Self-assembly of polychlorotriphenylmethyl organic radicals on surfaces

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Departament NMMO

ICMAB

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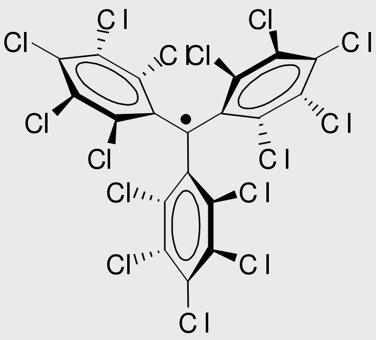
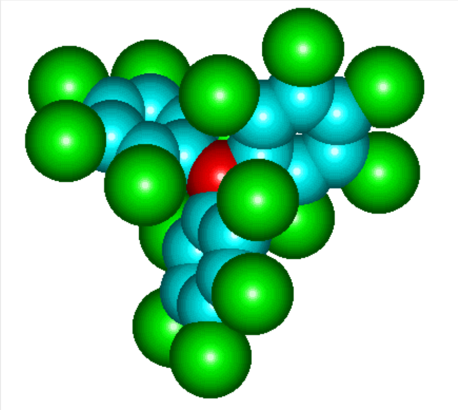
INTRODUCTION

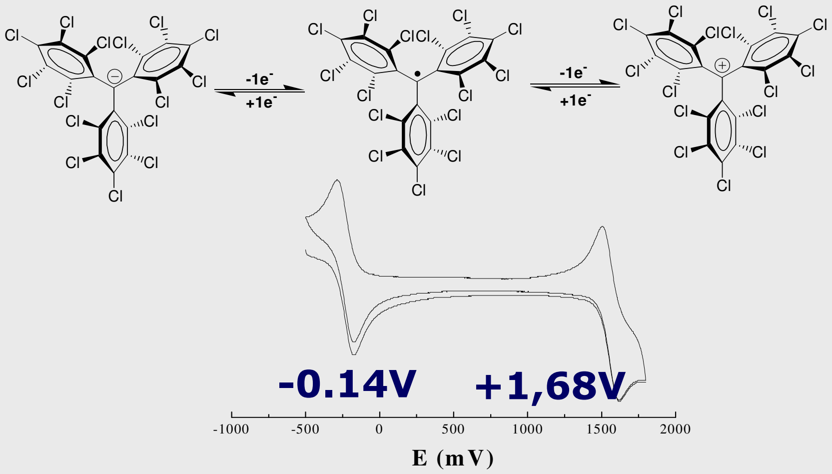
Polychlorotriphenylmetyl (PTMs) radicals.





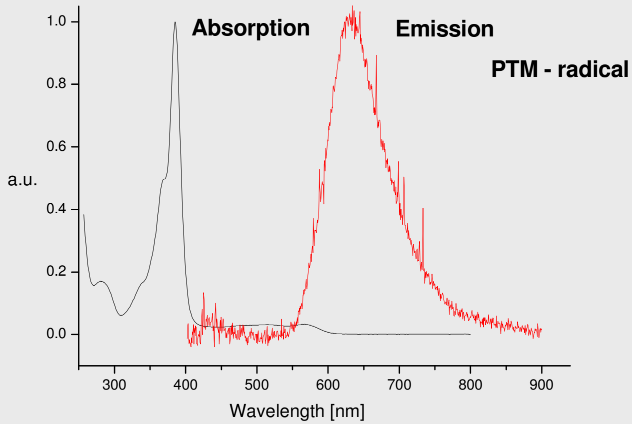
- Highly persistent
- Easily functionalized
- Open-shell structures (magnetism)

- Electroactive



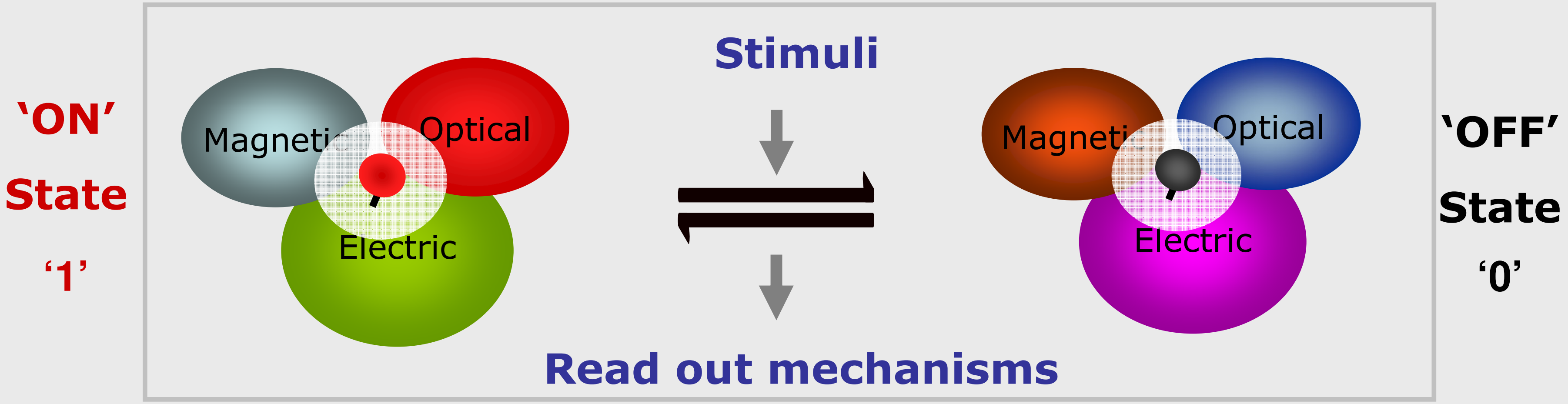
- Fluorescence

600nm (red)



Motivation

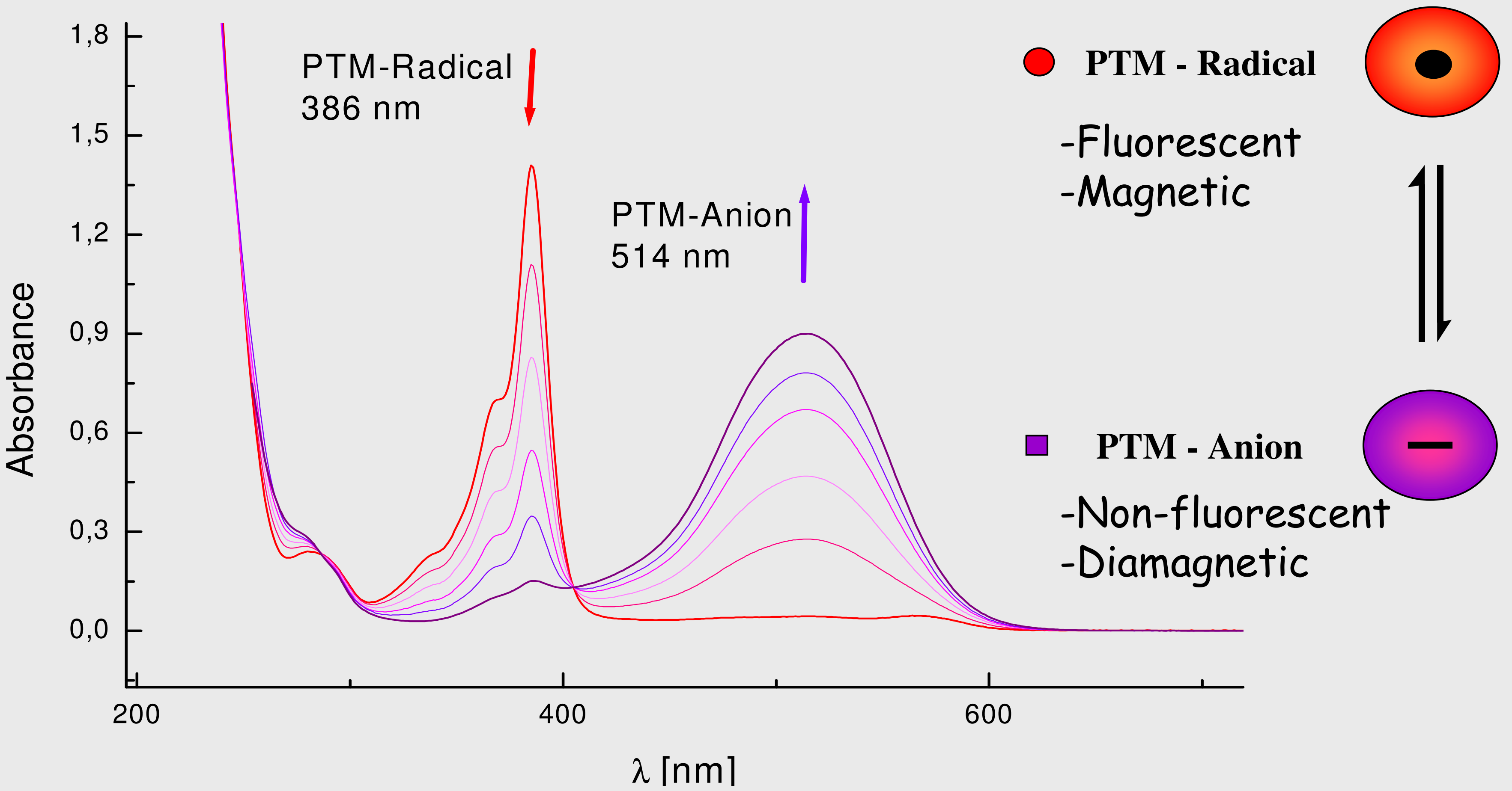
A switch or memory device mechanism → <u>Bistable systems</u>



A molecule having two stable and fully reversible states exhibiting different optical, magnetic or electrical properties

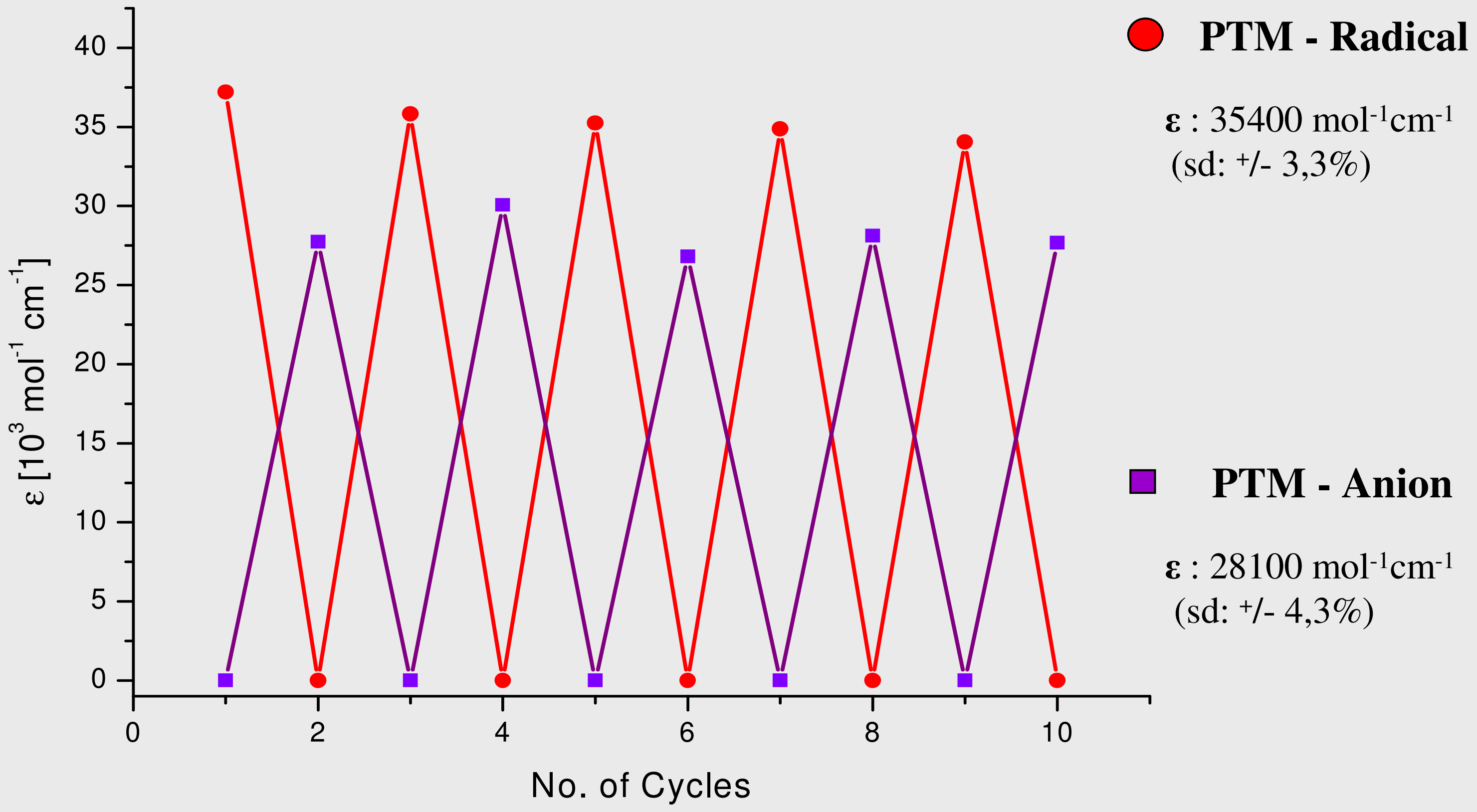
INTRODUCTION

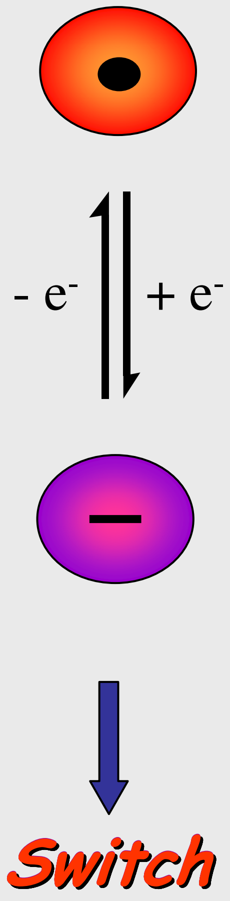
UV/Vis Spectra of the PTM Radical and Anion in a Chronoamperometric Experiment



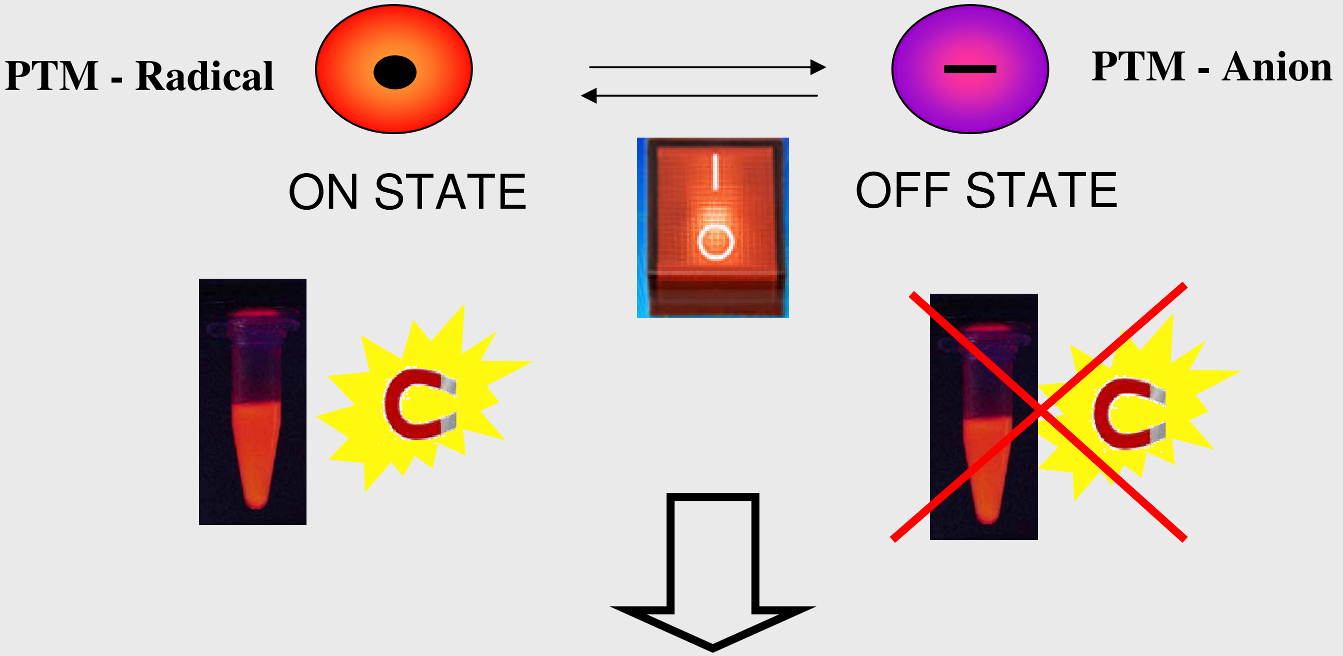
INTRODUCTION

Redox- Switching of the UV/Vis- Response between the PTM- Radical and the PTM- Anion



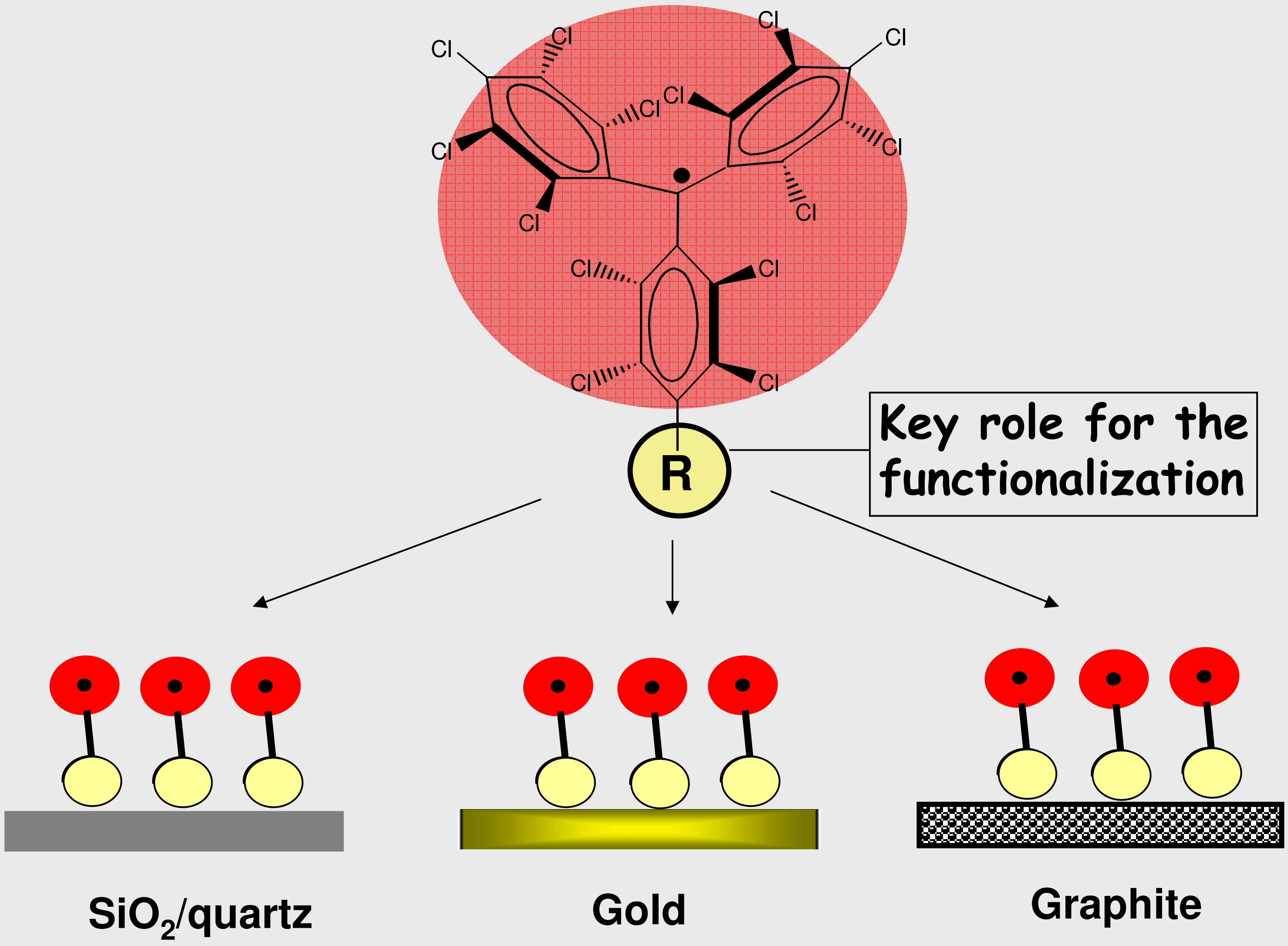


PTM RADICALS ARE GOOD BUILDING BLOCKS FOR PREPARING MULTIFUNCTIONAL MOLECULAR SWITCHES



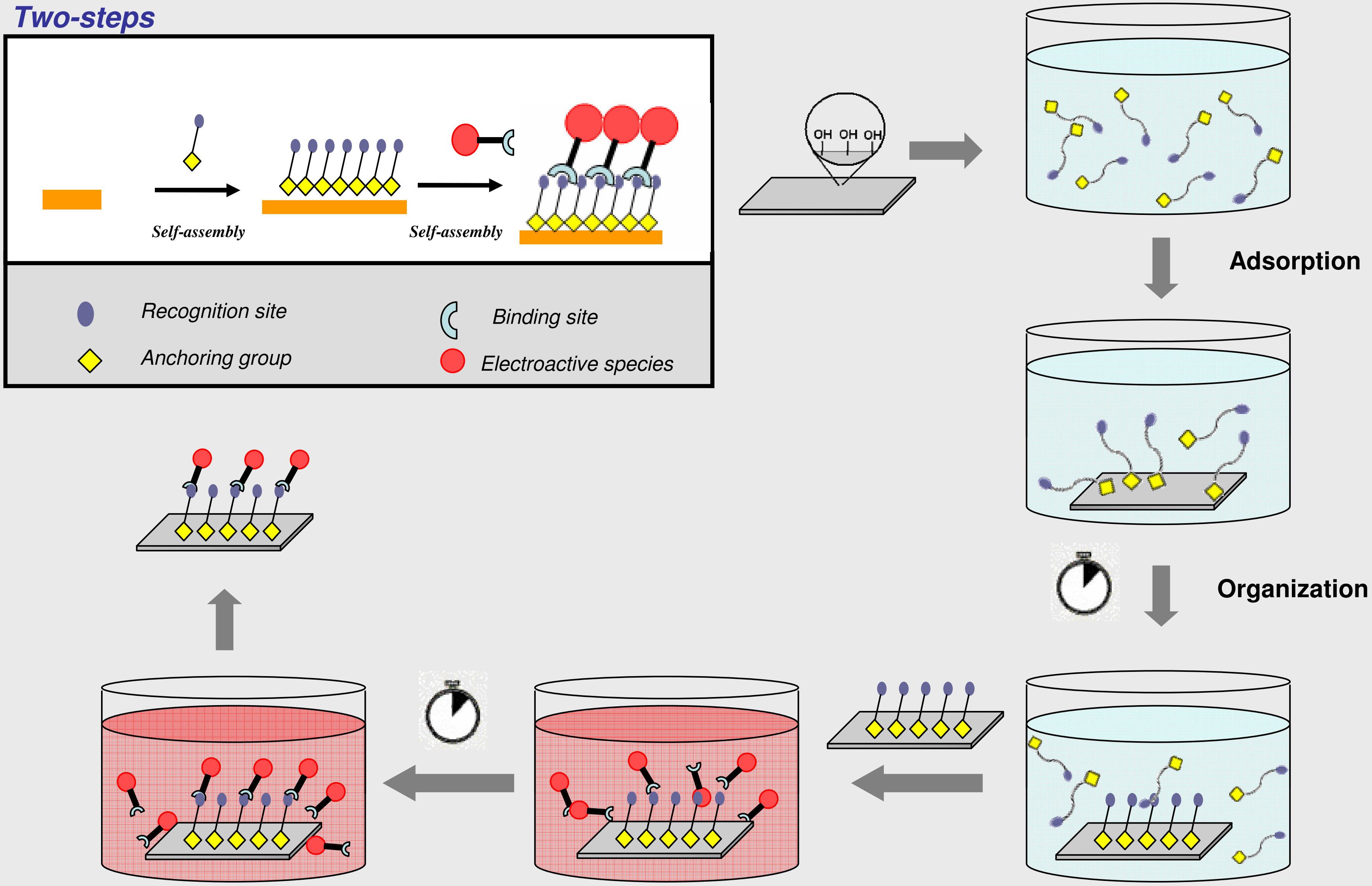
Functionalise surfaces with PTM radicals for memory devices/switches

Functionaliztion of different surfaces



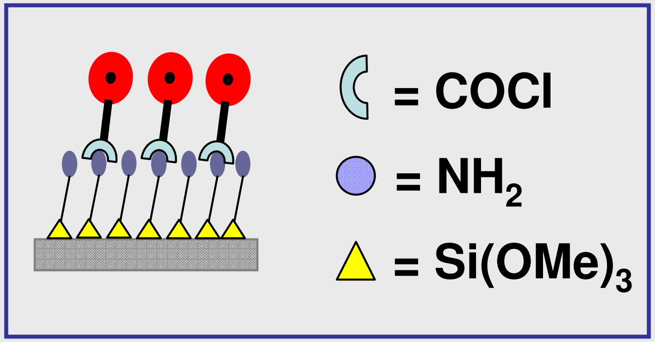
PREPARATION OF PTM SELF ASSEMBLED MONOLAYERS (SAMs) ON SILICON OXIDE AND QUARTZ SURFACES

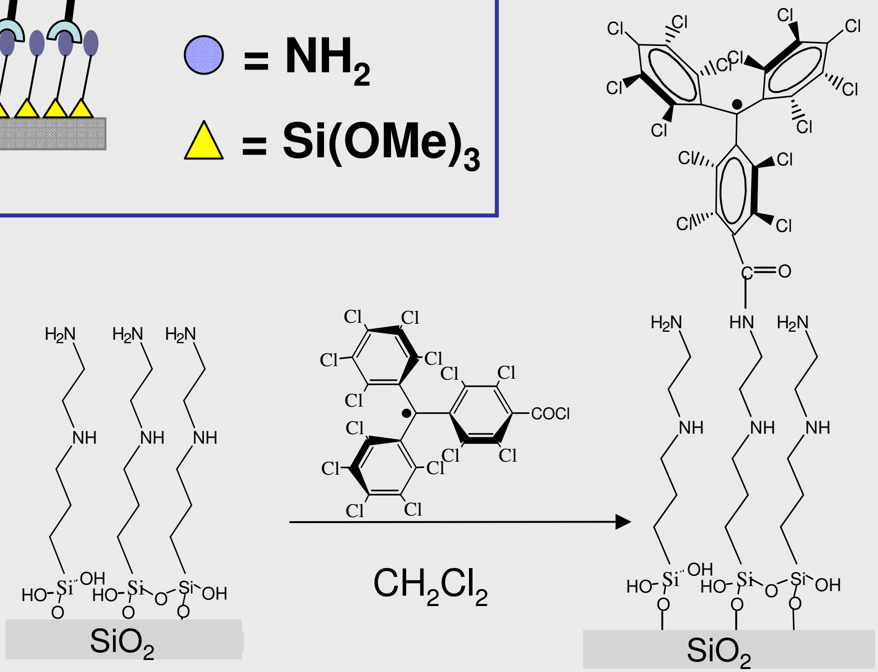
Two-steps



N. Crivillers, et al. *Angew. Chem. Int. Ed.* 2007, 46, 2215

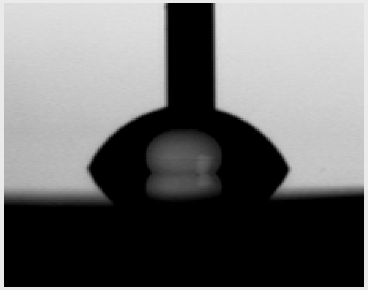
PTM SAM based on Covalent Bonding



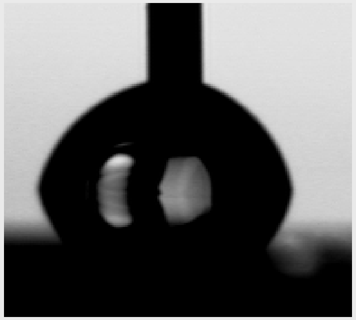


CONTACT ANGLE

NH$_2$-SAM ADVANCING



PTM-SAM ADVANCING

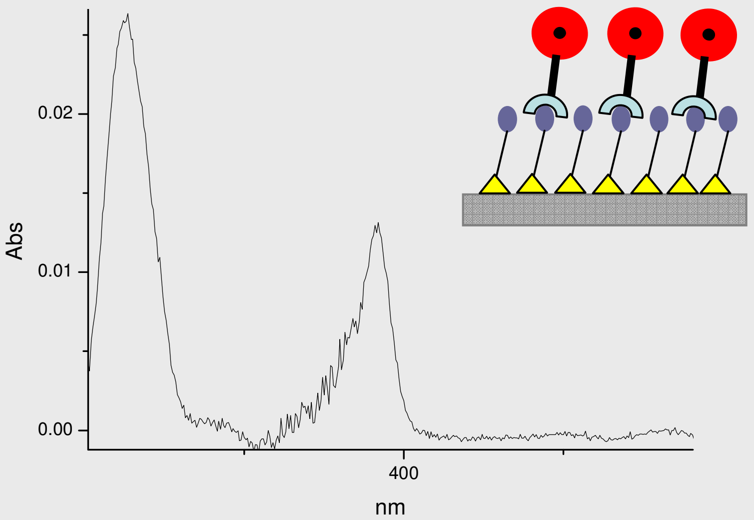


Contact angle, Ellypsometry, X-Ray photoelectron spectroscopy (XPS)

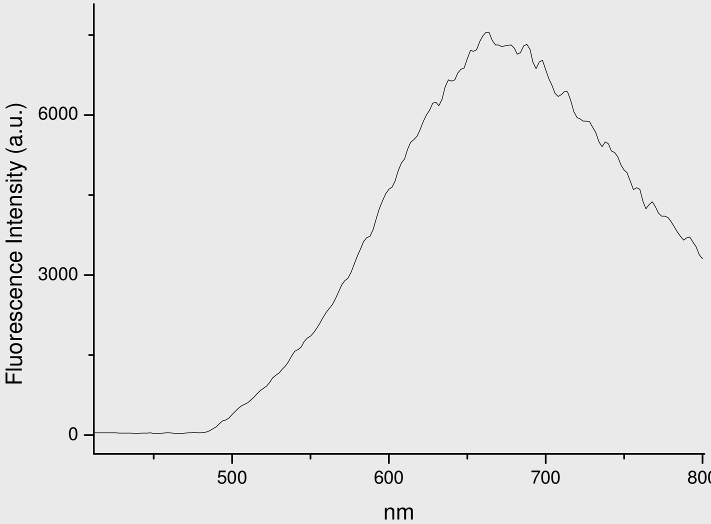
SAM	$\theta_{adv.}$ (°)	$\theta_{rec.}$ (°)	Ell.thick.(nm)	Cl/N (XPS)
NH_2	57.3±1.2	22.7±3.7	0.8	-
PTM	84.0±0.2	44.0±2.0	1.3	1.6 **1 PTM / 4.4 NH_2**

Optical Characterisation and EPR of the SAM (on quartz and glass)

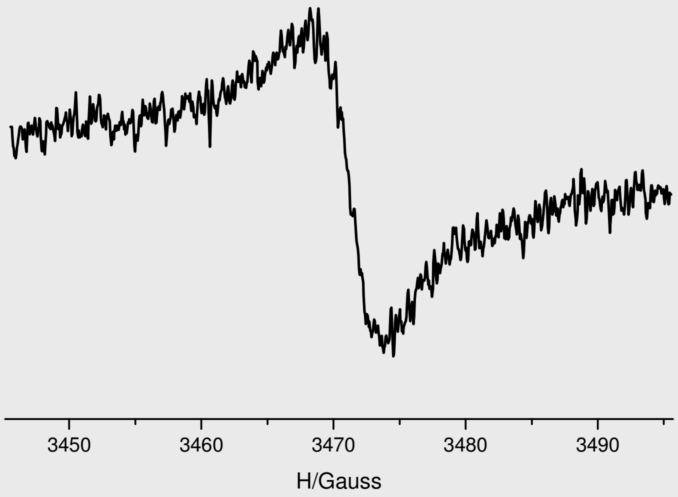
UV-vis spectra:



Fluorescence emission spectra:



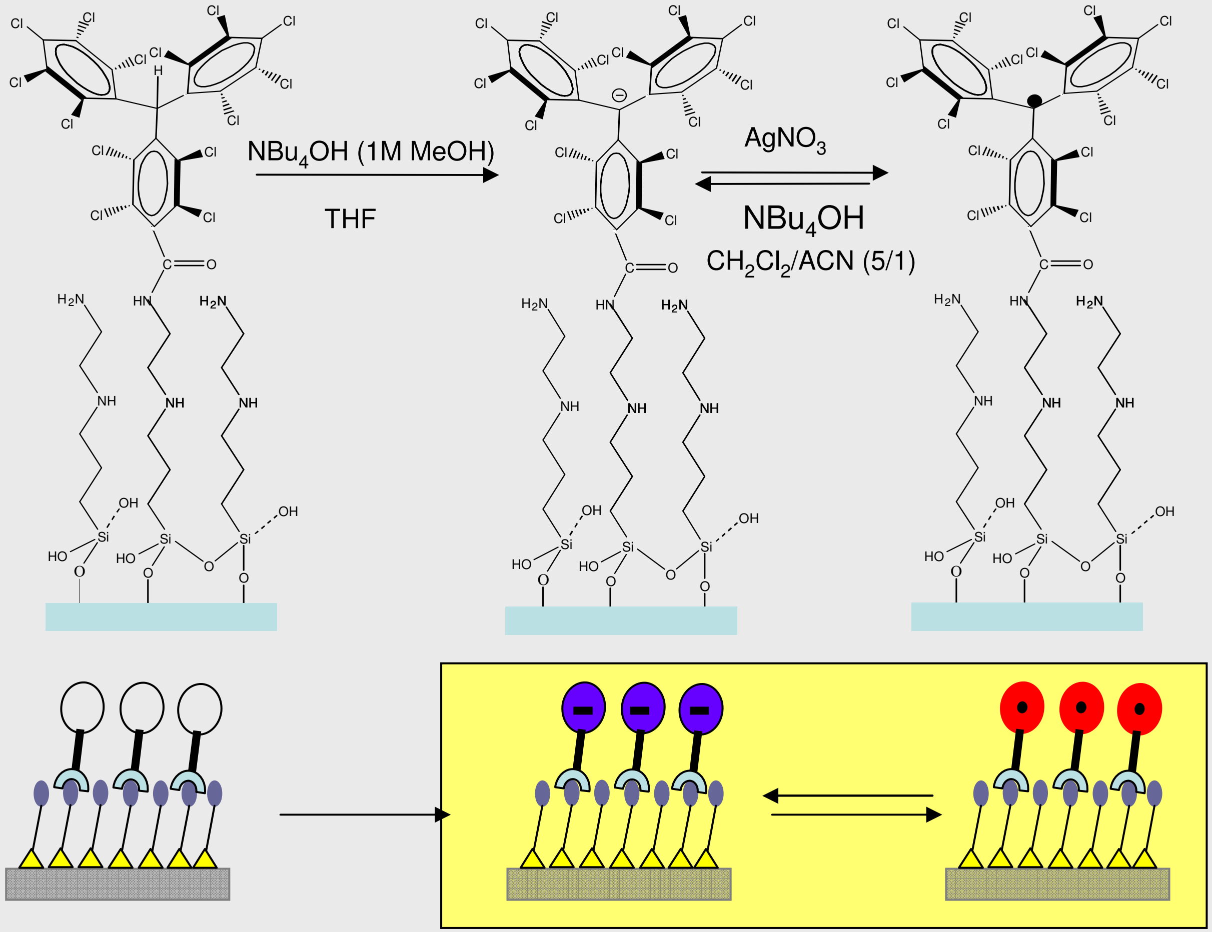
Electron paramagnetic resonance (EPR)



$g = 2.0024$

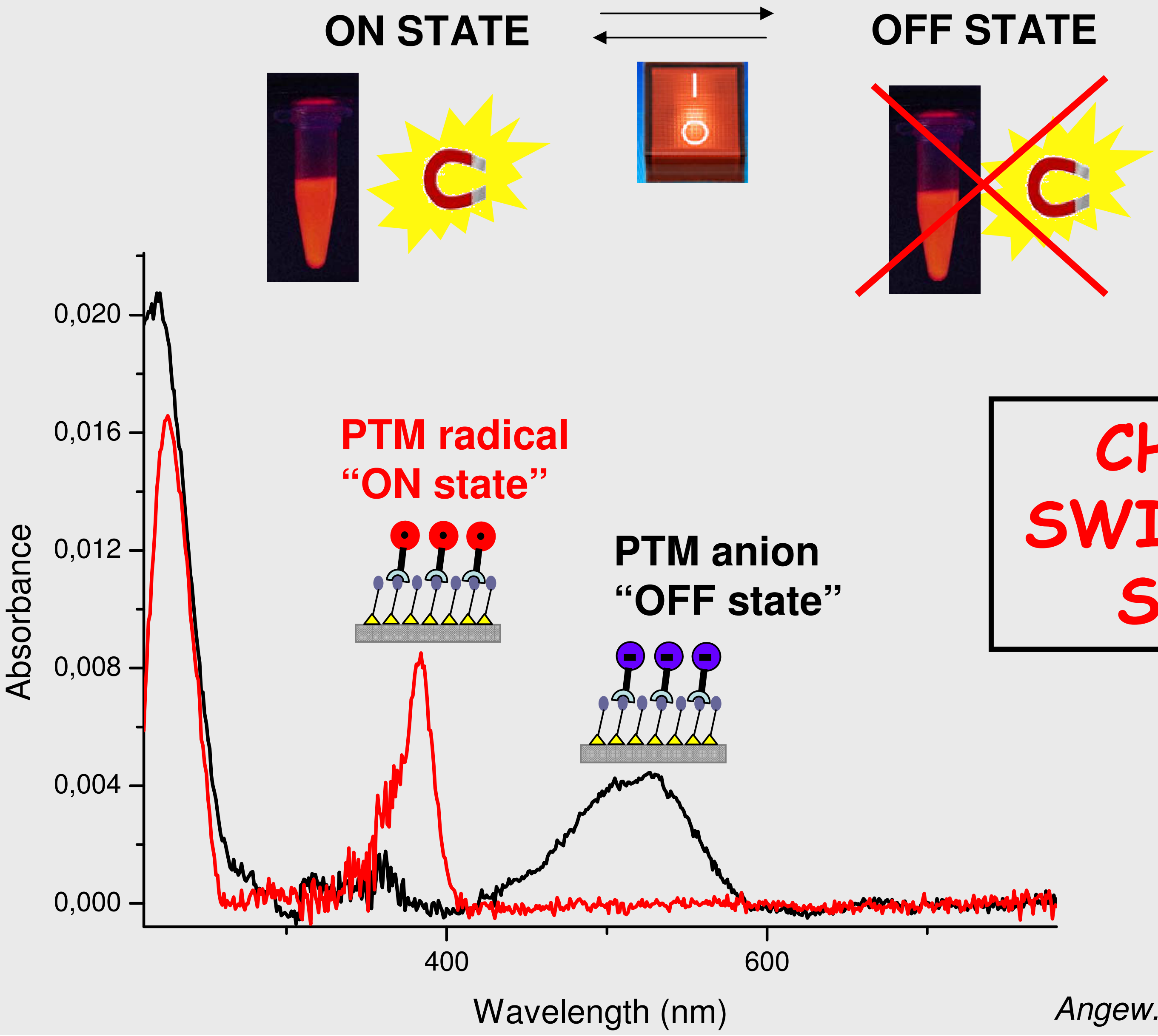
$\Delta H_{pp} \approx 5.2G$

PTM radical generated in situ on the surface



Possible to carry out chemical reactions on the PTM SAMs

Chemical Switch with Optical and Magnetic Response



CHEMICAL SWITCH ON A SURFACE

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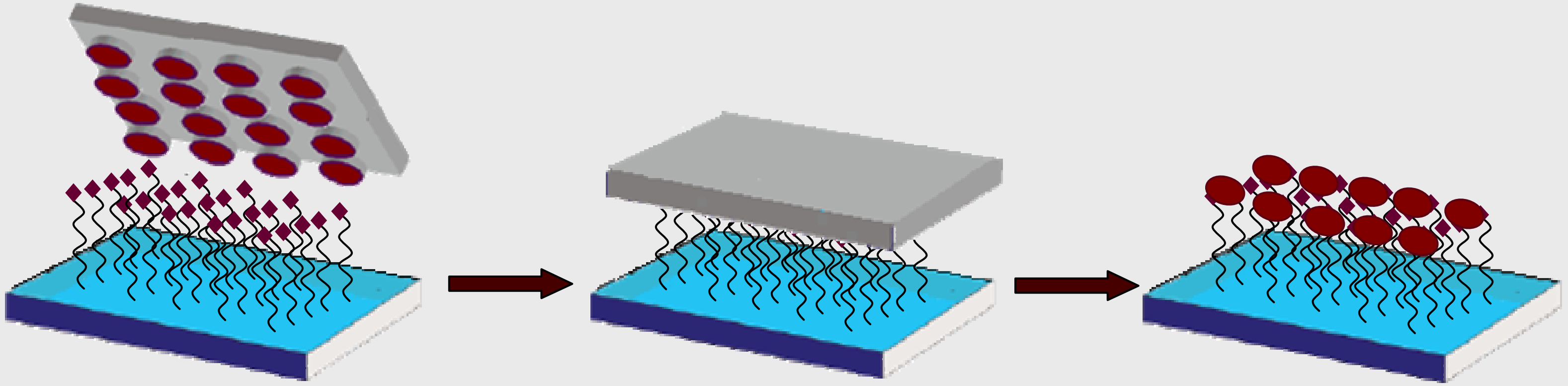
One step further...

Patterning of the surface: Fluorescent, magnetic and redox active patterned glass surface.

MICROCONTACT PRINTING:



1) Functionalization of a glass slide with the amino-terminated monolayer.

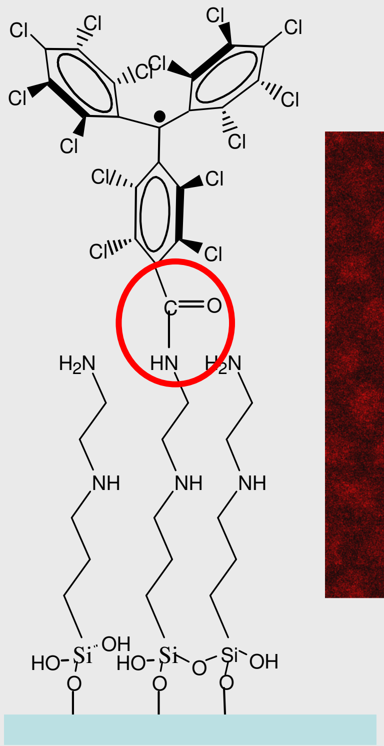
2) The stamp is dipped in the ink solution (PTM solution).

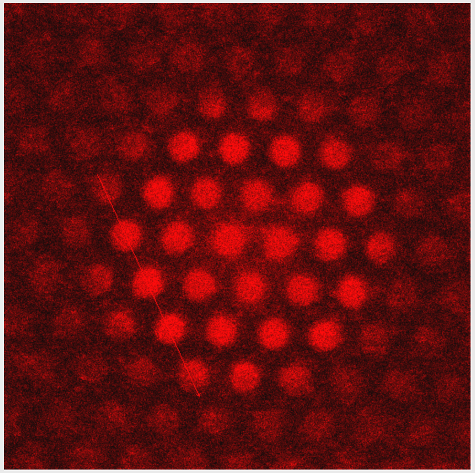
3) The stamp is brought in contact with the amino monolayer and kept for some minutes before careful removal.

Microcontact printing

Ink solution: 0.1 mM of PTM-COCl (radical) in DMSO

Confocal fluorescence microscopy image



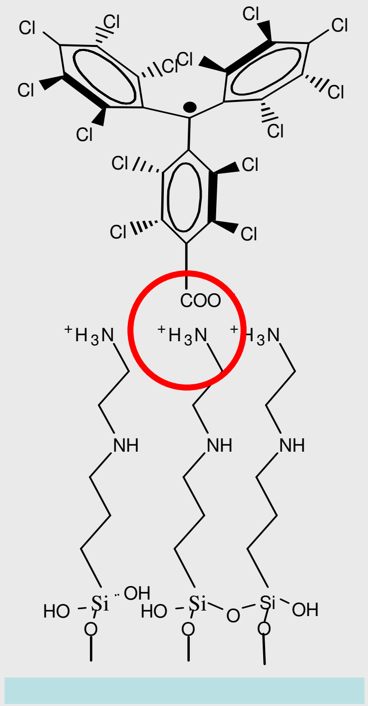


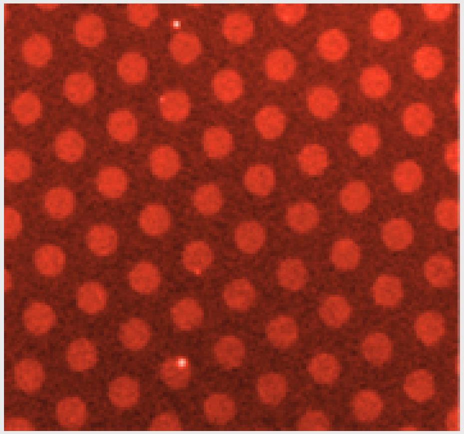
Spot size: 5µm

λexc = 488nm

Ink solution: 0.1mM of PTM-COOH (radical) in acetonitrile

Fluorescence microscopy image



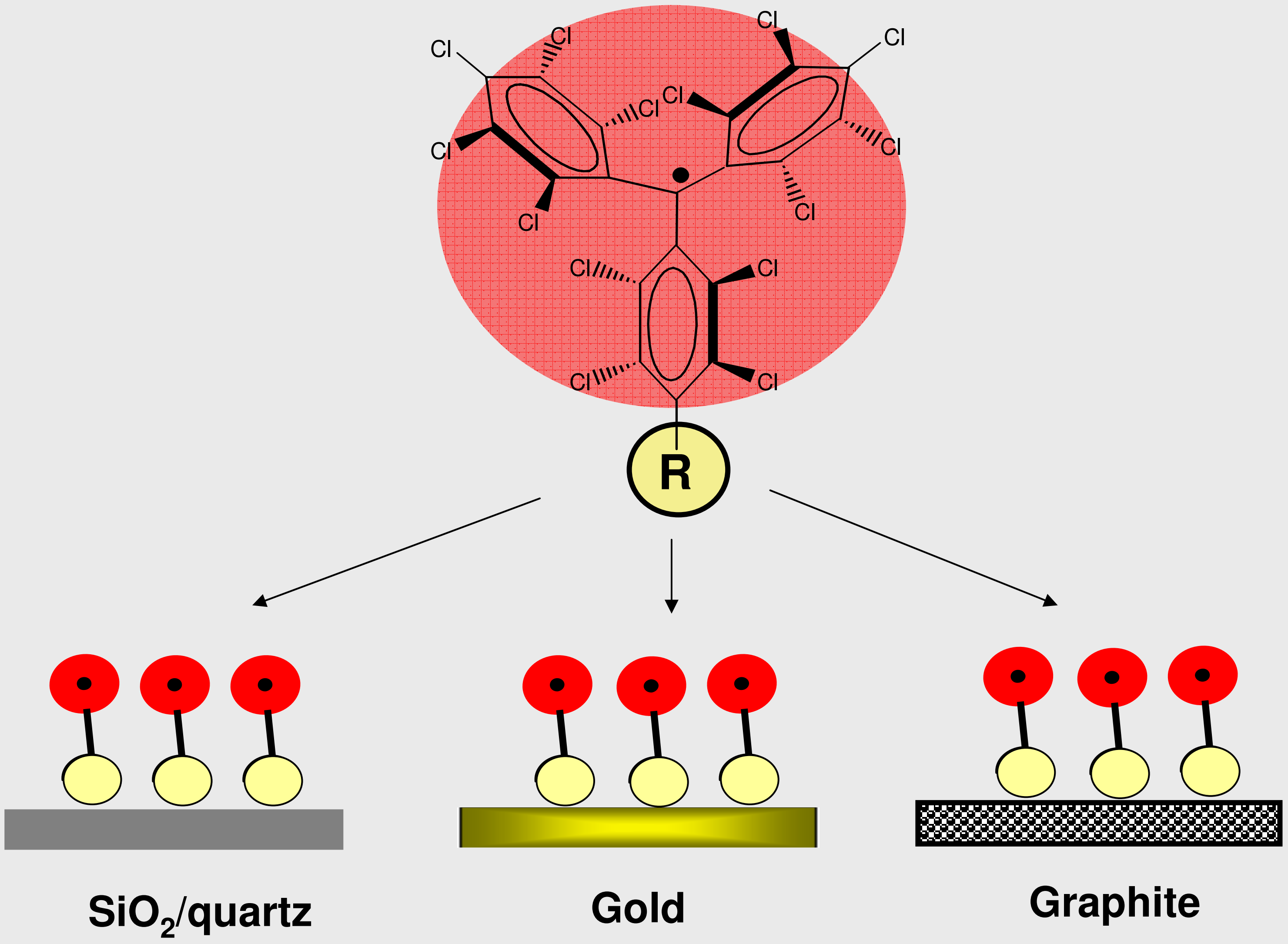


Spot size: 10µm

λexc = 340-370 nm

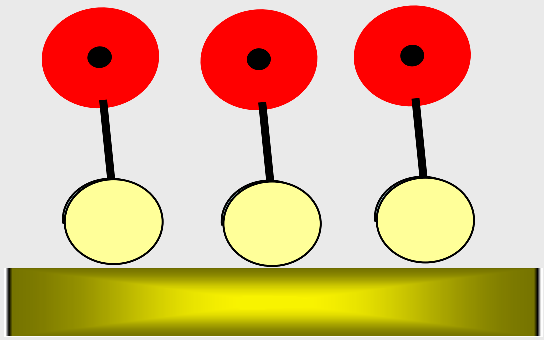
Both strategies (covalent and non-covalent) are good to obtain a patterned surface

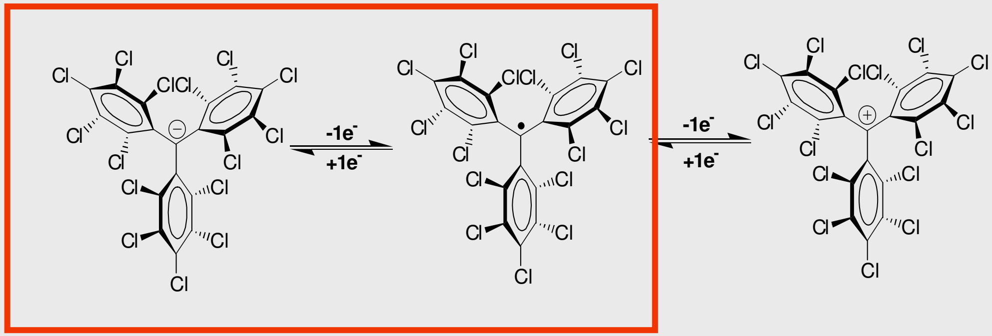
Functionaliztion of different surfaces

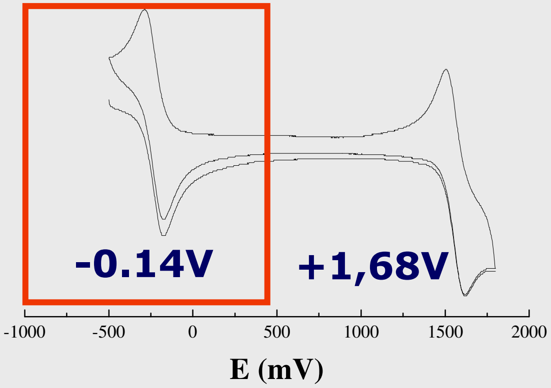


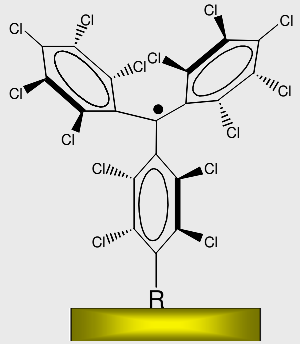
PREPARATION OF PTM SAMs ON GOLD

Electrochemical *in situ* characterization

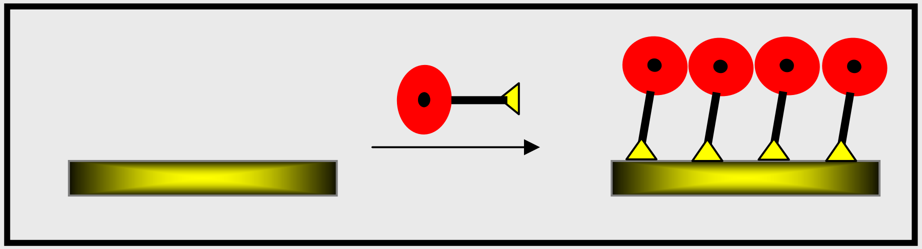


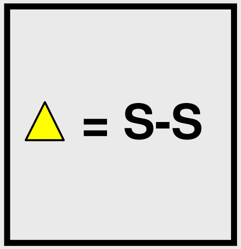




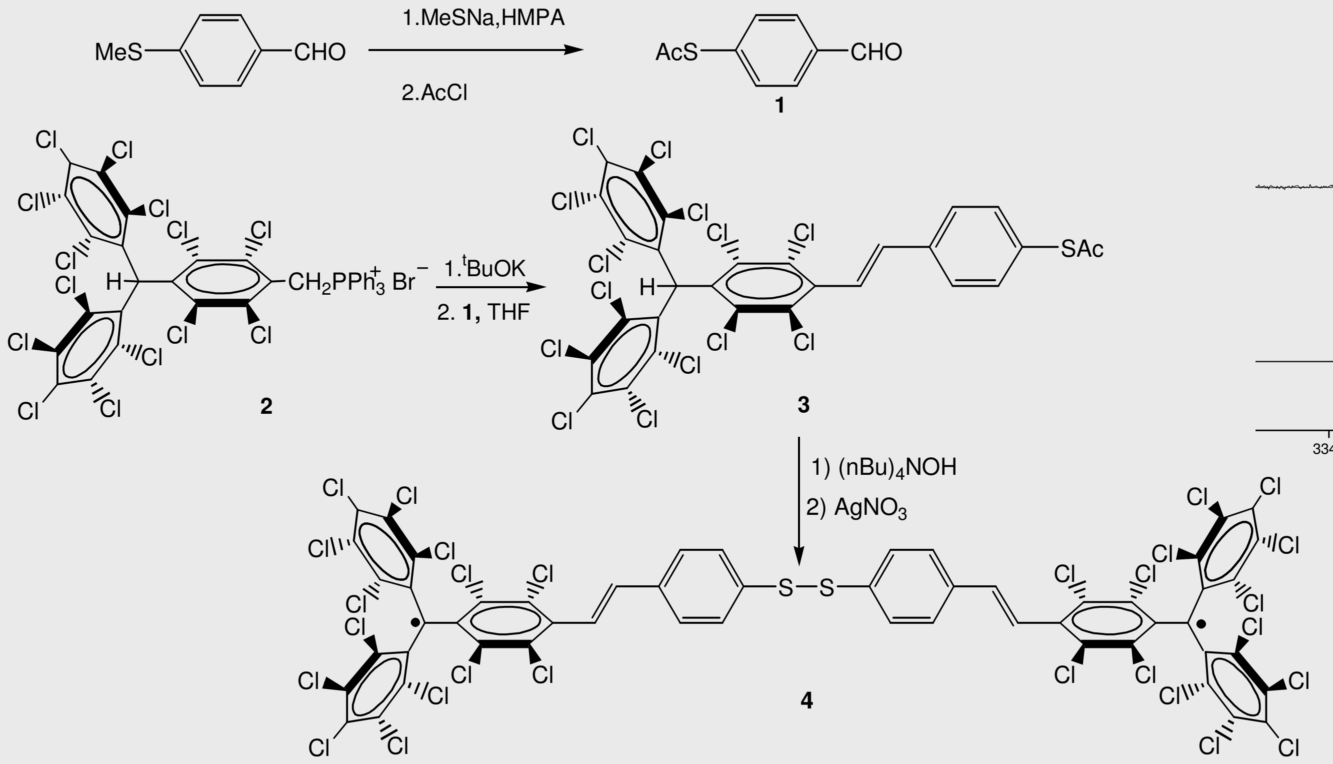


Direct Anchoring

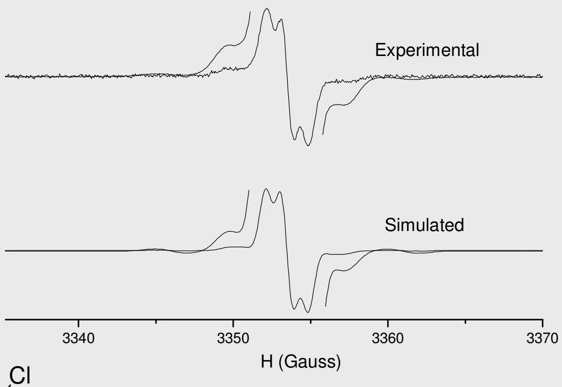




Synthesis:

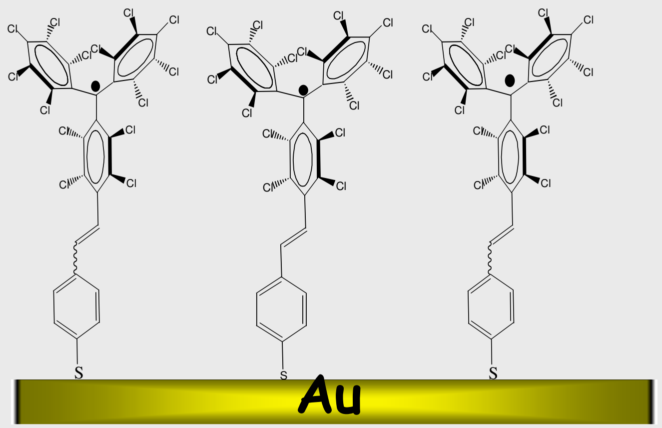


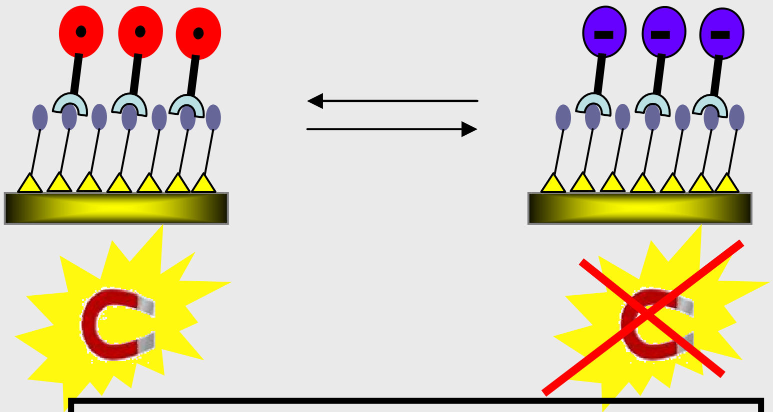
EPR



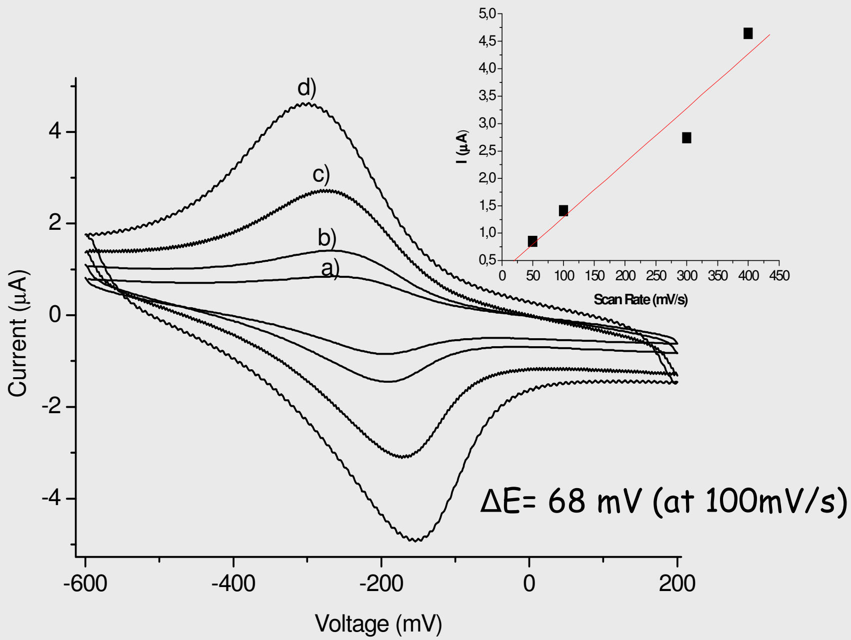
JACS, in press.

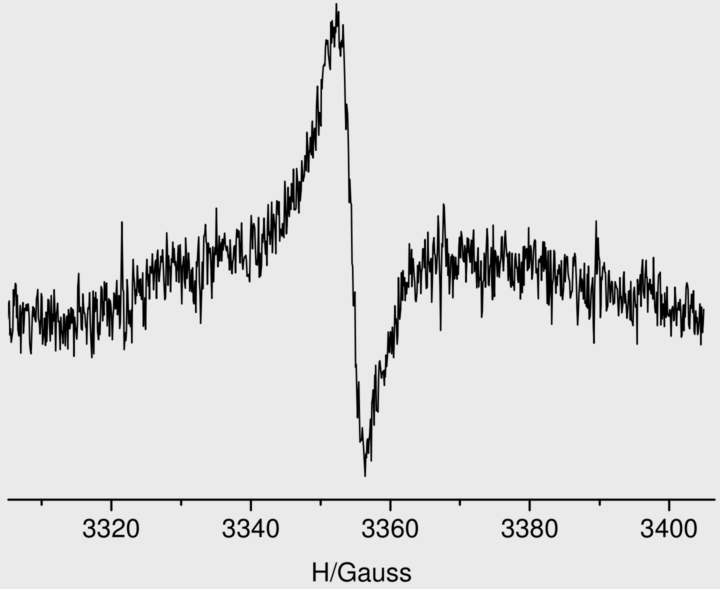
PREPARATION OF PTM SAMs ON GOLD. Direct anchoring





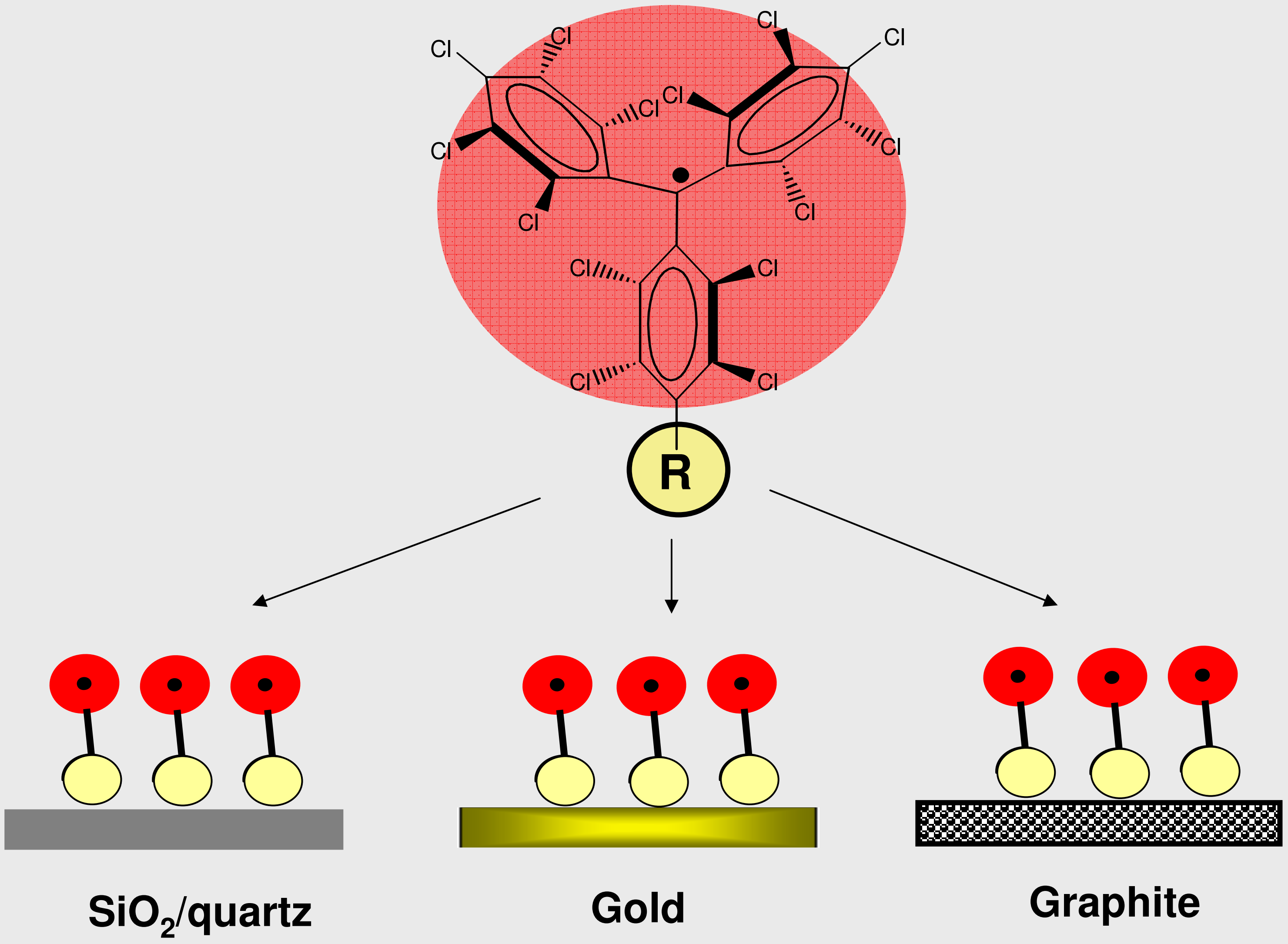
ELECTROCHEMICAL SWITCH ON SURFACE



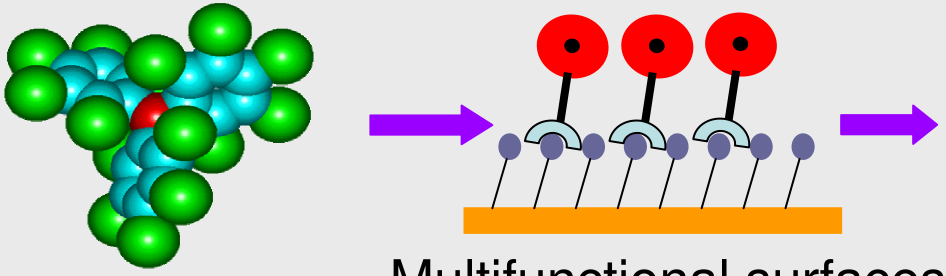


Crivillers et al. JACS, in press.

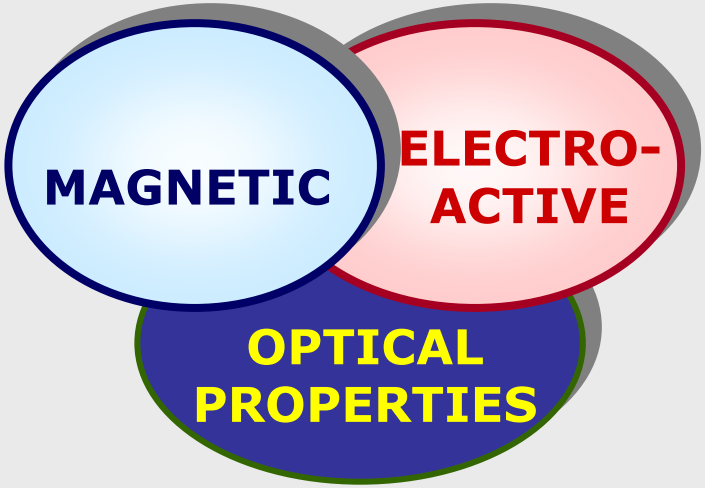
Functionaliztion of different surfaces

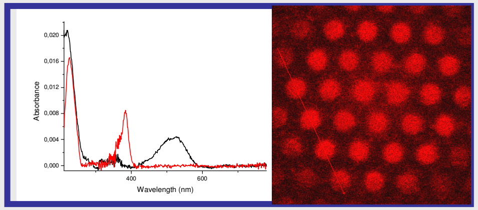


CONCLUSIONS

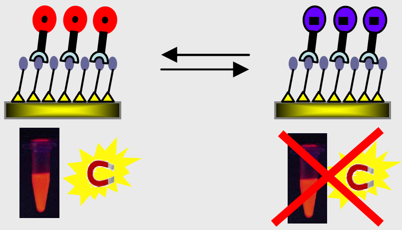


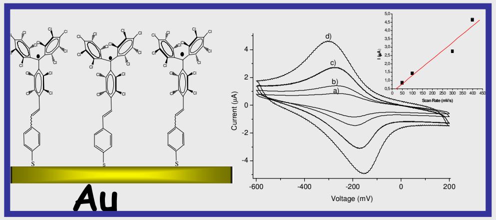
Multifunctional surfaces





Chemical switch





Electrochemical switch

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