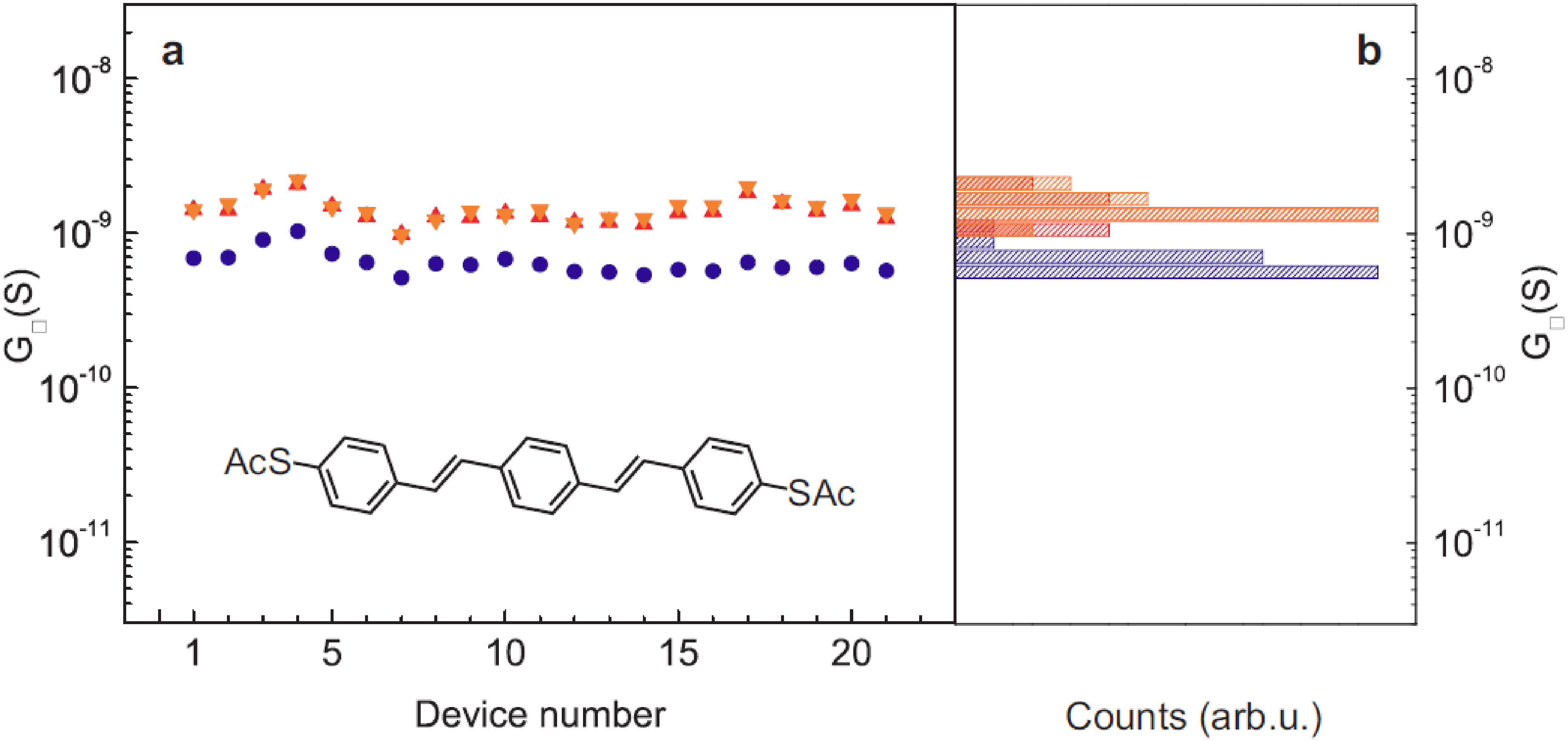
experiment: exchange → oxidation → reduction



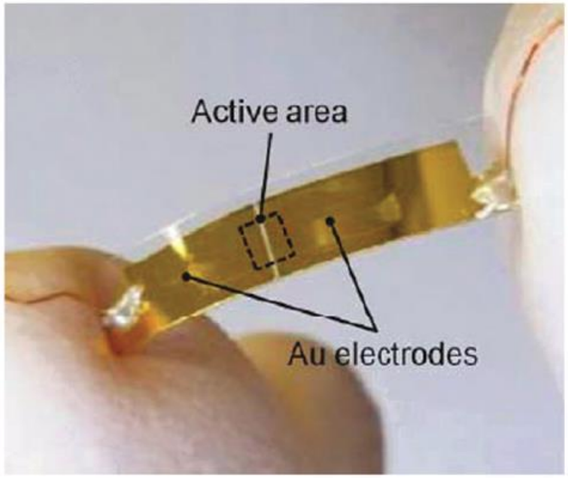
chemical modulation of the conductance

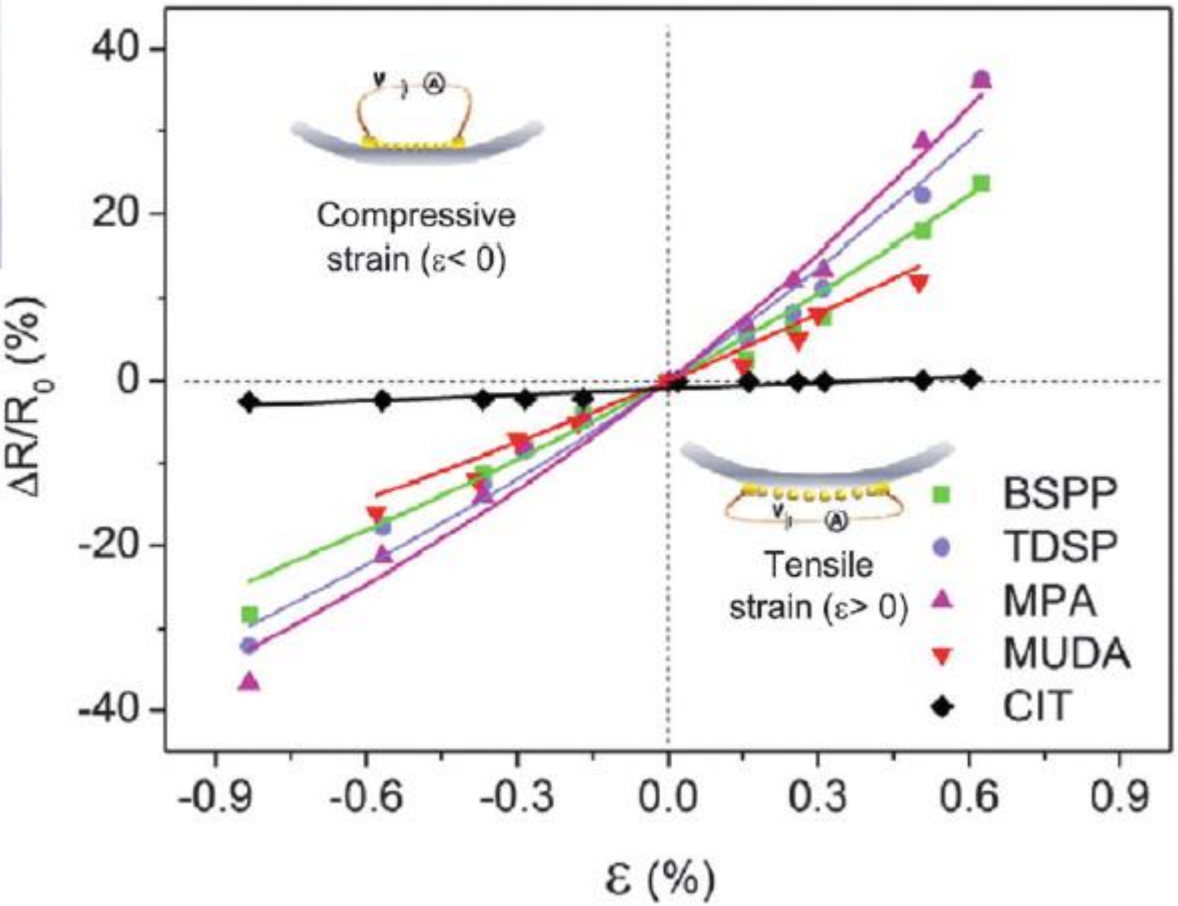
controls

experiment: exchange → oxidation → reduction



mechanical strain gauges based on NP arrays





L. Ressier et al., JPC 2011, Nanotech 2013