Molecular electronics

Lecture 3

Aviram-Ratner concept. Functional molecular electronics: rectification and memory

Non-linear Molecular elements

- To achieve **computing** with molecular elements we need to obtain non-linear elements:
  - diodes (rectifiers), or
  - negative differential resistance devices (NDR), or
  - three-terminal devices
- To obtain molecular **memory** we need **switching**

Molecular devices

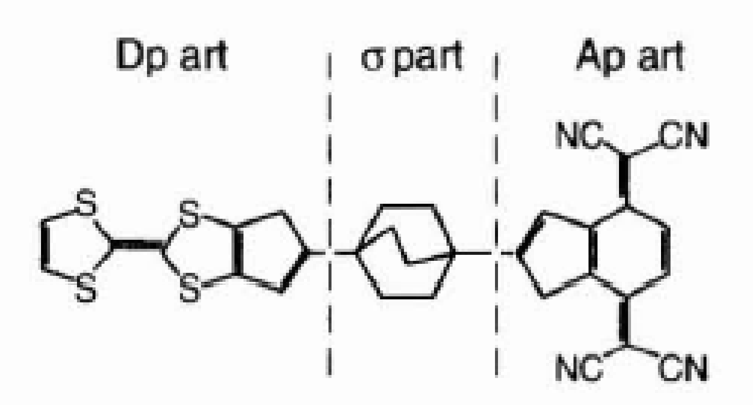
- The challenges:
  - how to attach molecules to the electrodes
  - how to arrange them in the same direction

Rectification processes

- **S-rectifiers**: rectification due to Shottky barrier formed at metal-organic interfaces
- **A-rectifiers**: rectification due to assymetric placement of the molecule (on part of the molecule has good MO overlap with the electrode and the other one not)
- **U-rectifiers**: unimolecular rectification due to assimetric transport between the MOs.

Molecular rectifier (Diode)

- The idea (Aviram and Ratner, 1974):
  donor-acceptor system separated by a spacer so their π-systems don't overlap.
- the system will have preferential charge transfer direction

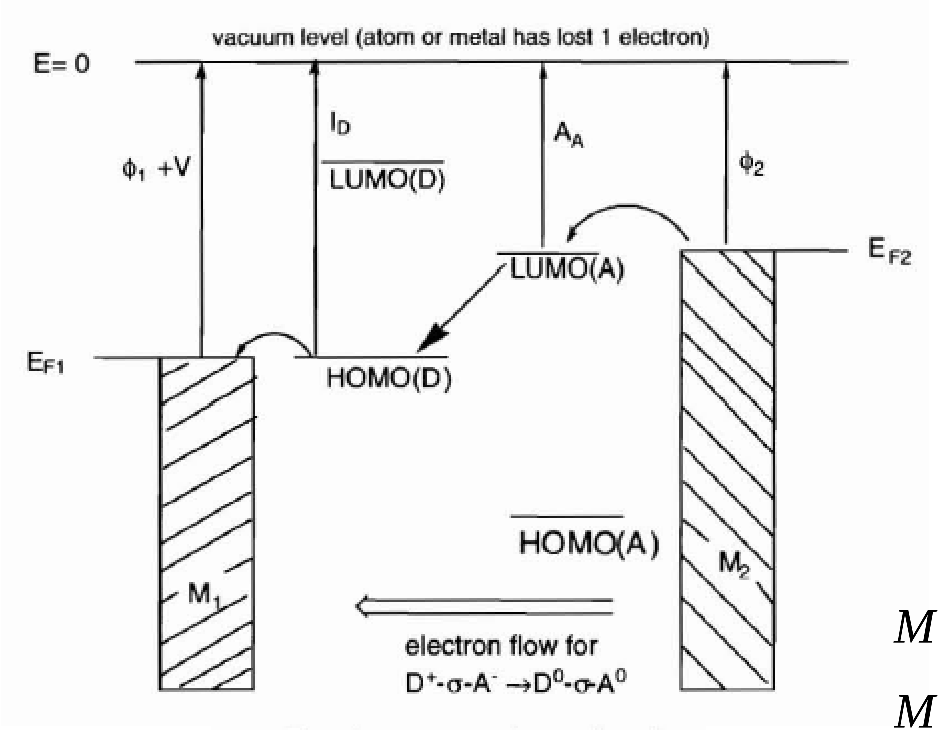


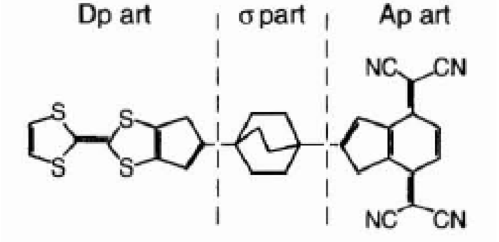
good one electron donor with low first ionisation potential

good one electron acceptor with a relatively high electron affinity.

saturated covalent bridge, decouples MO of D and A

Molecular rectifier





TTF

TCNQ

$$I_D - A_A = 6.83 - 3.3 = 3.5eV$$

$$I_A - A_D = 9.6eV$$

- Electron transport mechanism:
  1. Resonant transfer

$$HOMO_D \to M_1$$

$$M_2 \to LUMO_A$$

$$M_1 + D^0 - \sigma - A^0 + M_2 \to M_1^- + D^+ - \sigma - A^0 + M_2$$

$$M_1 + D^+ - \sigma - A^0 + M_2 \to M_1^- + D^+ - \sigma - A^- + M_2^+$$

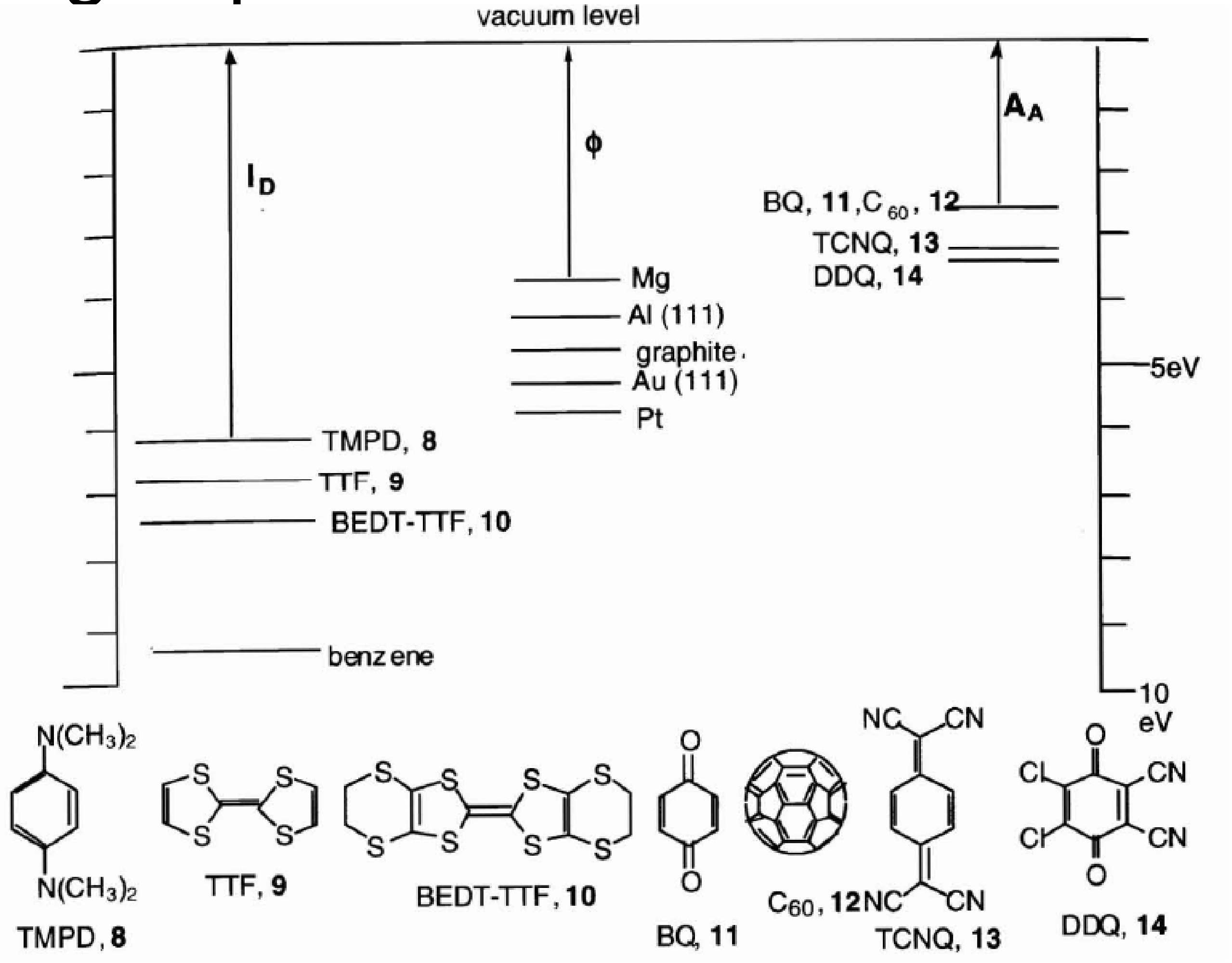
  2. Inelastic transfer

$$LUMO_A \to HOMO_D$$

$$M_1^- + D^+ - \sigma - A^- + M_2^+ \to M_1^- + D^0 - \sigma - A^0 + M_2^+$$

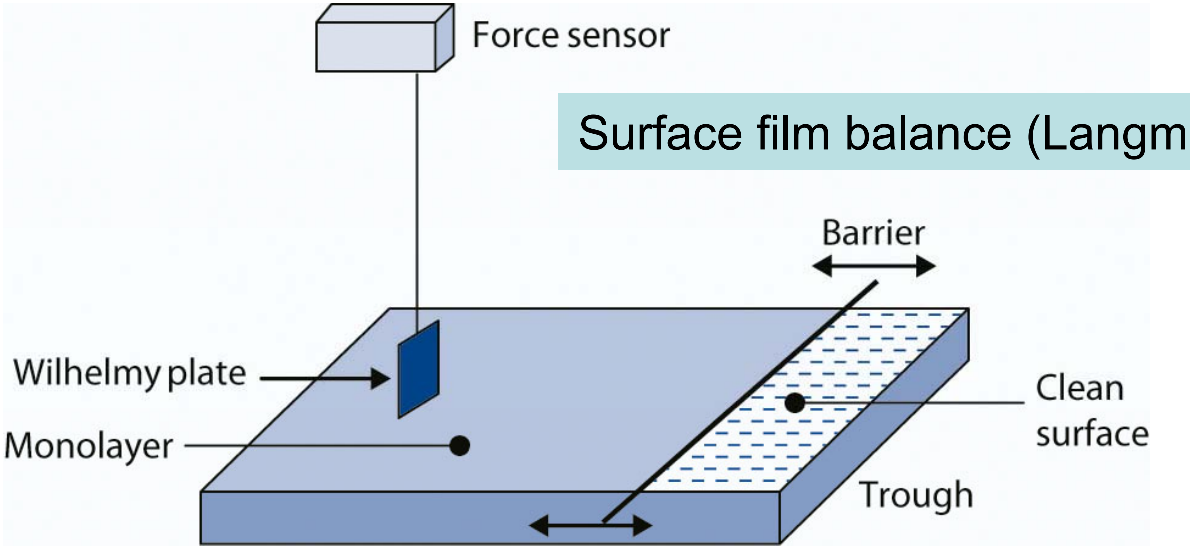
Molecular rectifier

- Energy levels for some common donor and acceptor groups:



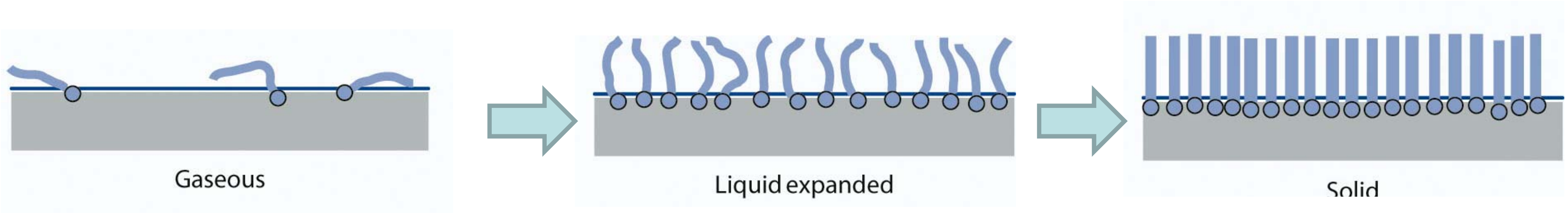
Molecular Rectifiers via LB process

- Langmuir-Blodgett technique can produce mono- (or multi-) layers of uniformly oriented molecules



Surface film balance (Langmuir trough)

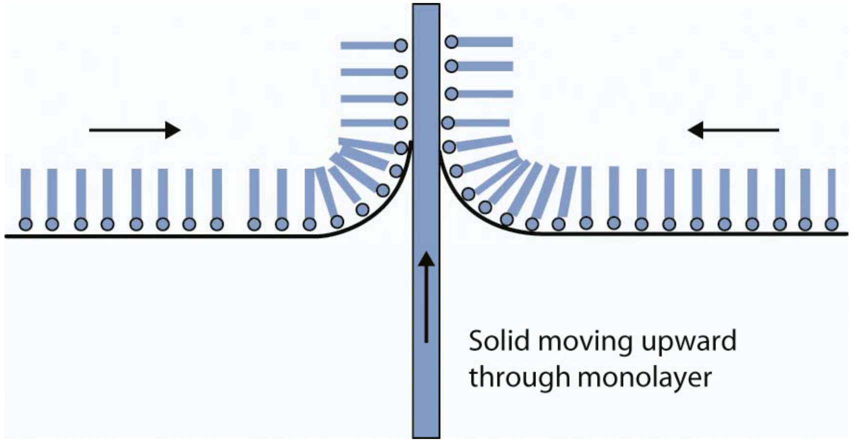
Monolayer compression:



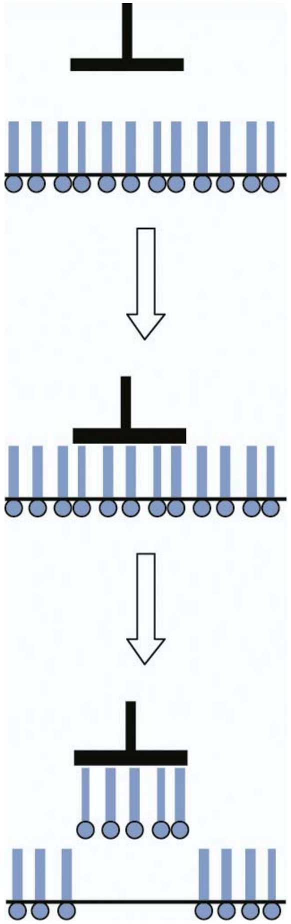
Molecular Rectifiers via LB process

- The monolayer could be than transferred to a solid support:

Vertical transfer



Langmuir-Schaefer



Molecular Rectifiers via LB process

LB (or LS) process occurs via physisorption

- Advantages:
  - monolayer density and arrangement can be controlled via LB process (prior to deposition)
  - Shottky barrier at the surface is avoided
- Disadvantages
  - monolayer structure can change after transfer
  - other adsorbates present on the surface are not displaced

Chemisorbed layers (SAMs)

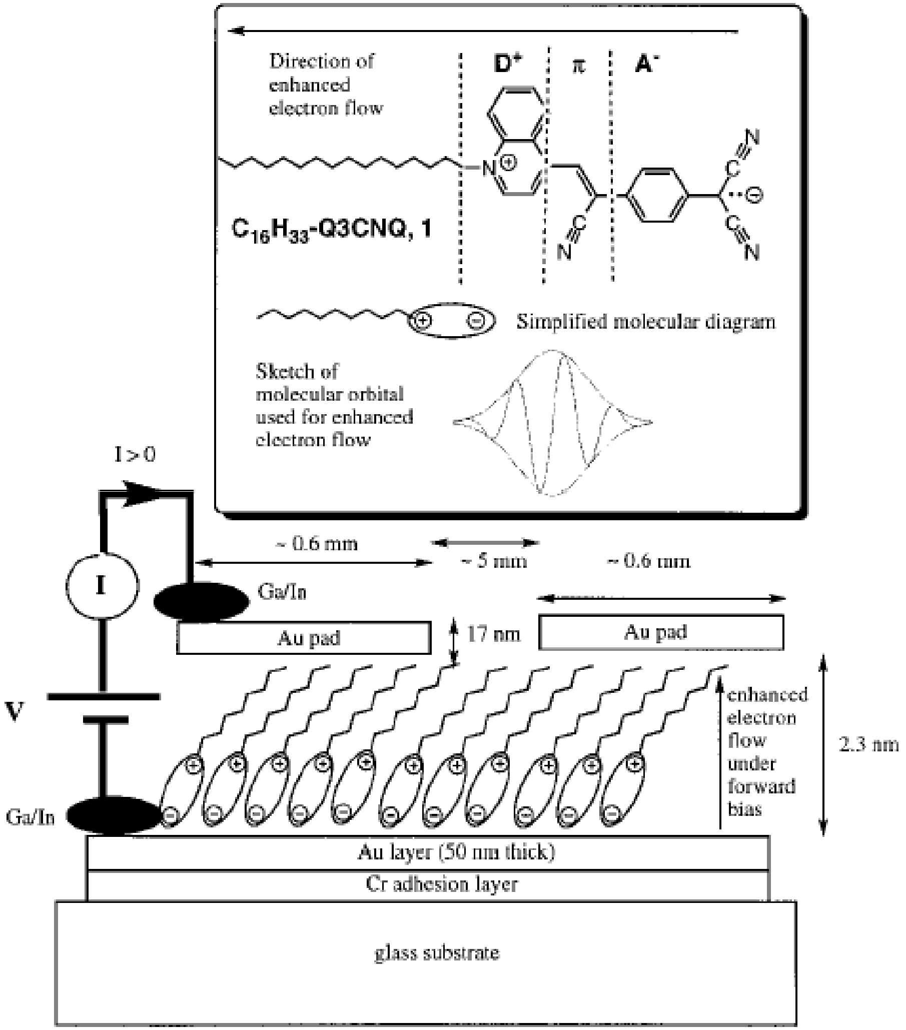
- Advantages
  - chemical reaction displaces adsorbates
  - once bound the adsorbed species are difficult to remove and re-arrange
- Disadvantages
  - uncertain degree of coverage
  - possibility of further chemical reactions
  - formation of surface dipoles (e.g. Au-thiol bond is particularly polarized)

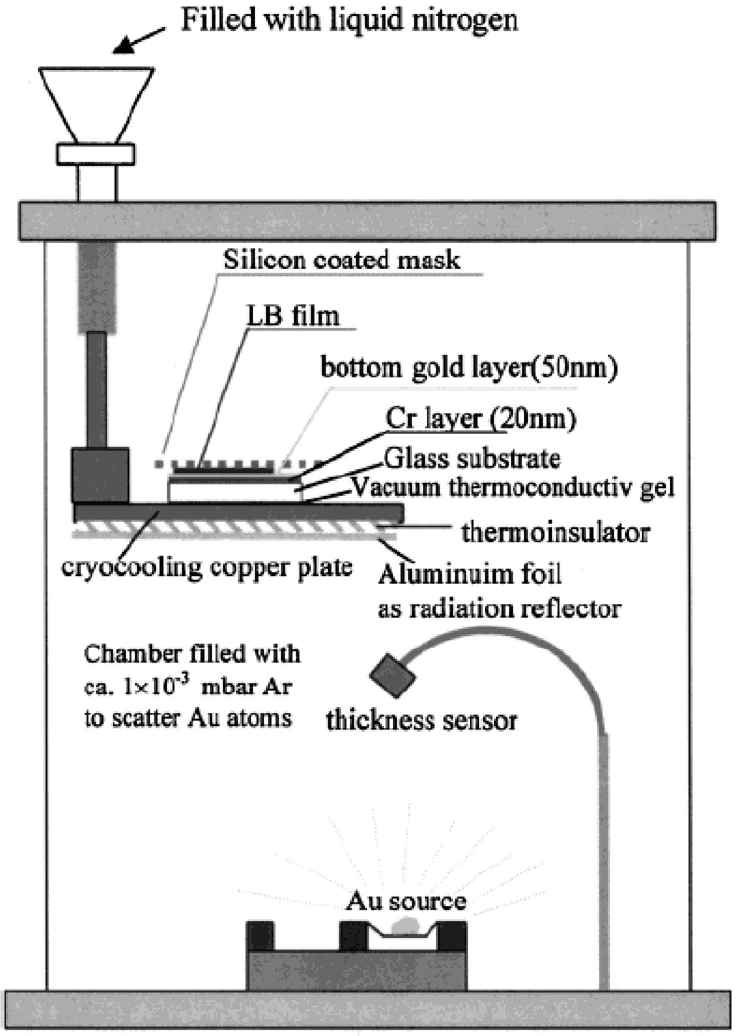
Rectification with Monolayers: Experimental

- The most challenging issue:
  Deposition of the **top metal electrode** in metal-organic-metal sandwich without damaging the organic layer or creating shorts
- First achieved by Roy Sambles group at Exeter University using Mg films
  Sambles et al, J.Chem.Soc.Chem.Commun. 1374 (1990)
  however, Mg film can create Shottky barrier on TCNQ due to interfacial salts $Mg^{+2}TCNQ^{-2}$and $Mg^{+2}(TCNQ^{-1})_2$.

Rectification with Monolayers: Experimental

- ”Cold gold” evaporation
  Metzger et al, J.Phys.Chem B105, 7280 (2001)

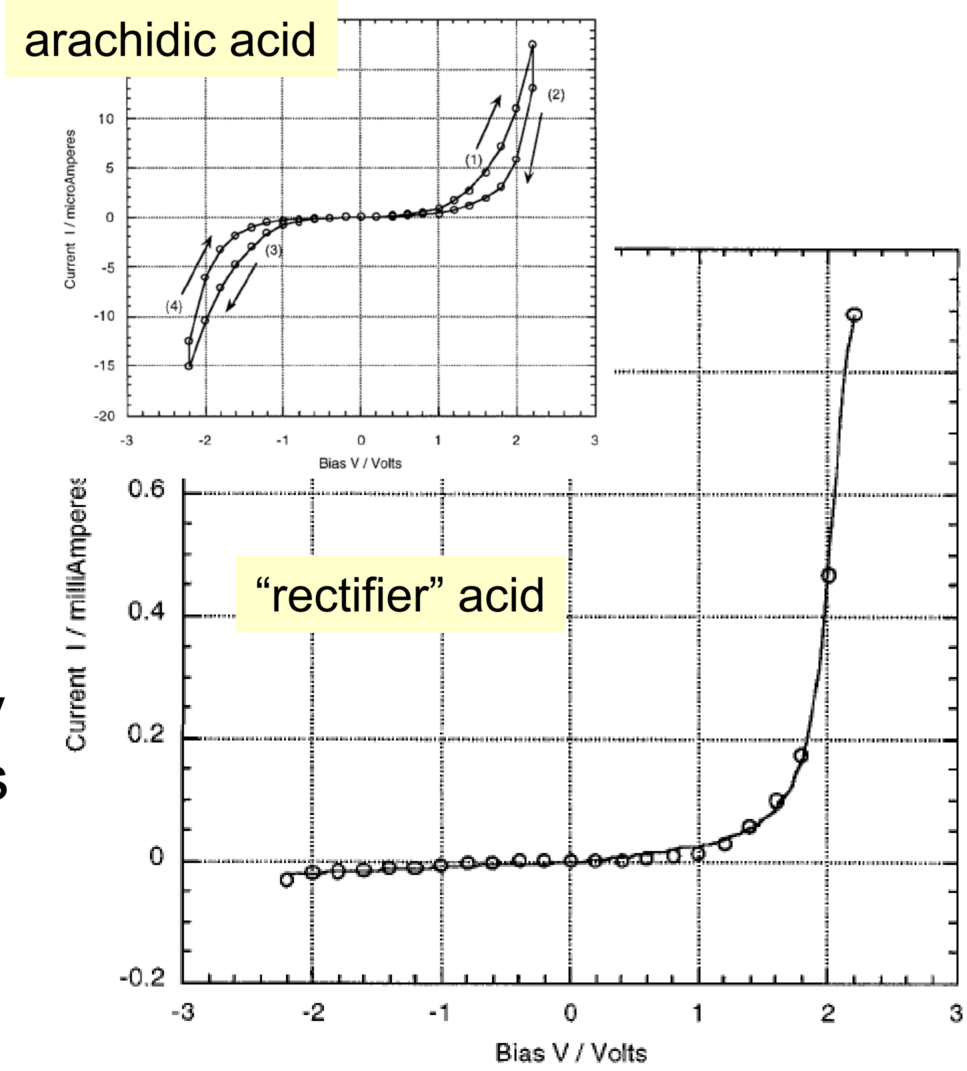




Langmuir-Blodgett Approach to MR

- Molecular rectifier:
  Metzger, R. M.; Xu, T.; Peterson, I. R.,. Journal of Physical Chemistry B 2001, 105, (30), 7280-7290.

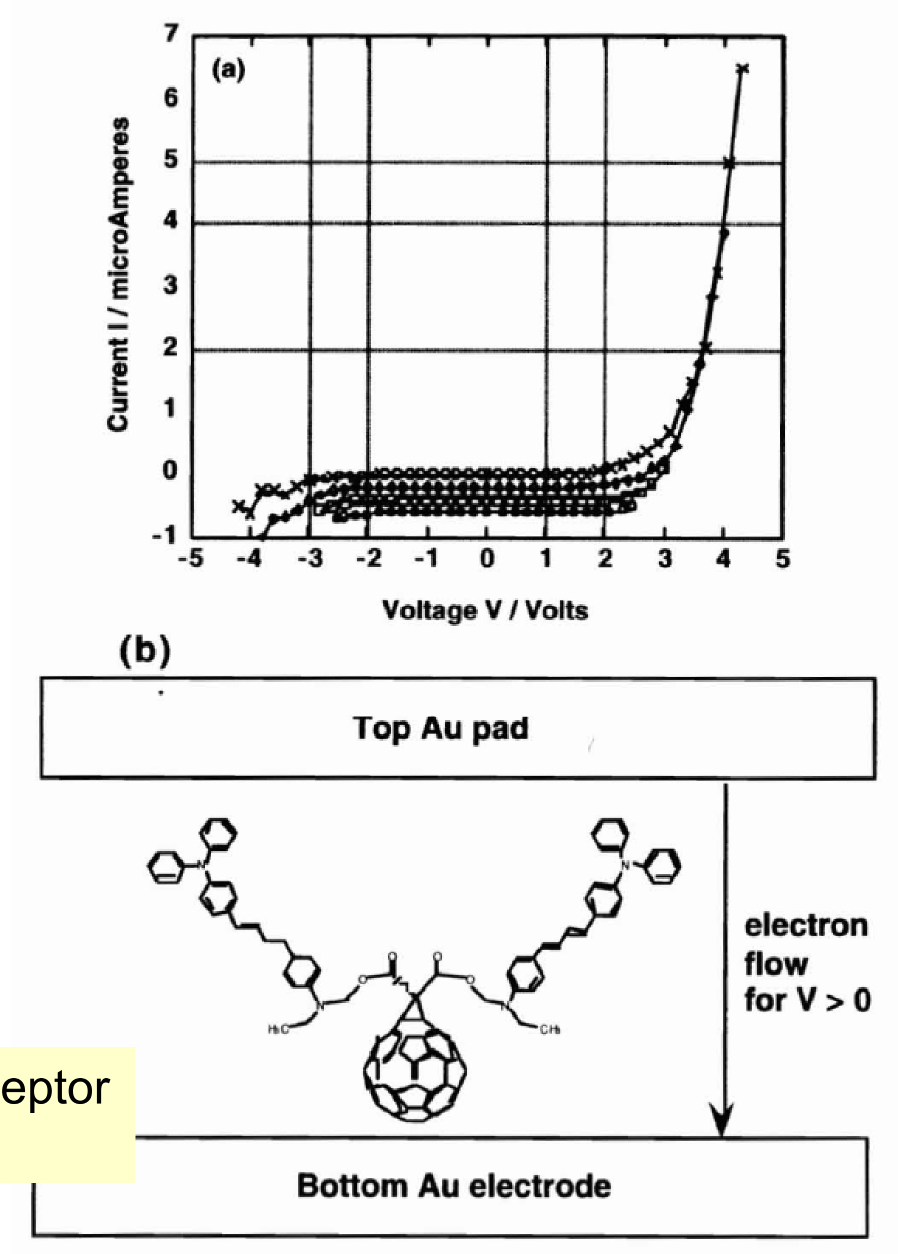
- Arachidic acid $C_{19}H_{39}COOH$ deposited with the same technique produces symmetric IV-curves
- $C_{16}H_{22}Q\text{-}3CNQ$ produces asymmetric curves with rectification ratio **RR= 26 @** 1.5V
- Repeated cycles reduce rectification ration presumably due to “flipping” the molecules in high electric field (1.5V across 2.3 nm = 0.65 GV/m !)



Langmuir-Blodgett Approach to MR

- Very rigid monolayer with stable rectification ratio based on C60

  Metzger et al, J.Phys.Chem B107, 1021 (2003).

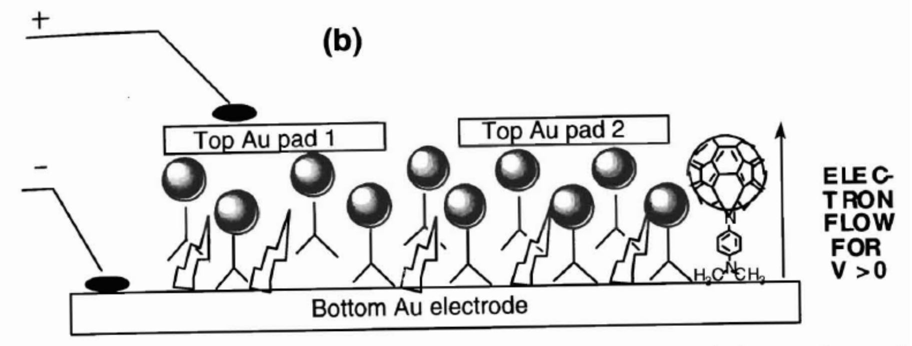


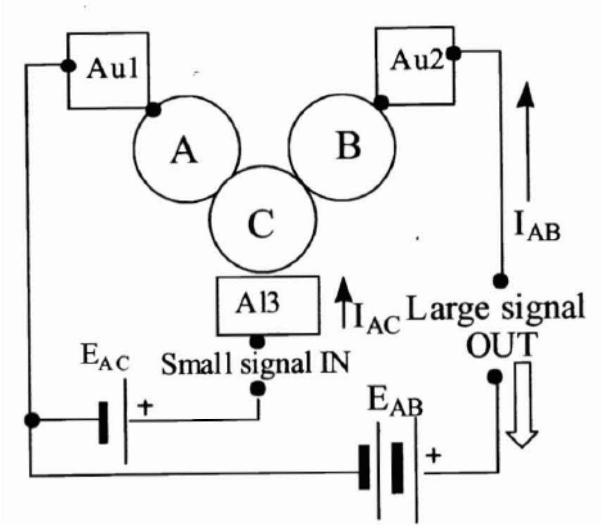
one-electron donors (triphenylamine)

weak one-electron acceptor (fullerene)

Langmuir-Blodgett Approach to MR

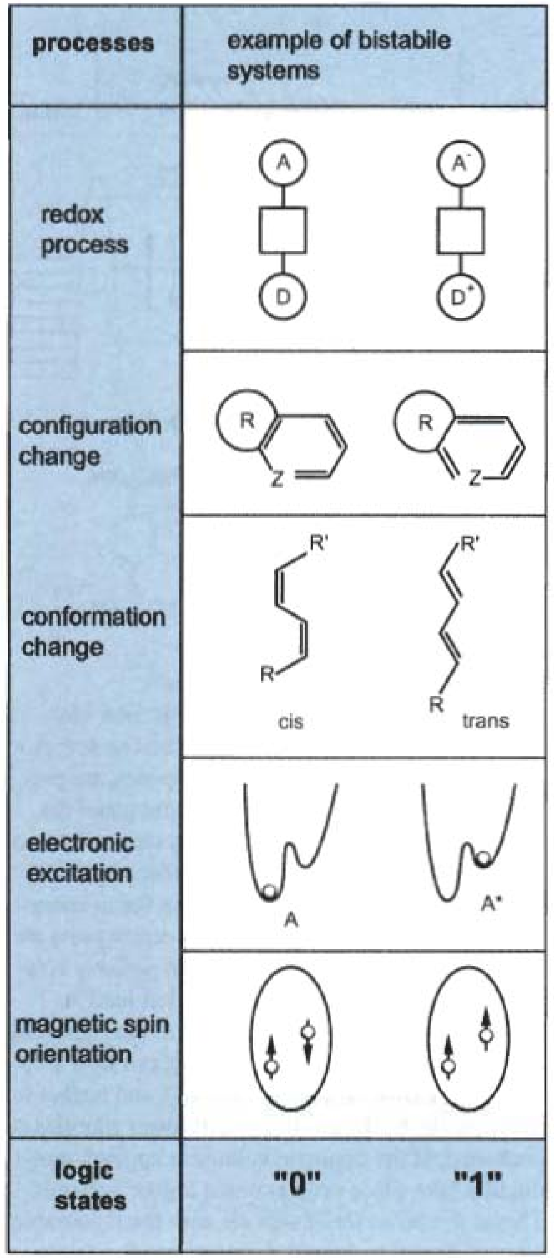
- Results and Challenges
  - Current always flows better from Donor to Acceptor as predicted by Aviram and Ratner.
  - Many devices are plaqued by filamentary growth at gold electrodes
  - Can we measure properties of the current carrying monolayer?
  - What happens when the molecule goes from ground to excited state (image dipoles in metal electrodes)?
  - Can a three-terminal build using this technique?





Switches and Memory

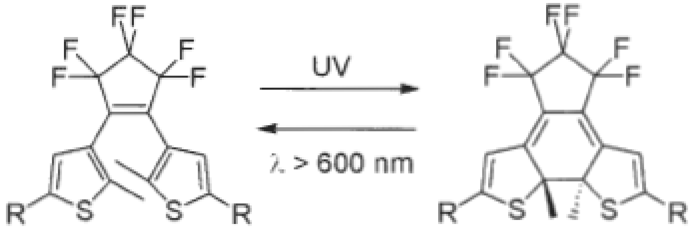
- Bistable molecular systems: molecules that can exist in 2 (meta)stable states with different properties
- switches can be triggered by light, pH etc.



processes	example of bistabile systems	
redox process		
configuration change		
conformation change		
electronic excitation		
magnetic spin orientation		
logic states	"0"	"1"

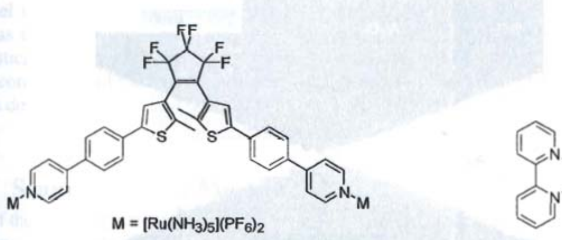
Switches and Memory

- light triggered switch

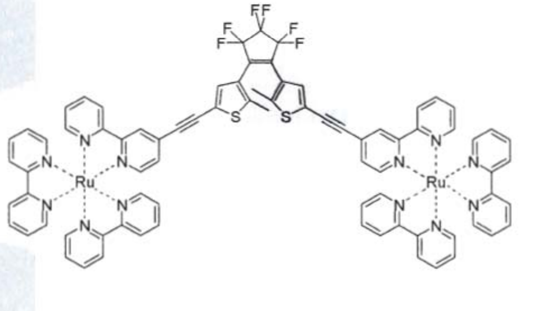


14
open form

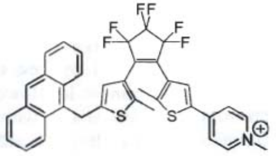
14
closed form



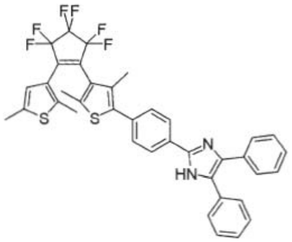
A. Fernández-Acebes, J.-M. Lehn, Chem. Eur. J.,5,3285(1999)



S. Fraysse, C. Coudret, J.-P. Launay, Eur. J. Inorg. Chem.,1581(2000)



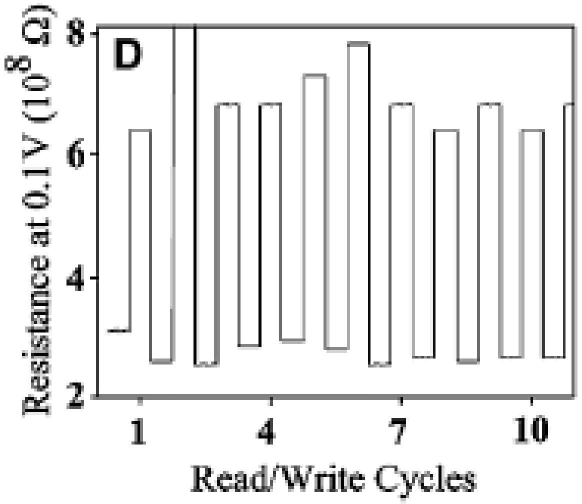
J. M. Endtner, F. Effenberger, A. Hartschuh, H. Port, J. Am. Chem. Soc.,122,3037(2000)

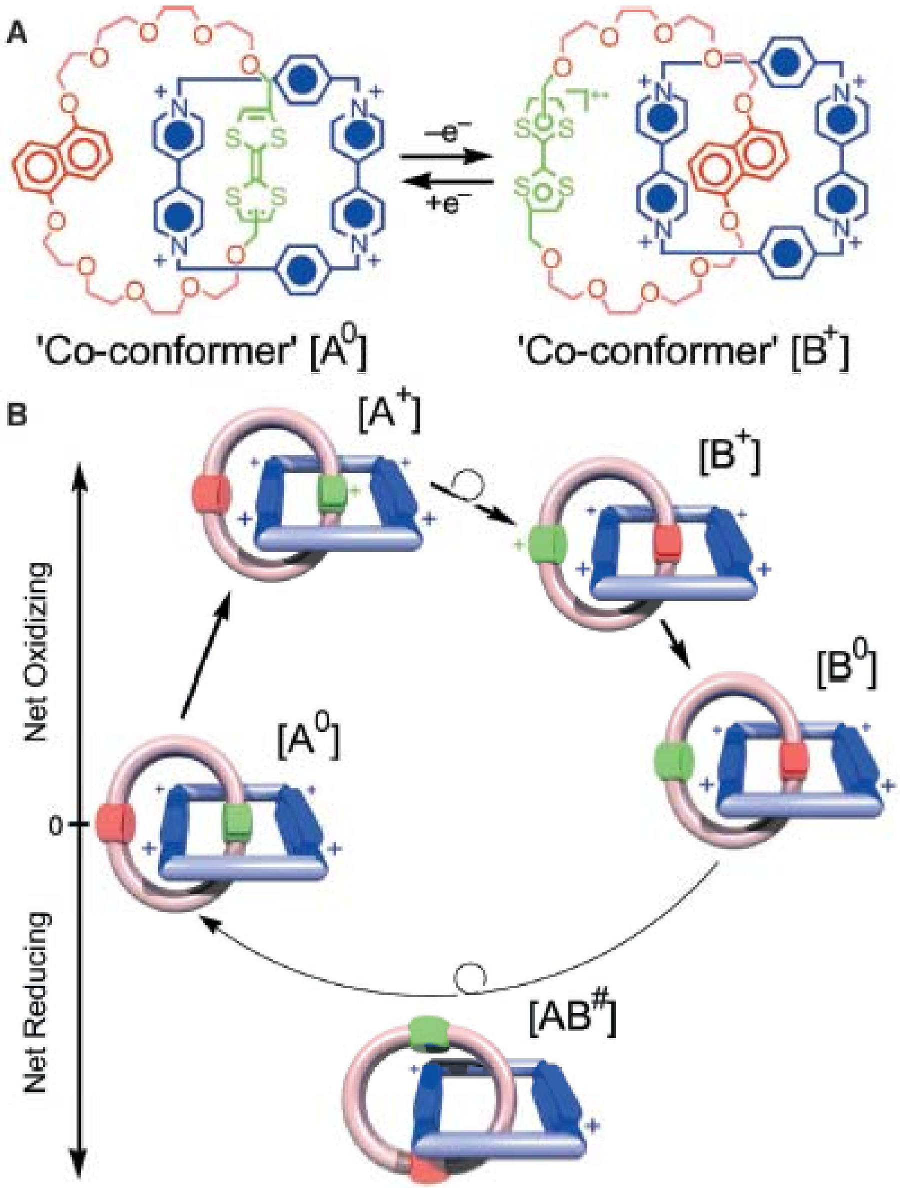


K. Yagi, C. F. Soong, M. Irie, J. Org. Chem.,66,5419(2001)

Switches and Memory

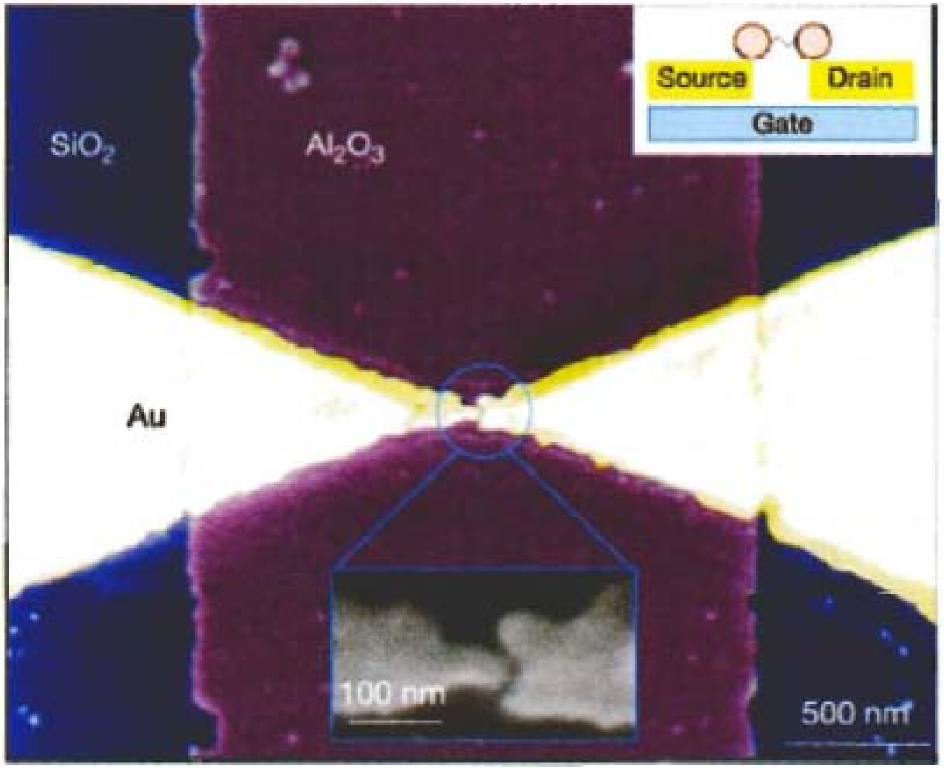
- Voltage triggered switch:
  catenane molecule can be switched between two state (rotation of a ring) by applying positive (+2V) or negative pulses (-2V), reading voltage is 0.1V





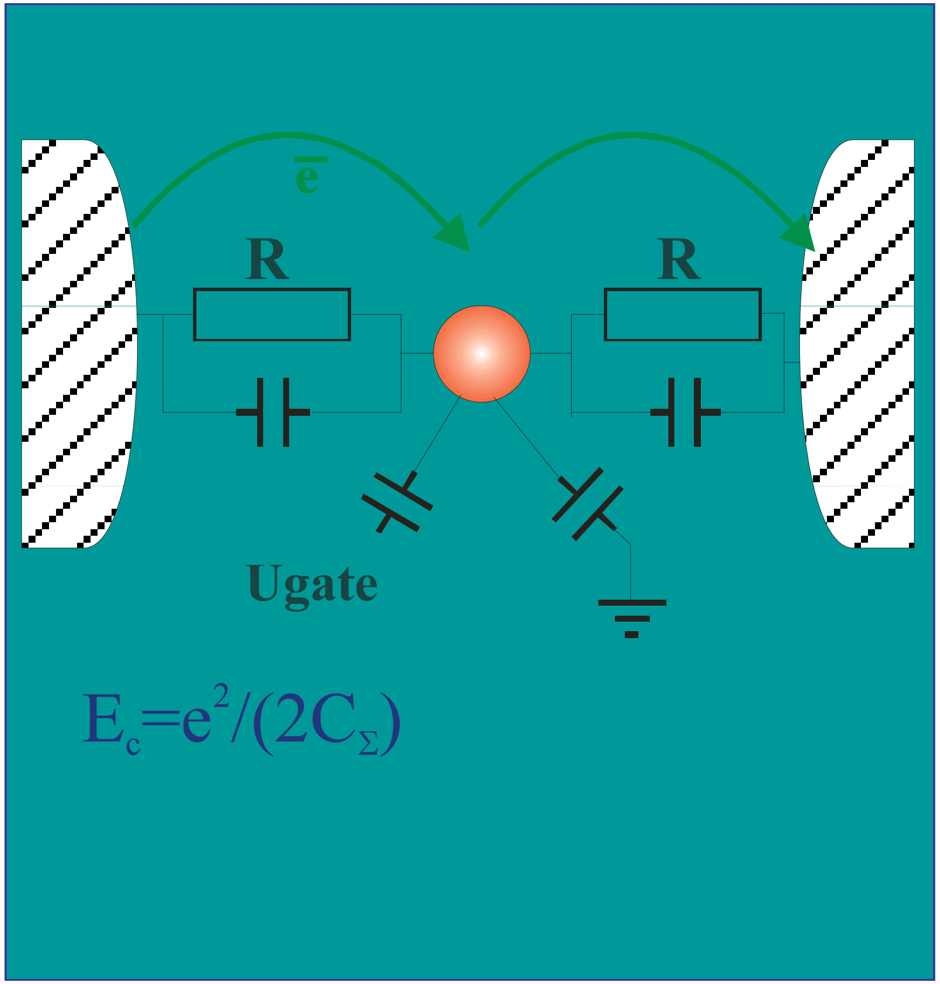
Collier et al, Science 289, 1172 (2000)

Fixed three terminal technique



Theory considerations: Coulomb blockade

- Charging effects on the nanoscale are important



Geometrical effect:

depends on the particle size and geometry of the contacts

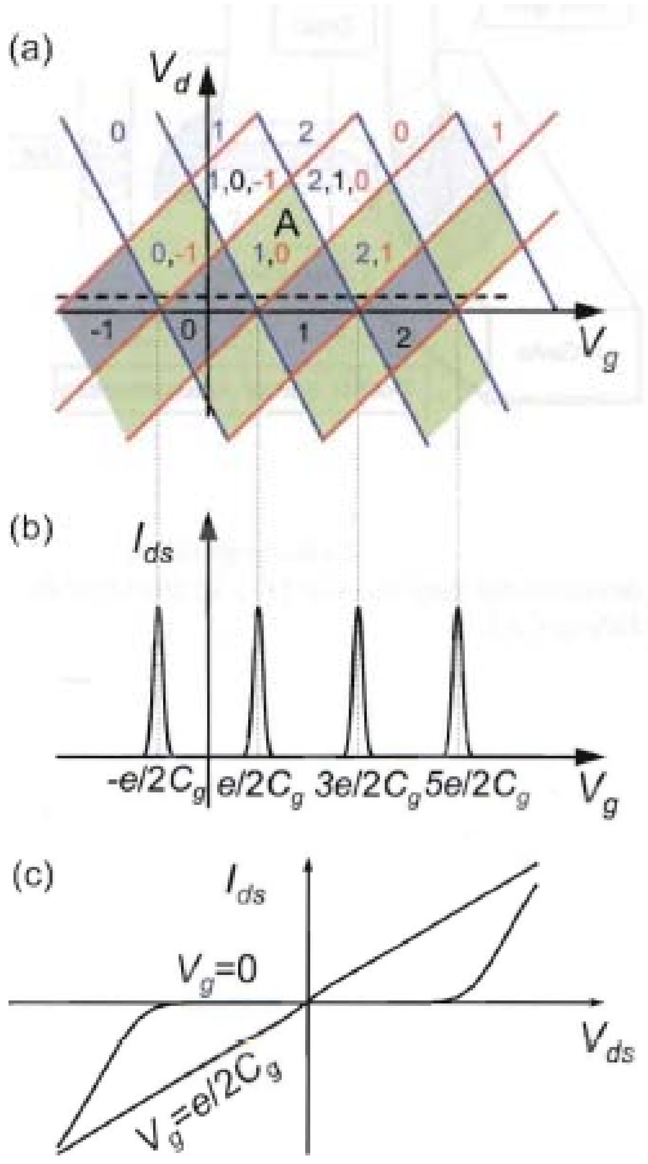
1nm cluster: Ec ~ 0.5 eV

Coulomb blockade

- ”diamond” plot for an SET

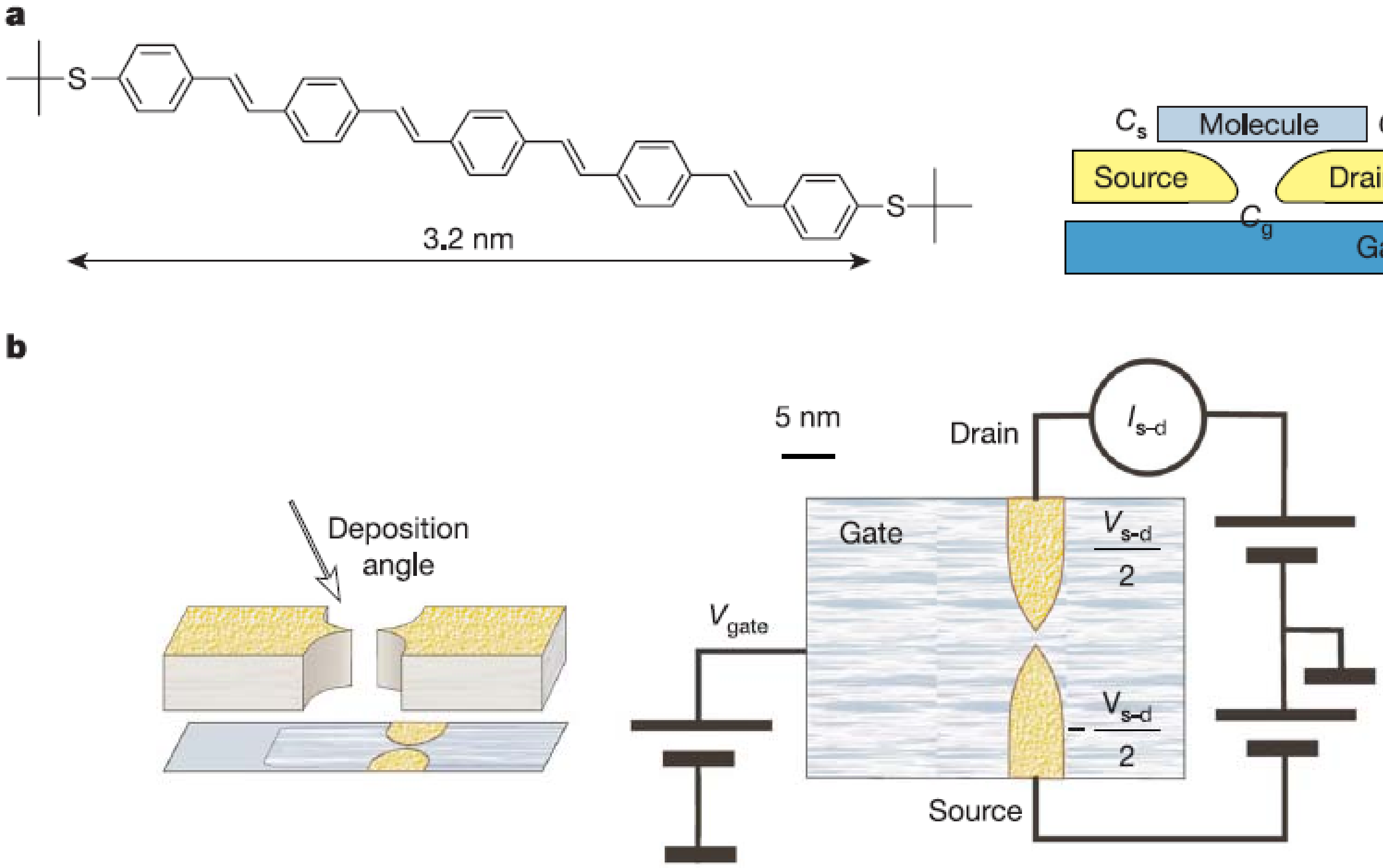
- current vs gate voltage

- current vs bias voltage



SET on a single molecule

- *Kubatkin et al, Nature 425, p.698 (2003)*



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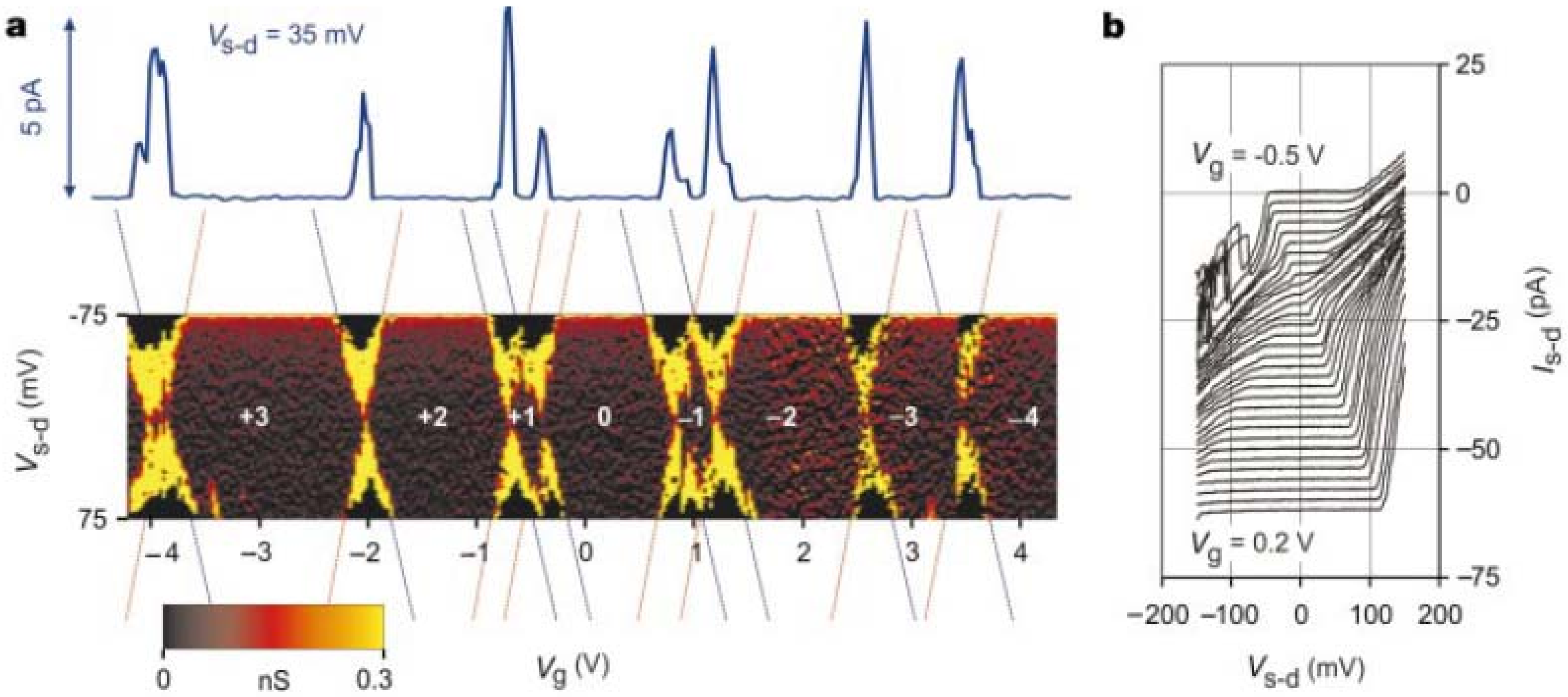

- Only two slopes are present, meaning we have a single island SET
- size of the diamonds is different, meaning we have smth on top of the Coulomb blockade

SET on a single molecule

- *Kubatkin et al, Nature 425, p.698 (2*

- Modelling results: due to image charges the charge in the molecule is localized close to the electrodes