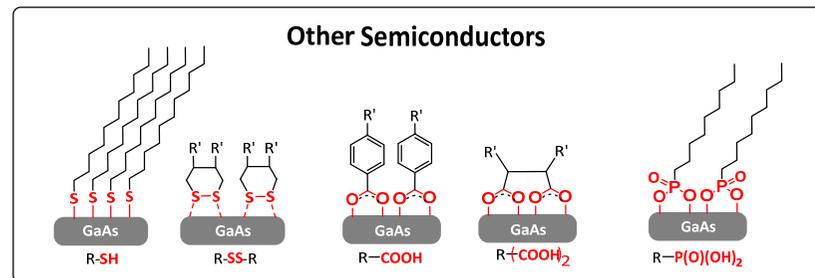
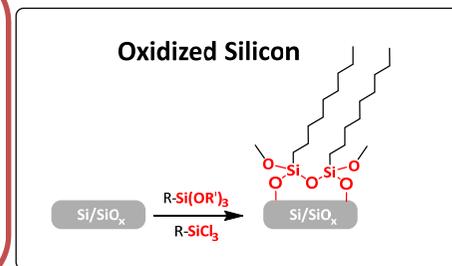
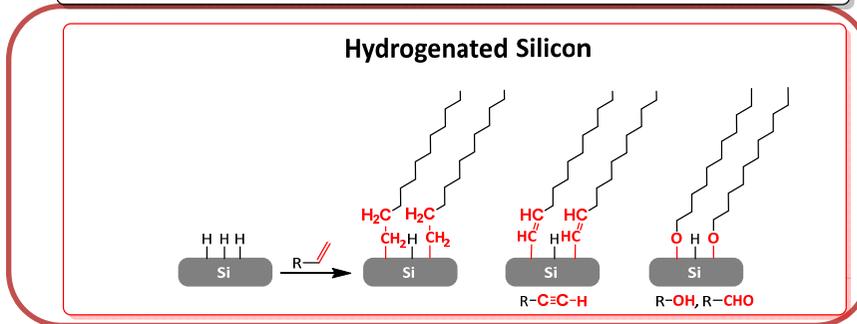
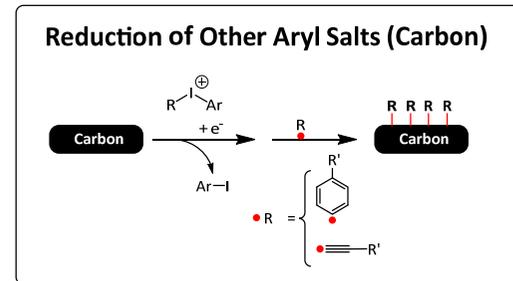
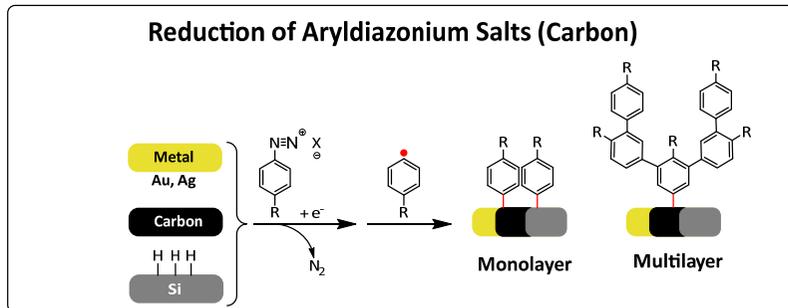
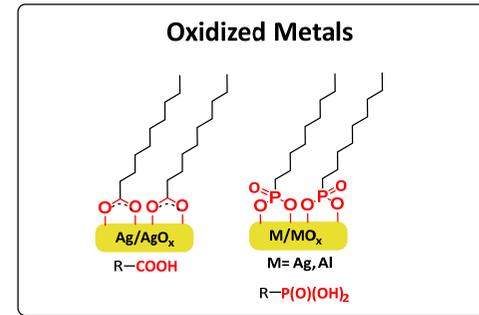
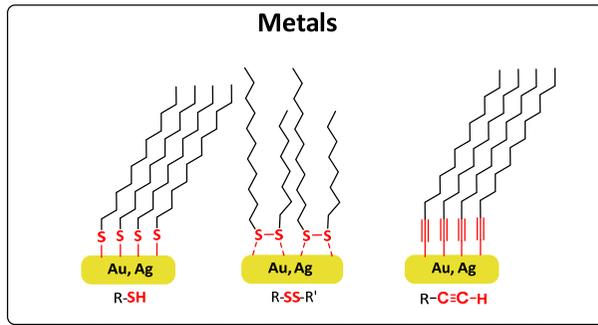
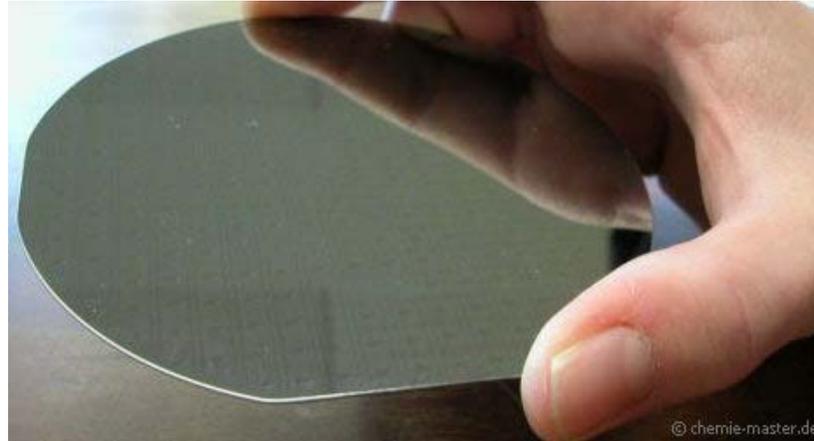




# Surface Modification



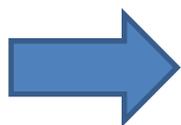
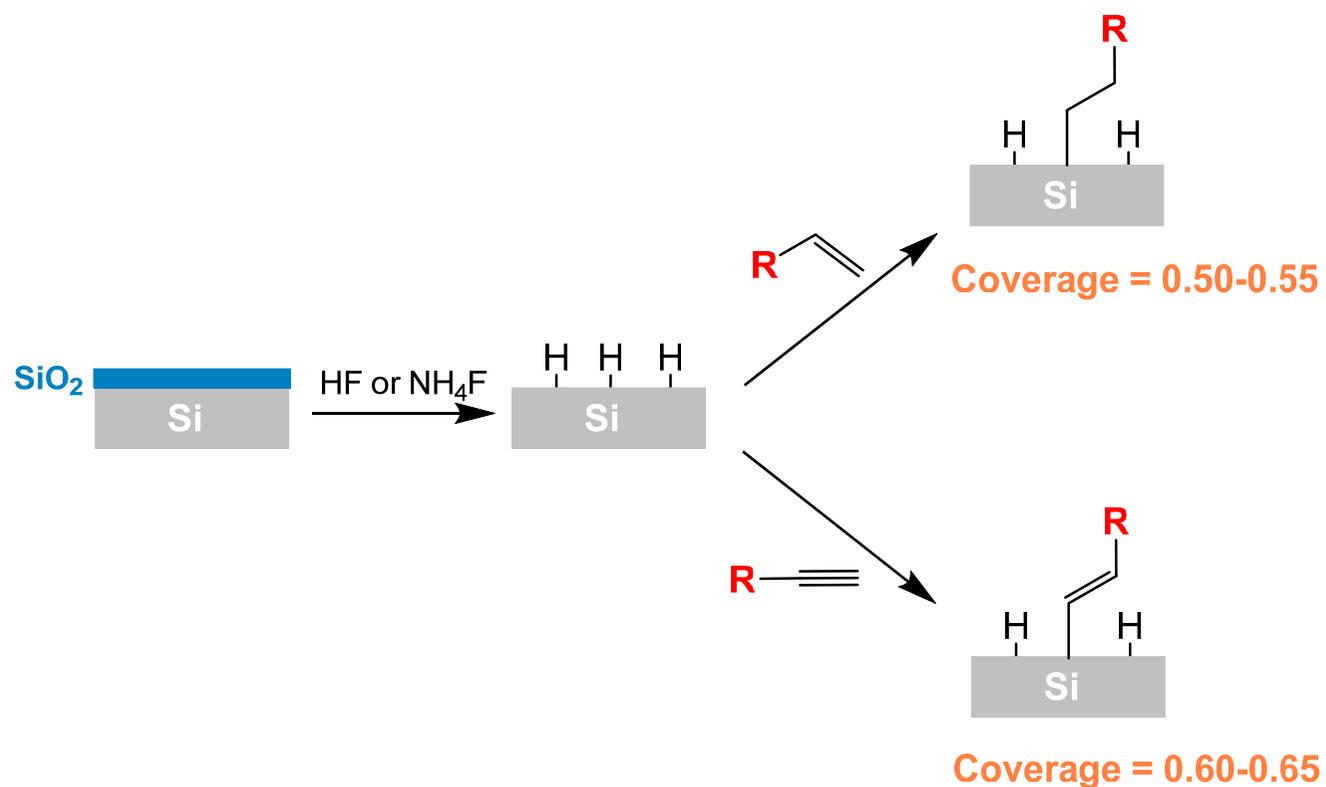
# Silicon as Immobilization Substrate



- **High purity substrate and well-defined structure**
- **Unlike metals (e.g. gold), the electronic properties of silicon can be tuned** (doping type, dopant density, photogenerated electron-hole pairs)
- **Technological processes used for the micro- and nanopatterning of silicon are numerous and mature**
- **Controlled and robust hybrid molecule/silicon assemblies**

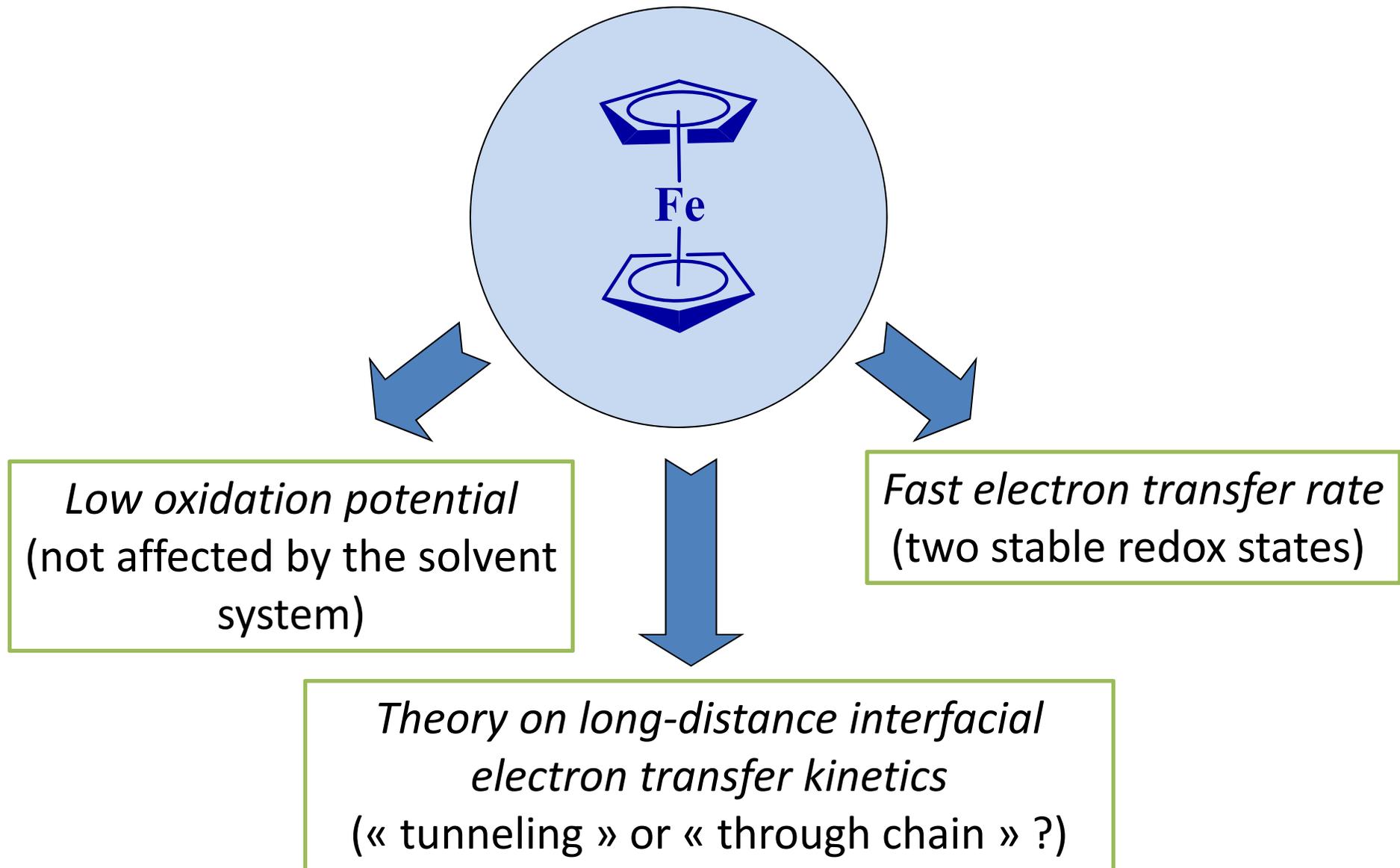
# Covalent Grafting onto Si-H Surfaces

## Hydrosilylation reaction with Si-H



**Highly ordered, densely packed monolayers**  
Si-C interfacial bonds, not electrically defective

# Ferrocenyl Monolayers

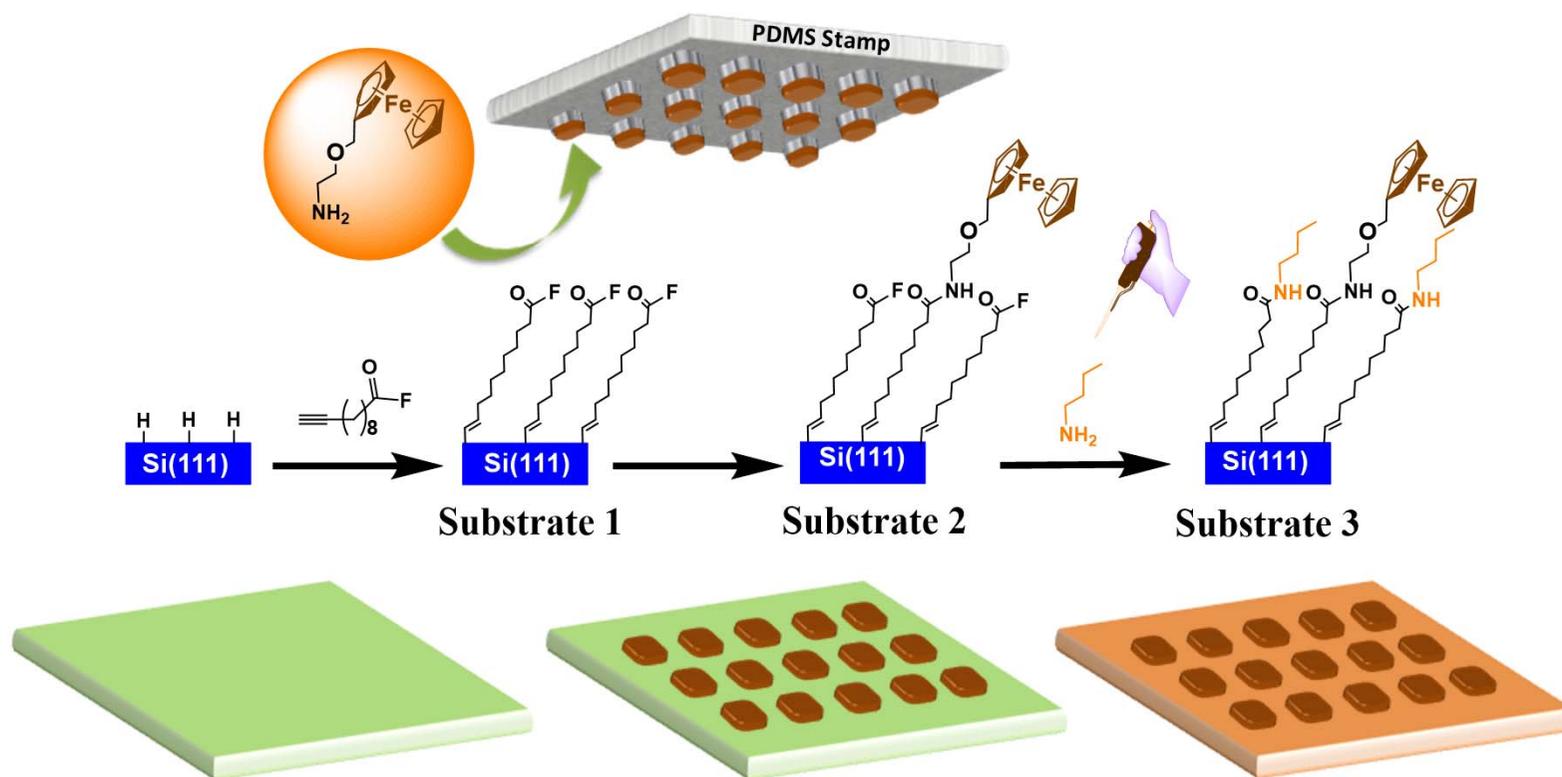


# Ferrocenyl Monolayers

## Light-Activated Electrochemical Addressing of Grafted Redox Centers

n-type Si  $\longrightarrow$  Photoanode

For oxidation processes, insulator in the dark and quasi-conductor upon illumination



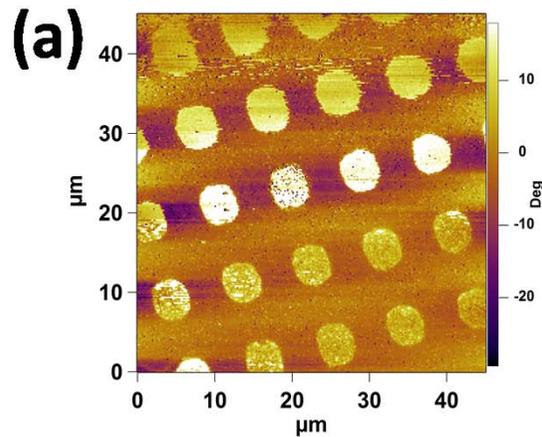
Collab. H. Zuilhof, Wageningen Univ., The Netherlands

# Ferrocenyl Monolayers

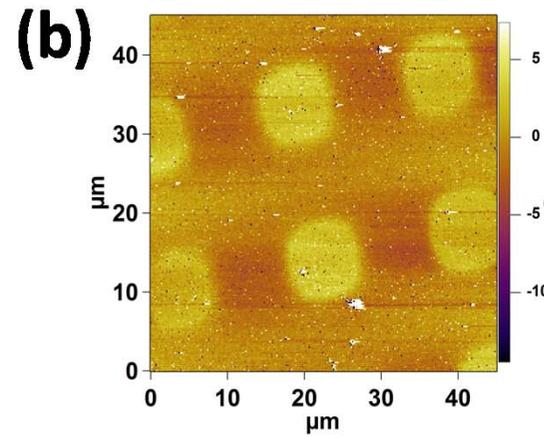
## Light-Activated Electrochemical Addressing

Collab. H. Zuilhof, Wageningen Univ., The Netherlands

AFM phase images

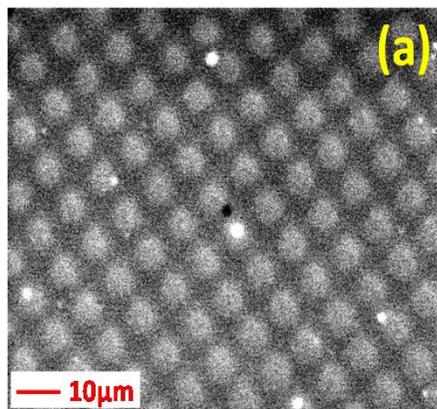


$5 \times 5 \mu\text{m}^2$

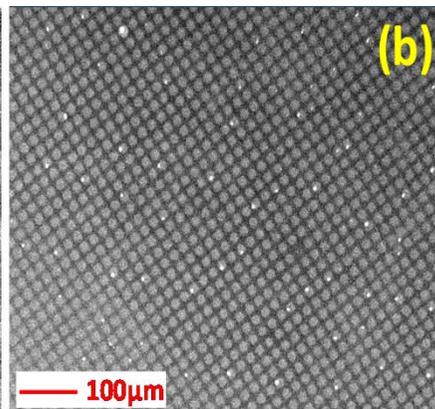


$10 \times 10 \mu\text{m}^2$

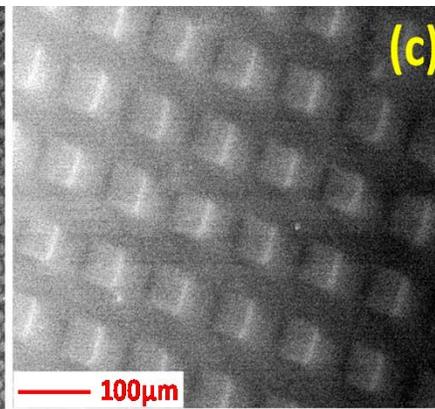
SEM images



$5 \times 5 \mu\text{m}^2$



$10 \times 10 \mu\text{m}^2$

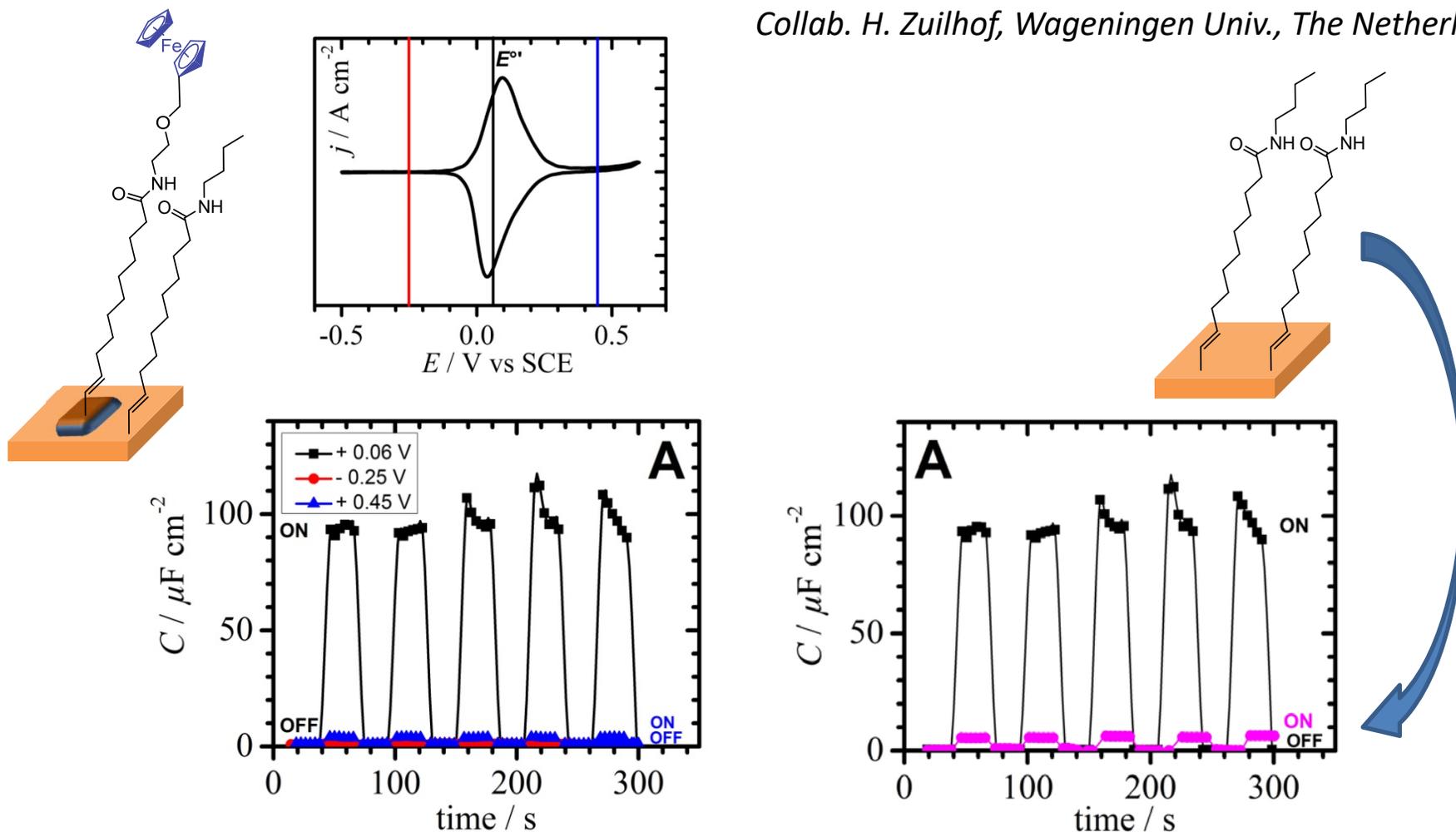


$20 \times 20 \mu\text{m}^2$

# Ferrocenyl Monolayers

## Light-Activated Electrochemical Addressing

Collab. H. Zuilhof, Wageningen Univ., The Netherlands



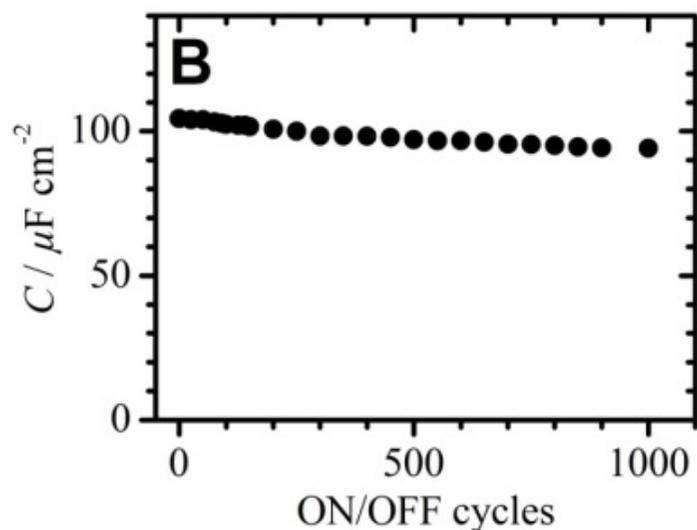
*C* - time profiles measured at 50 Hz for different applied potentials during several dark (OFF state)/illumination (ON state) switching cycles.

# Ferrocenyl Monolayers

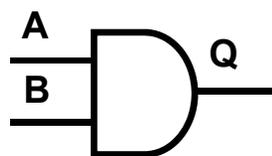
## Light-Activated Electrochemical Addressing

Collab. H. Zuilhof, Wageningen Univ., The Netherlands

### Stability of the photocapacitance



Truth table for  
AND logic gate



Input A (Illum)	Input B ( $E_{\text{app}}$ )	Output Q (Capa)
0	0	0
0	1	0
1	0	0
1	1	1

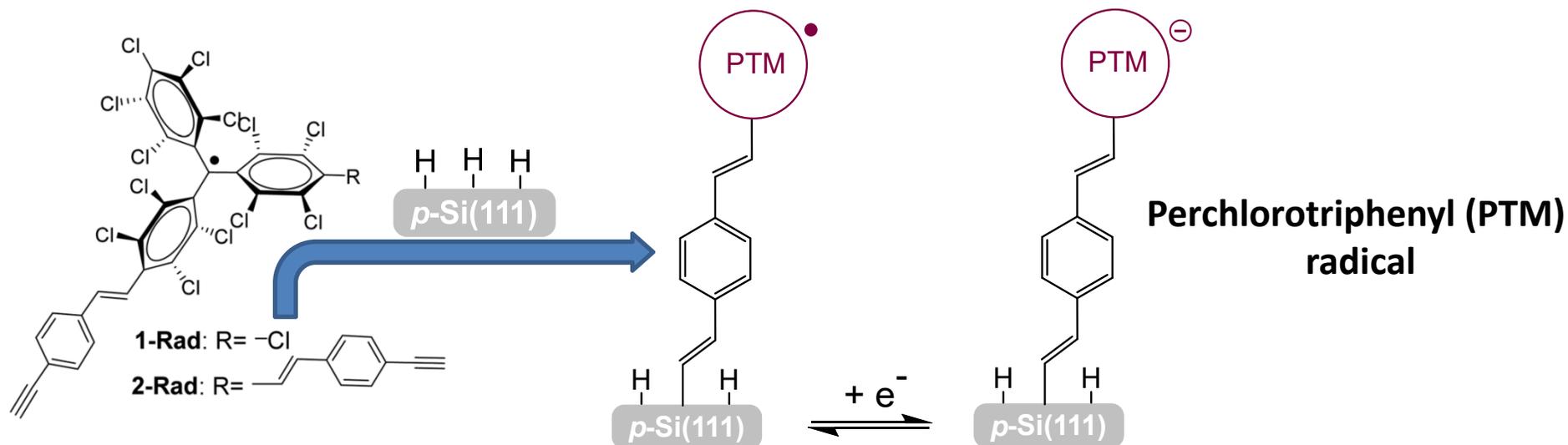
0 : dark    0 : -0.25 V    0 :  $<2 \mu\text{F/cm}^2$   
1 : illum    1 : 0.06 V    1 :  $>80 \mu\text{F/cm}^2$



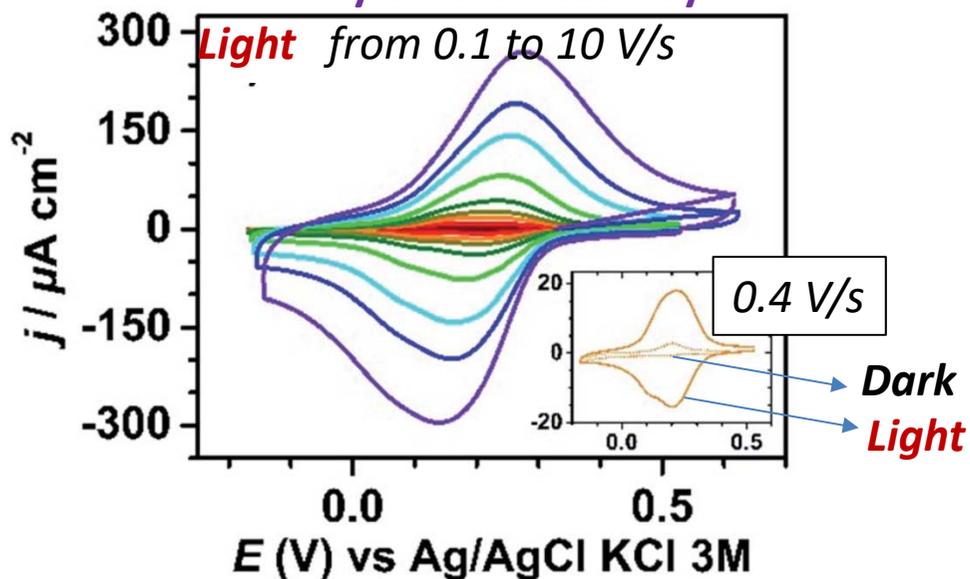
All solid-state molecular AND gate

# Organic Radical Monolayers

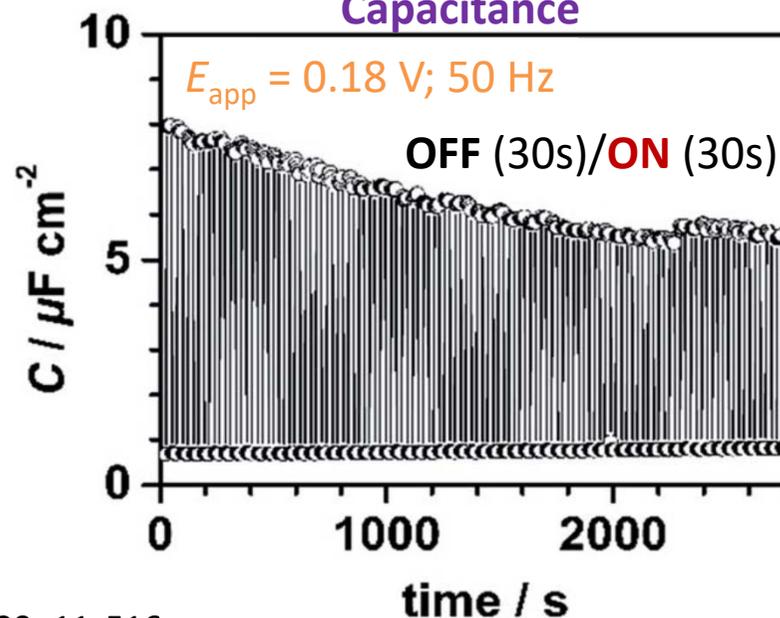
Collab. N. Crivillers and C. Rovira, Institut de Ciència de Materials de Barcelona, Spain



Cyclic voltammetry

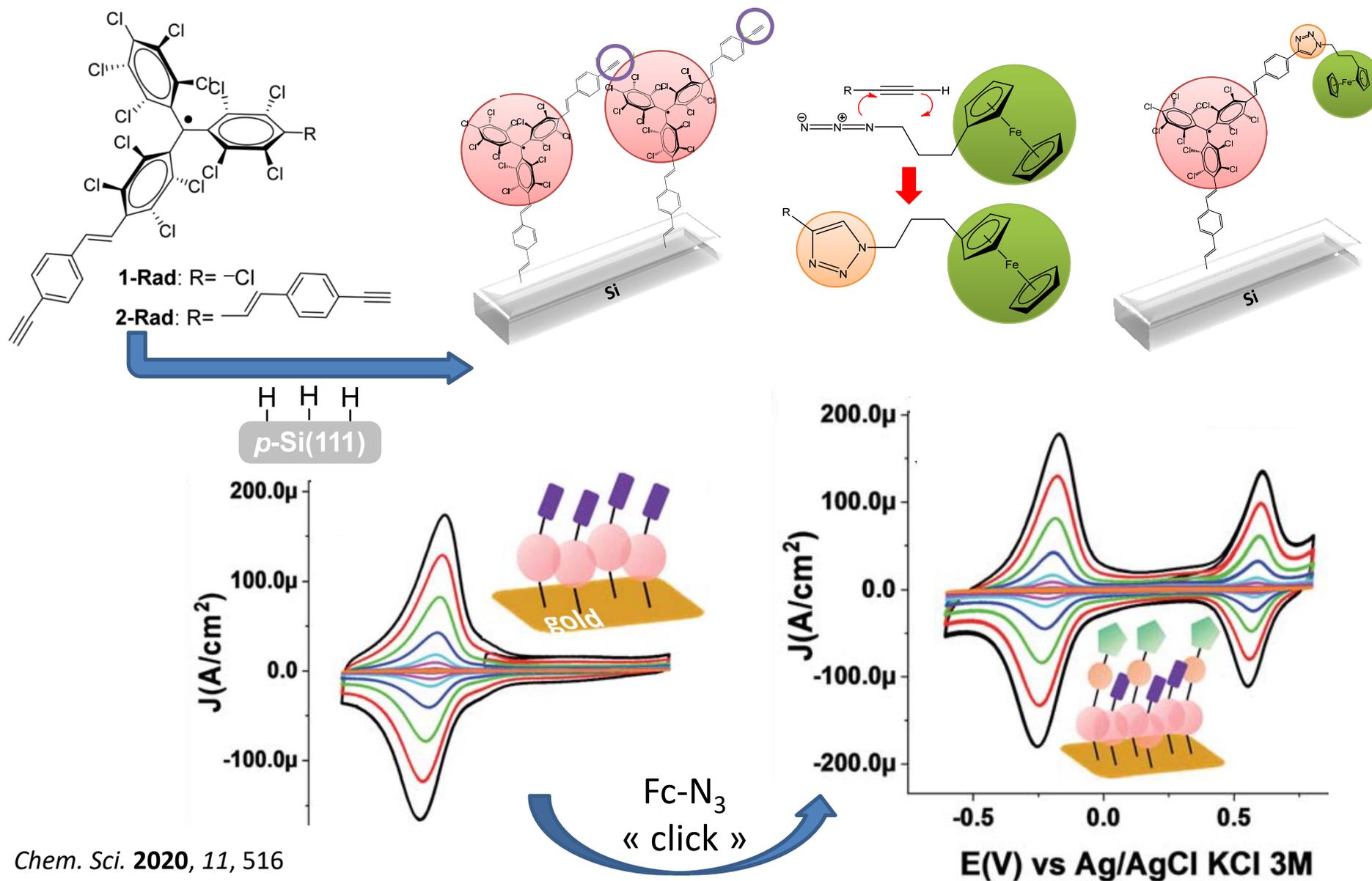


Capacitance



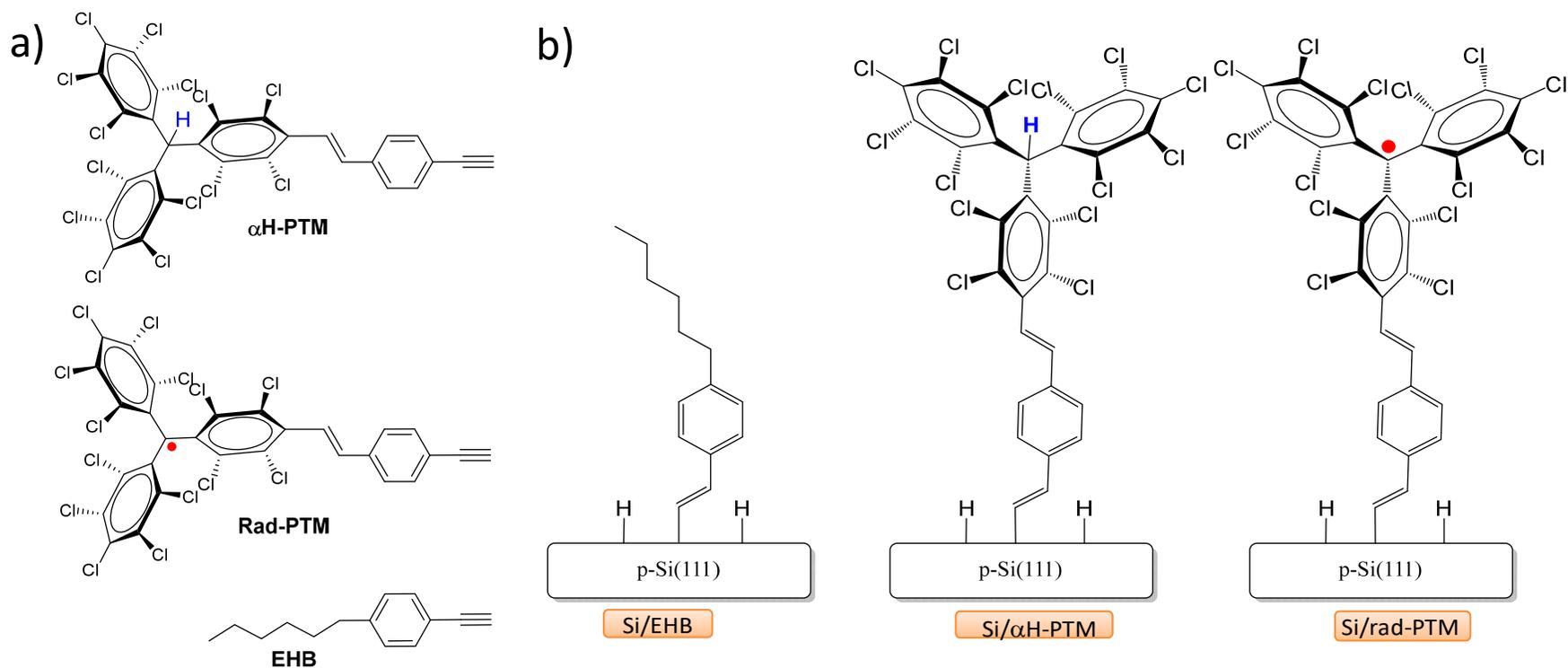
# Biredox Monolayers

Collab. N. Crivillers and C. Rovira, Institut de Ciència de Materials de Barcelona, Spain



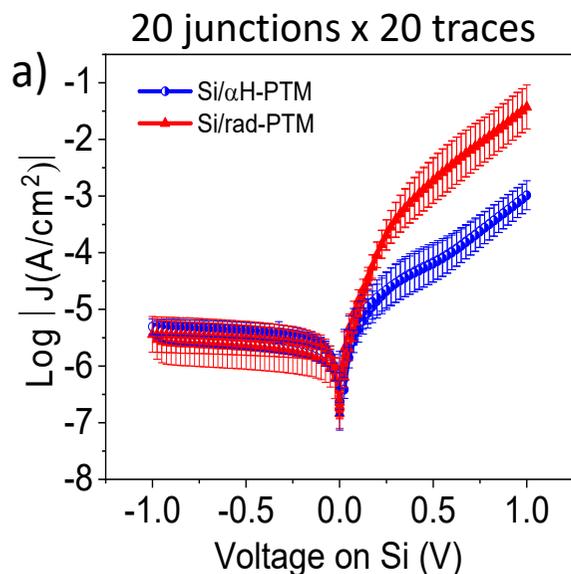
# Metal-Molecule-Semiconductor Junctions Incorporating Stable Organic Radical

Collab. N. Crivillers and C. Rovira, Institut de Ciencia de Materials de Barcelona, Spain



# Charge Transport Through Junctions

Collab. N. Crivillers and C. Rovira, Institut de Ciència de Materials de Barcelona, Spain



$$\phi_{\text{eff}}(\text{Si/rad-PTM}) = 0.74 \pm 0.01 \text{ eV}$$

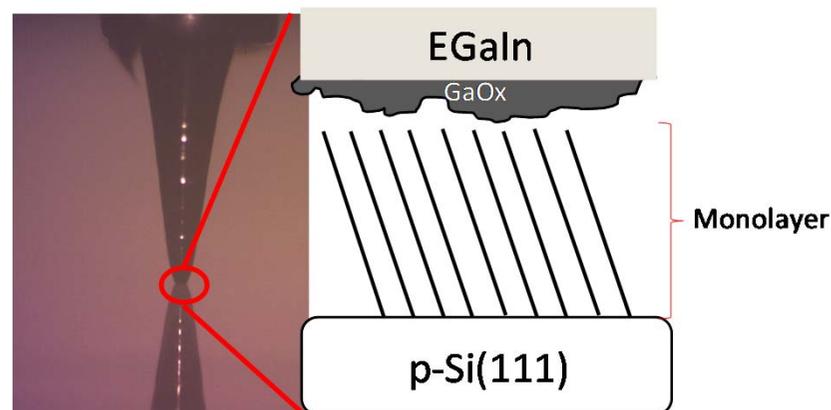
$$n = 1.3$$

$$d_{\text{monolayer}} = 21.8 \pm 1.0 \text{ \AA}$$

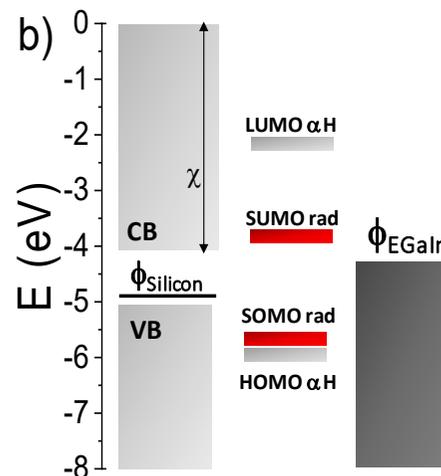
$$\phi_{\text{eff}}(\text{Si}/\alpha\text{H-PTM}) = 0.74 \pm 0.01 \text{ eV}$$

$$n = 1.4$$

$$d_{\text{monolayer}} = 21.0 \pm 1.0 \text{ \AA}$$



Nijhuis, Whitesides and co-workers,  
*J. Am. Chem. Soc.* **2009**, *131*, 17814

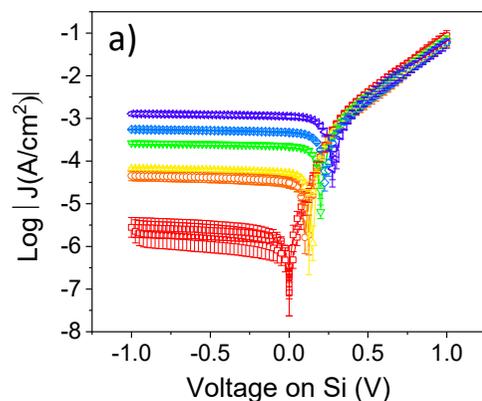


**Presence of the SOMO-SUMO molecular orbitals for the radical-based junction impacts on the device performance**

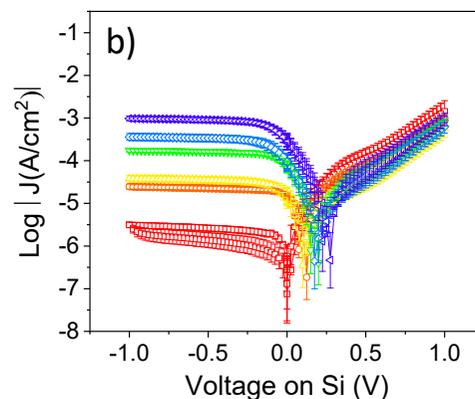
# Photoresponse behavior of the junctions

Collab. N. Crivillers and C. Rovira, Institut de Ciencia de Materials de Barcelona, Spain

Si/rad-PTM



Si/ $\alpha$ H-PTM



4200  $\mu\text{W}/\text{cm}^2$

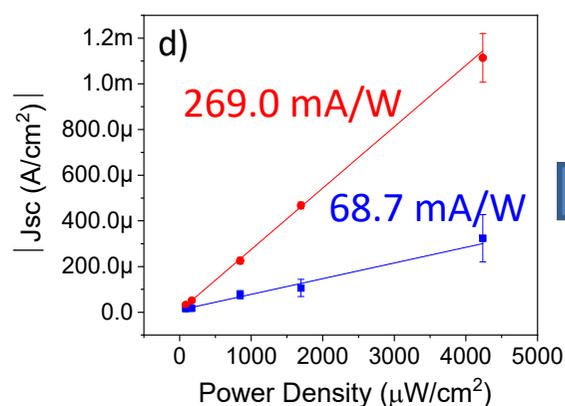
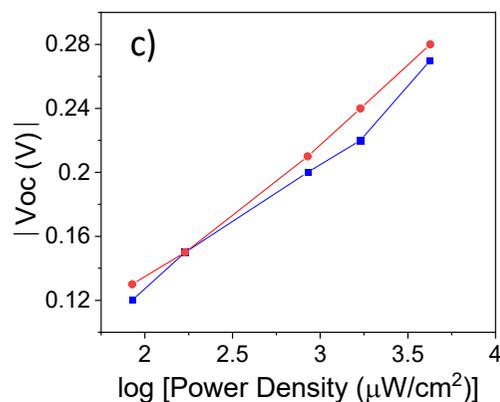
0  $\mu\text{W}/\text{cm}^2$

Red laser  $\lambda = 635 \text{ nm}$  (1.95 eV)

$\approx$  PTM radical SUMO-SOMO bandgap

•  $>$  Bandgap of Si

• no radical decomposition

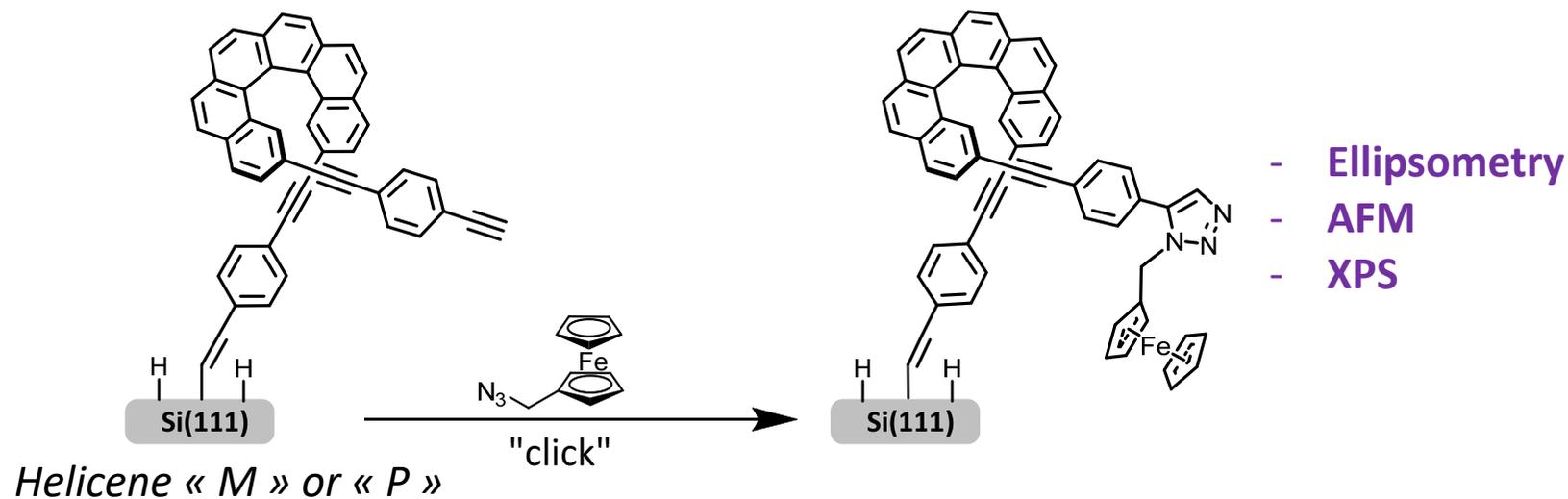


Improvement of the photodiode properties by the incorporation of low-band gap molecules in the visible spectrum at the interface

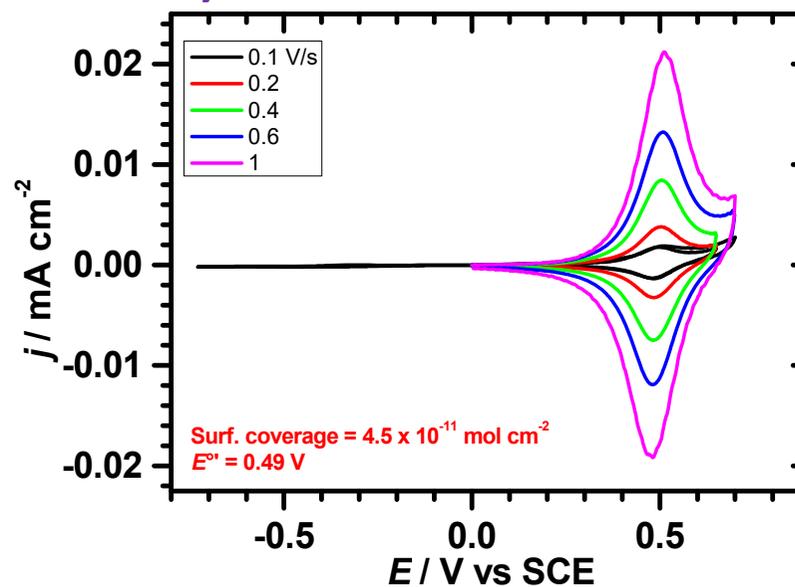
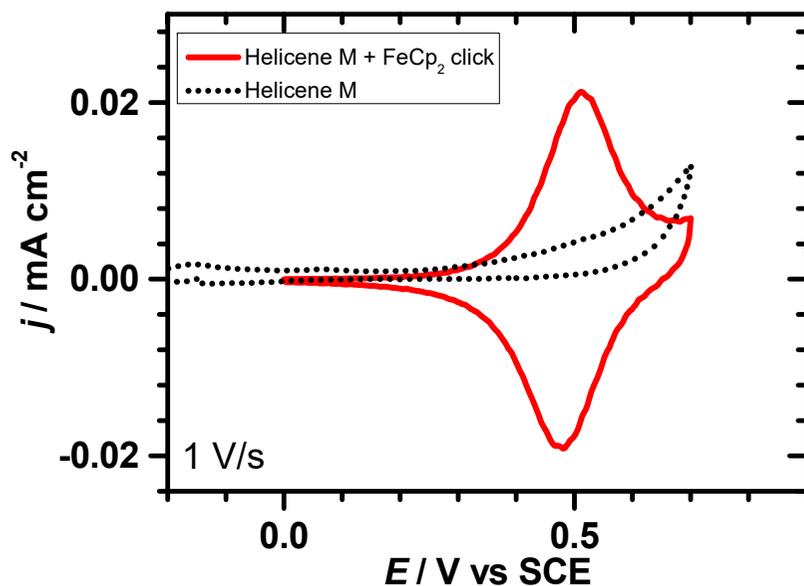
Linear fits as expected for typical photodiode characteristics

# Chiral Molecule-Modified Si-H Surfaces for Spintronics

Collab. J. Crassous, Institut des Sciences Chimiques de Rennes (ISCR), OMC



## Cyclic voltammetry



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## Institut de Ciència de Materials de Barcelona

F. Bejarano, J. Alejandro De Sousa, M. Mas-Torrent, N. Crivillers, C. Rovira

(PTM monolayers)

