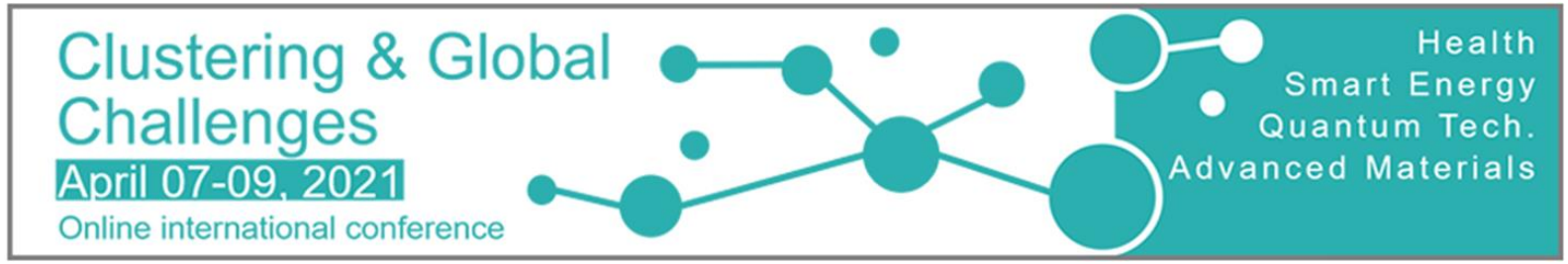

Reversible Switching of the Au (111) Work Function by Near Infrared Irradiation with a Bistable SAM based on a Radical Donor-Acceptor Dyad

Nerea González Pato

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Spain

07/04/2021

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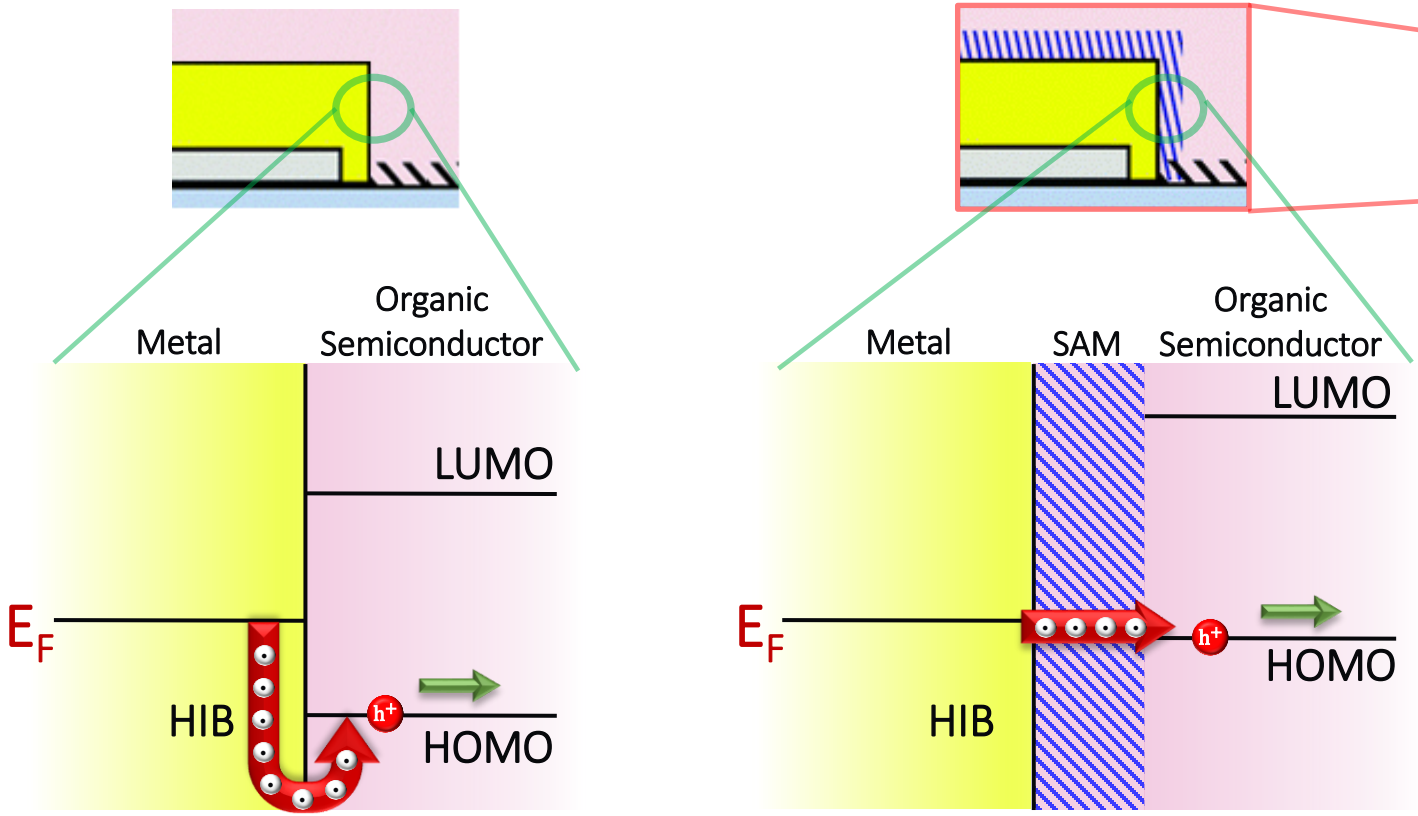
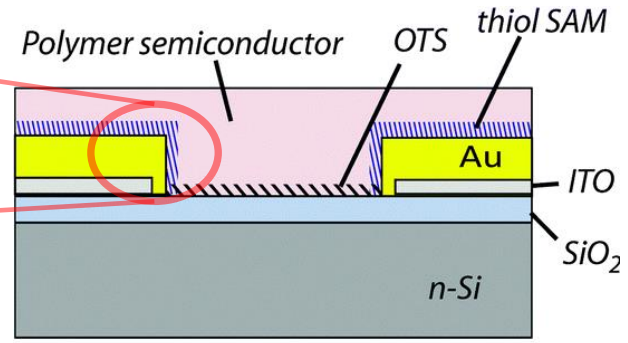
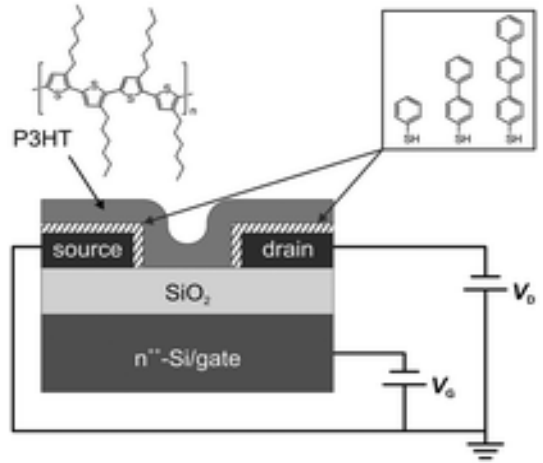
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Molecular electronics: charge injection barrier





Fenwick, O. *et al. J. Mater. Chem. C* **3**, 3007–3015 (2015).



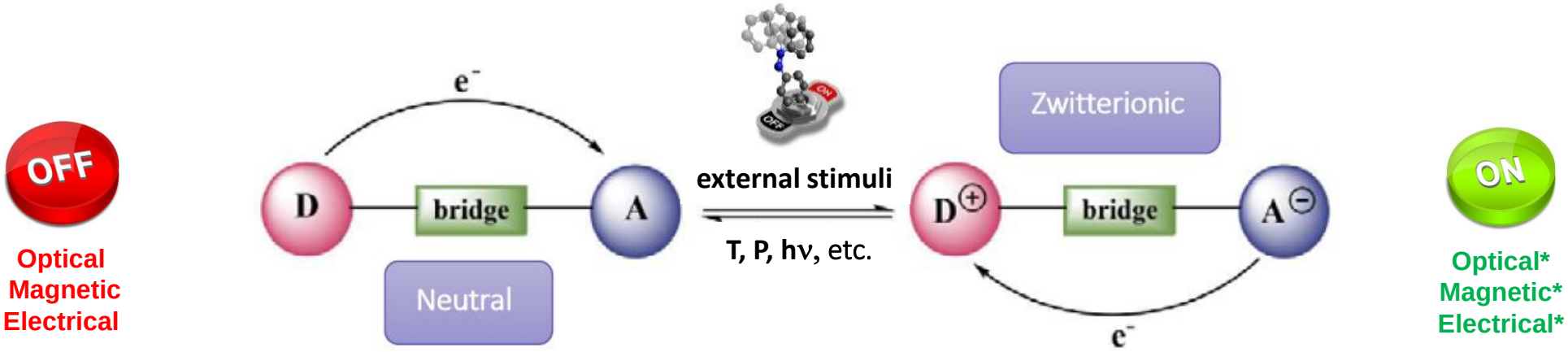
Orgiu, E., Crivillers, N., Rotzler, J., Mayor, M. & Samorì, P. *J. Mater. Chem.* **20**, 10798–10800 (2010).

Charge injection barrier in OFETs can be overcome by tuning **work function** of metals, by the presence of an interfacial **dipole** created by organic molecules arranged on the metal surface as **Self Assembled Monolayers** (SAMs).

Molecular electronics: charge injection barrier

Molecular Switch

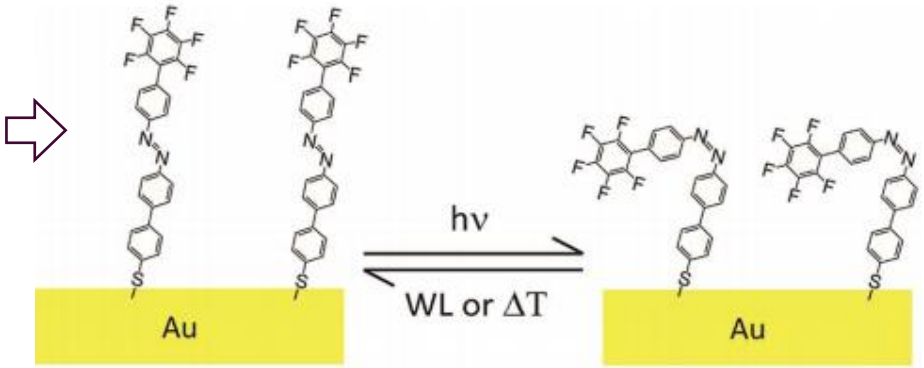
- Bistability: property of a molecular system able to evolve from a stable electronic state to another electronic state in a reversible and detectable fashion when applying an appropriate and controllable perturbation.



Interesting applications: Electronics, optics, magnetism, biological applications

Molecular electronics: molecular switch

Switch ⇨ Conformational change ⇨



$\Delta\phi_{CT}$= 220meV

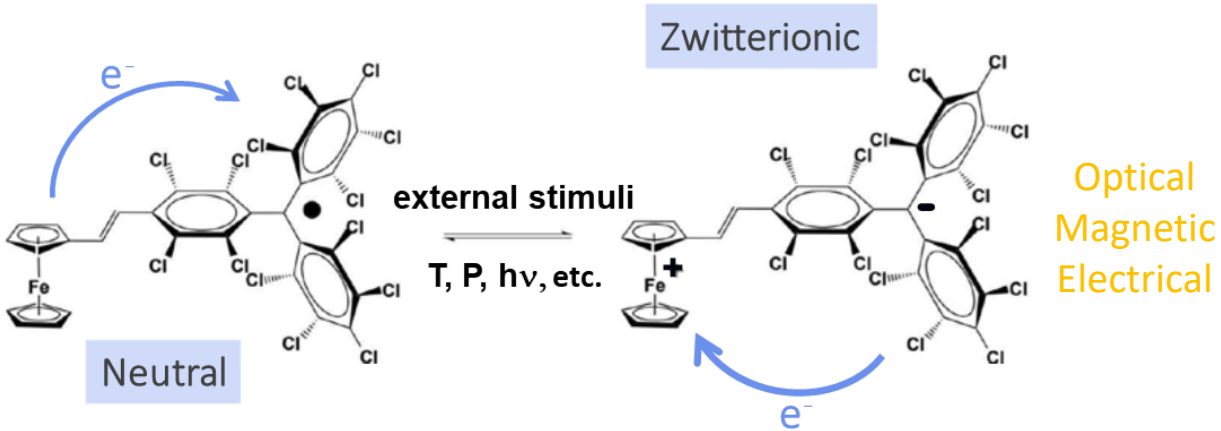
⇩

Charge reorganization

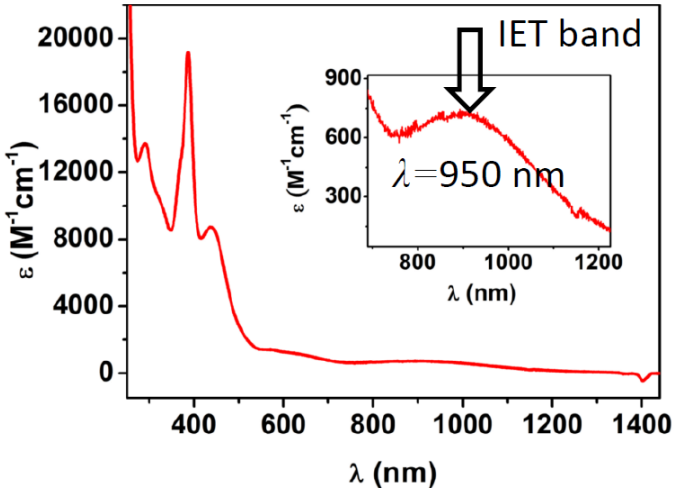
⇩

A. M. Masillamani, S. Osella, A. Liscio, O. Fenwick, F. Reinders, M. Mayor, V. Palermo, J. Cornil and P. Samor`ı *Nanoscale* 6, 8969–8977 (2014).

Optical
Magnetic
Electrical



Optical
Magnetic
Electrical ⇨



J. Guasch, L. Grisanti, S. Jung, D. Morales, G. D'Avino, M. Souto, X. Fontrodona A. Painelli, F. Renz, I. Ratera, and J. Veciana, *Chem. Mater.* **25**, 808–814 (2013)..

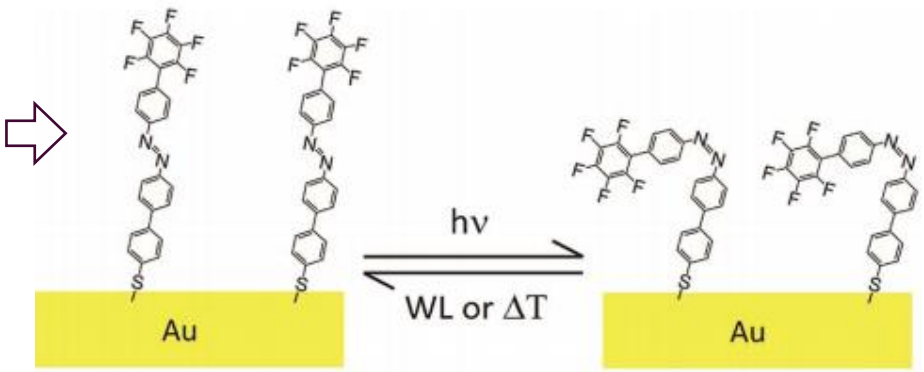
Molecular electronics: molecular switch

Switch ⇨ Conformational change

⇩

Charge reorganization

⇩

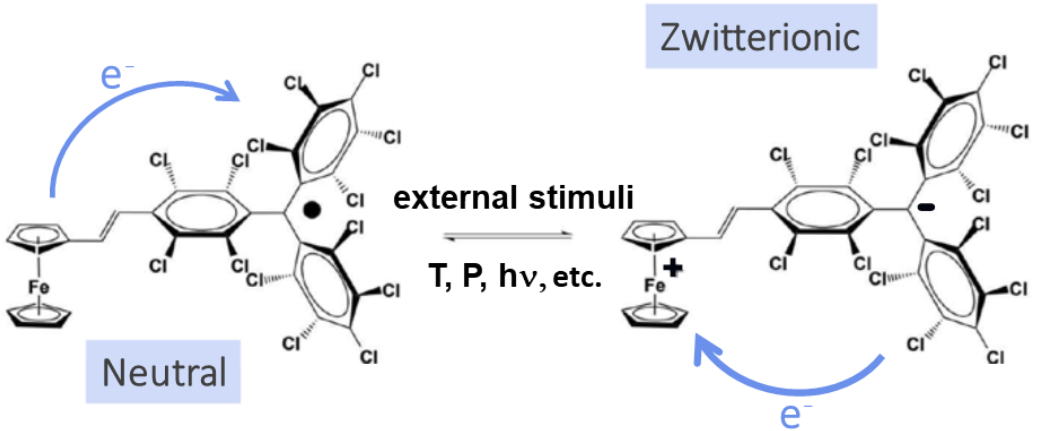


$\Delta\phi_{CT}$= 220meV

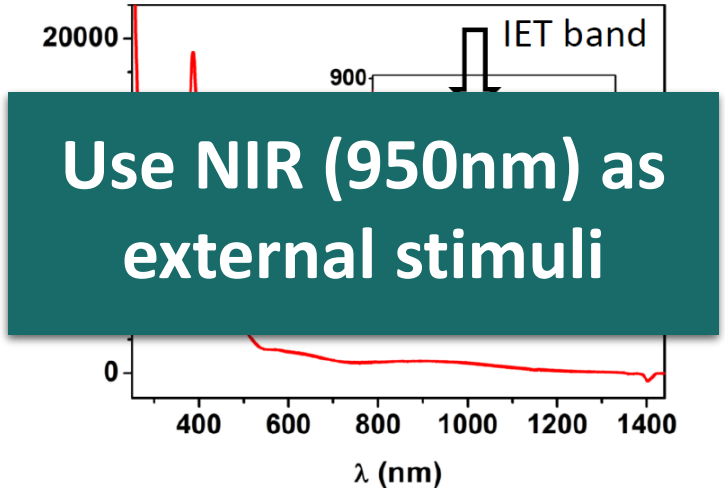
UV-Vis light inducing conformational changes

A. M. Masillamani, S. Osella, A. Liscio, O. Fenwick, F. Reinders, M. Mayor, V. Palermo, J. Cornil and P. Samor`ı *Nanoscale* 6, 8969–8977 (2014).

Optical
Magnetic
Electrical



Optical
Magnetic
Electrical



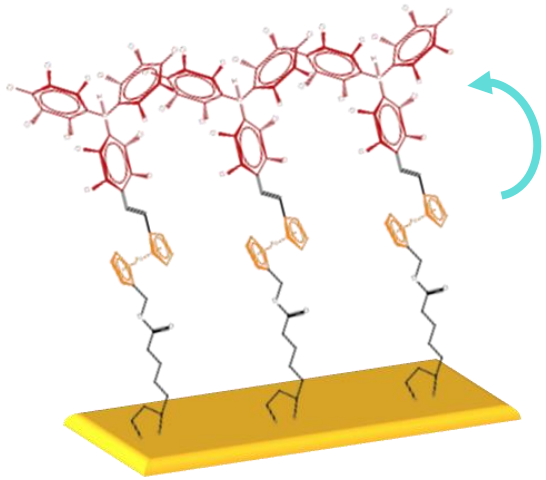
Use NIR (950nm) as external stimuli

J. Guasch, L. Grisanti, S. Jung, D. Morales, G. D'Avino, M. Souto, X. Fontrodona A. Painelli, F. Renz, I. Ratera, and J. Veciana, *Chem. Mater.* **25**, 808–814 (2013)..

Preparation of SAMs and Characterization

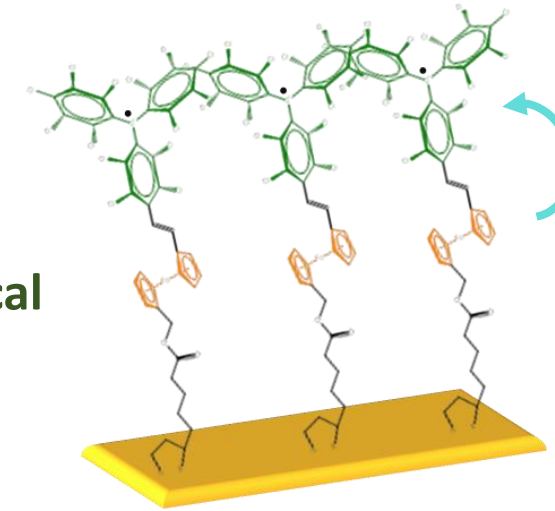
Self-Assembled Monolayers (SAMs)

SSFcPTM αH



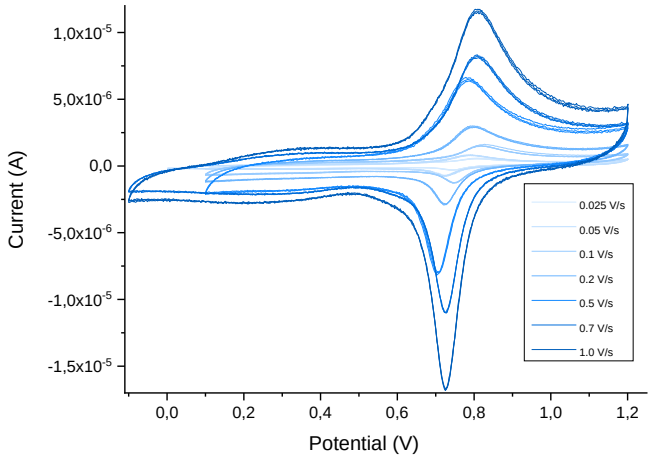
~~Internal Electron Transfer (IET)~~

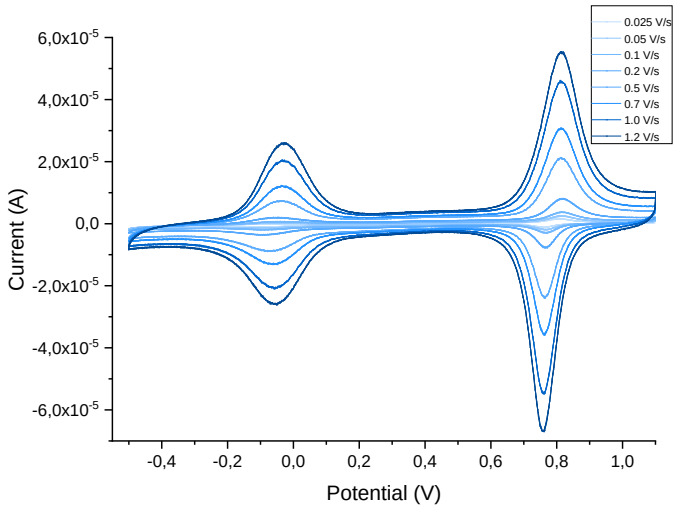
SSFcPTM radical

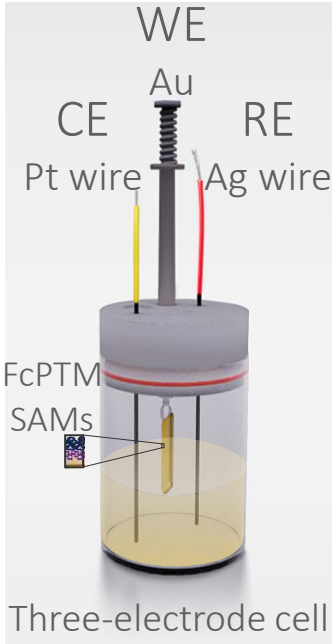


Internal Electron Transfer (IET)

Cyclic Voltammograms







Depolarization Effect and Contact Potential Difference (CPD)

Depolarization effect refers to a reduction in the magnitude of the dipole moment due to interactions between neighbouring molecules

Calculated magnitudes in isolated molecules

Sample	μ_z[D]	$\alpha_{zz}10^{-24}$ [cm^3]
Fc	2.01	39.7
Fc-PTM (αH)	-0.3	120.7
Fc-PTM •	-1.24	151.6

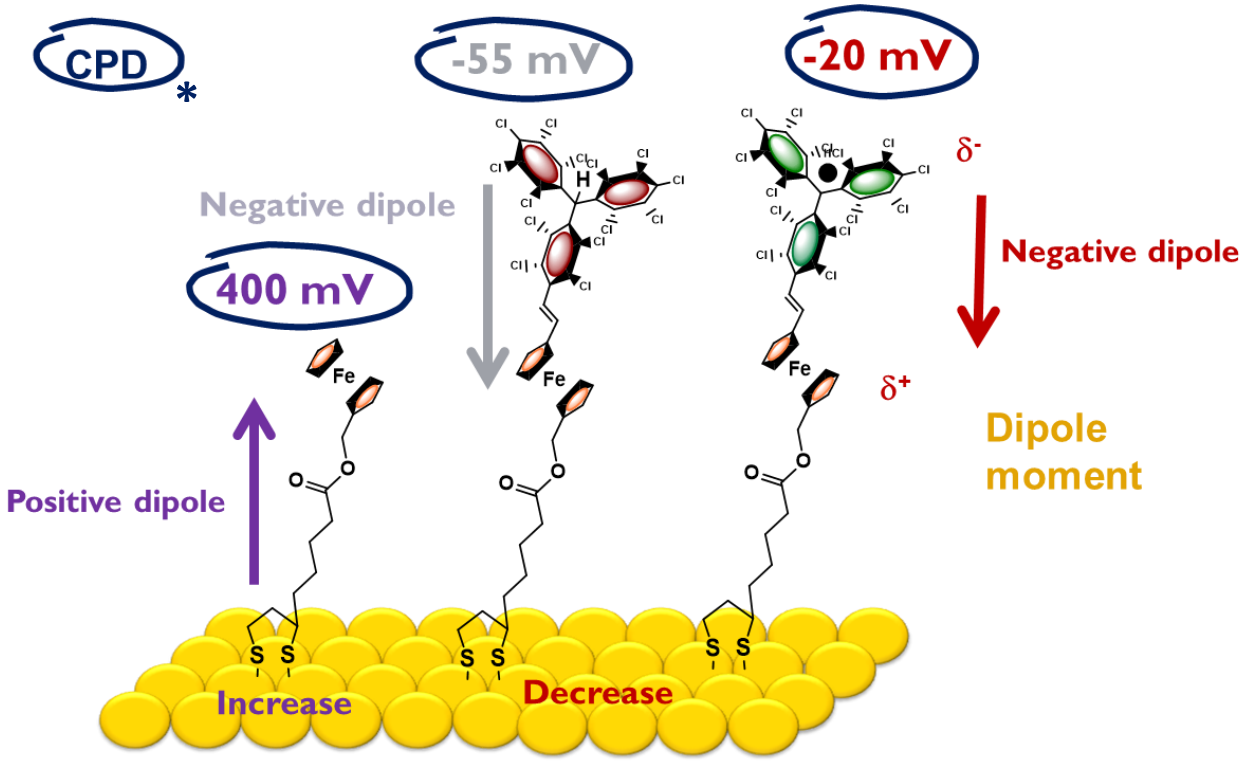
Dipole moment

$\mu_{1\text{-H}} < \mu_1$

Polarizability

$\alpha_{1\text{-H}} < \alpha_1$

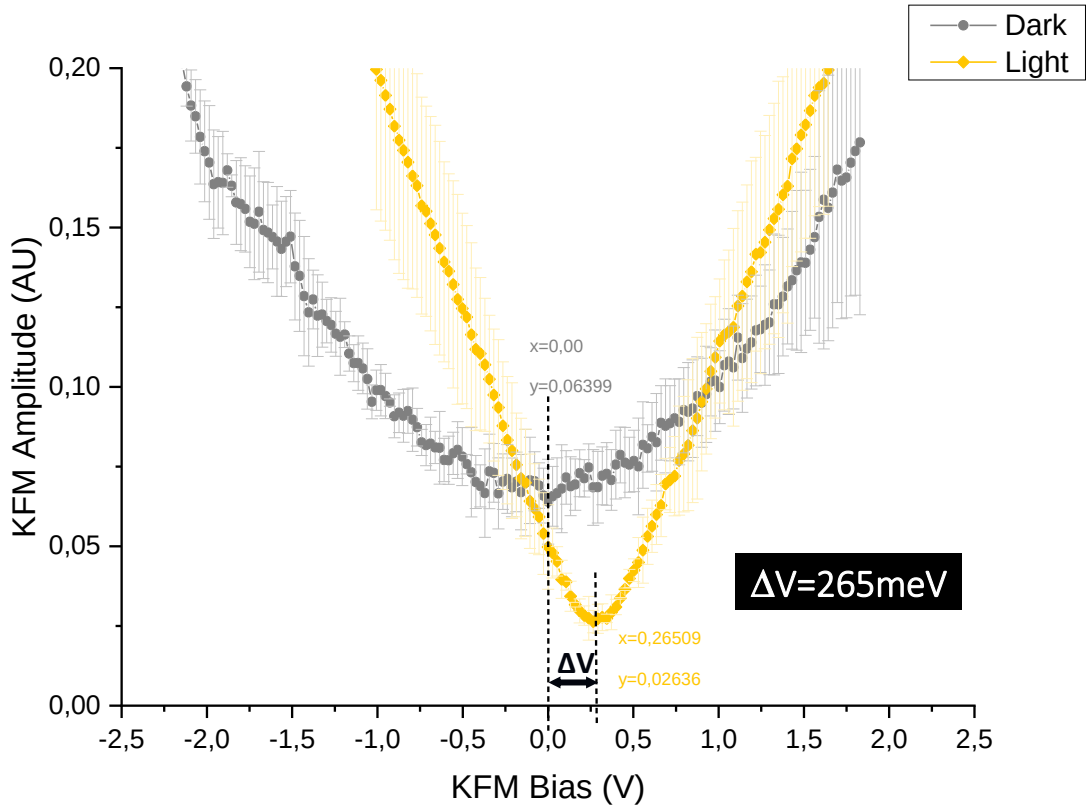
Why the interface dipole is lower for the radical?

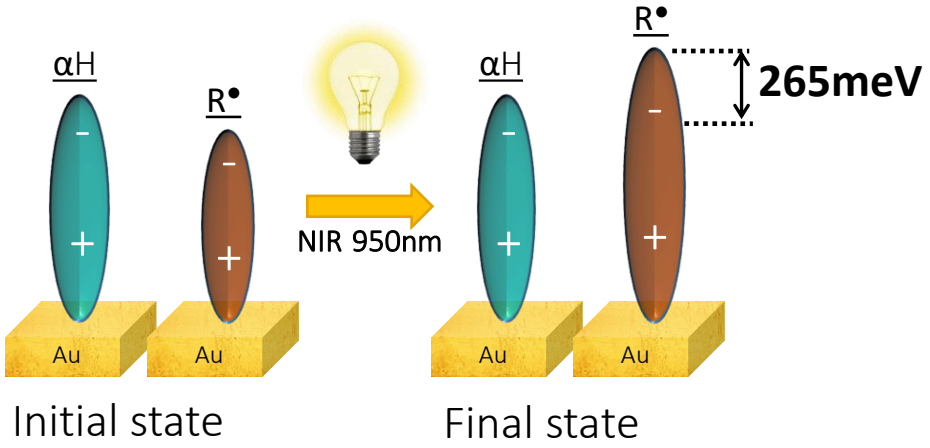


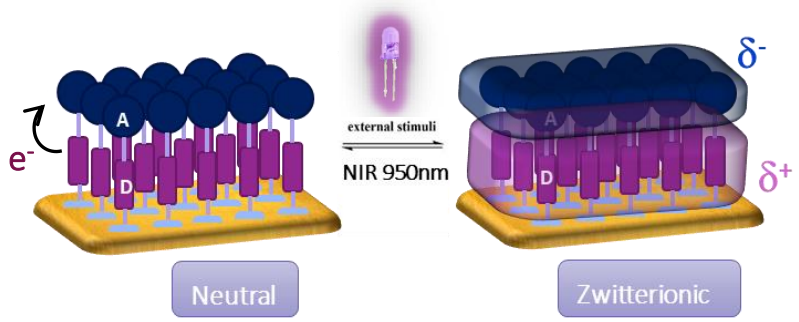
***Behaviour when forming SAMs**

V. Diez-Cabanes, D. C. Morales, M. Souto, M. Paradinas, F. Delchiaro, A. Painelli, C. Ocal, D. Cornil, J. Cornil, J. Veciana, I. Ratera, *Adv. Mater. Tech.*, **2018**

KPFM: Work Function Modification







Molecular systems with high polarizabilities, like the radical, are able to trigger a charge reorganization working forward the dipole induced by NIR light.

V. Diez-Cabanesa, A. Gómez, M. Souto, N. González-Pato, J. Cornil, J. Veciana, I. Ratera, ***J. Mater. Chem. C,*** 2019, 7, 7418

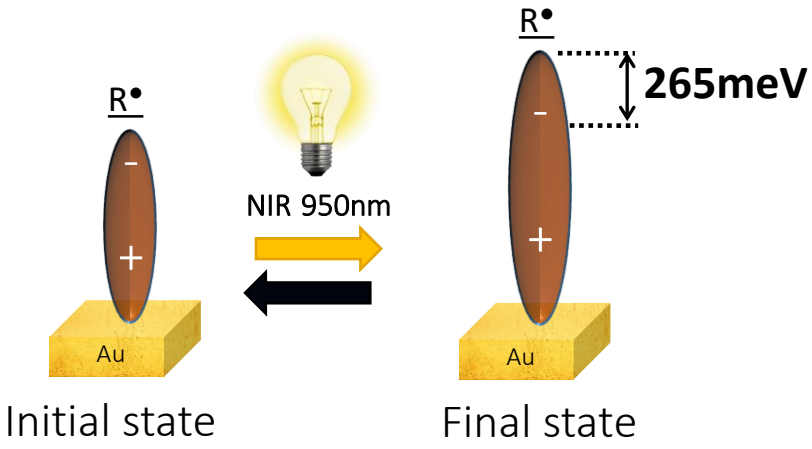
KPFM: Work Function Modification pulse

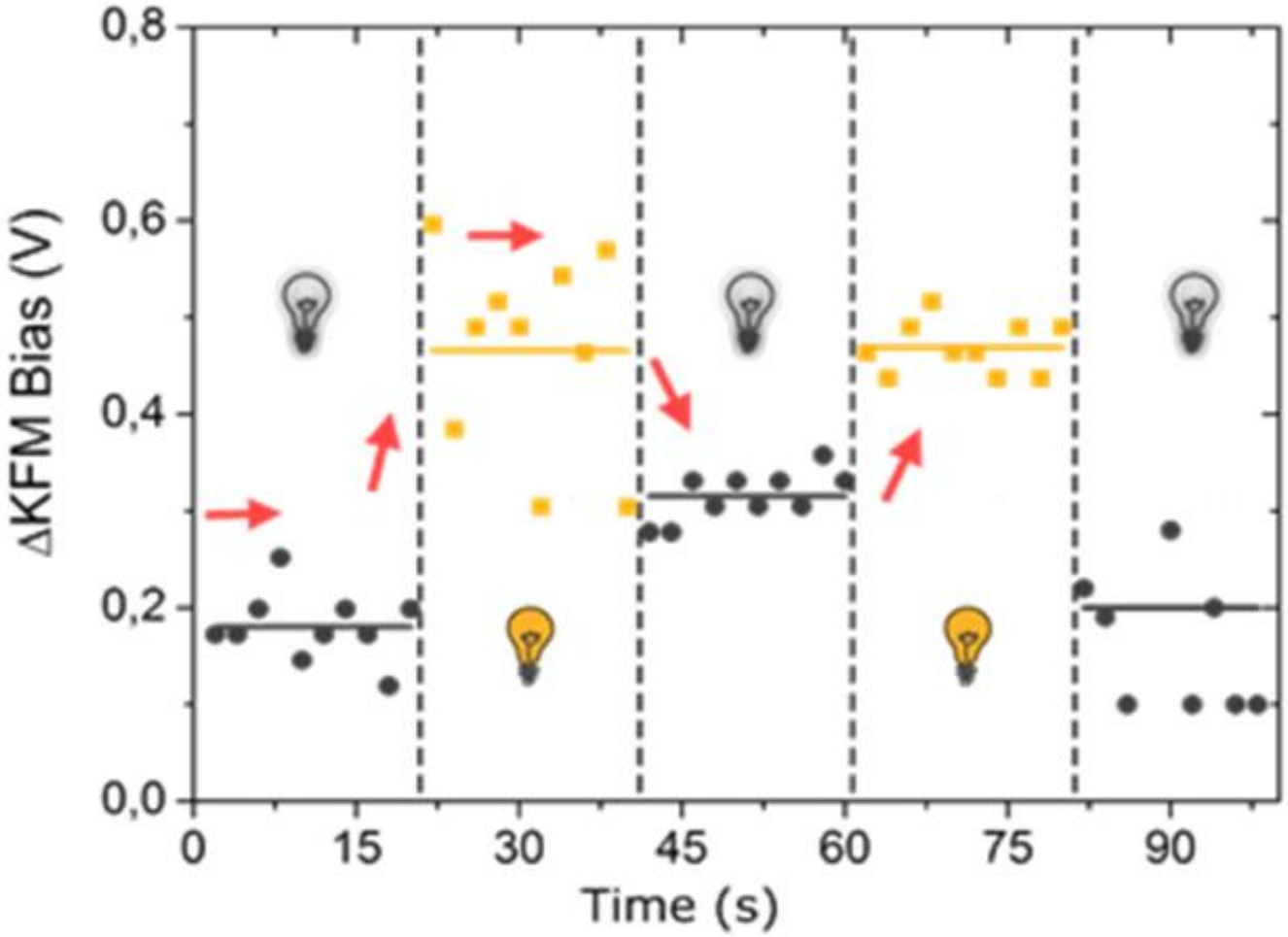
Switch pulse

10 first curves with LED OFF

10 curves with LED ON

Repeated four times in a row, during 100 seconds in total.

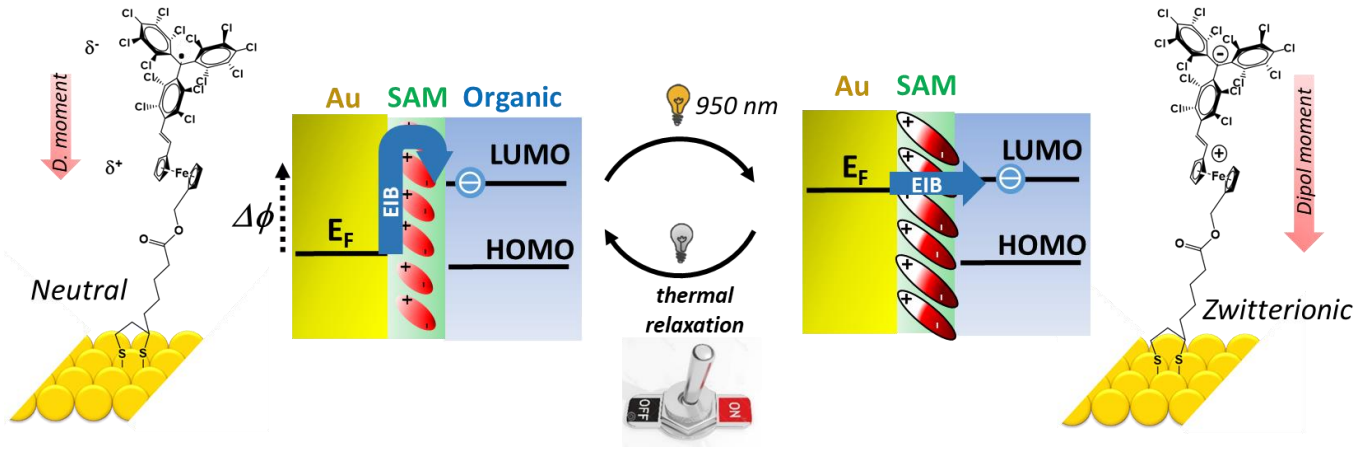




V. Diez-Cabanesa, A. Gómez, M. Souto, N. González-Pato, J. Cornil, J. Veciana, I. Ratera, ***J. Mater. Chem. C,*** 2019, 7, 7418

Conclusions

1. Control of metal Work Function switch by applying an external stimulus
2. Work Function change due to charge reorganization inside the molecule
3. ΔV= 265meV, highest value reported in literature
4. First work function switch controlled by Near-Infrared (NIR) irradiation



Acknowledgements

Prof. J. Veciana

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V. Diaz-Cabanes

Dr. D. Morales

Dr. A. Kyvik

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Prof. C. Rovira

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V. Diaz-Cabanes

Anna Painelli

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Thank you for your kind attention!

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Health
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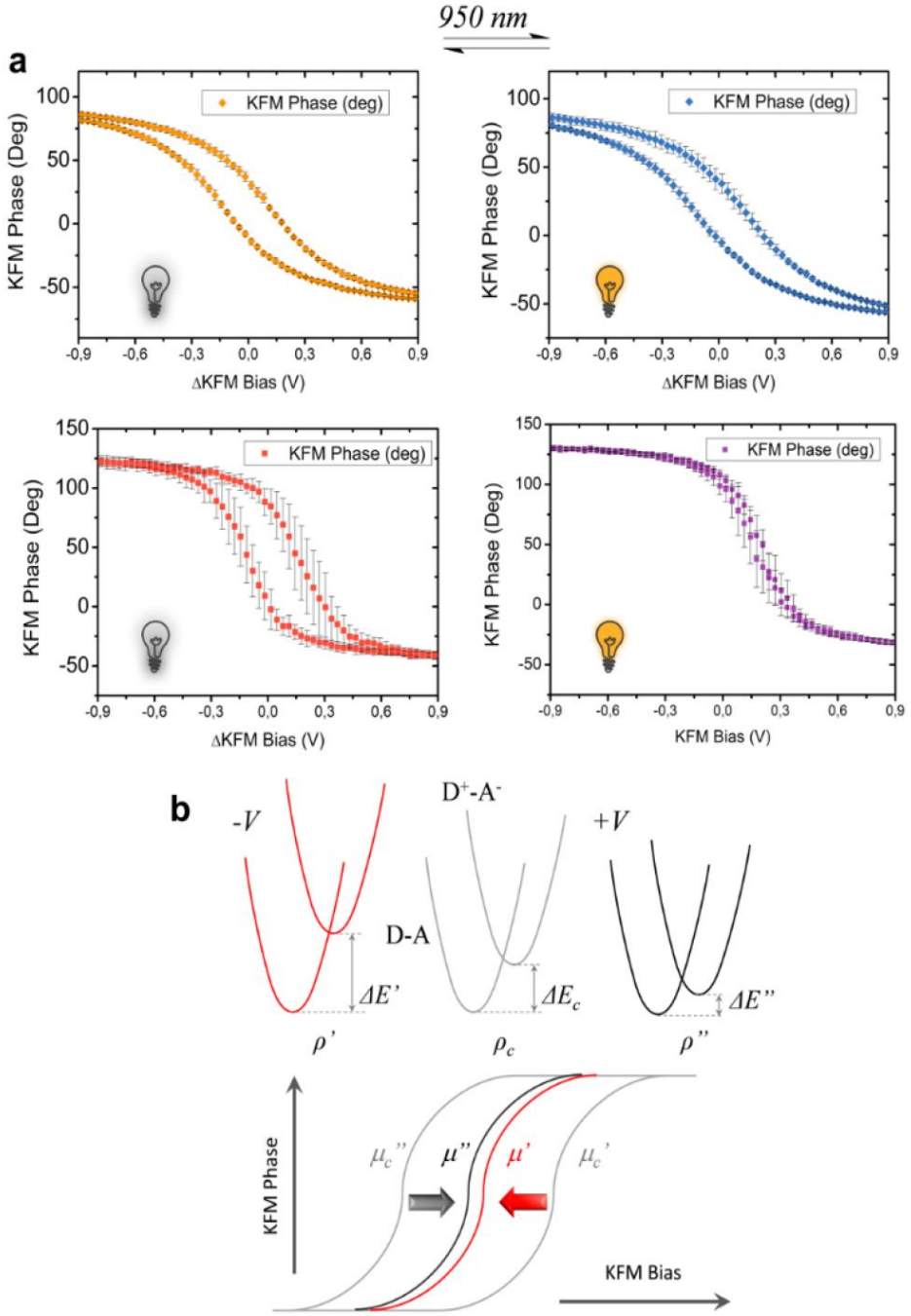
Advanced Materials

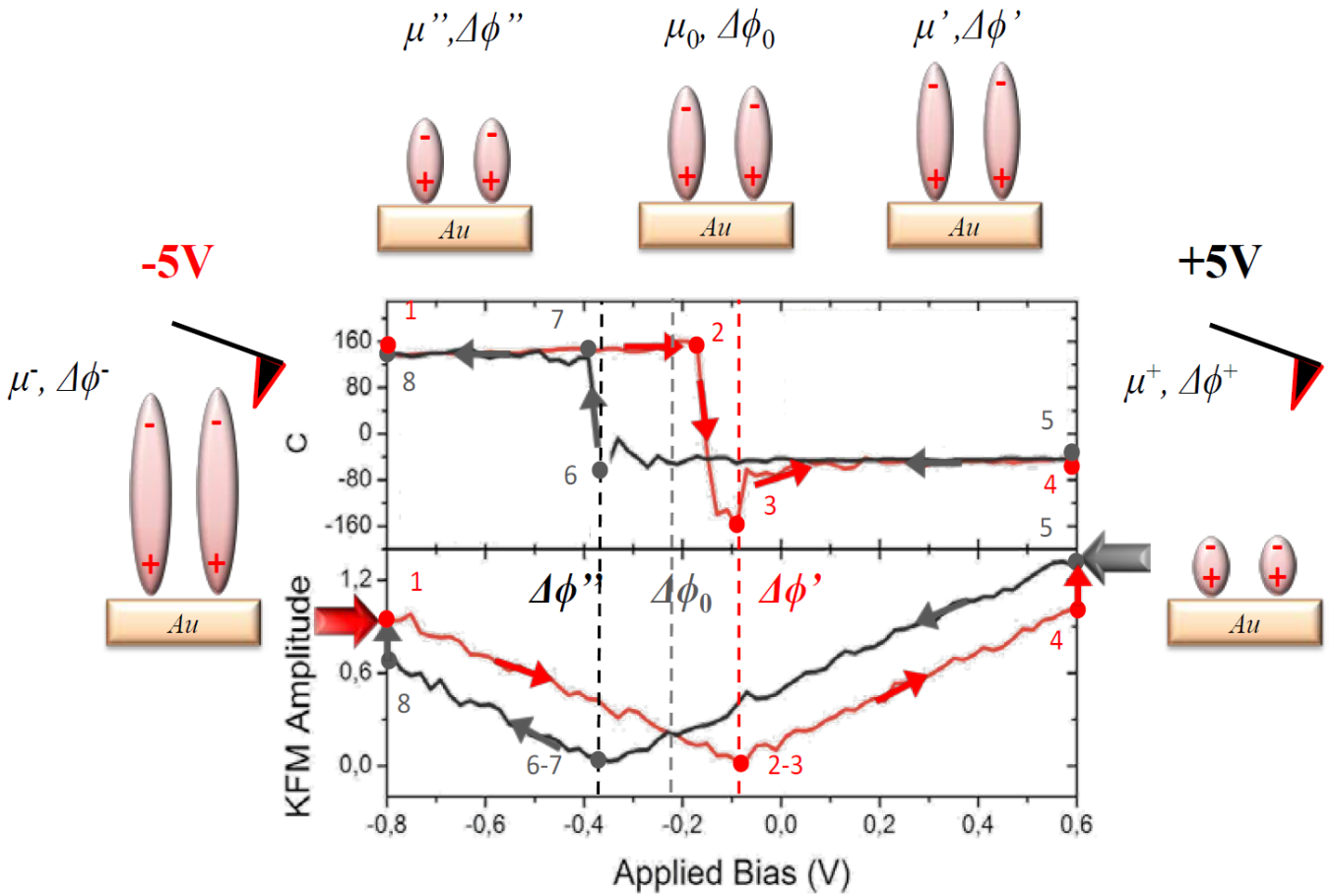
Nerea González Pato

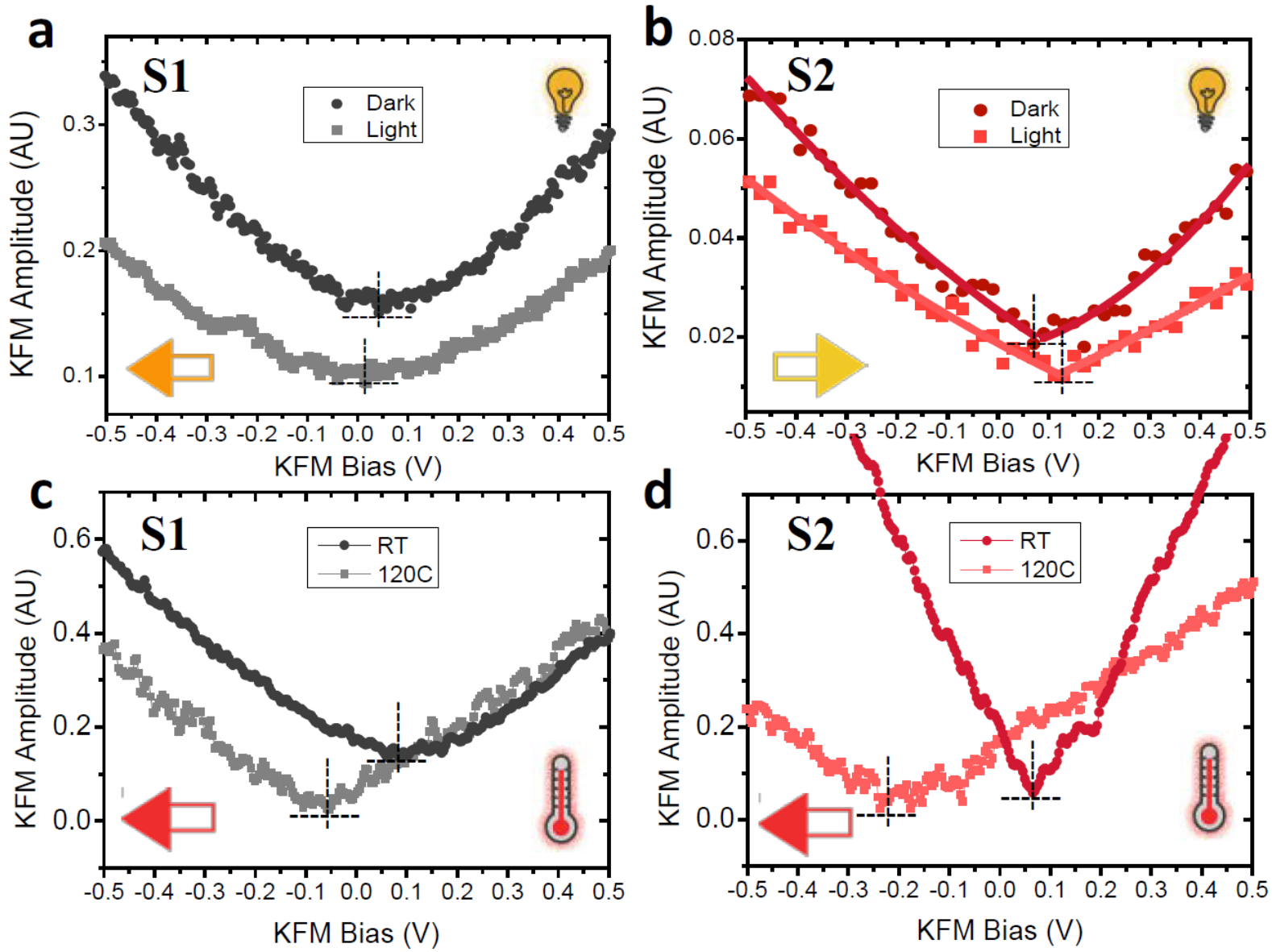
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)

ngonzalez@icmab.es

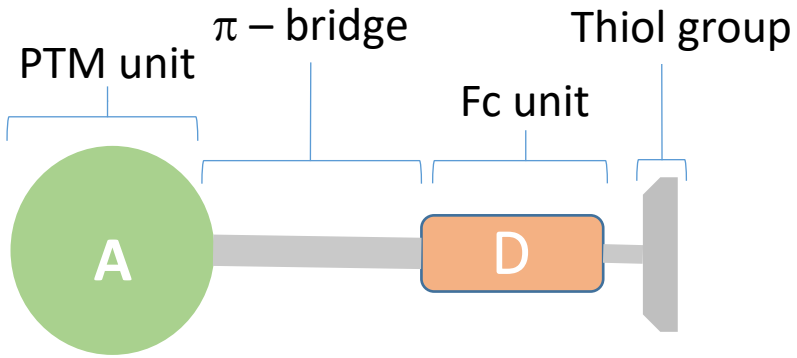
Supporting Slides


950 nm
a
KFM Phase (deg)
KFM Phase (Deg)
ΔKFM Bias (V)
KFM Bias (V)
b
-V
D⁺-A⁻
+V
D-A
ΔE'
ΔE_c
ΔE''
ρ'
ρ_c
ρ''
KFM Phase
KFM Bias
μ_c''
μ''
μ'
μ_c'

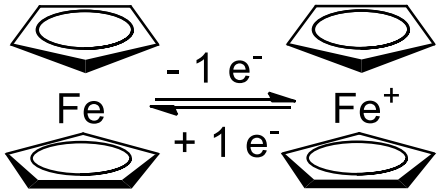

μ'',Δφ''
μ0, Δφ0
μ',Δφ'
Au
-5V
+5V
μ-, Δφ-
μ+, Δφ+
C
KFM Amplitude
Δφ''
Δφ0
Δφ'
Applied Bias (V)

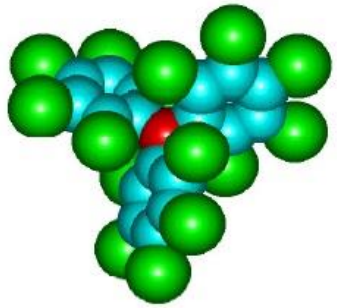

a
S1
Dark
Light
KFM Amplitude (AU)
KFM Bias (V)
b
S2
Dark
Light
KFM Amplitude (AU)
KFM Bias (V)
c
S1
RT
120C
KFM Amplitude (AU)
KFM Bias (V)
d
S2
RT
120C
KFM Amplitude (AU)
KFM Bias (V)

Donor-Acceptor systems



Building block – DONOR

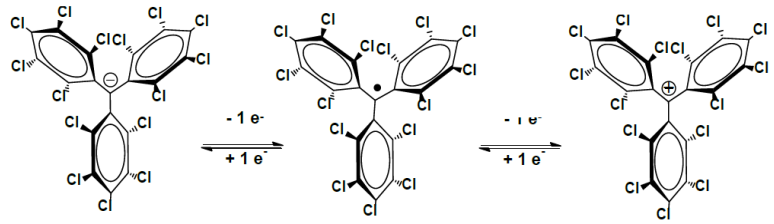




Ferrocene (Fc)

- Electroactive molecule
- Behaviour like aromatic electron-rich organic compound
- Thermal stability: stable at room temperature

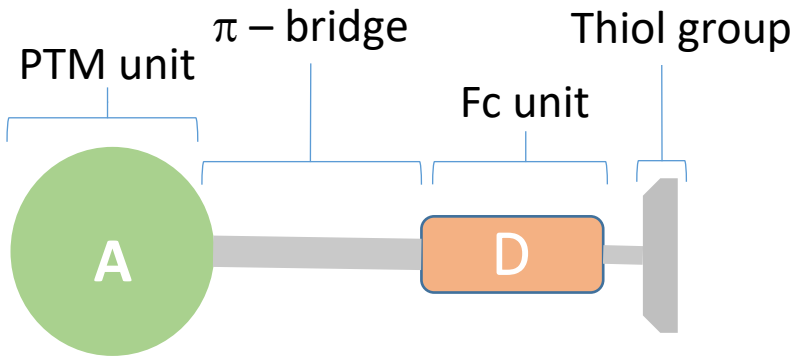
Building block – ACCEPTOR



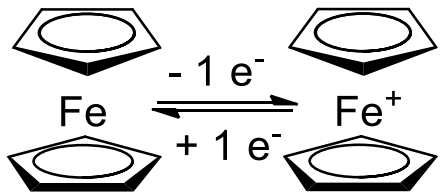
Polychlorotriphenylmethyl radical (PTM)

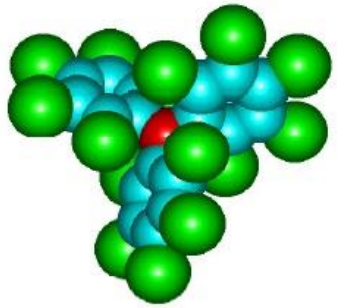
- Chemical and thermal stability
- Electroactive with low reduction potential
- Magnetically active

Donor-Acceptor systems



Building block – DONOR





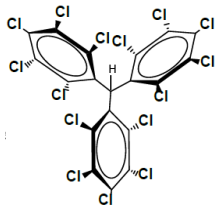
Ferrocene (Fc)

- Electroactive molecule
- Behaviour like aromatic electron-rich organic compound
- Thermal stability: stable at room temperature

Energy

Building block – ACCEPTOR

Closed shell

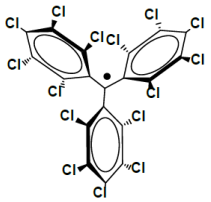


LUMO

HOMO

α-H

Open shell



SOMO

HOMO

• rad

Preparation of SAMs

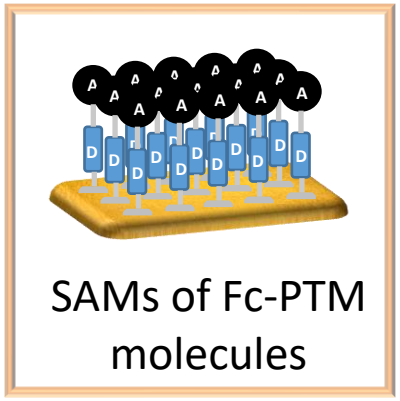
Gold substrate

Adsorption

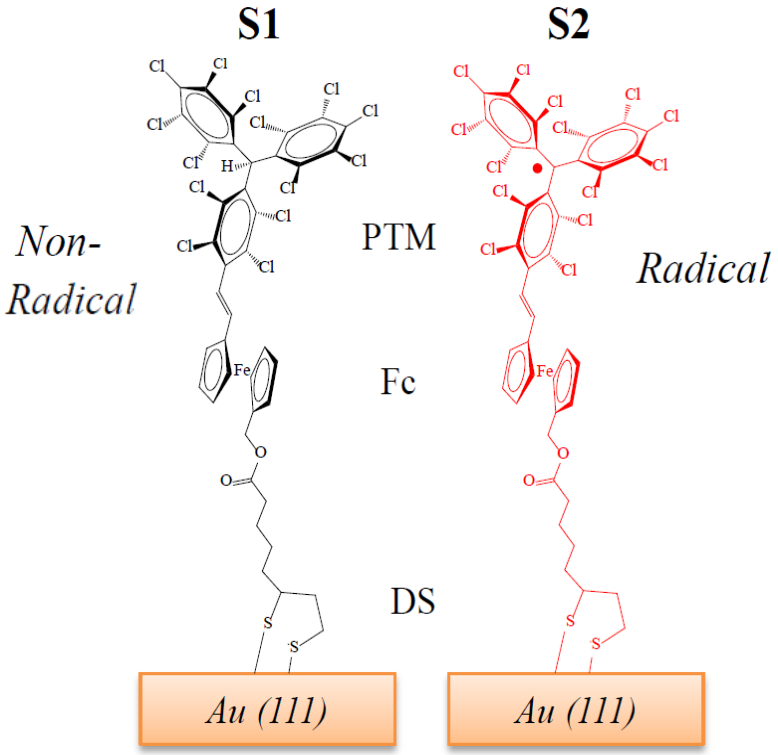
1mM solution in Toluene

Organization:
40ºC (1h)
R.T. (24h)

Rinse and dry



SAMs of Fc-PTM molecules

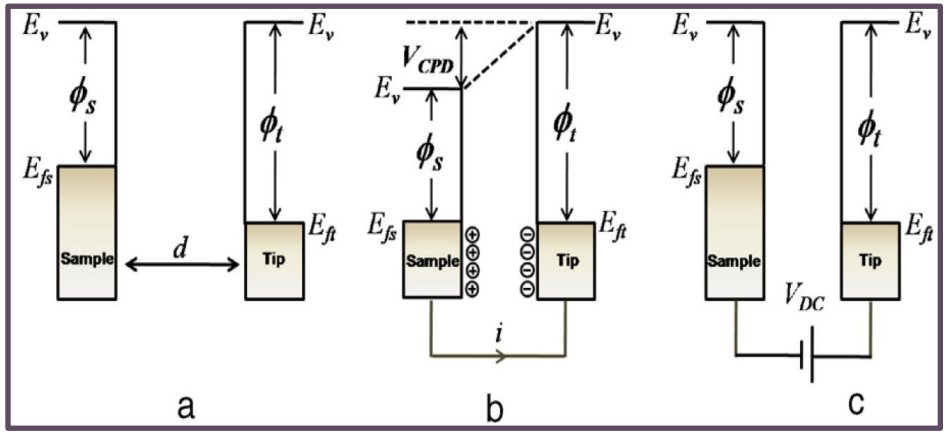


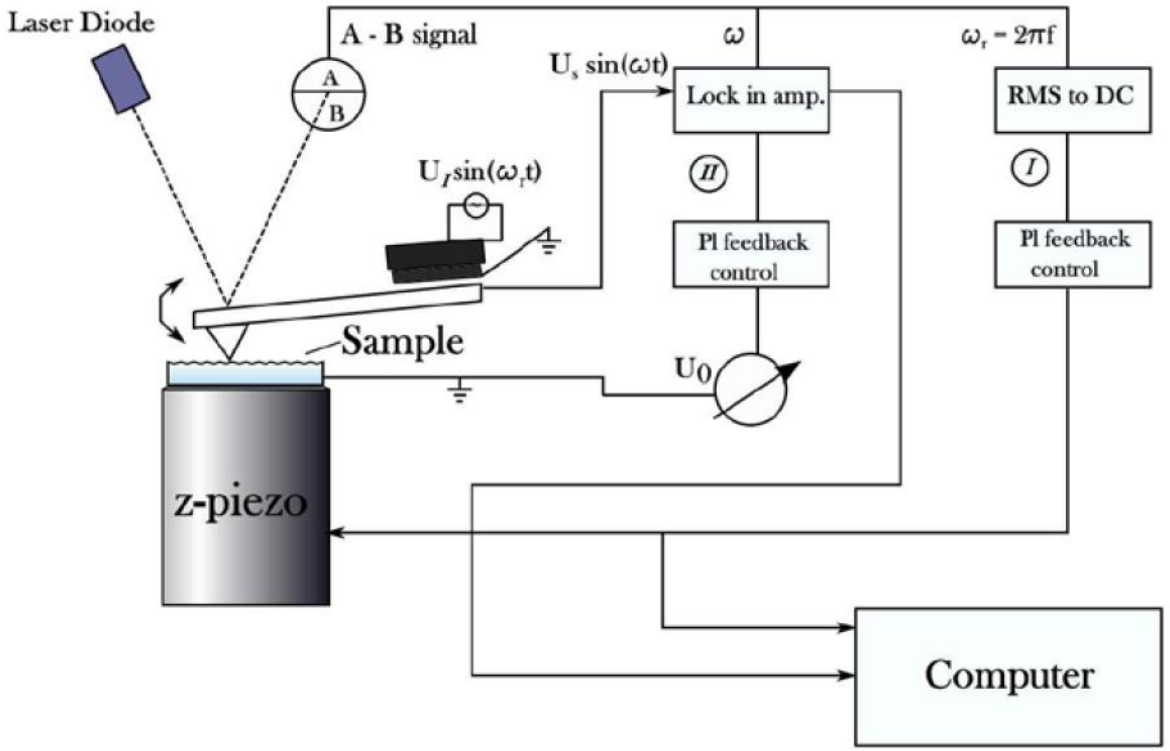
Experiments were performed in absence of light and under inert atmosphere.

KPFM: Work Funcion Modification

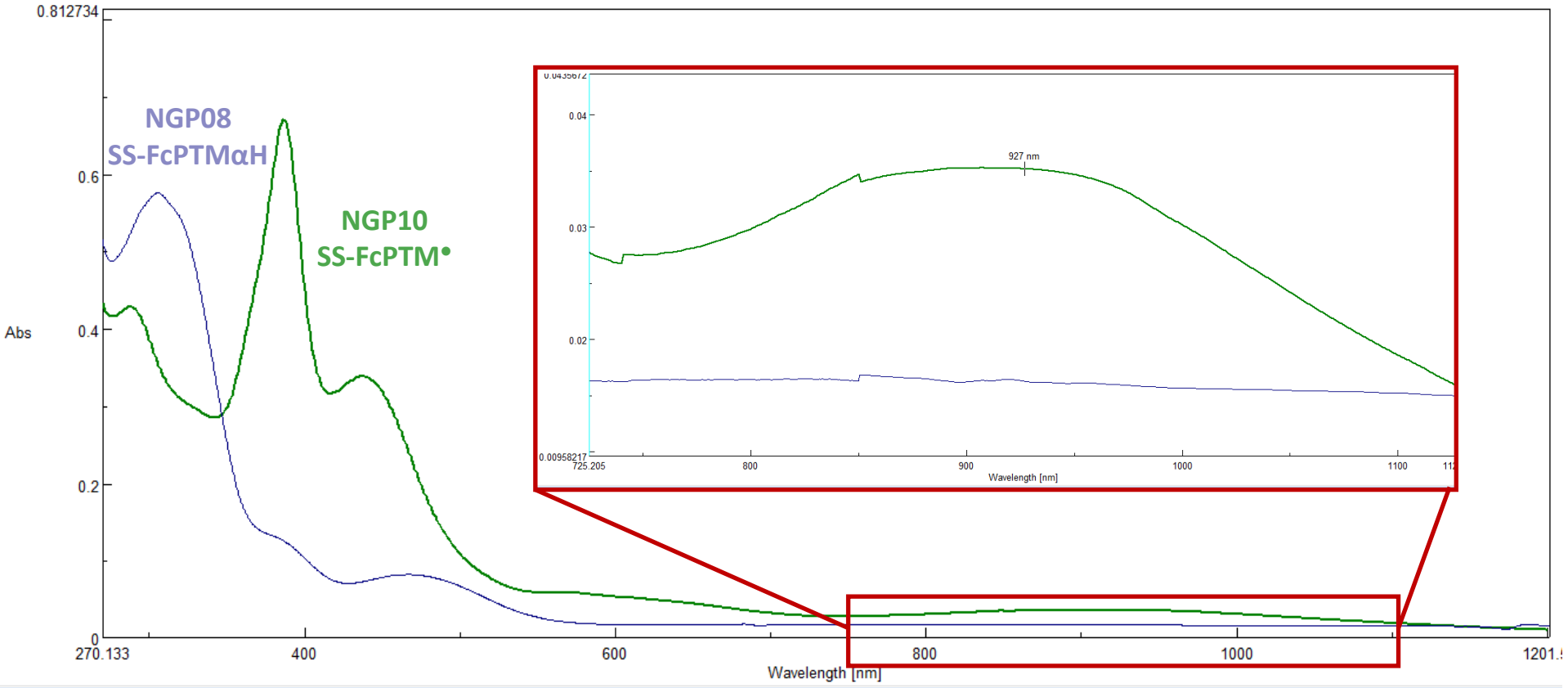
- Measures the contact potential difference between the tip and the sample.
- Tapping mode

$$V_{CPD} = \phi_{tip} - \phi_{sample}$$





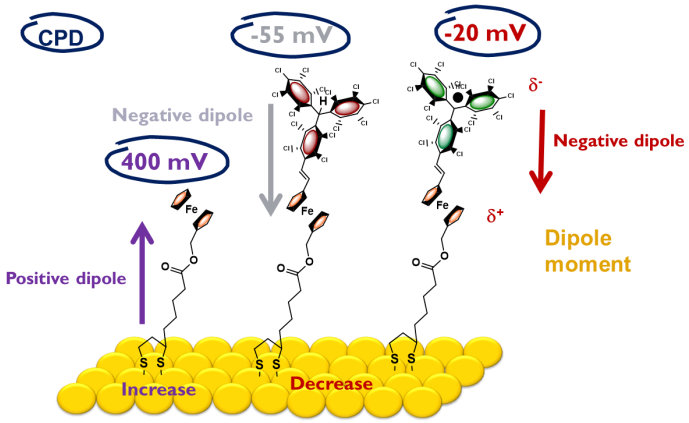
UV-Vis spectra of SS-Fc-PTM: intramolecular electron transfer (IET), 950 nm



Previous works of the group

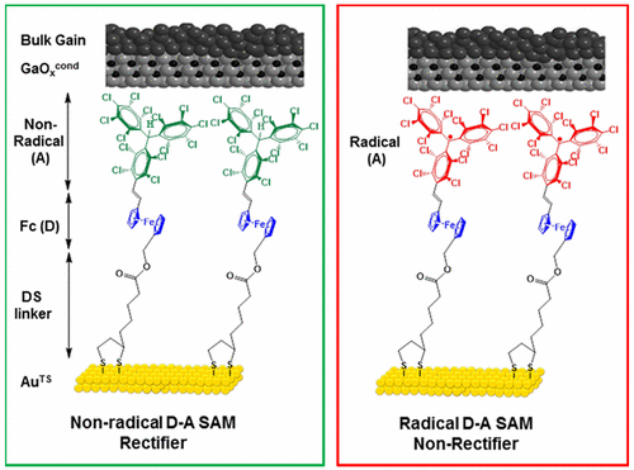
Effect of the Molecular Polarizability of SAMs on the Work Function Modification of Gold: Closed- versus Open-Shell Donor–Acceptor SAMs

Adv. Mater. Technol. **2018**, 1800152



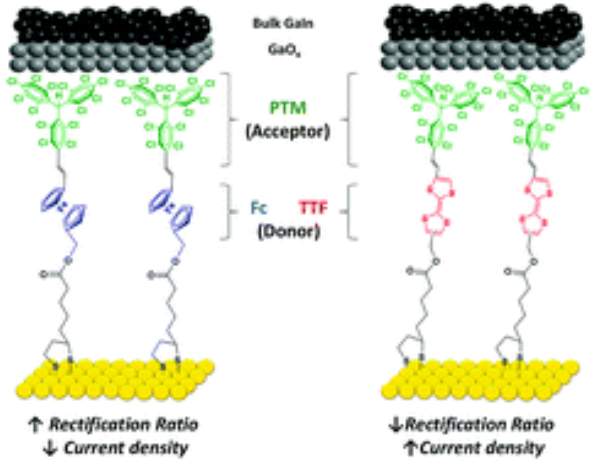
Tuning the Rectification Ratio by Changing the Electronic Nature (Open-Shell and Closed-Shell) in Donor–Acceptor Self-Assembled Monolayers

J. Am. Chem. Soc. 2017, 139, 4262–4265

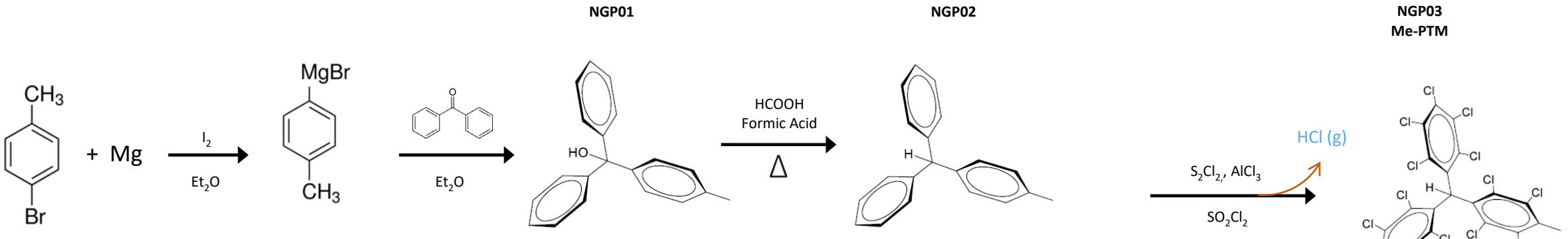


Influence of the donor unit on the rectification ratio in tunnel junctions based on donor– acceptor SAMs using PTM units as acceptors

Phys. Chem. Chem. Phys., 2018, 20, 25638



Synthesis of SS-Fc-PTM



Yield 37.2%

Yield 43%
Yield 50%

Yield 44%
Yield 56.3%

Reduction

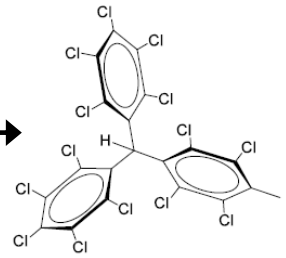
Aromatic Halogenation

Grignard reaction

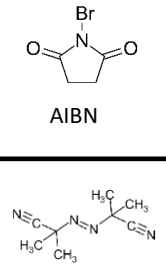
R–Mg–X
X=halogen
R= organic group usually alkyl or aryl.
Form new C-C bonds

Synthesis of SS-Fc-PTM

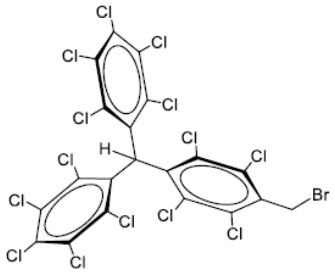
NGP03
Me-PTM



AIBN

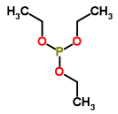


NGP04
Br-CH_2-PTMαH

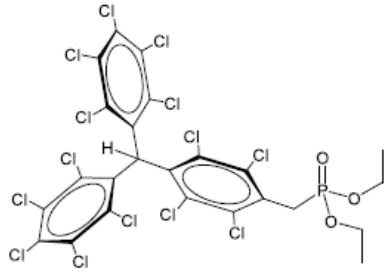


Yield 97.4%

$PO(OEt)_3$



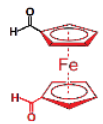
NGP05
$PO(OEt_2)$-CH_2-PTMαH



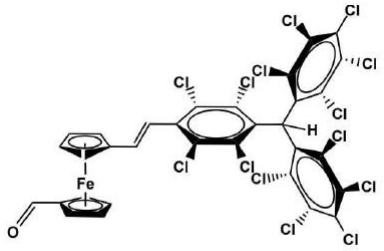
Yield 91.8%

t-BuOK

THF, -78ºC

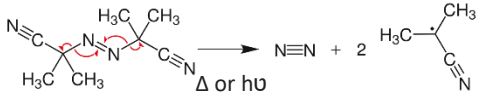


NGP06
OHC-Fc-PTMαH



Yield 25%
Yield 62%

Wohl–Ziegler bromination



Through radical initiator, above 70ºC

Michaelis-Arbuzov Reaction

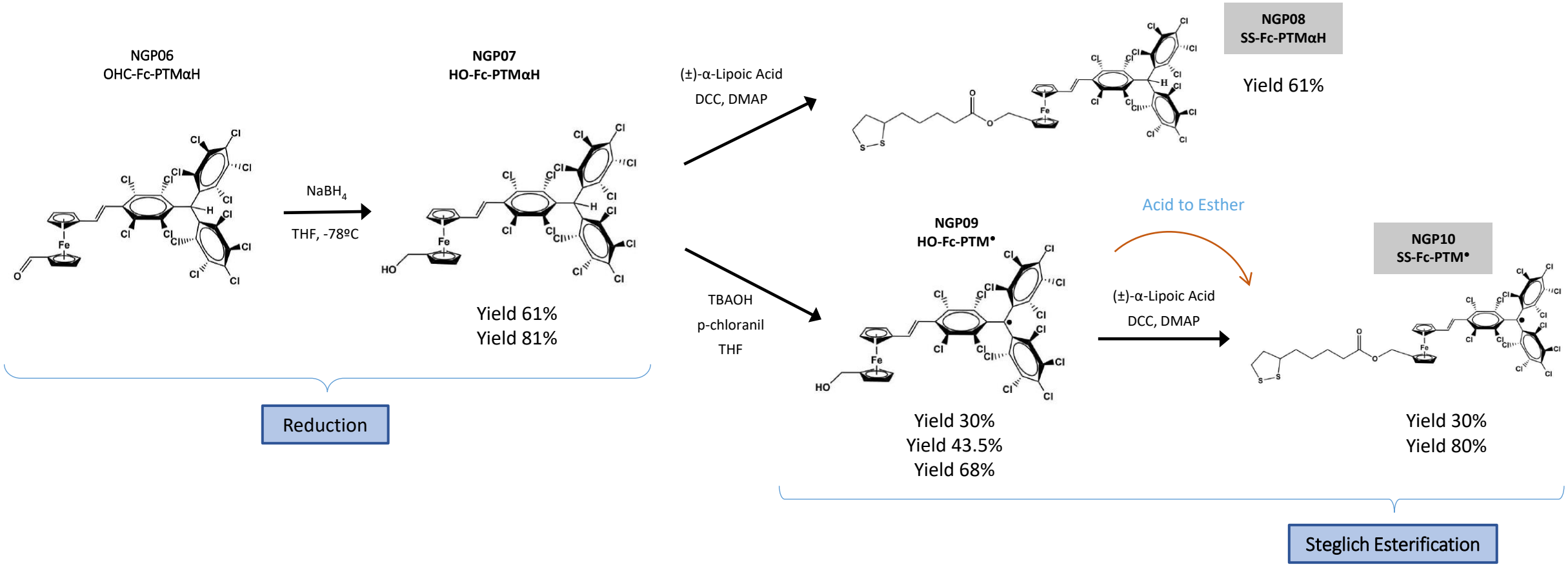
To form the phosphonate

Wittig-Horner reaction

TRANS product, intermediate is thermodynamically more stable.

Wittig reaction: instead of phosphonate is used the triphenylphosphine

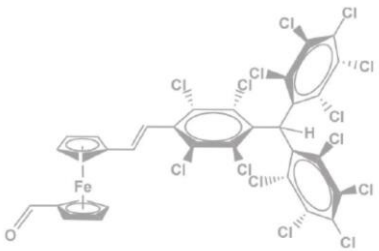
Synthesis of SS-Fc-PTM



p-chloranil instead of AgNO3, because AgNPs are formed and passed through the column. Is a mild oxidant

Synthesis of SS-Fc-PTM

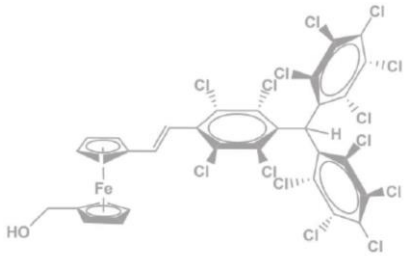
NGP06
OHC-Fc-PTMαH



$NaBH_4$

THF, -78ºC

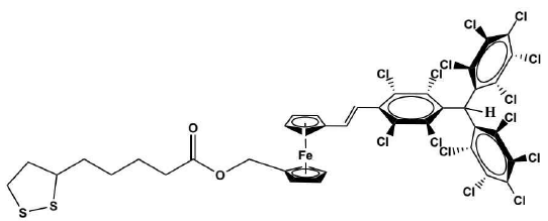
NGP07
HO-Fc-PTMαH



Yield 61%
Yield 81%

Reduction

(±)-α-Lipoic Acid
DCC, DMAP

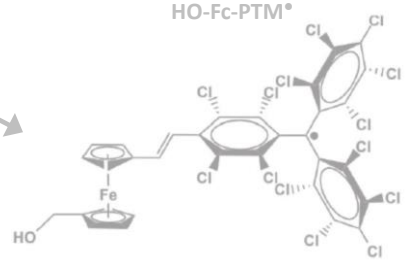


NGP08
SS-Fc-PTMαH

Yield 61%

TBAOH
p-chloranil
THF

NGP09
HO-Fc-PTM•

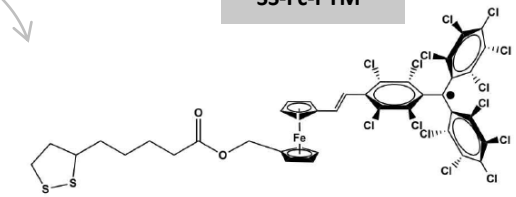


Yield 30%
Yield 43.5%
Yield 68%

Acid to Esther

(±)-α-Lipoic Acid
DCC, DMAP

NGP10
SS-Fc-PTM•



Yield 30%
Yield 80%

Steglich Esterification

p-chloranil instead of AgNO3, because AgNPs are formed and passed through the column. Is a mild oxidant