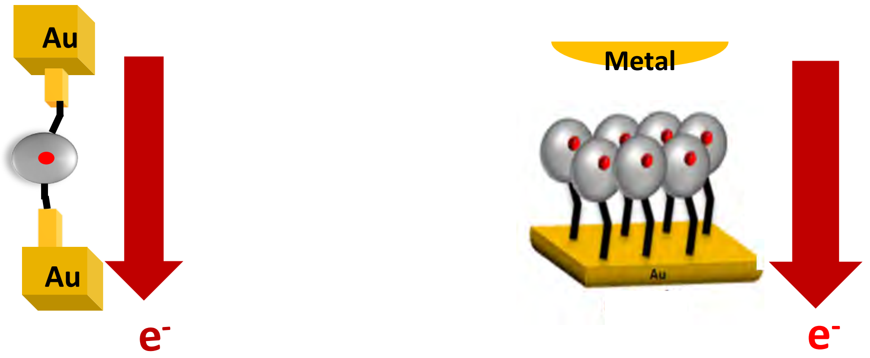
Organic Free Radicals on Surfaces. A way to manipulate electronic properties of surfaces

Jaume Veciana
vecianaj@icmab.es

Institut de Ciència de Materials de Barcelona-CSIC/CIBER-BBN (Spain)



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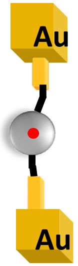
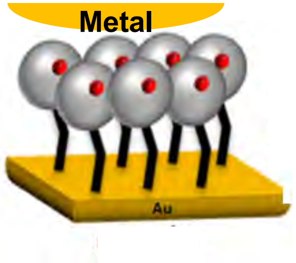
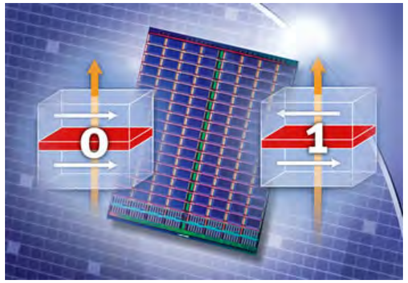
Organic Radical Molecules for Spintronics

Study of injection, transport, and manipulation of electron spins into organic radical-based solid state systems

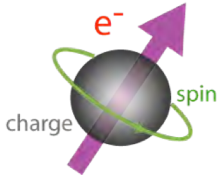






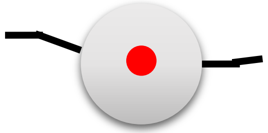
Why organic molecules?

Organic molecules are considered to be ideal media for spin transport due to their **weak spin-orbit coupling and hyperfine interactions**, in which **spin coherence over time and distance are preserved much longer** than in inorganic materials.



Why organic radical molecules?

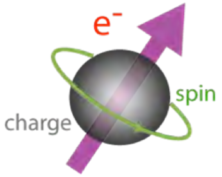
Organic radicals may act as spin filters in the coherent tunneling regime due to the **spin polarization of their unpaired electrons**

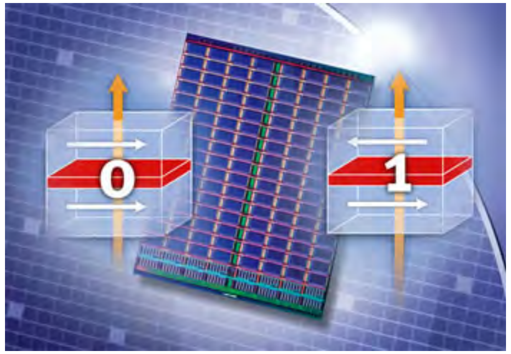


M. A. Ratner and col. *J. Am. Chem. Soc.* 2010, *132*, 3682

Organic Radical Molecules for Spintronics

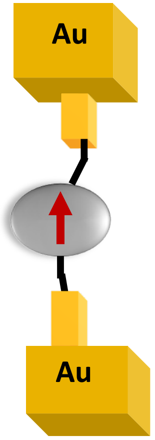
Study of injection, transport, manipulation and detection of electron spins into organic radical-based solid state systems





Final objective:

A spin filter device based on organic radicals



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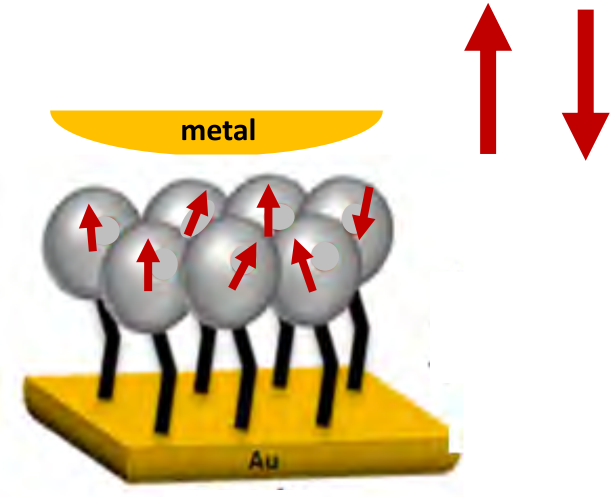
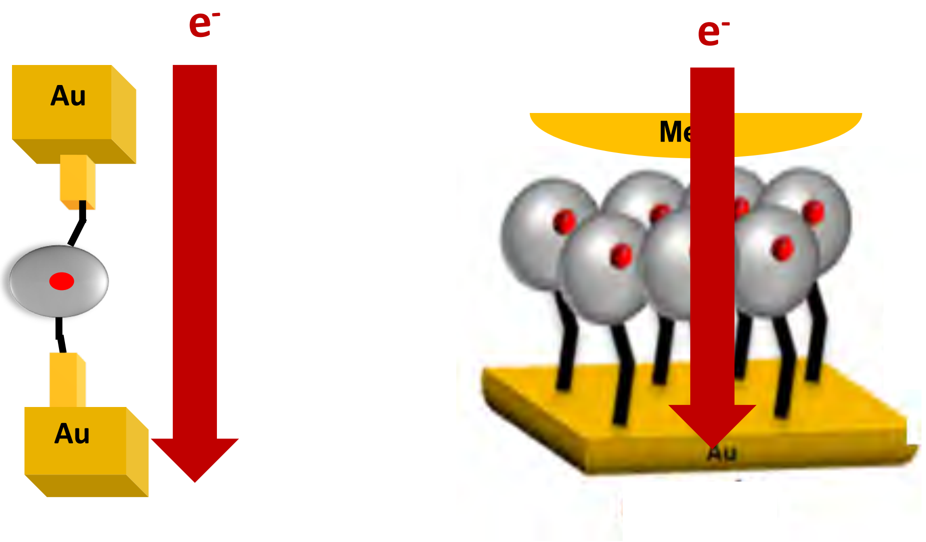


Filtering spin-up e^-

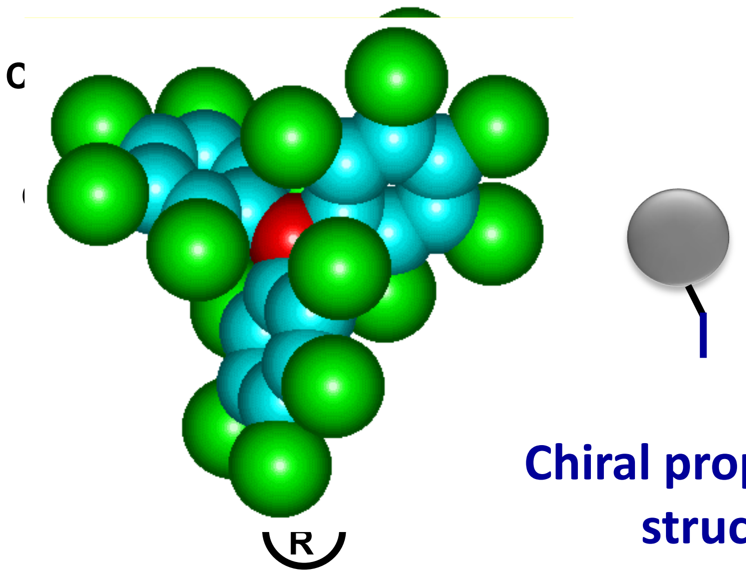
Organic Radical Molecules for Spintronics

Charge transport through PTM radical molecules



Solid-state junctions made of a single-molecule or of a self-assembled monolayer (SAM) of organic radicals anchored to Au

Polychlorinated triphenylmethyl (PTM) radicals



Chiral propeller-like structure

PTM advantages:

- **Functionalization (R)**
- **Persistent and stable radicals**
- **Non-radical derivative (HPTM)**
- Ultra-long coherence time (> 1 μs)
- Chiral polarized luminiscent emitter

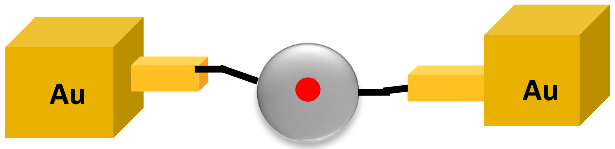
P. Mayorga-Burrezo et al. *Angew. Chem. Int. Ed.* 2019, DOI: 10.1002/anie.201909398

Y.-Z. Dai et al. *ChemPhysChem* 2018, 19, 2972-2977

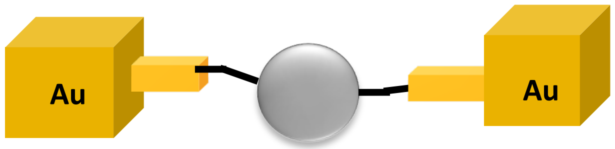
Electrical properties of PTM radical-based materials

Charge transport through a single PTM radical molecule

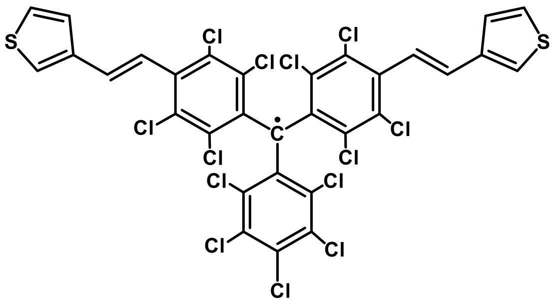
Single molecule junctions

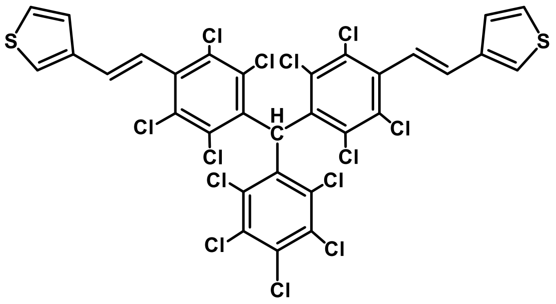


PTM radical molecule

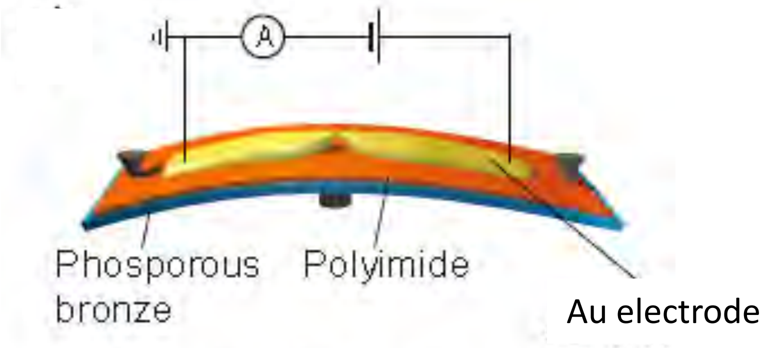


PTM non-radical molecule

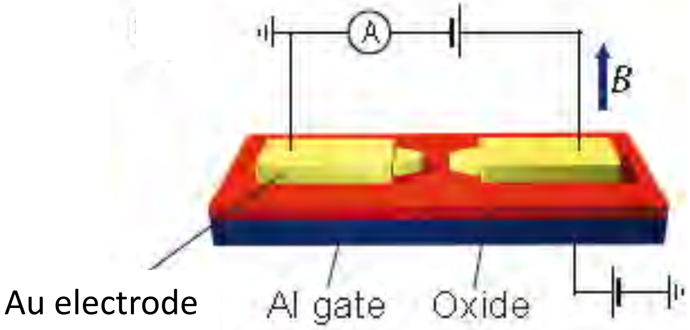




Junctions



Mechanically Controlled Break Junction (MCBJ)

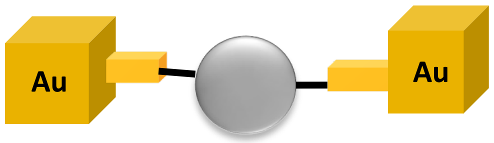


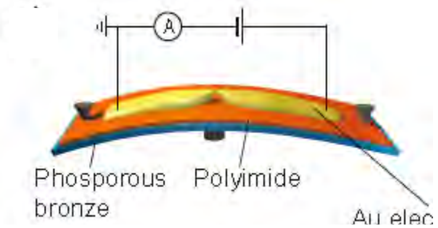
Electro-Migrated Break Junction (EMBJ)

In collaboration with H.S.J. van der Zant and E. Burzurí (Delft Univ. Tech)

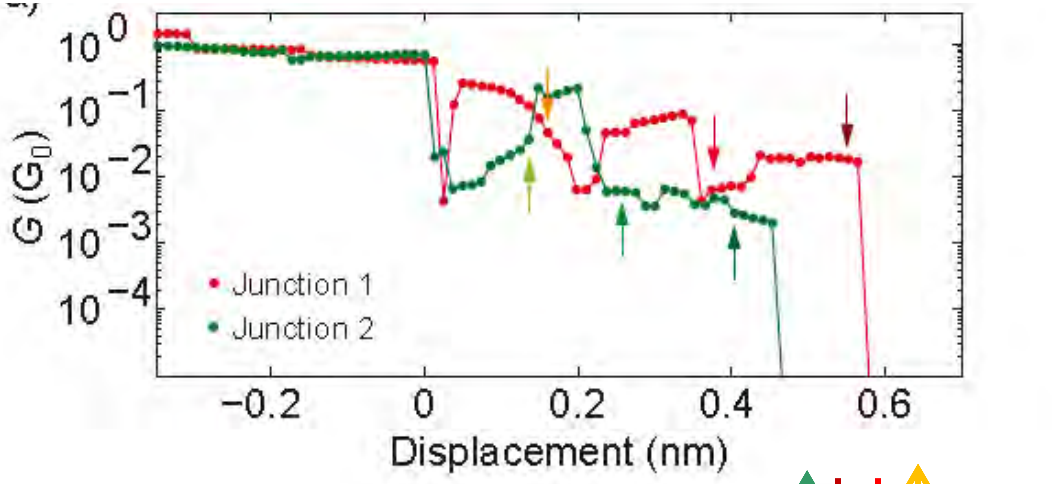
Electrical properties of PTM radical-based materials

Charge transport through a single PTM radical molecule

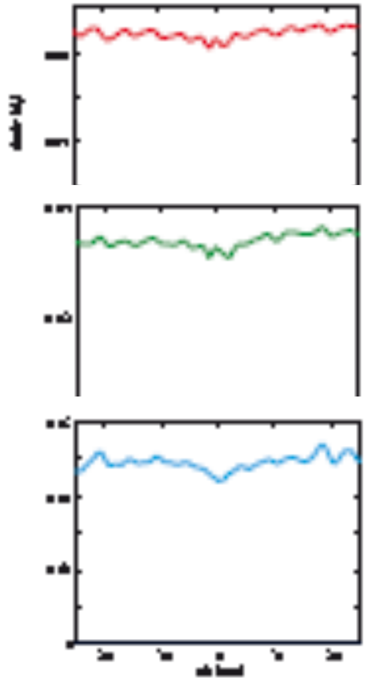




Conductance breaking traces of two PTM radical junctions with MCBJ at 6K



Trapped radical molecules ↑↓↓↑



- **No zero-bias anomaly at differential conductances**
- **Non-radical molecules show lower conductances than the radical ones**

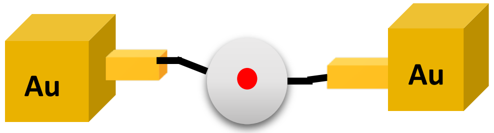
Two conductance channels:

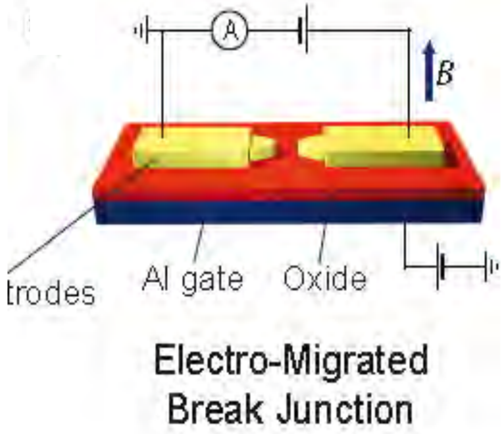
a) **A background transport channel that changes with stretching**
b) **Another channel responsible of zero-bias anomaly independent on stretching**

Electrical properties of PTM radical-based materials

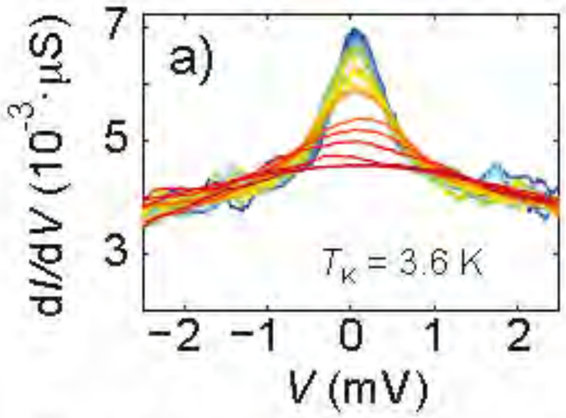
Charge transport through a single PTM radical molecule

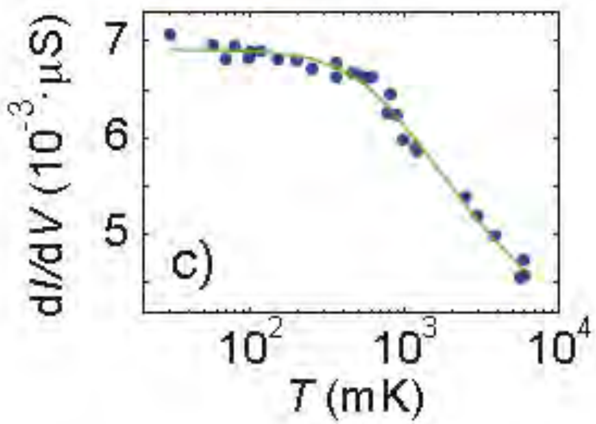
Conductances at temperatures between 30 mK and 4.5 K of a PTM radical junction with EMBJ

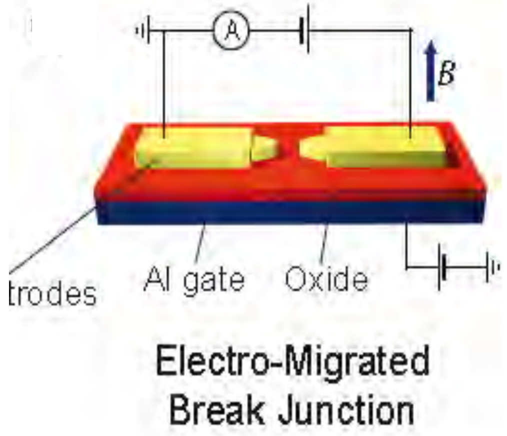


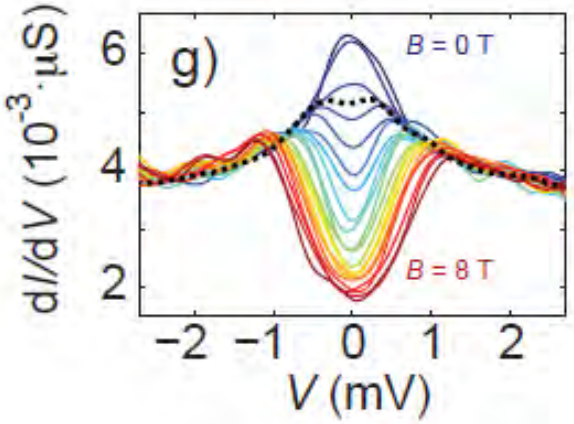


Zero-bias anomaly









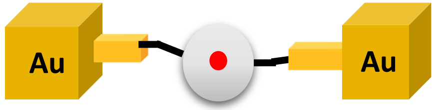
Kondo temperature; T_K = 3.0 K

Onset of Kondo splitting at B = 1.2 T

R. Frisenda, et al. *Nano Lett*, 2015, 15, 3109

Electrical properties of PTM radical-based materials

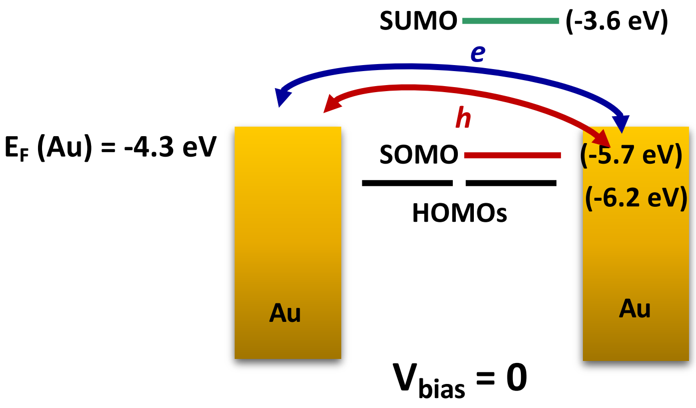
Charge transport through a single PTM radical molecule



2 Off-resonant conductance channels:

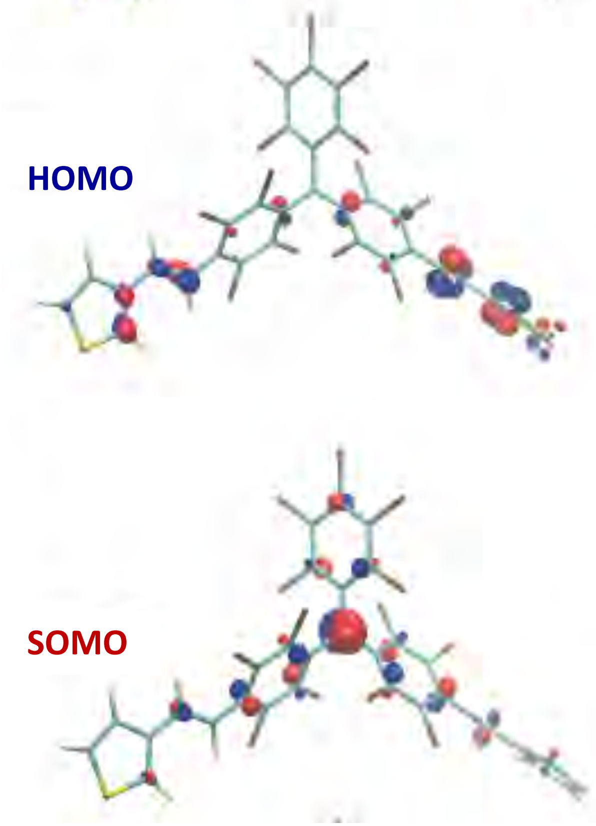
SUMO-assisted transport channel

SOMO-assisted transport channel



The strong localization of the SOMO makes the Kondo resonance stable under large molecular stretchings/distorsions

DFT calculations of energy levels with B3LYP hybrid functional



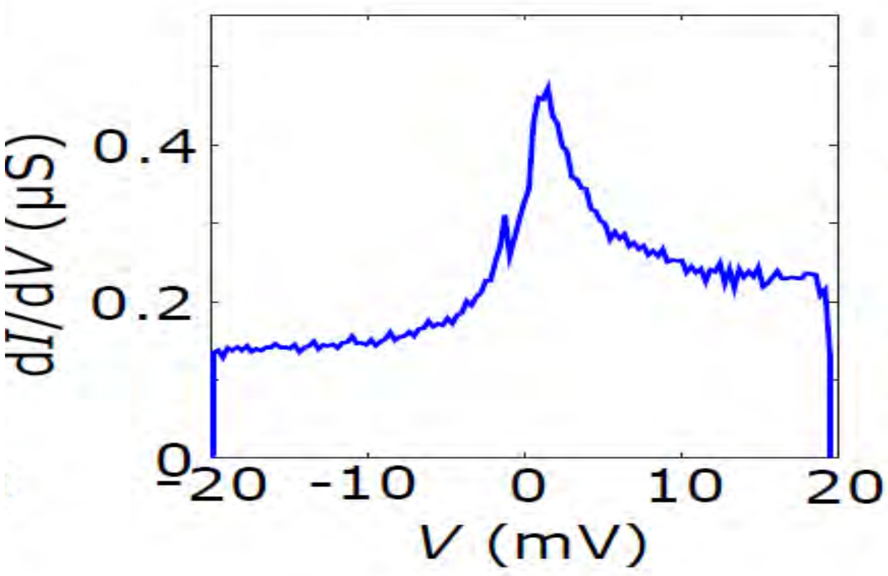
<u>SUMO-assisted transport channel</u> is responsible for the spin-independent <u>conductance background</u>

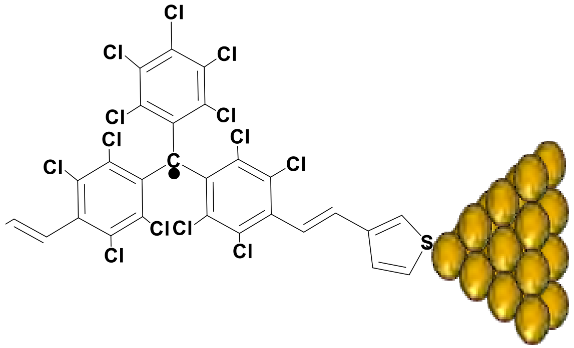
<u>SOMO-assisted transport channel</u> is responsible for the <u>Kondo-correlated phenomena</u>

Electrical properties of PTM radical-based materials

Molecule/electrode contact dependance of transport through single PTM radical molecules

Zero-bias resonance at 4 K
(Kondo correlation)





Conductances are more spread, a signature of a weaker Au-S bonds with ill-defined molecule-metal contacts

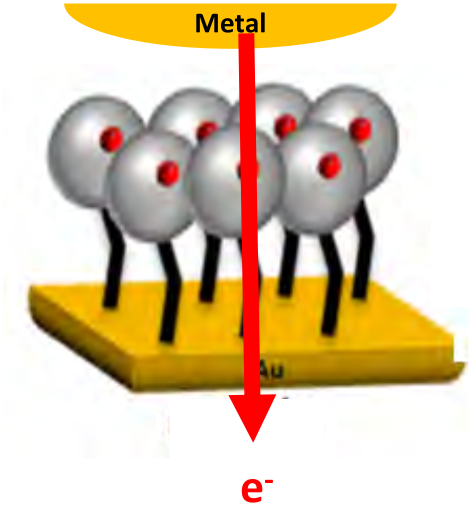
σ Au-C bonds are more robust and have less variability in conductance values ¡¡¡¡

F. Bejarano et al, *J. Am. Chem. Soc.* 2018, *140*, 1691

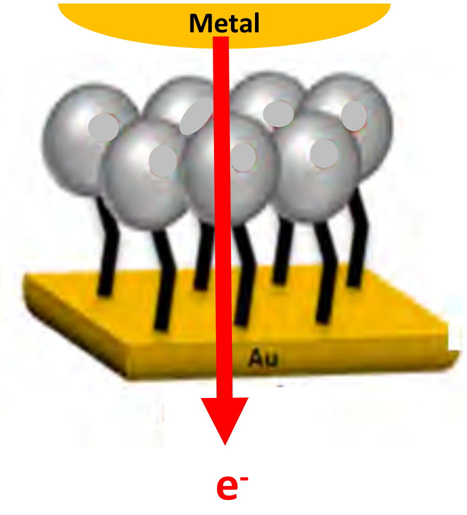
Electrical properties of PTM radical-based self-assembled monolayers

Charge transport through organic radicals anchored to metals

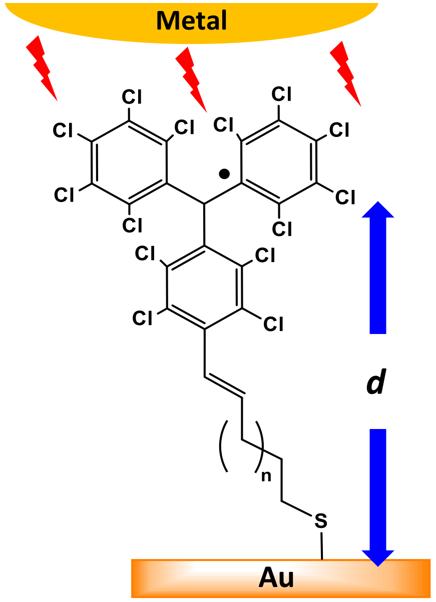
PTM SAM junctions



PTM radical SAM junctions (R-SAMs)



PTM non-radical SAM junctions (NR-SAMs)



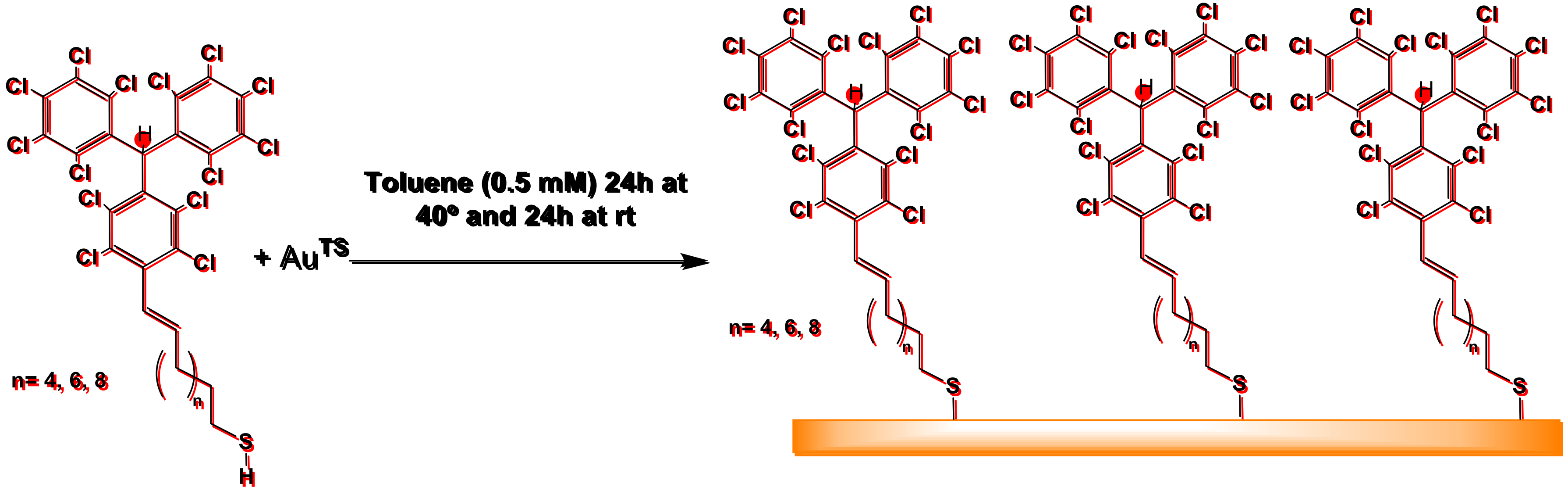
Characteristics of junctions:

- PTM heads are decoupled from the Au bottom-electrode via long alkyl chains guaranteeing the same work functions of in both junctions
- Controlling the PTM distance to Au, *d*, changing $(CH_2)_n$; n = 4, 6, 8
- Similar PTM head/top-electrode interactions via van der Waals interfaces

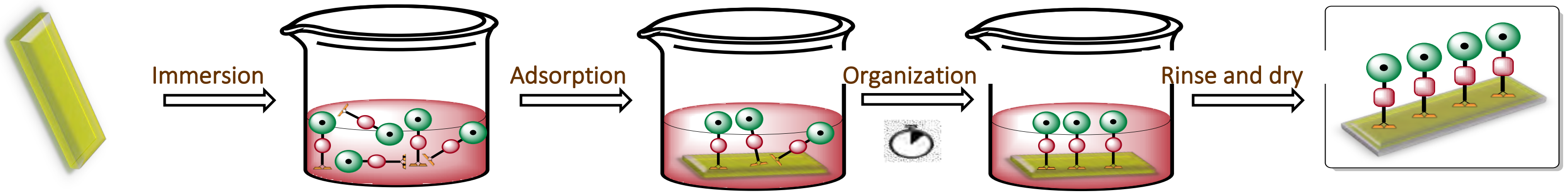
In collaboration with C. A. Nijhuis and Y. Li (Nat. Univ. Singapore)

Electrical properties of PTM radical-based materials

Preparation of PTM radical SAM (R-SAM) and non-radical SAM (NR-SAM)on Au(111)



Au^{TS}-SC$_8$PTM$_{non\text{-}rad}$..... Au^{TS}-SC$_{12}$PTM$_{non\text{-}rad}$



Ultra-flat Au substrate

Immersion

Toluene 0.5 mM solution of molecules

Adsorption

40 ºC (1h) /r.t. (48 h)

Organization

Rinse and dry

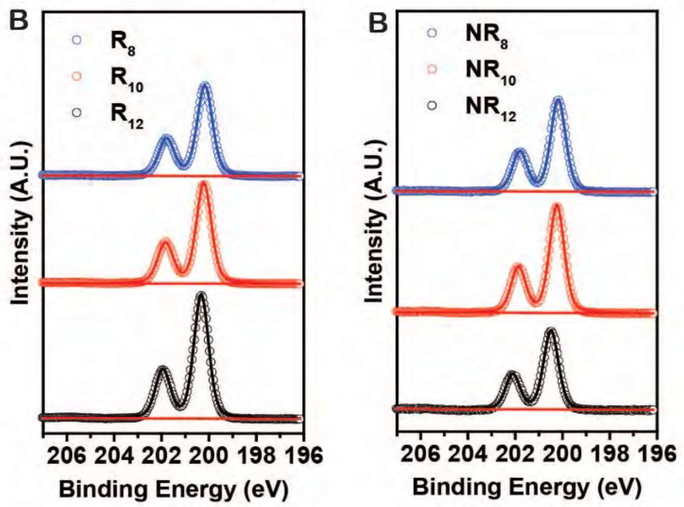
Formed SAM

Charge transport through PTM radical molecules anchored to metal surfaces

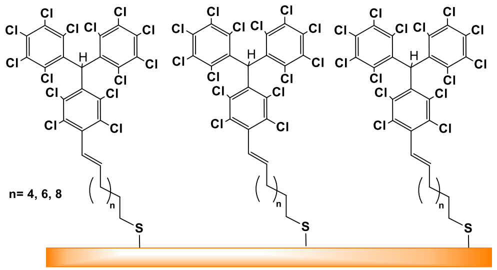
Supramolecular structure characterizations of PTM radical and non-radical SAMs on Au(111)

Angle resolved XPS (Cl 2*p* spectra)

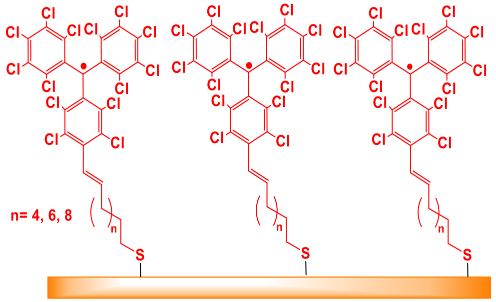
R-SAMs **NR-SAMs**



NR-SAMs

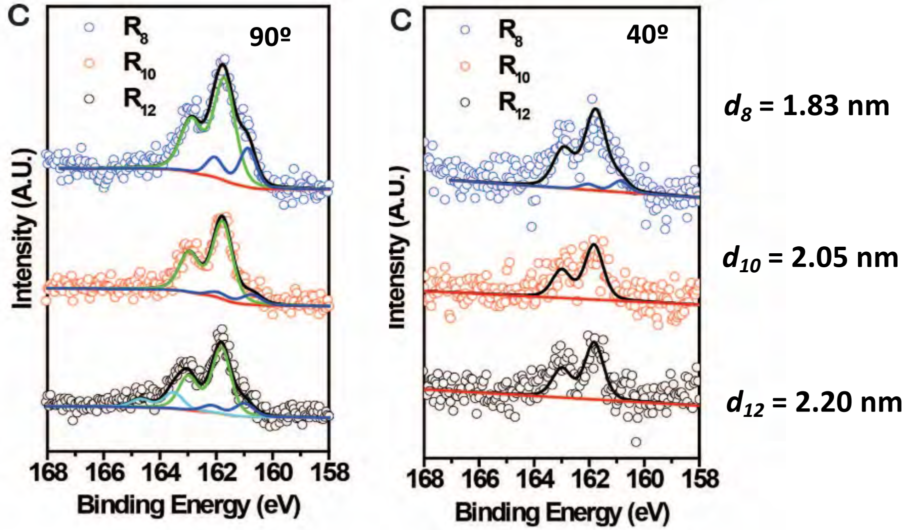


R-SAMs



Angle resolved XPS (S 2*p* spectra)

I_θ ratios of S 2*p* at take-off angles of 90º and 40º of SAMs



Radical and non-radical SAMs are laterally packed with similar molecular densities (0.15×10^{-9} mol/cm^2)

Molecules are standing-up on the surfaces with thickness, d, that scales with the number, n, of C atoms of alkyl chains of R-SAMs and NR-SAMs

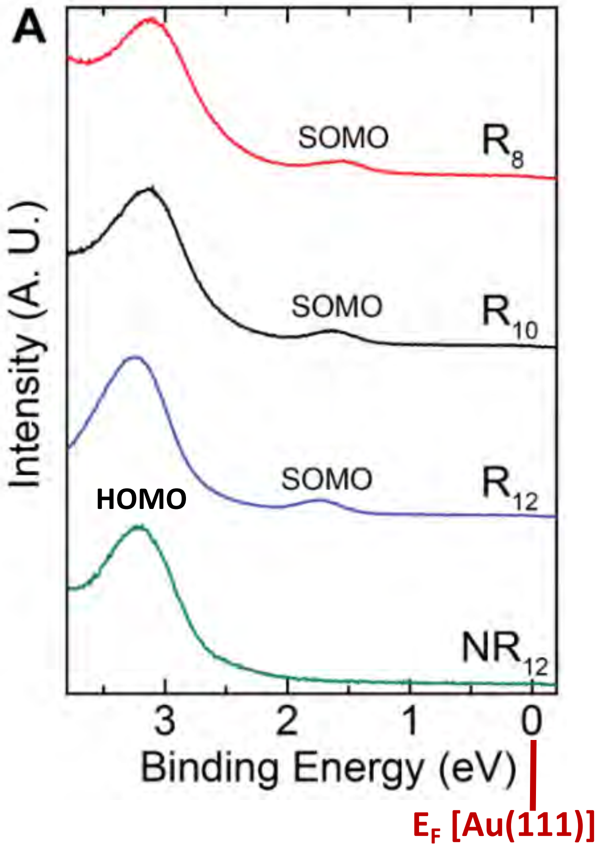
R-SAMs and NR-SAMs have similar supramolecular structures

Other characterizations of SAMs: CA, ESR, CV

Electrical properties of PTM radical-based materials

Electronic structure determinations of PTM R-SAM and NR-SAMs on Au(111)

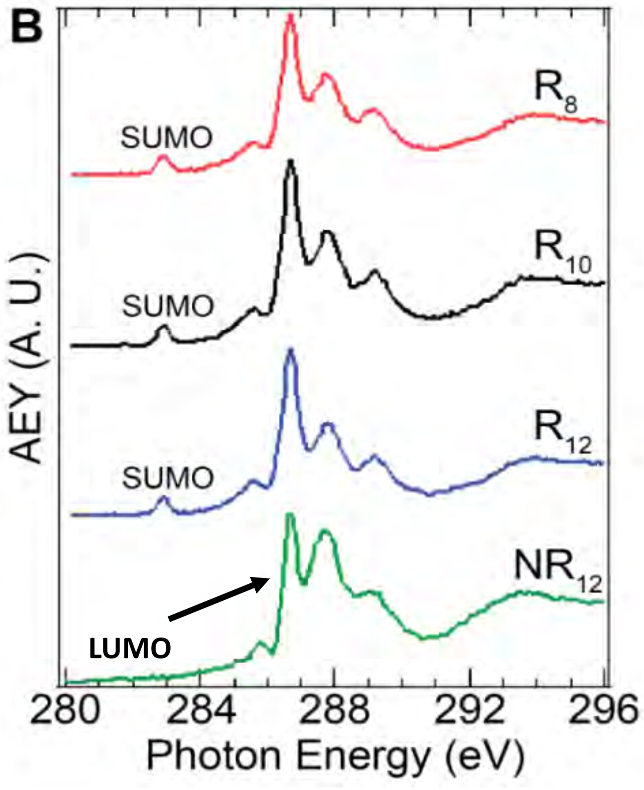
UPS



UPS, Ultra-violet photoelectron spectroscopy

Occupied levels

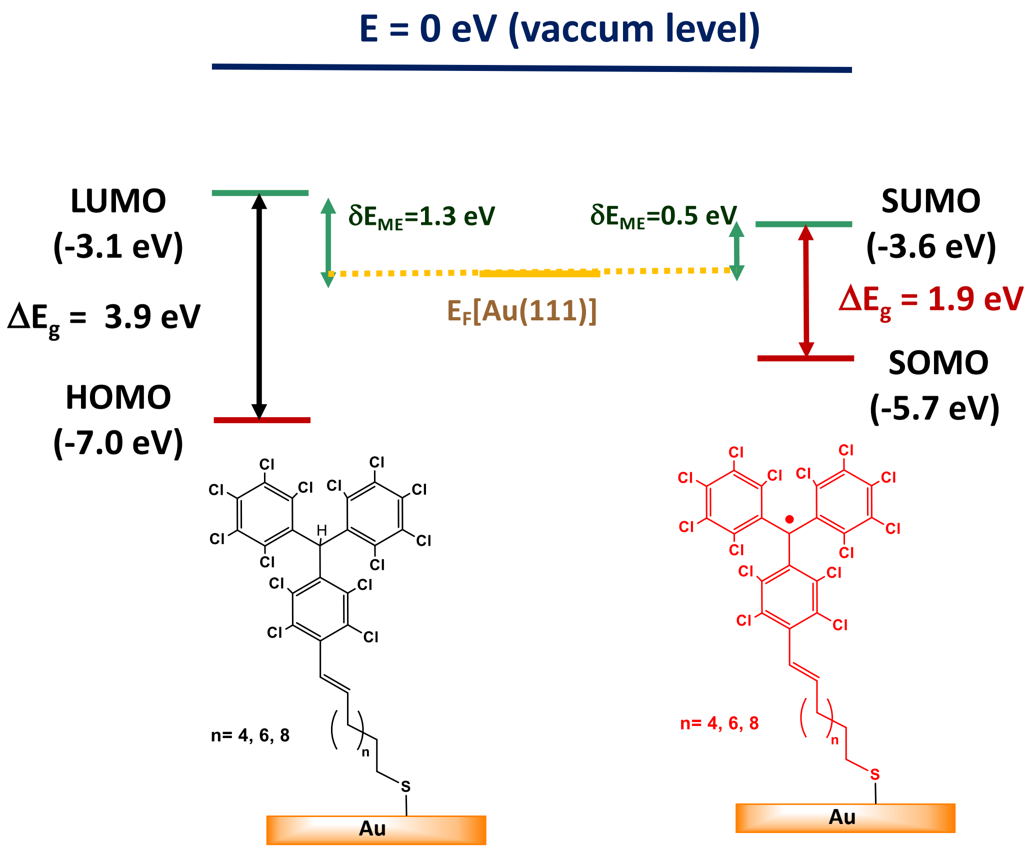
C K-edge NEXAFS



NEXAFS, Near edge X-ray adsorption fine structure spectroscopy

Unoccupied levels

Energy diagrams of frontier orbitals of SAMs



E = 0 eV (vaccum level)

LUMO
(-3.1 eV)

ΔE_g = 3.9 eV

HOMO
(-7.0 eV)

δE_{ME}=1.3 eV

δE_{ME}=0.5 eV

E_F[Au(111)]

SUMO
(-3.6 eV)

ΔE_g = 1.9 eV

SOMO
(-5.7 eV)

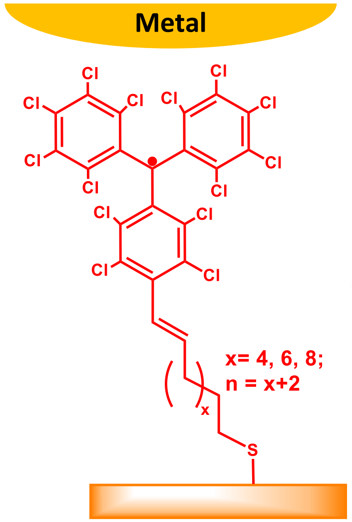
NR-SAMs

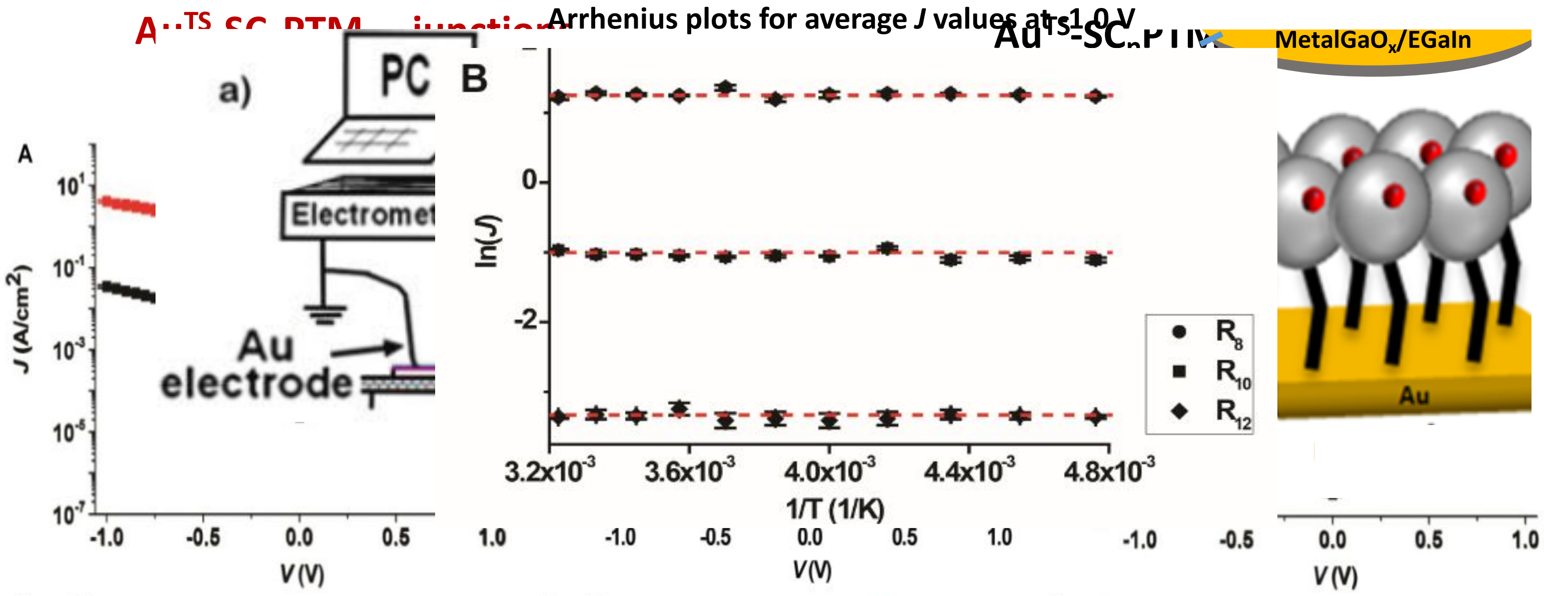
R-SAMs

Charge transport through PTM radical molecules anchored to metal surfaces

Charge transport measurements on Au^{TS}-PTM SAM//Ga_2O_3/EGaIn junctions

Current densities of radical and non-radical junctions at voltage bias range of -1.0 V/+1.0 V





Current densities at -1 V do not depend on temperature (210-340 K) confirming a charge transport through a coherent tunneling mechanism

In all three junctions and in the whole measured bias range the mean values $<|J|>_G$ for R-SAMs are 100 times higher than for NR-SAMs ¡¡¡¡

Current densities, J, of both SAMs decrease exponentially for larger chains suggesting that charge transport mechanism is in the coherent tunneling regime for both SAMs

Yuan Li et al., *Nature Comm.*, 2016, *7*, 12066

Charge transport through PTM radical molecules anchored to metal surfaces

Charge transport measurements on junctions as function of tunneling distances

Tunneling regime:

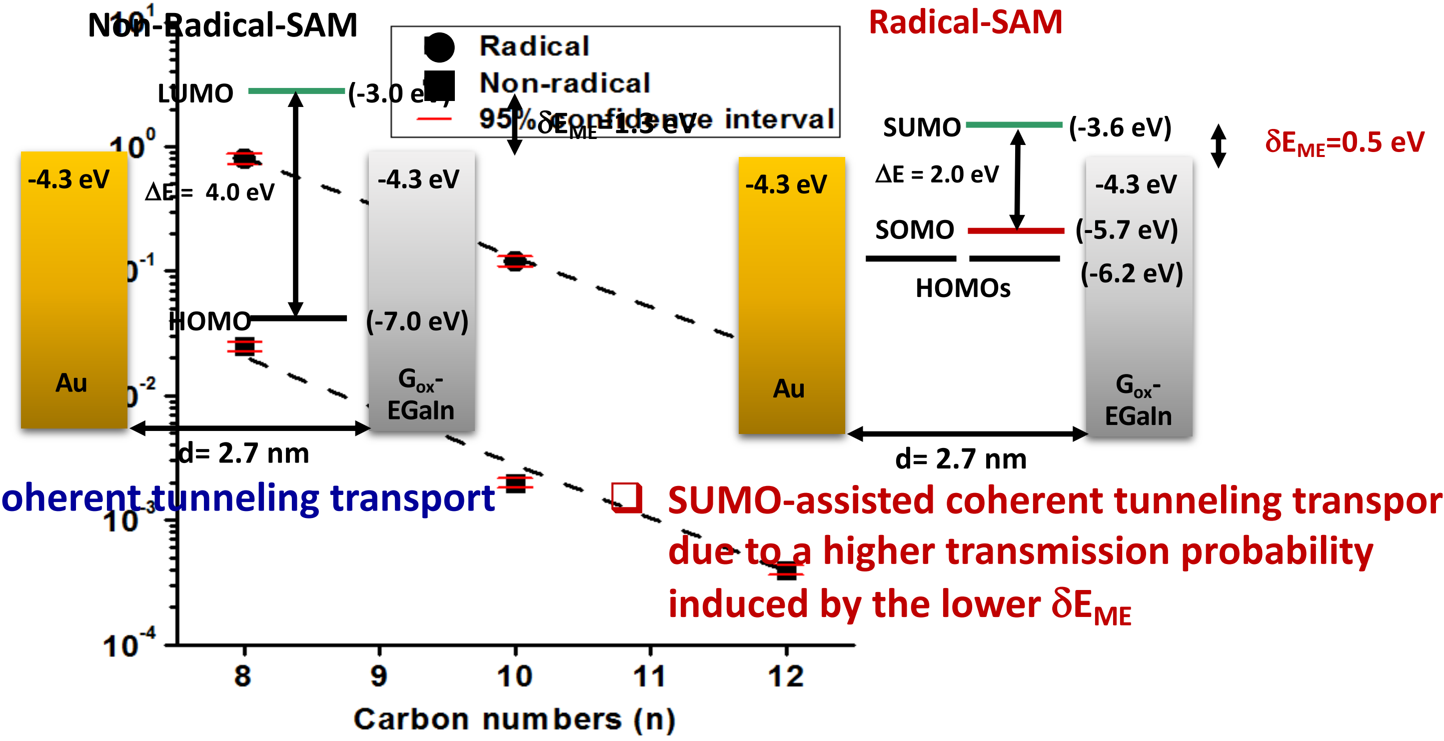
Current density J (A/cm^2) depends on the nº carbons (n_c) or the distance, d

$$J = J_0 e^{-\beta d}$$

β = tunneling decay constant

J_0 = pre-exponential factor

$\langle \log|J| \rangle_G$ values determined at -1.0 V



- ☐ **Coherent tunneling transport**
- ☐ **SUMO-assisted coherent tunneling transport due to a higher transmission probability induced by the lower δE_{ME}**

Radical SAMs;	**J_0^R = 1018 A/cm^2 β_R = 0.89±0.01 n_c^{-1} (β = 0.72 Å^{-1})**
Non-radical SAMs;	**J_0^{NR}= 78 A/cm^2 β_{NR} = 1.03±0.03 n_c^{-1} (β = 0.82 Å^{-1})**

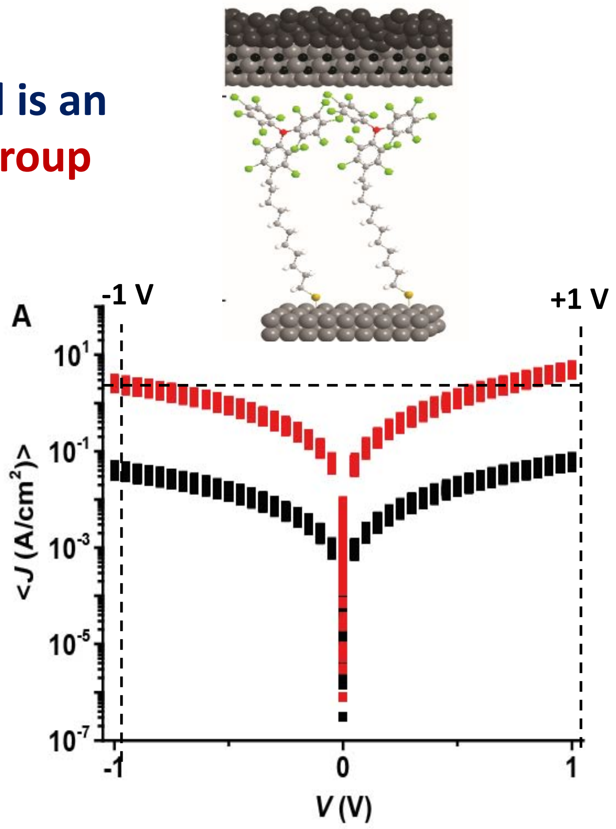
Transport through a coherent tunneling mechanism in both kinds of SAMs

Y. Li, N. Crivillers et al. *Nature Commun.*, 2016, *7*, 12066

Charge transport through PTM radical molecules anchored to metal surfaces

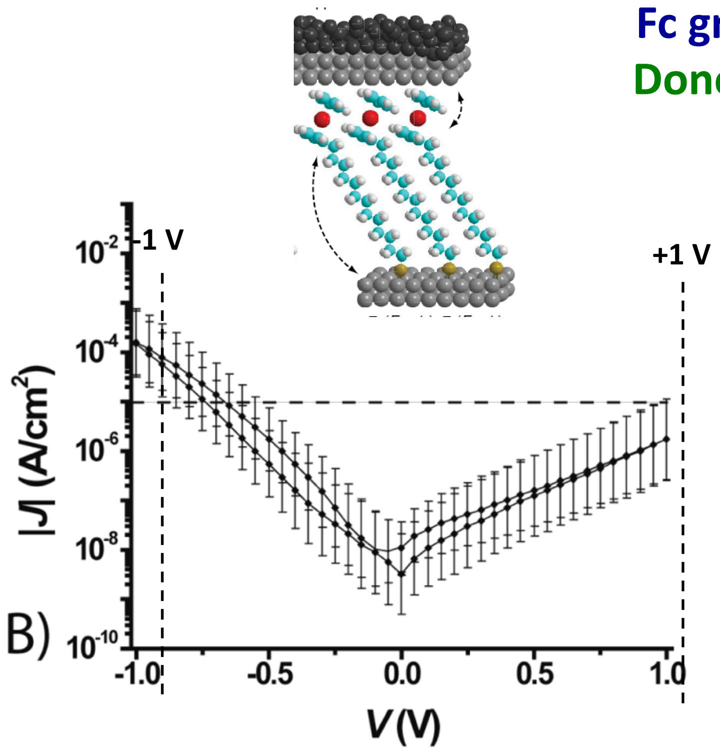
Current rectification in junctions with asymmetrically located electroactive groups

PTM radical is an
Acceptor group



R =|J(-1V)|/|J(+1V)| = 0.7

Fc group is a
Donor group



RR =|J(-1V)|/|J(+1V)| = 150

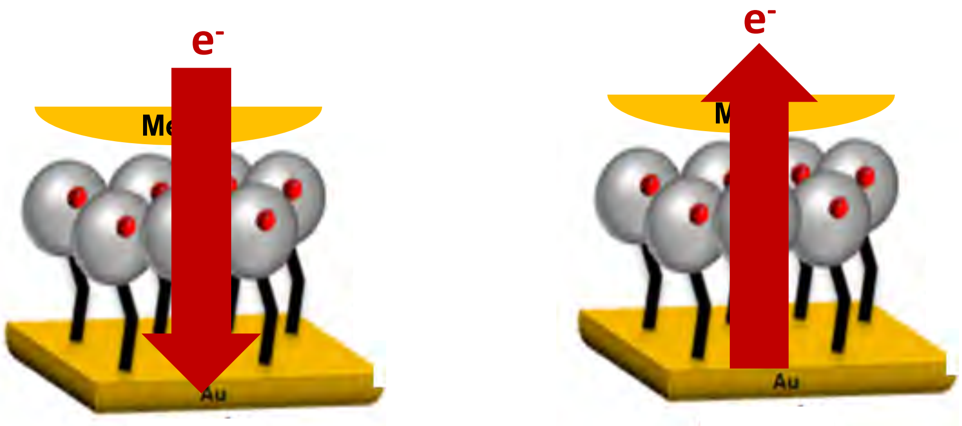
C. A. Nijhuis and col. *Nat. Commun.*, 2015, *6*, 6324

The lack of rectification in R-SAM and NR-SAM contrasts with the behavior of SAMs with electroactive groups energetically and spatially close to the top electrode and separated from the bottom one, like in Fc-SAMs

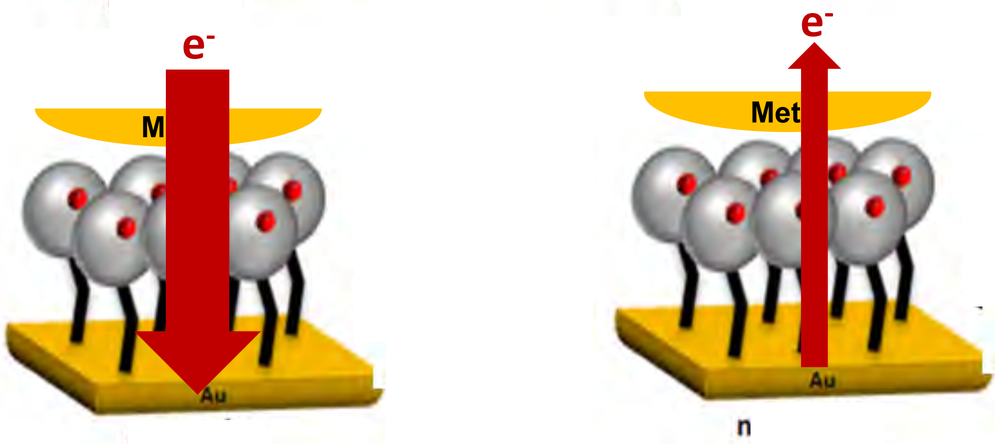
Charge transport through PTM radical molecules anchored to metal surfaces

Manipulation of charge transport through organic radicals anchored to metals

Radical SAMs on Au efficiently transport electrons:



How to achieve a rectifying Radical SAMs? :

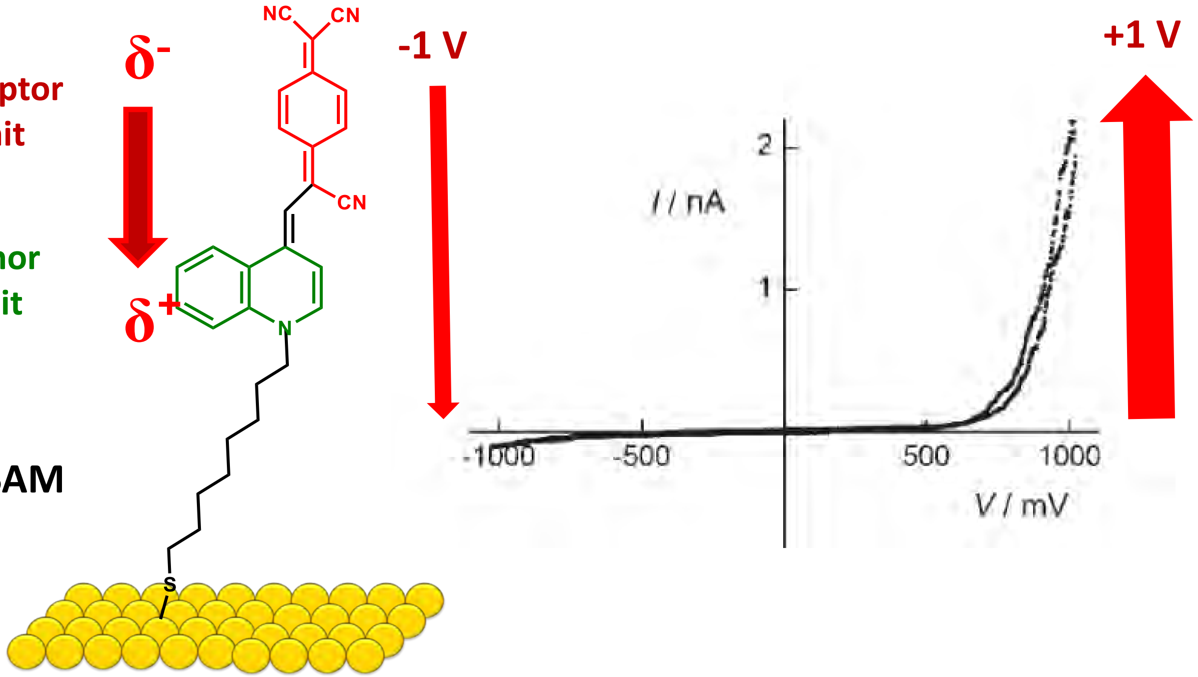


Charge transport through PTM radical molecules anchored to metal surfaces

Current rectification through SAMs based on Donor-π-Acceptor dyads

D-π-A dyad

$R = |J(+1V)|/\log|J(-1V)| = 30$



δ-

Acceptor unit

Donor unit

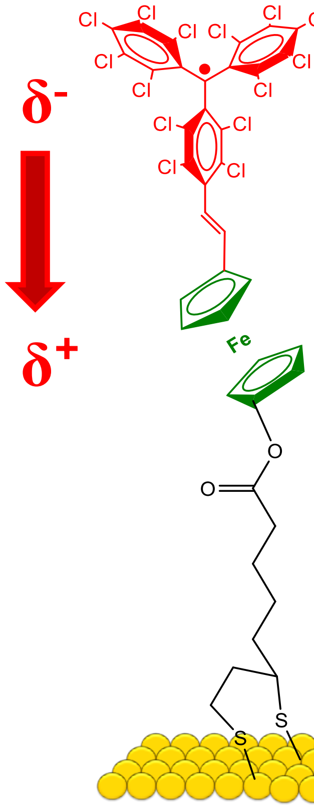
δ+

SAM

-1 V

+1 V

D-π-A dyad



δ-

δ+

PTM as an Acceptor unit

Fc as a Donor unit

R-SAM

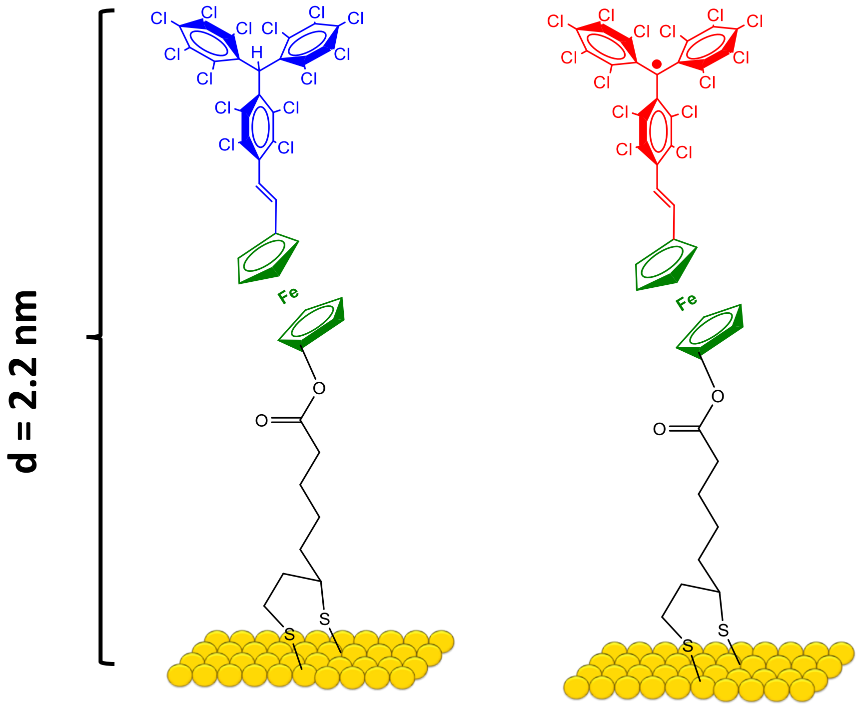
A. Girlando et al., *ChemPhysChem*, 2007, *8*, 2195–2201

Charge transport through PTM radical molecules anchored to metal surfaces

Charge transport through Au^{TS}-Fc-π-PTM$_{rad}$ dyad SAM//Ga$_2$O$_3$/EGaIn junctions

Preparation of radical and non-radical D-π-A SAMs

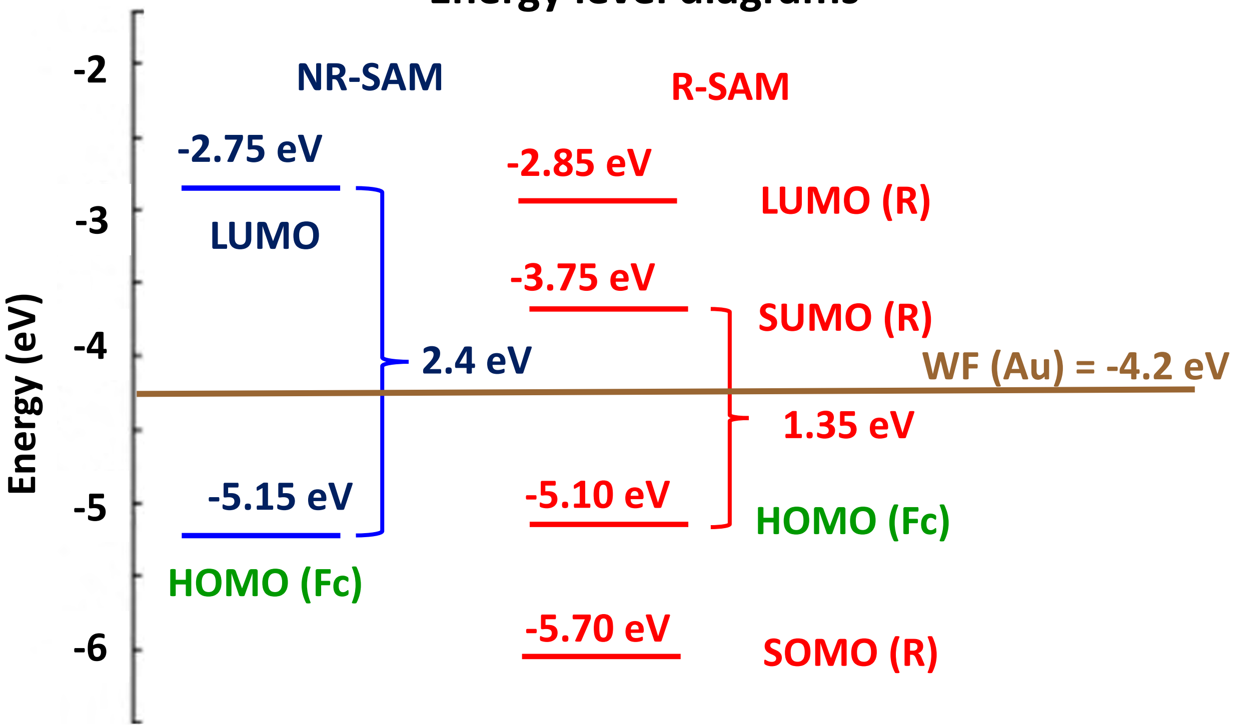
$\Gamma_{SAM} = 1.5 \times 10^{-10}$ mol/cm^2



NR-SAM **R-SAM**

Similar supramolecular structures of dyads (thickness, surface coverage)
Calculated from angle resolved XPS

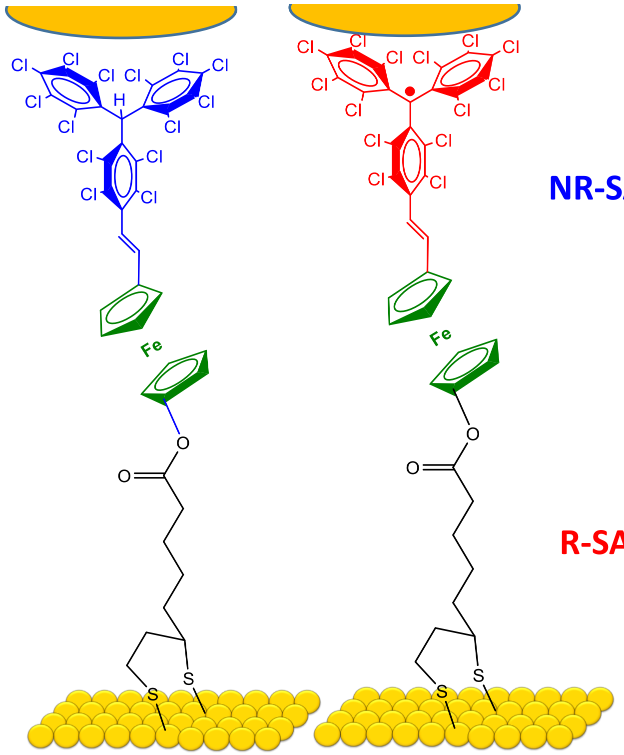
Energy level diagrams



Different electronic structures of dyads (frontier molecular orbital levels)
Calculated from CV, UPS and NEXAFS

Charge transport through PTM radical molecules anchored to metal surfaces

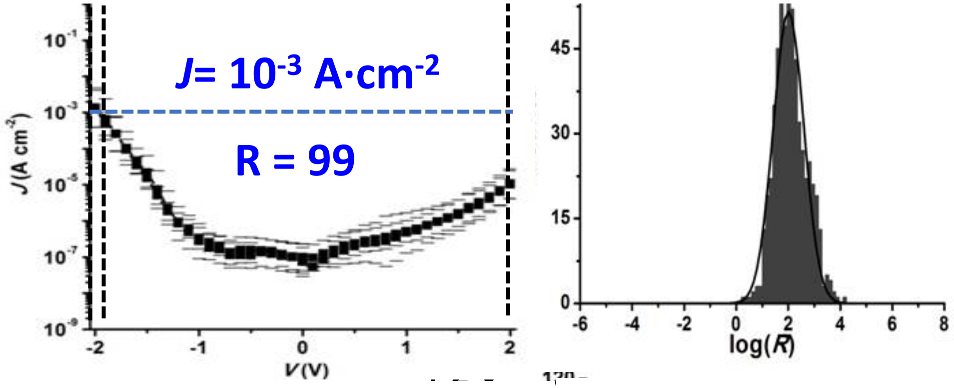
Current rectification through Au^{TS}-Fc-π-PTM dyad SAM//Ga_2O_3/EGaIn junctions



NR-SAM **R-SAM**

NR-SAM

R-SAM



Rectification ratio

$R = |J(-2.0V)| / |J(+2.0V)|$

Parameter	NR-SAM
Nº of junctions	25
Nº of shorts	3
Nº of traces	528
No shorting junctions (%)^a	88
Rectification ratio (R) (*d*log)^b	99 (0.7)

***J* values of R-SAM are 100 times higher than those of NR-SAM at all assayed bias voltages**

The rectification ratio is 99 for NR-SAM while it is only 6 for the R-SAM

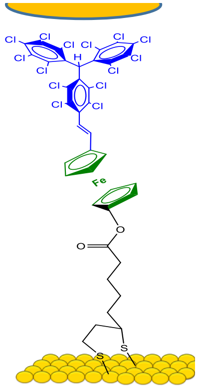
M. Souto et al. *J. Am. Chem. Soc.*, 2017, *139*, 4262

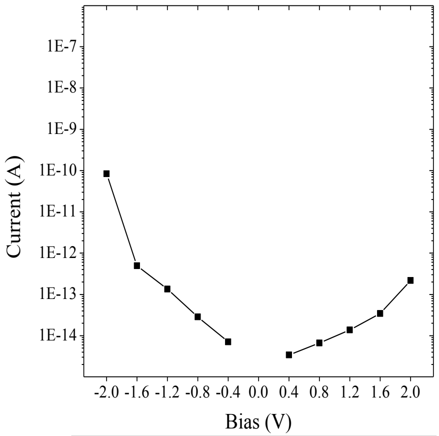
Charge transport through PTM radical molecules anchored to metal surfaces

Proposed mechanisms for the current rectification through Au^{TS}-Fc-π-PTM dyads SAM//Ga_2O_3/EGaIn junctions

Calculated current densities

NR-SAM

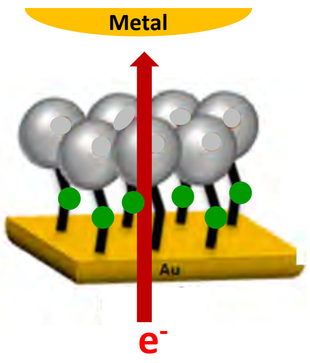




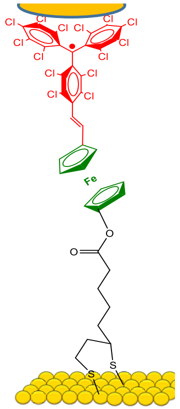
NR-SAM

$R_{SAM}(2V)=384$

+2 V

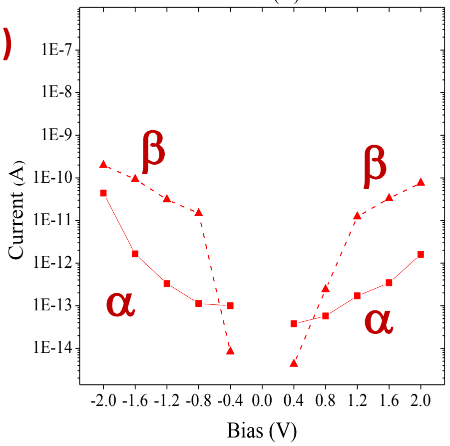


R-SAM



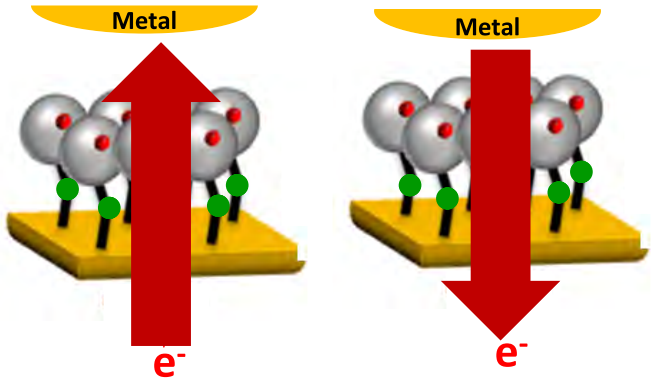
R-SAM (β-SUMO)

$R_{SAM\text{-}\beta}(2V)=3$



R-SAM (α-SOMO)

$R_{SAM\text{-}\alpha}(2V)=28$



Presence of SUMO orbital turns off the typical rectification properties of assimetric junctions because this orbital always is inside the Fermi window of electrodes.

Calculations at the DFT level with the SIESTA 3.2 package by J. Cornil (Mons Univ.)

M. Souto et al., *J. Am. Chem. Soc.*, 2017, *139*, 4262–4265

Electrical properties of PTM radical-based materials

Manipulation of the work function of a metallic surfaces using polar SAMs

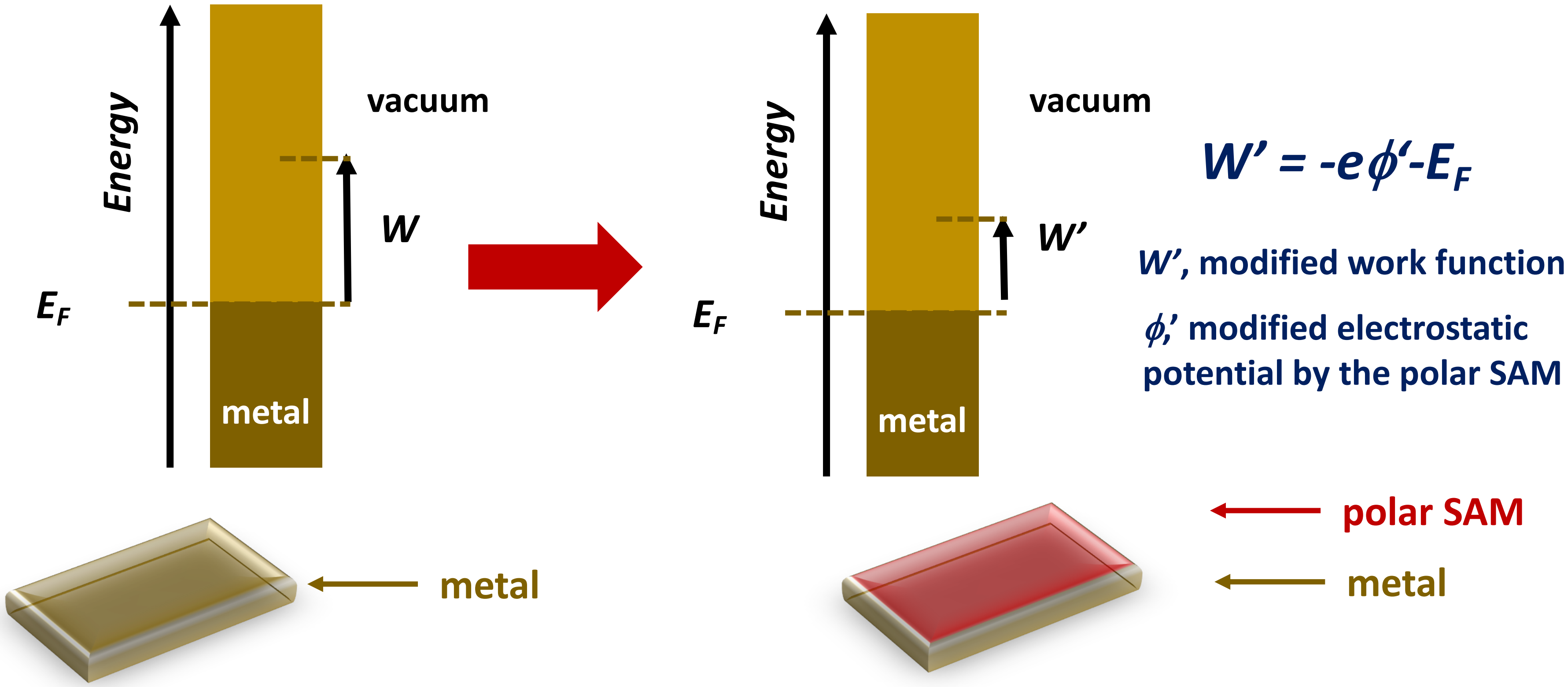
Work function (*W*) of a metal is the thermodynamic work required to remove an electron (*e*) from inside the metal to at state at rest in the vaccum nearby its surface

$$W = -e\phi - E_F$$

W, work function of metal

E_F, Fermi level of metal

ϕ, electrostatic potential in the vacuum nearby the metal surface



$$W' = -e\phi' - E_F$$

W', modified work function

ϕ,’ modified electrostatic potential by the polar SAM

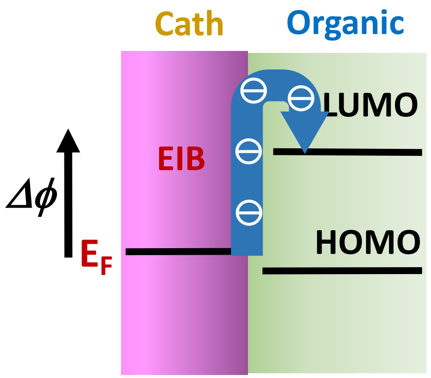
Work function shift: $W' - W = \Delta\phi$

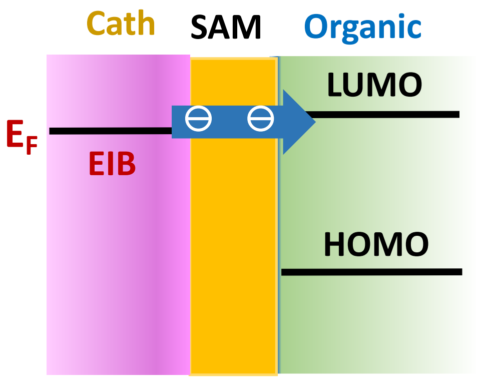
Electrical properties of PTM radical-based materials

Metallic work functions and charge injection barriers can be modified by dipolar SAMs

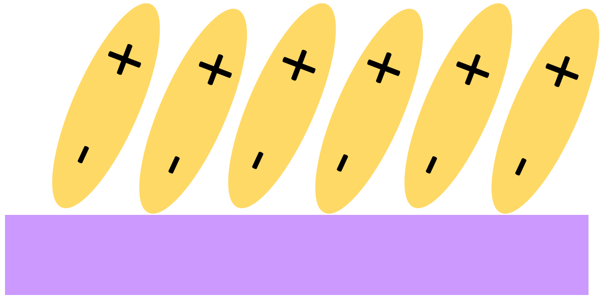
Manipulation of work function is important because the efficiency of molecular electronic devices (OFETs, OPVs) are dictated by the charge injection barriers

Dipolar SAMs

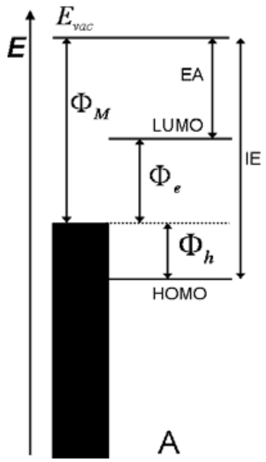




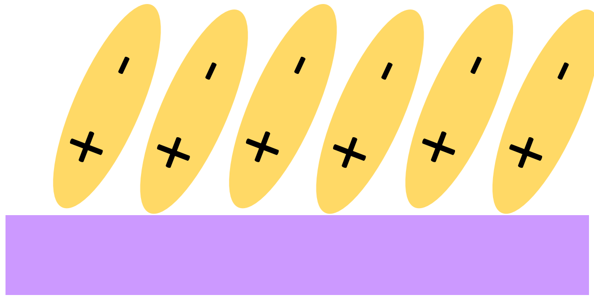
SAM with Positive Interfacial Dipole



Negative Work Function Shift (Δϕ <0)



SAM with Negative Interfacial Dipole



Positive Work Function Shift (Δϕ >0)

J.L. Bredas and col., *Acc. Chem. Res.* 2008, *41*, 721-729

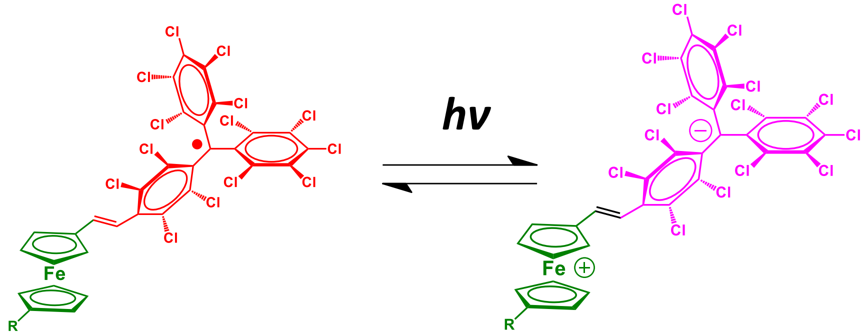
Electrical properties of PTM radical-based materials

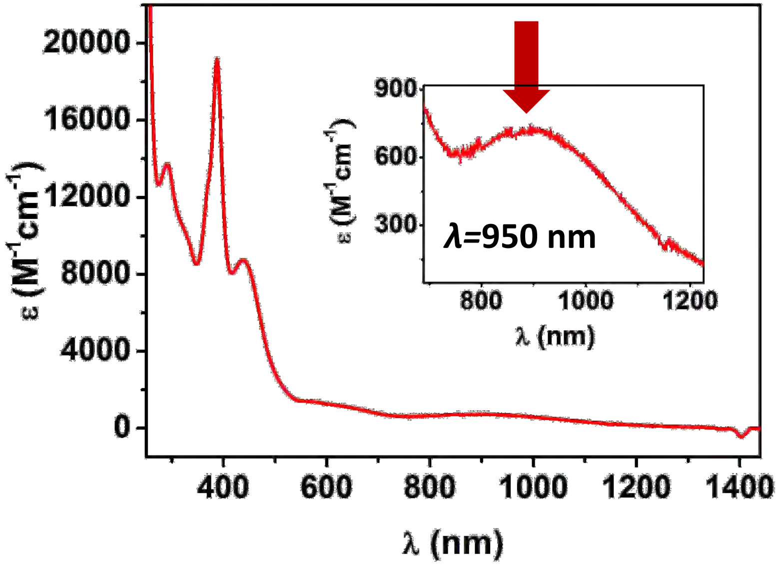
Manipulation of the work function of a gold surface, Au(111), using a bistable polar SAM

Bistable push-pull radical molecules

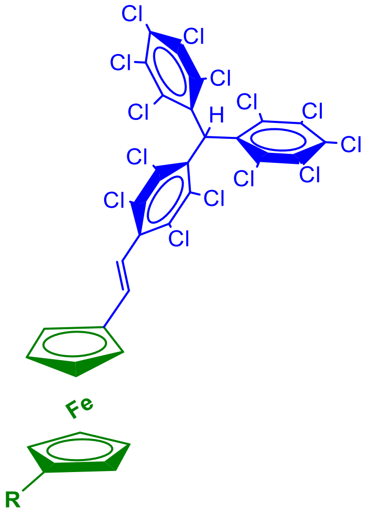
Neutral

D-π-A





Molecular bistability of Fc-π-PTM radical dyads

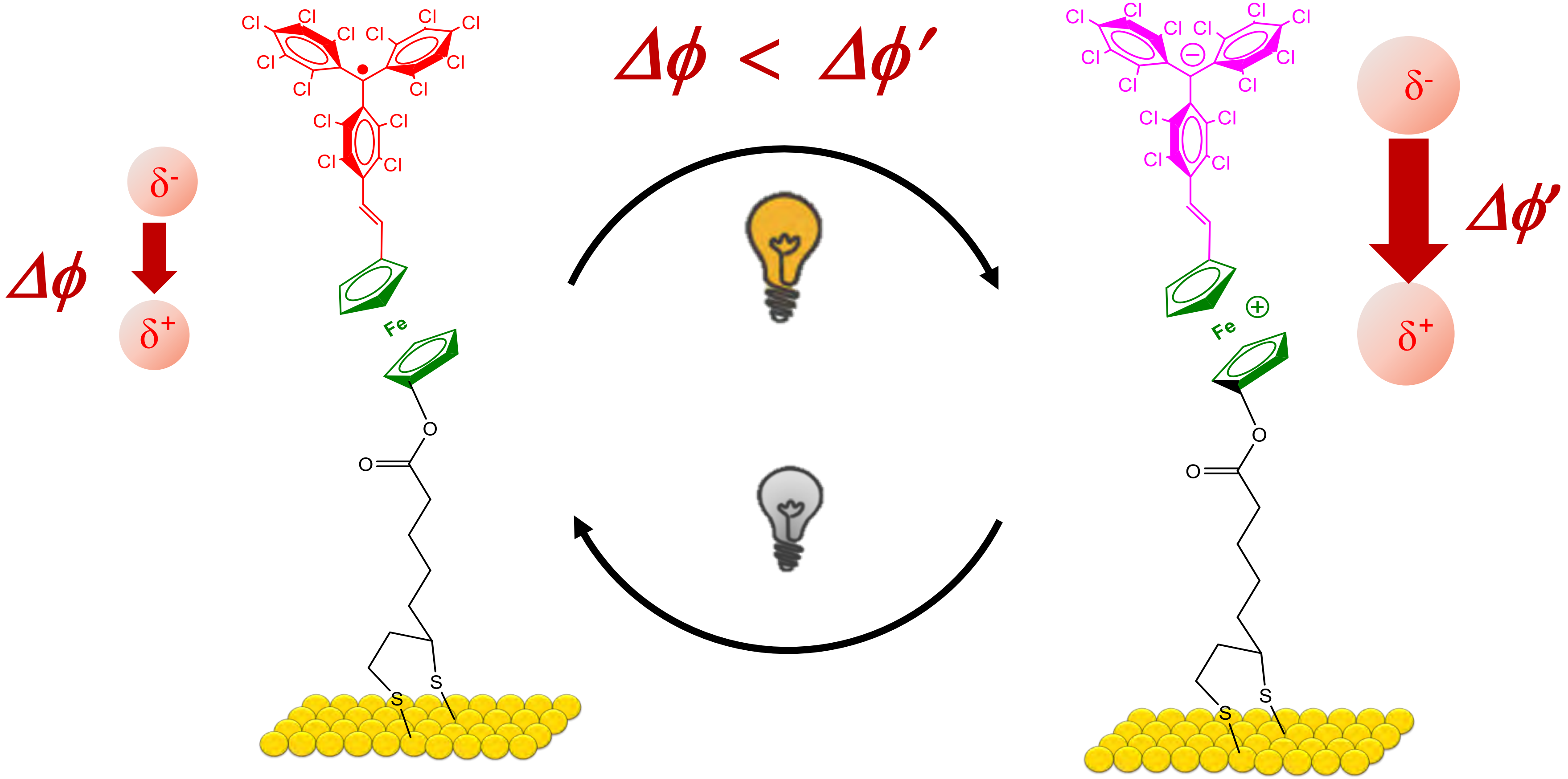


Non-radical derivative lacks of bistability

J. Guasch *et al. Chem. Mater.* 2013, *25*, 808

Electrical properties of PTM radical-based materials

Manipulation of the work function of a gold surface, Au(111) by an external stimulus, using a **bistable R-SAM**

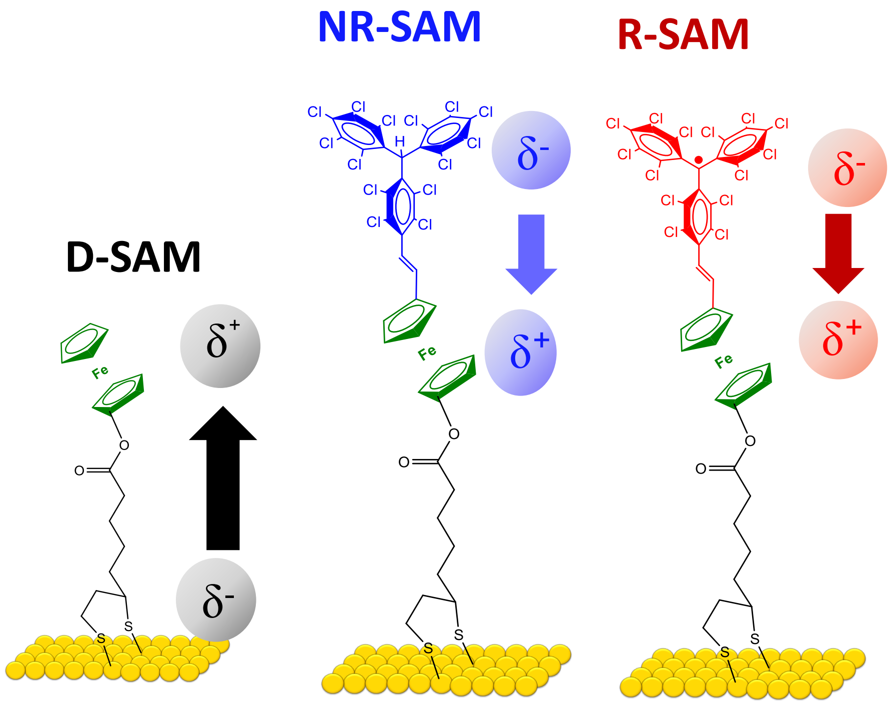


Switching the Au(111) work function

Electrical properties of PTM radical-based materials

Manipulatiion of the work function of a gold surface, Au(111), using dipolar SAMs

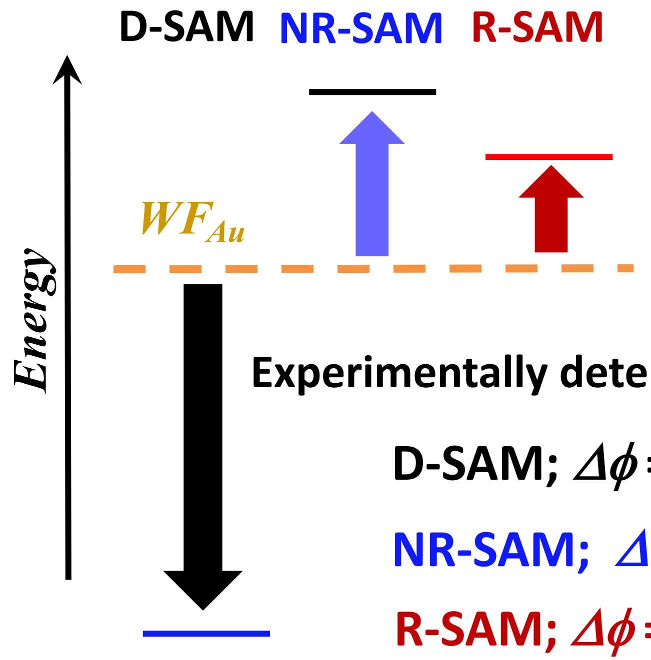
Work functions measured by the Contact Potential Difference (CPD) using Kelvin Probe Force Microscopy (KFPM) with an in-situ reference



Donor (D)

D-A closed-shell

D-A open-shell



Experimentally determined Δϕ values by KFPM

D-SAM; $\Delta\phi$ = -400 meV

NR-SAM; $\Delta\phi$ = +55 meV

R-SAM; $\Delta\phi$ = +20 meV

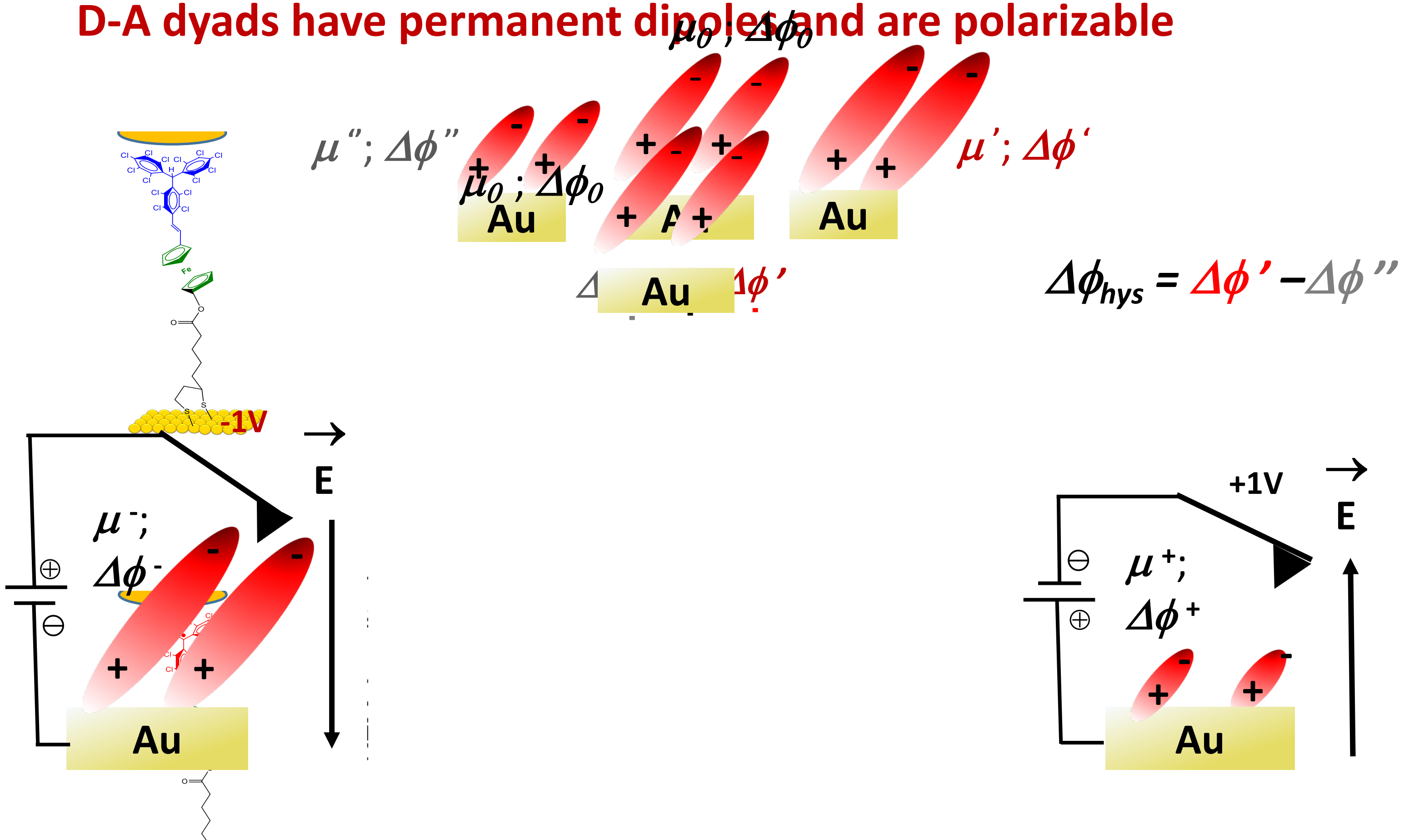
Work function shifts (Δϕ) are in accordance with DFT calculated dipole moments of D-A dyads, their polarizabilities and the depolarization effects

V. Diez-Cabanes et al. *Adv. Mater. Tech.*, 2018, 1800152

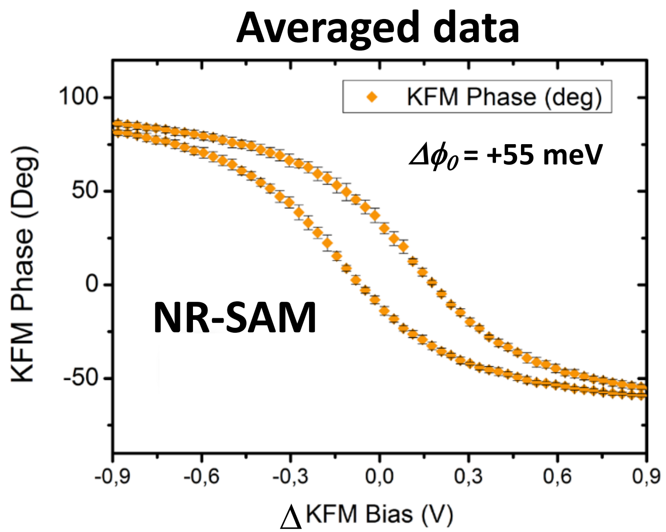
Electrical properties of PTM radical-based materials

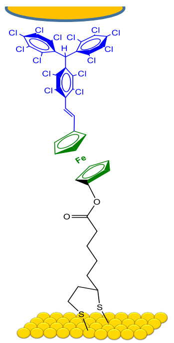
Modification of the work function of a gold surface with polarizable Fc-π-PTM SAMs by an external electrical potential generated in KPFM

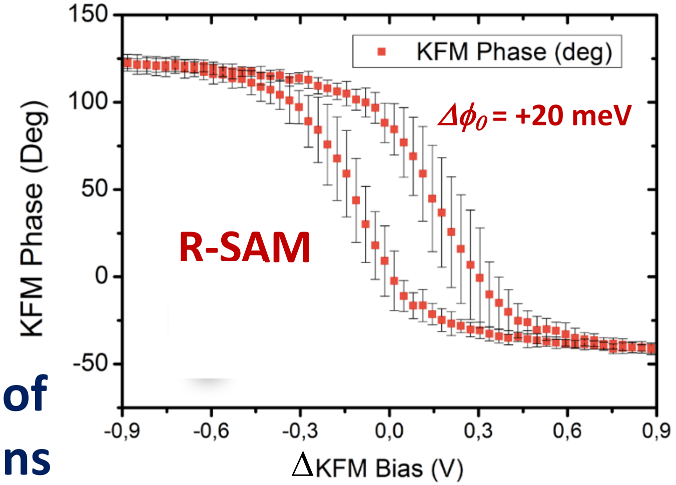
D-A dyads have permanent dipoles and are polarizable

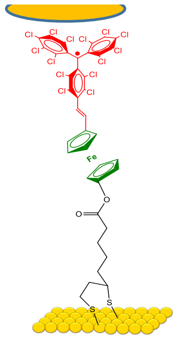


$$\Delta\phi_{hys} = \Delta\phi' - \Delta\phi''$$





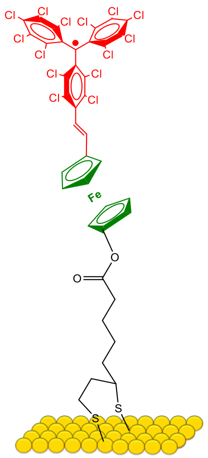




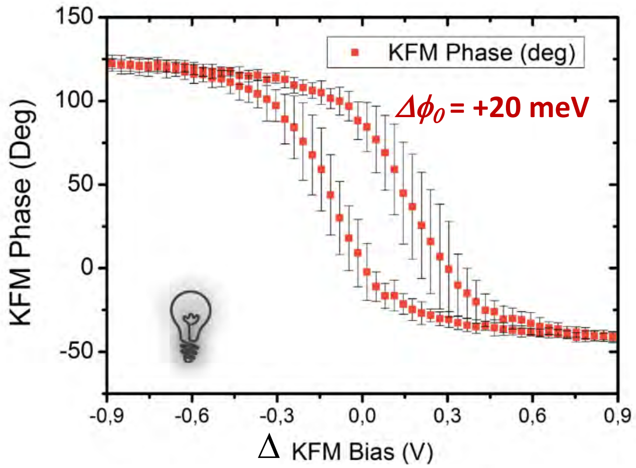
Hysteretic behaviours of WFs for both SAMs due to the polarizability of molecular dyads and the presence of intermolecular dipole interactions

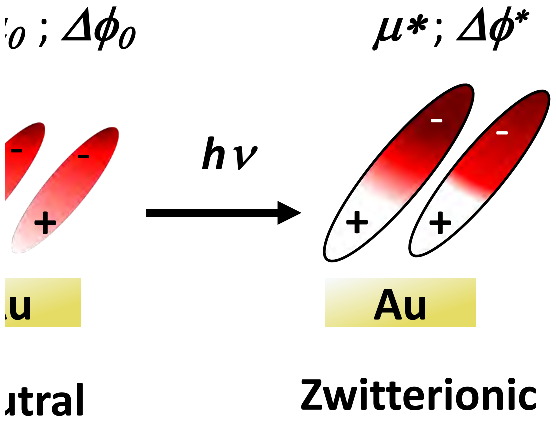
Electrical properties of PTM radical-based materials

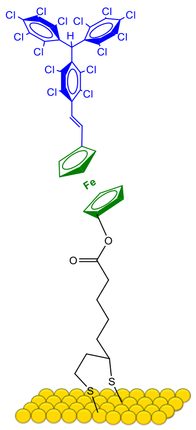
Modification of surface potential with Fc-π-PTM SAM under an external stimulus by a NIR (950 nm) irradiation



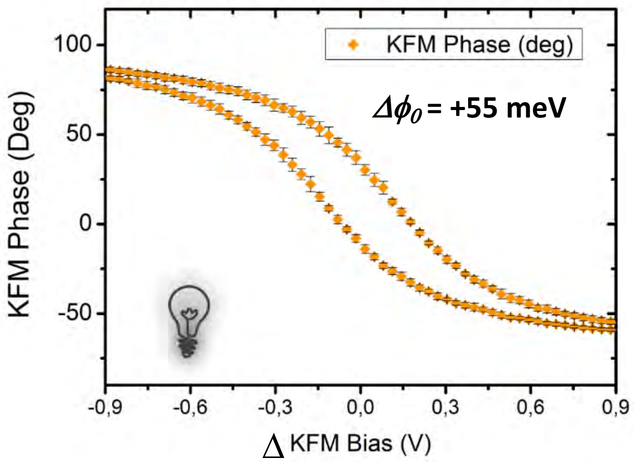
R-SAM

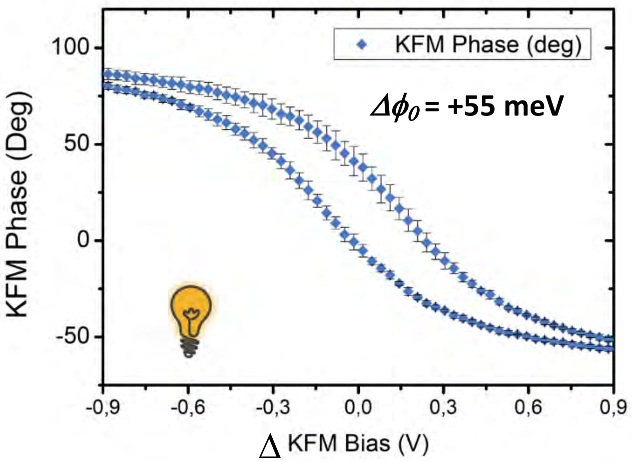


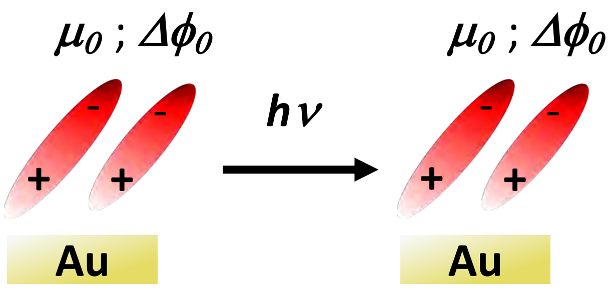




NR-SAM



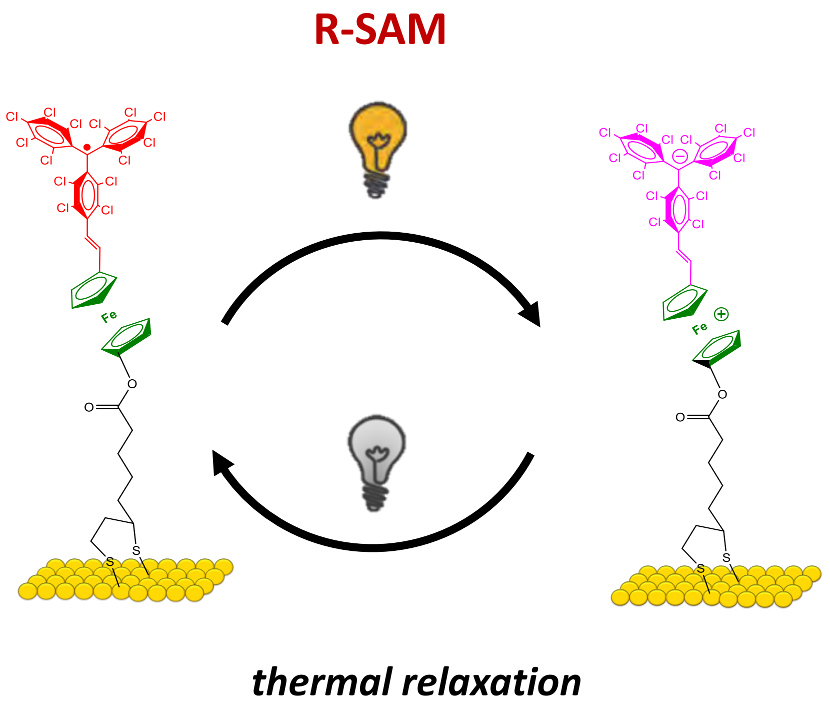


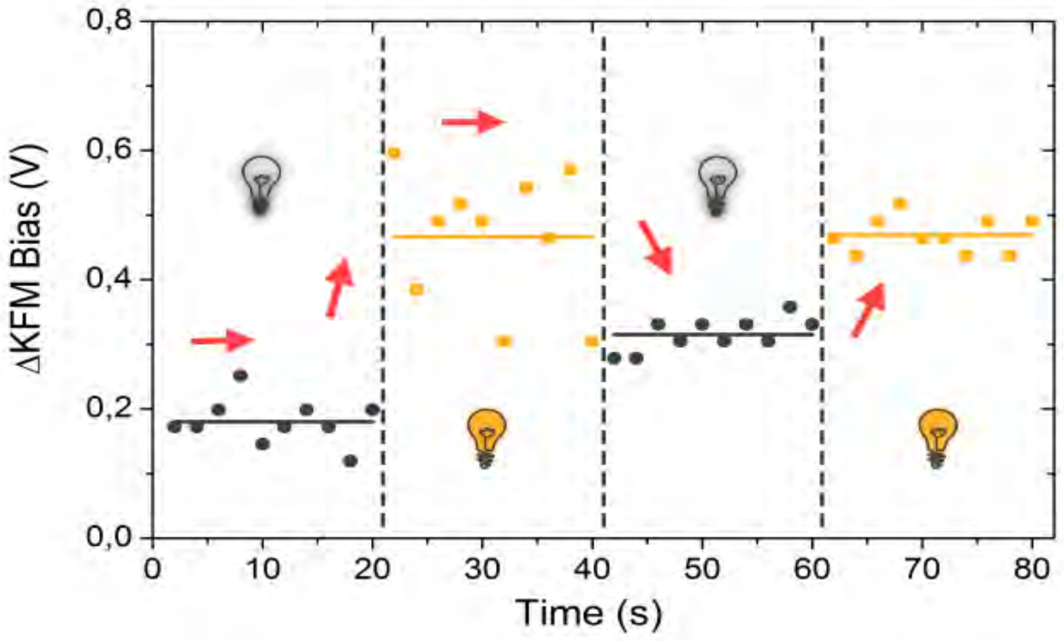


V. Diez-Cabanes et al. *J. Mater. Chem. C*, 2019, *7*, 7418-7426

Electrical properties of PTM radical-based materials

Metallic surfaces with photoswitchable work function using a dipolar Fc-π-PTM radical SAM



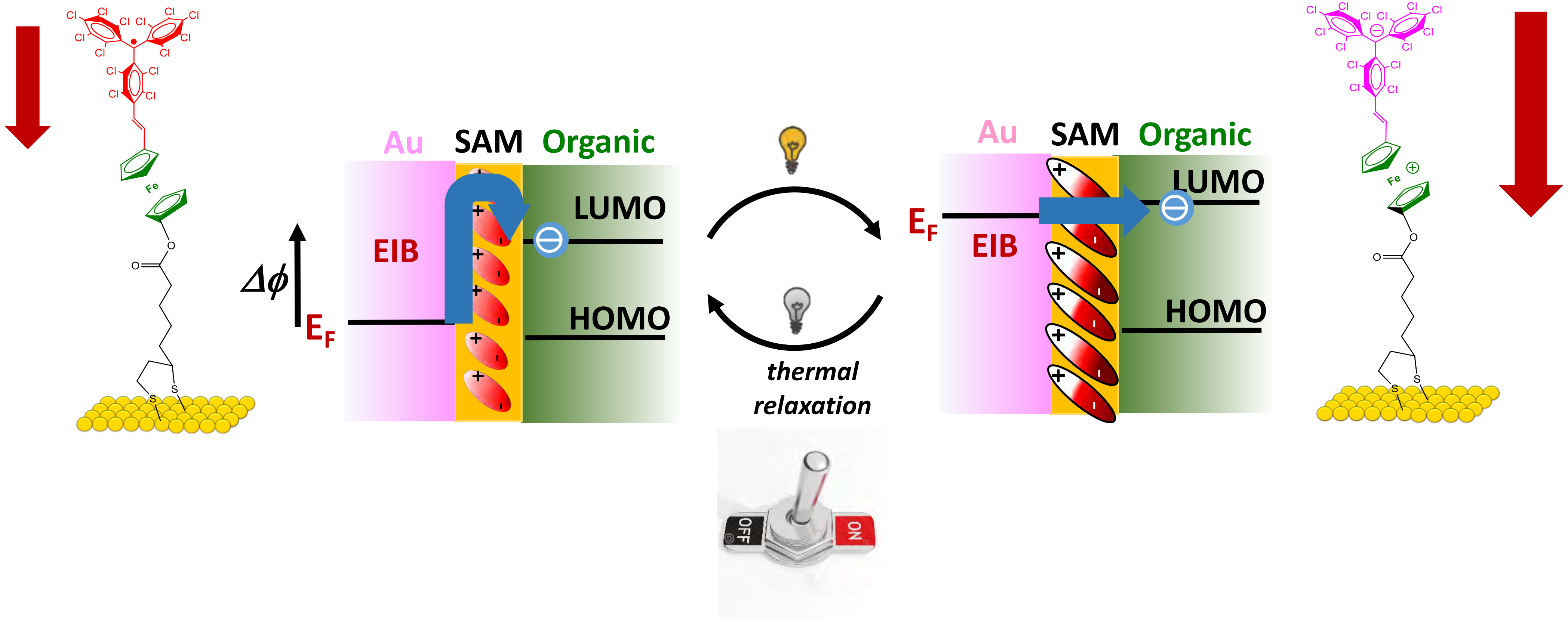


Reversible photoswitchable work function….

Why is interesting this reversible switchability of WFs?

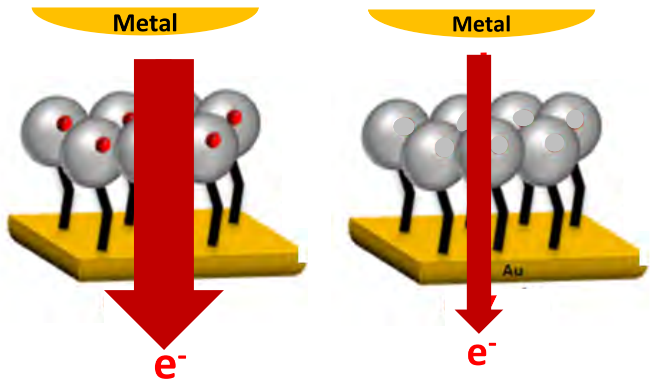
Possible aplications of PTM radical-based materials

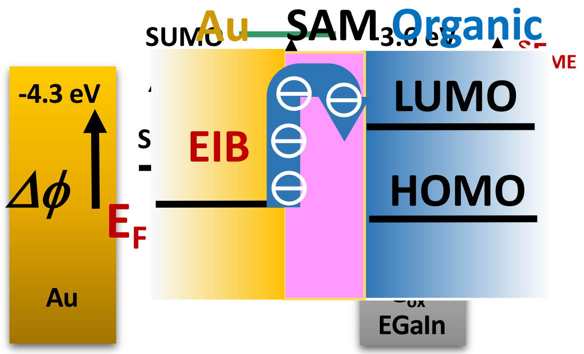
Metallic surfaces with photoswitchable work function using a dipolar Fc-π-PTM radical SAM

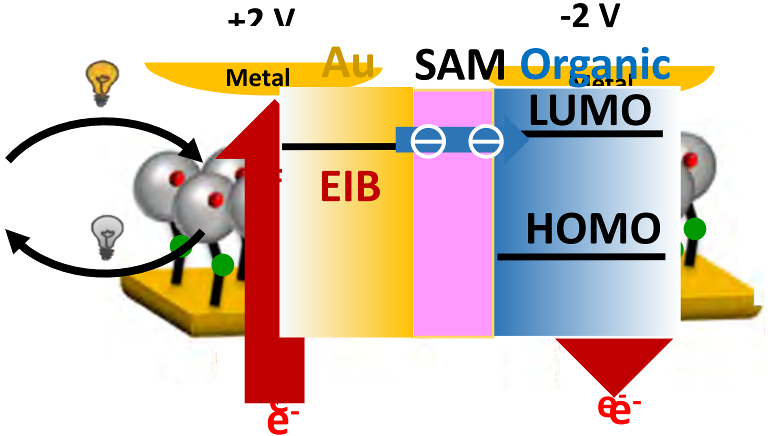


***WORK IN PROGRESS*: Photoswitching of charge injection barriers in organic electronic devices (OFETs, OPVs….) controlling their efficiency…**

Conclusions







❑ **Radical SAMs** in junctions are significantly more conducting (two orders of magnitude) than the **Non-Radical SAMs.**

❑ **Presence of accessible SUMO orbital close to metal WF enhances the transport of open-shell (radical) molecules.**

❑ **Non-radical SAMs with donor units (Fc) show considerable rectification values typical of junctions with electroactive groups energetically and spatially close to the top electrode and separated from the bottom one.**

❑ **Presence of accessible SUMO orbital of radicals, in radical SAMs, even with donor units (Fc), kills the typically expected rectification properties.**

❑ **Metallic surfaces with NIR photoswitchable work functions using dipolar Fc-PTM radical SAMs**

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Generalitat de Catalunya

EXCELENCIA
SEVERO
OCHOA

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UMONS

TUDelft
Delft University of Technology

NUS
National University of Singapore

ICMAB

CSIC

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Bioingenieria, Biomateriales y Nanomedicina

EXCELENCIA
SEVERO
OCHOA

Acknowledgements

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NANOMOL

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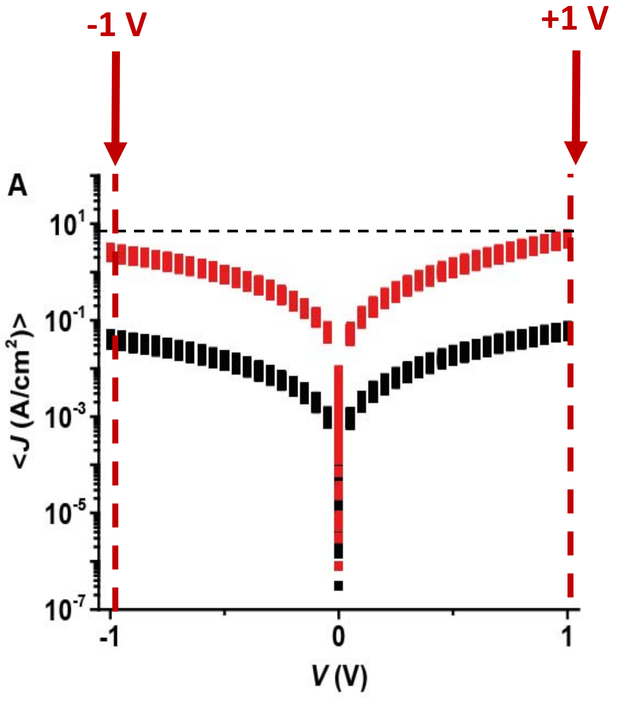
SEVERO
OCHOA

Thanks for you attention……

Charge transport through PTM radical molecules anchored to metal surfaces

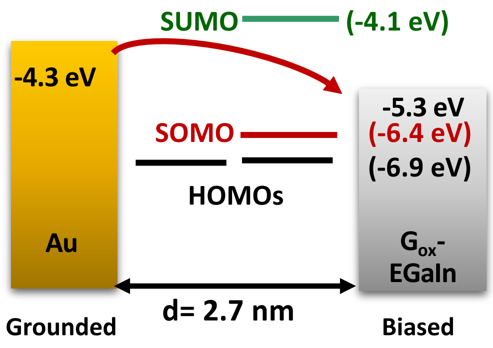
Charge transport through organic radicals anchored to metals

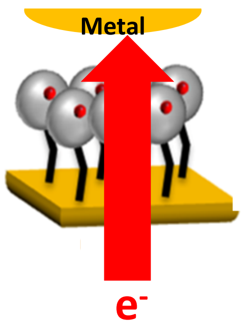


R =|J(-1V)|/log |J(+1V)| = 0.7

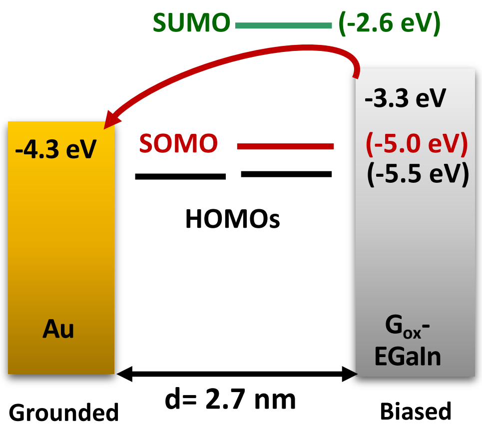
Radical-SAM

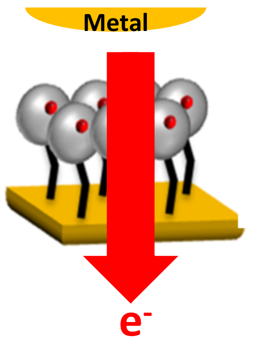
+1 V





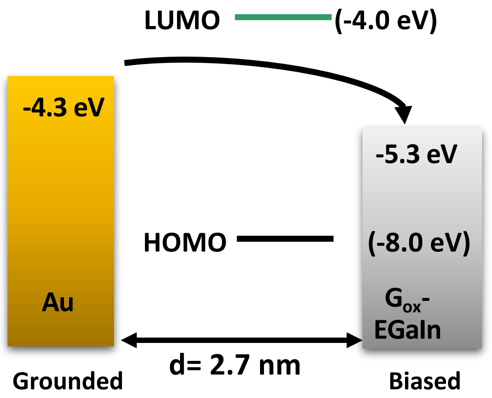
-1 V

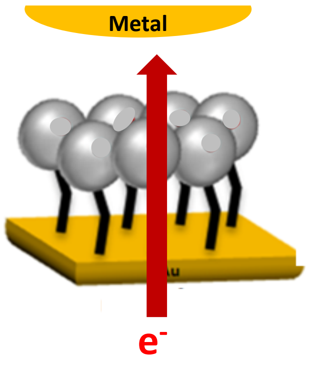




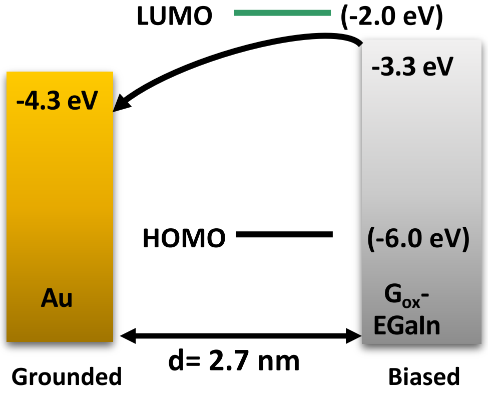
Non-Radical-SAM

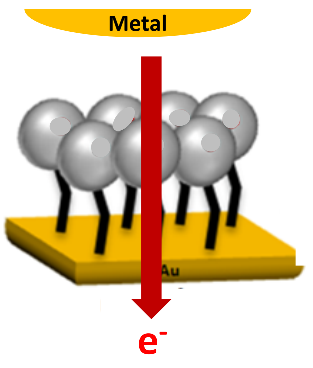
+1 V





-1 V





*Radical SAMs in junctions are two orders of magnitude more conducting than **Non-Radical SAMs** but there is no rectification in both SAMs*

Electrical properties of PTM radical-based materials

Charge/spin transport modelisation through a single PTM radical molecule

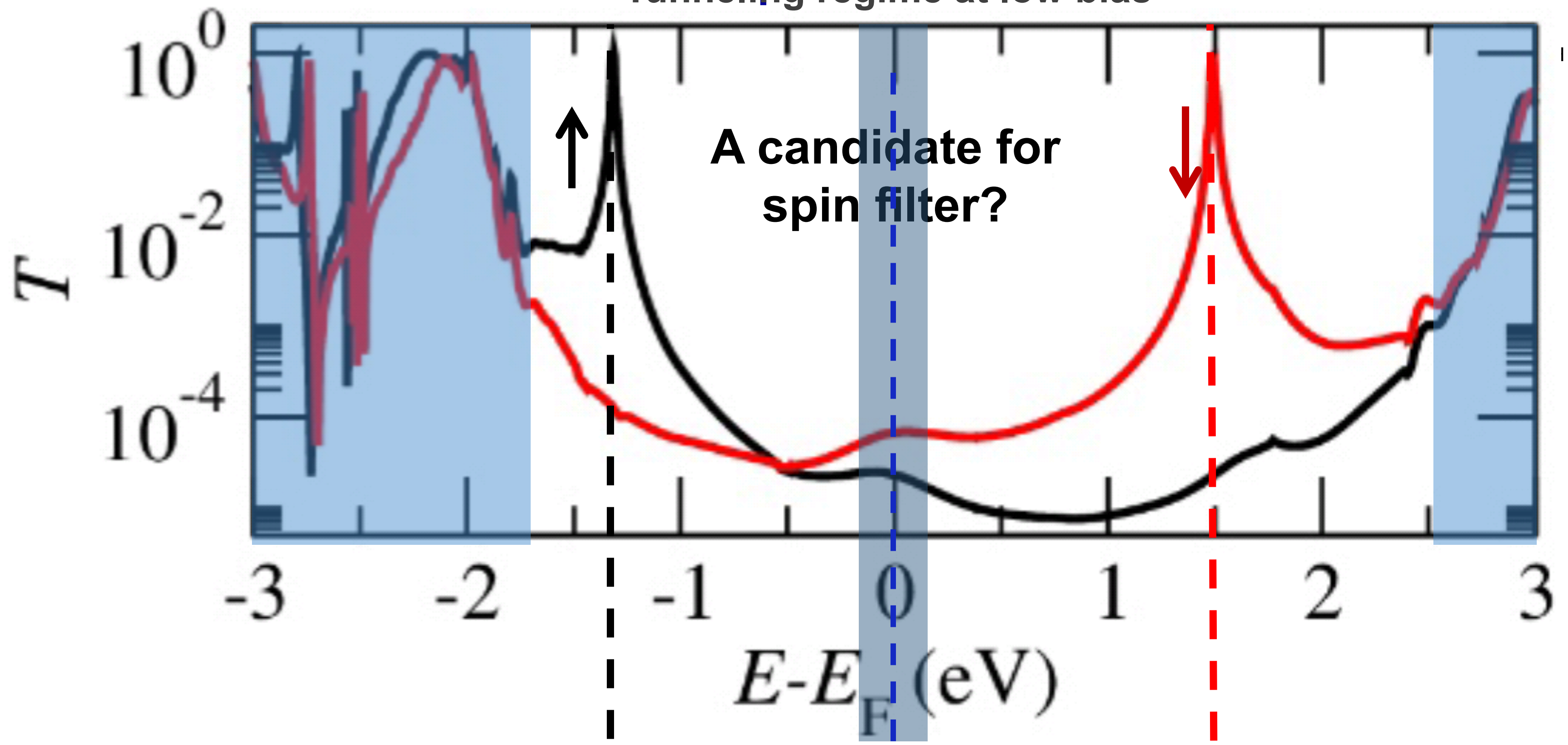
Up-spins transmission due to resonant transport through the filled SOMO level

Transmission is unpolarized for energies below -2 eV and above +2.5 eV

Down-spins transmission due to resonance transport through the empty SUMO

DFT calculated spin-resolved transmissions

Tunneling regime at low bias

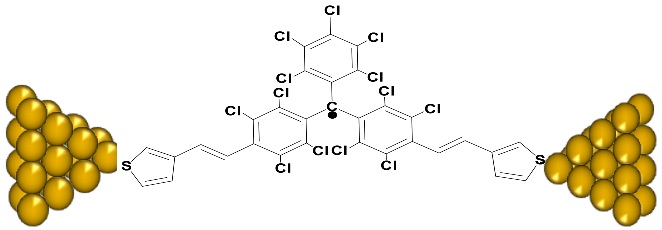


A candidate for spin filter?

SOMO

at V_{bias} ~ ±0.1 V
G ~$10^{-4.3}$ G_0

SUMO



DFT-based transport simulations with *Smeagol code*

by A. Droghetti (UPV-EHU, San Sebastian) and I. Rungger (NPL, London)

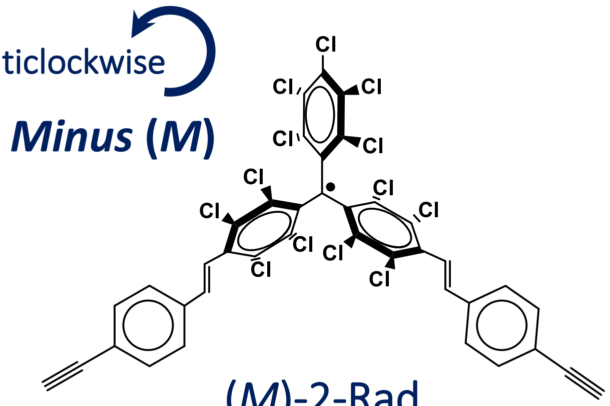
N. Crivillers et al. unpublished

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

Resolution of the racemic mixture of disubtituted 2-Rad PTM radical

anticlockwise

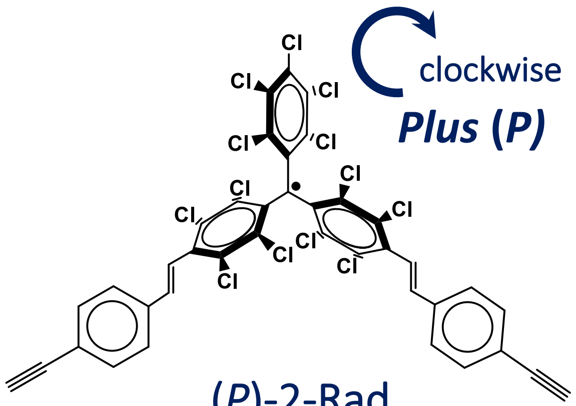
***Minus* (*M*)**



(*M*)-2-Rad

clockwise

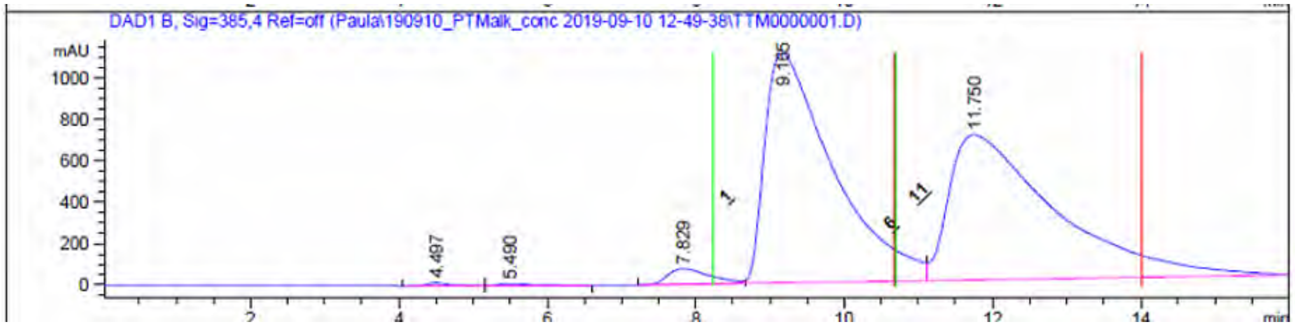
***Plus* (*P*)**



(*P*)-2-Rad

“propeller” conformation of the PTM● moiety

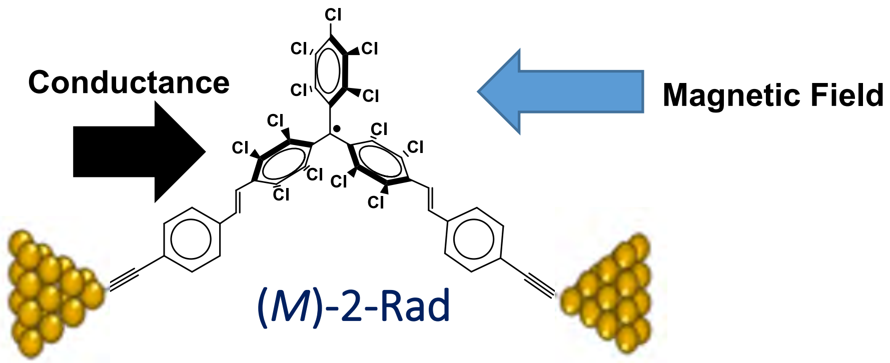
Chiral stationary phase (CSP) HPLC



After the resolution of the racemic mixture by CSP HPLC, the conductance through the two possible enantiomers can be explored

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

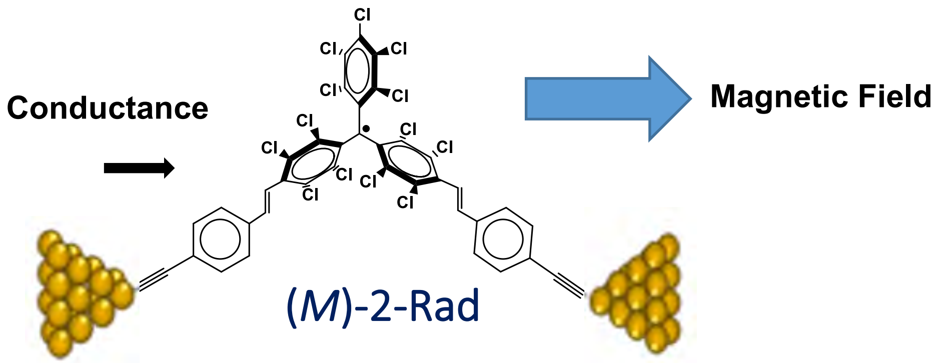
Evaluation of the chiral-induced spin selectivity (CISS) effect using a chiral single radical molecule with EMBJ



Conductance

Magnetic Field

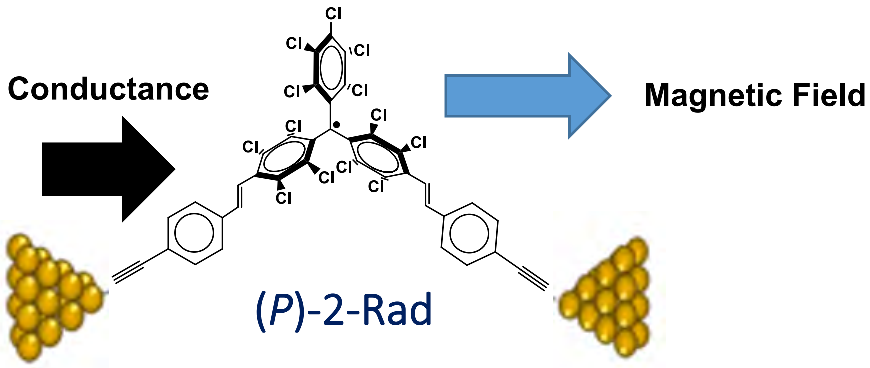
(*M*)-2-Rad



Conductance

Magnetic Field

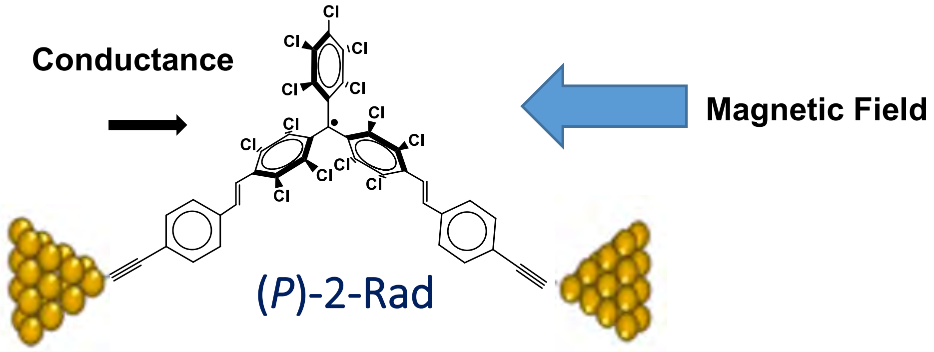
(*M*)-2-Rad



Conductance

Magnetic Field

(*P*)-2-Rad



Conductance

Magnetic Field

(*P*)-2-Rad

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

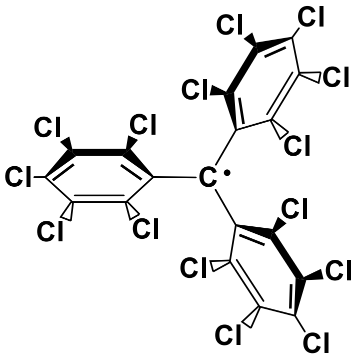
Trityl-based radical derivatives with intrinsic chirality

clockwise

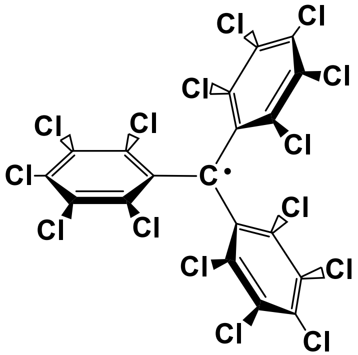
Plus (*P*)

anticlockwise

Minus (*M*)

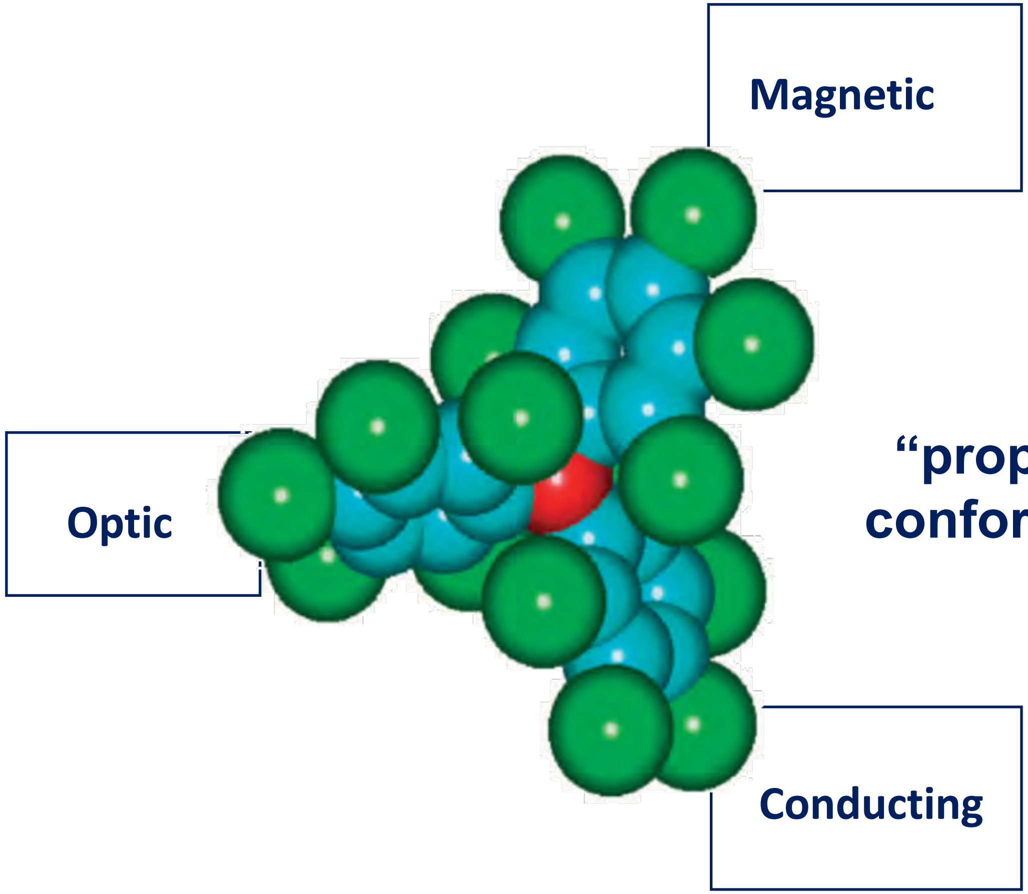


(*P*)-PTM



(*M*)-PTM

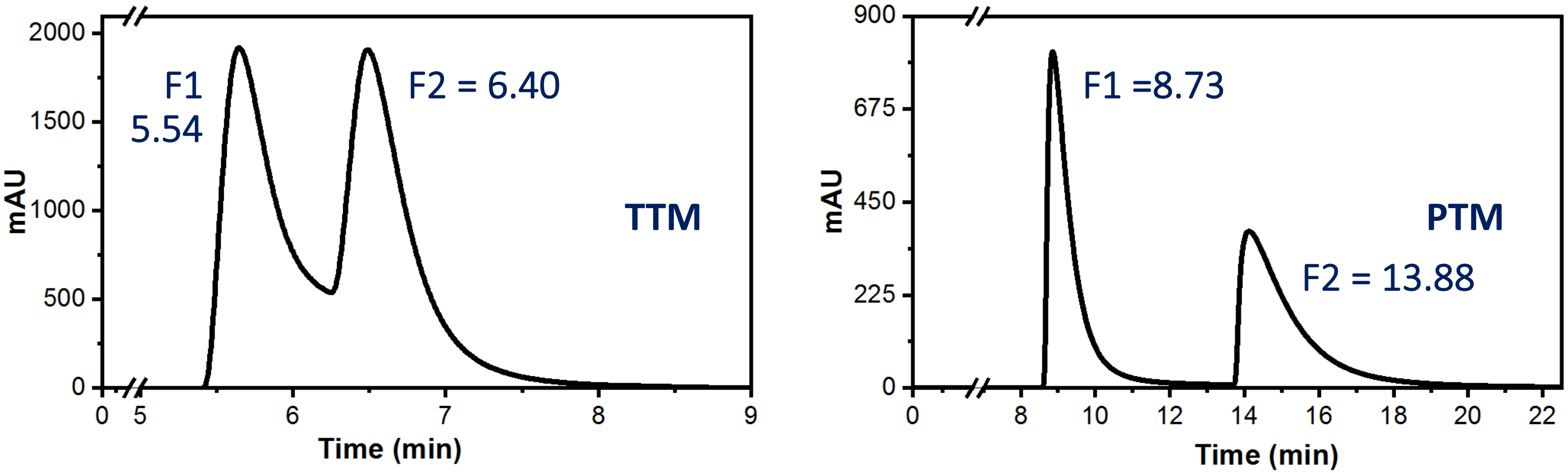
Polychlorotriphenylmethyl (PTM) radical

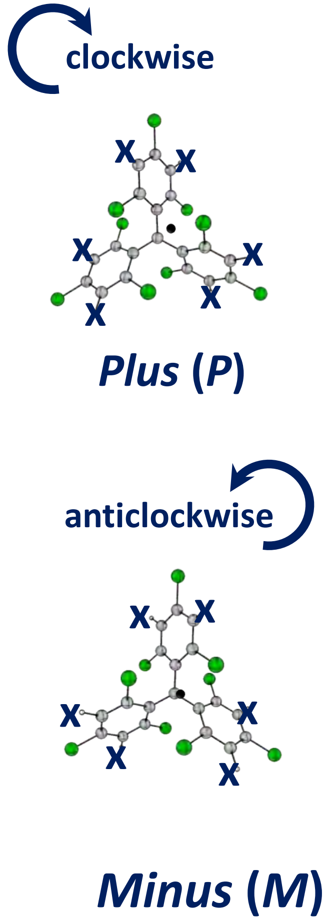


“propeller” conformation

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

Resolution of racemic PTM and TTM radical samples





Chiral stationary phase (CSP) HPLC: Daicel Chemical Industries, Ltd. (250 x 4.6 mm, 5 µm). Sample injection: 200 µL in n-hexane ~1 mg/mL. Separation conditions: eluent: n-hexane/DCM (99.9:0.1), flow rate: 1 mL/min, 20 °C.

X:

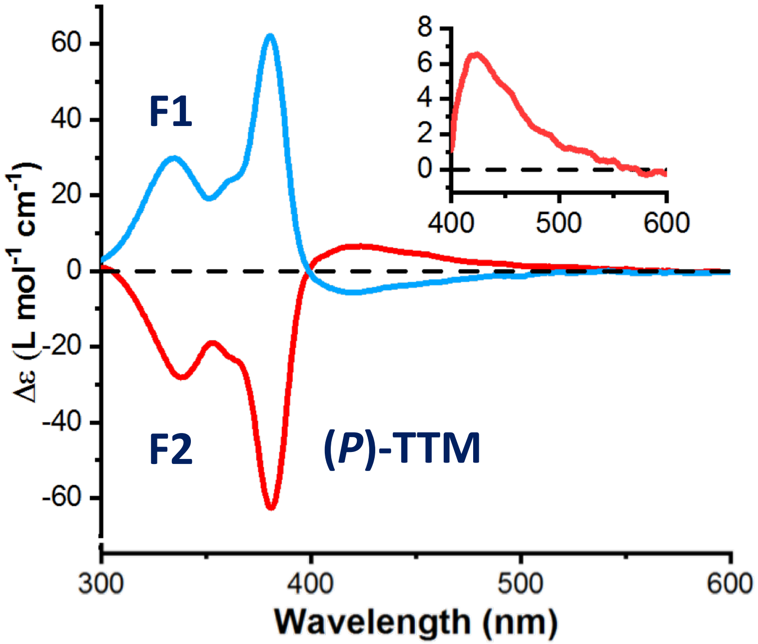
● = chlorine atoms **(PTM)**

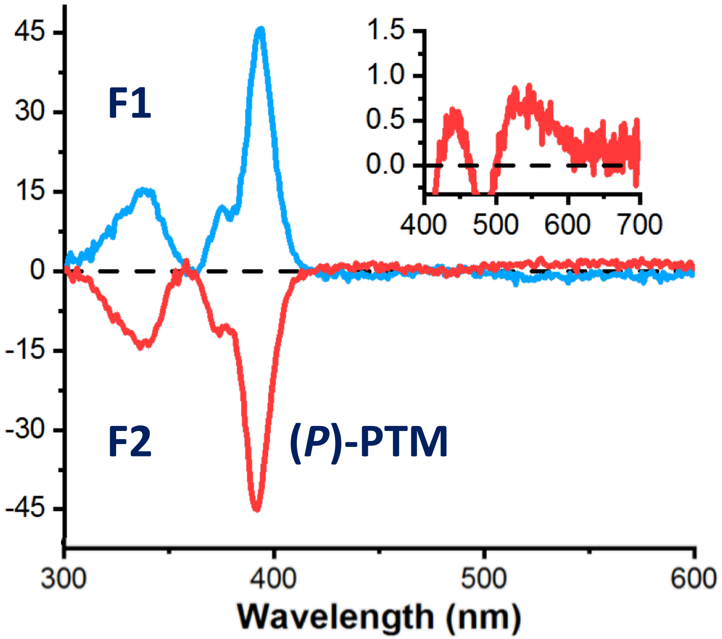
○ = hydrogen atoms **(TTM)**

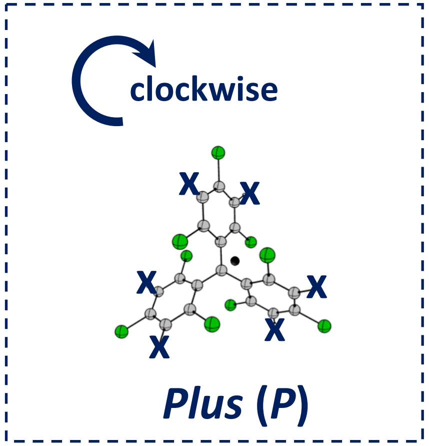
Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

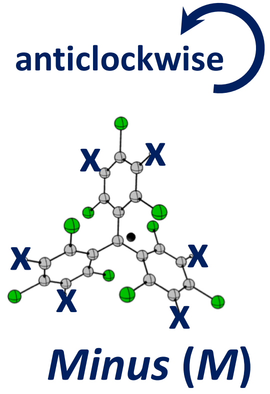
Determination of the absolute configuration of chiral radicals

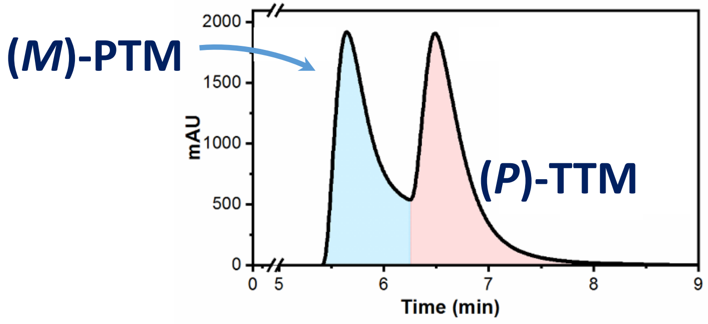
ELECTRONIC CIRCULAR DICHROISM (ECD) SPECTRA

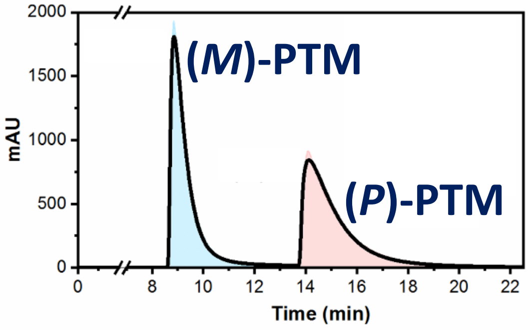












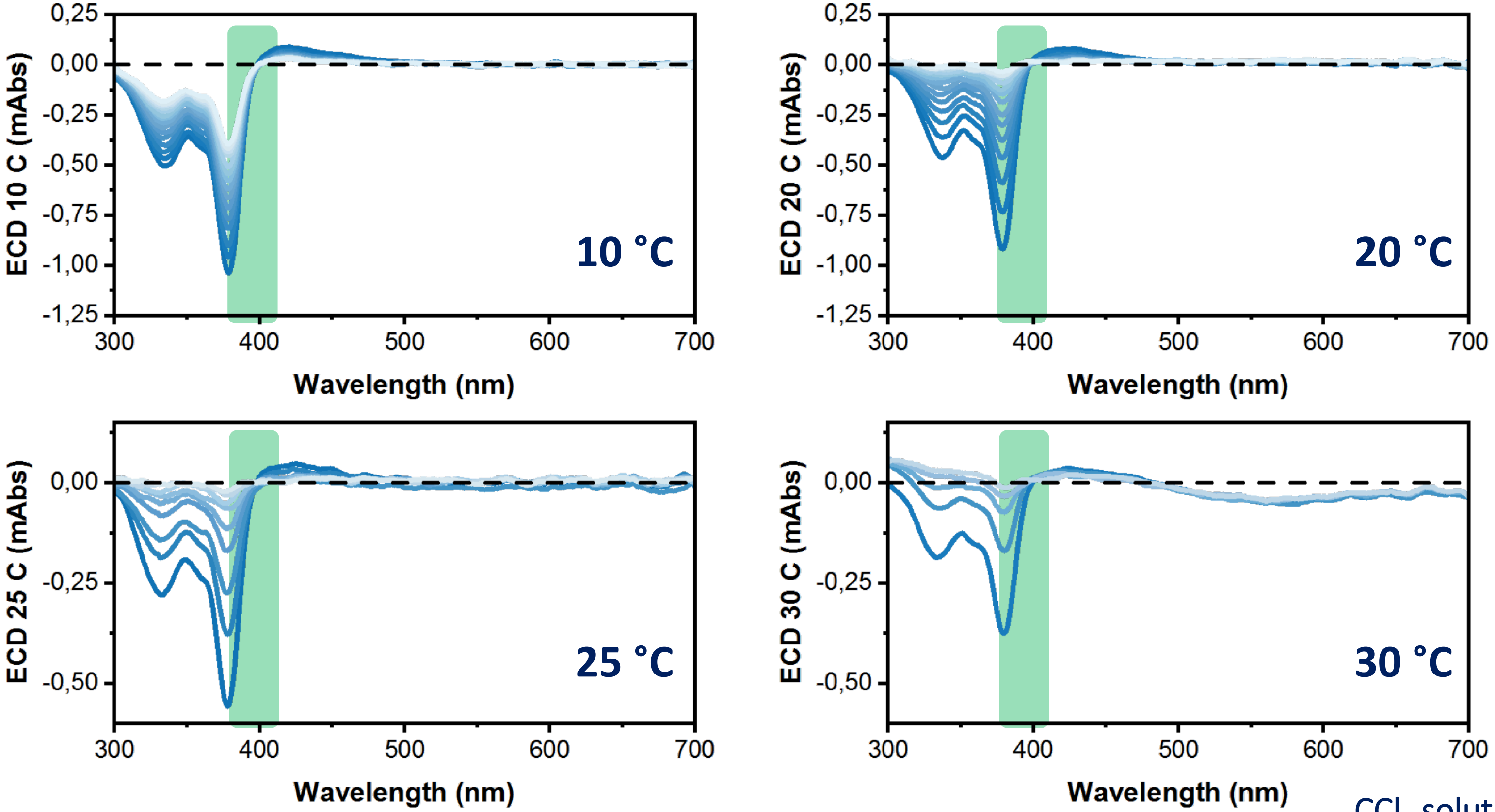
x:

● = chlorine atoms (PTM)

○ = hydrogen atoms (TTM)

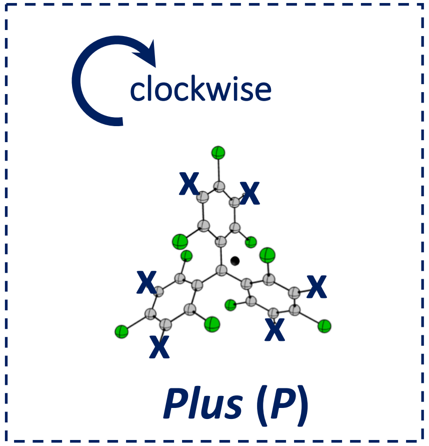
Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

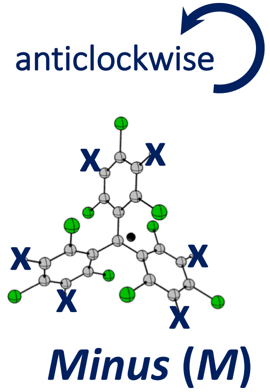
Racemization kinetics of enantiopure radical samples



TTM

CCl$_4$ solutions





DYNAMIC (d) ECD signal decays with time at different temperatures)

Racemization energy barriers

	$\Delta G^{\ddagger}_{303K}$ (kcal/mol)	Error
(P)-TTM	21.12	1.77
(P)-PTM	22.36	1.92

x:

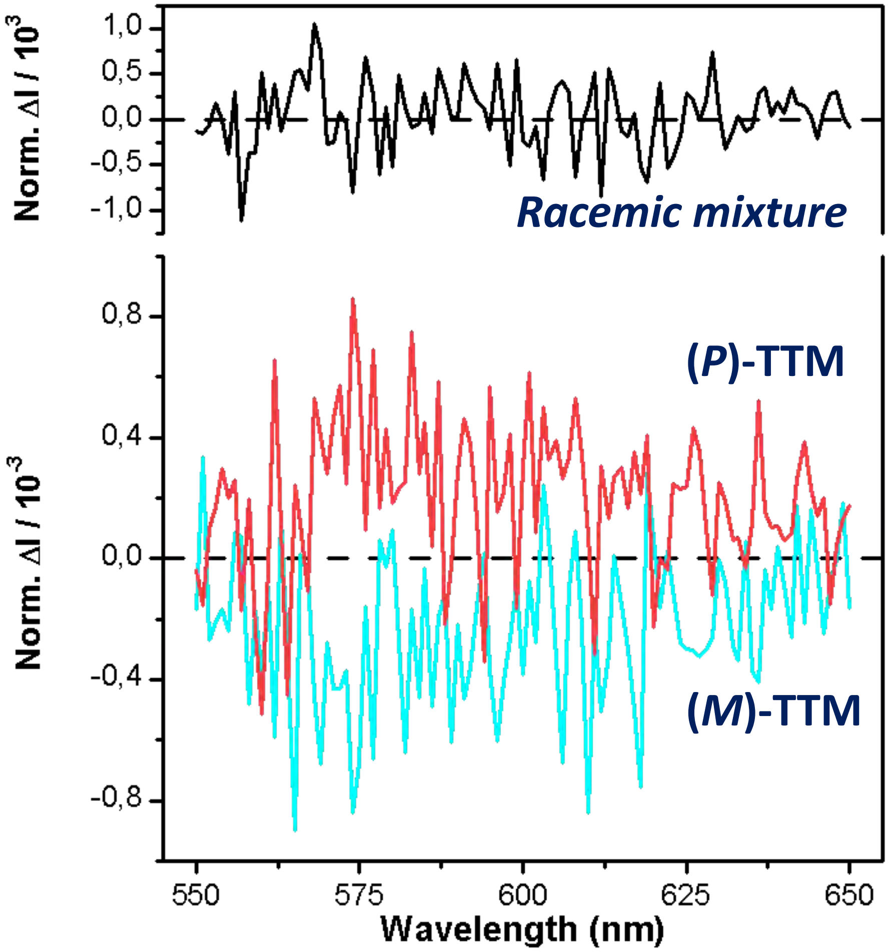
● = chlorine atoms **(PTM)**

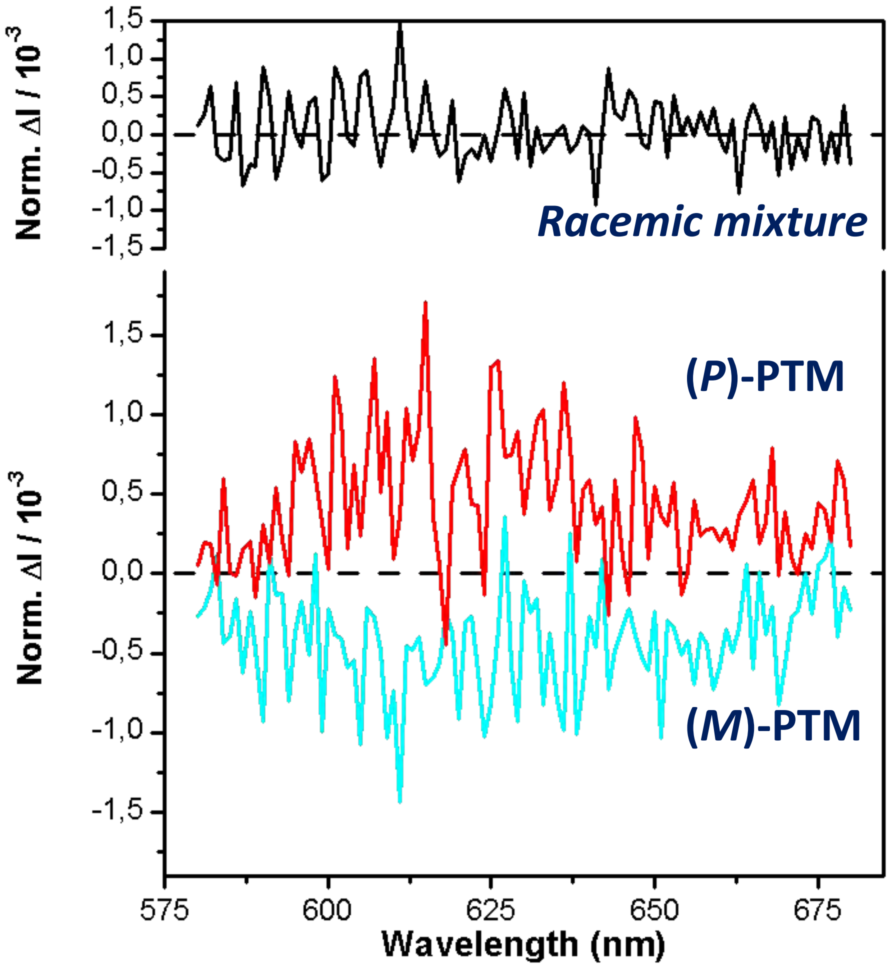
○ = hydrogen atoms **(TTM)**

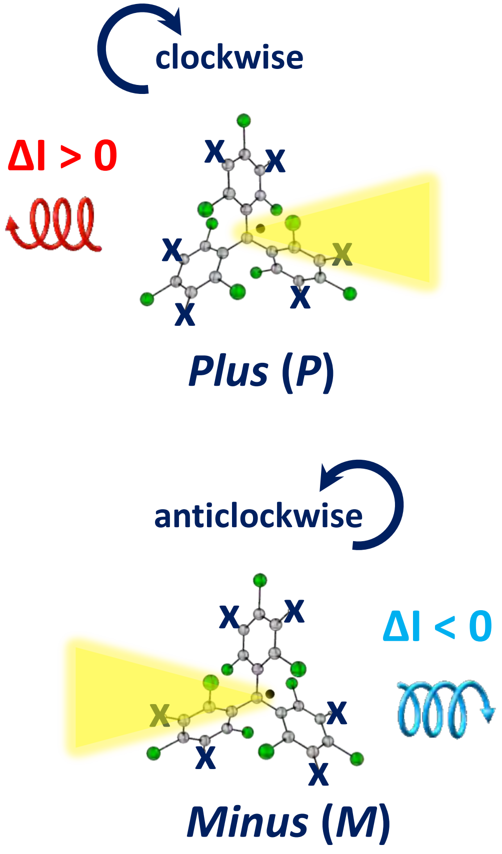
Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

Evaluation of the Circularly Polarized Luminiscence (CPL) activity

CCl_4 solutions, -20 °C







clockwise

ΔI > 0

Plus (*P*)

anticlockwise

ΔI < 0

Minus (*M*)

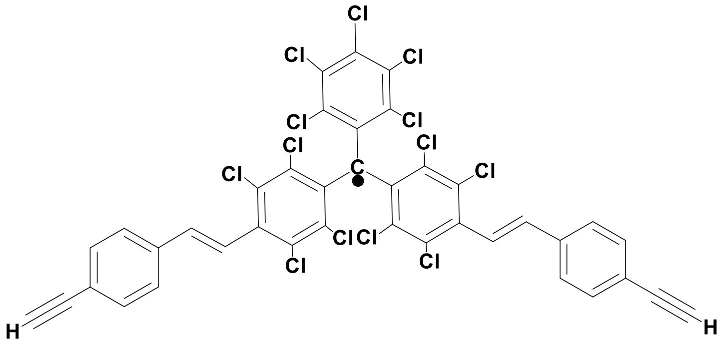
x:

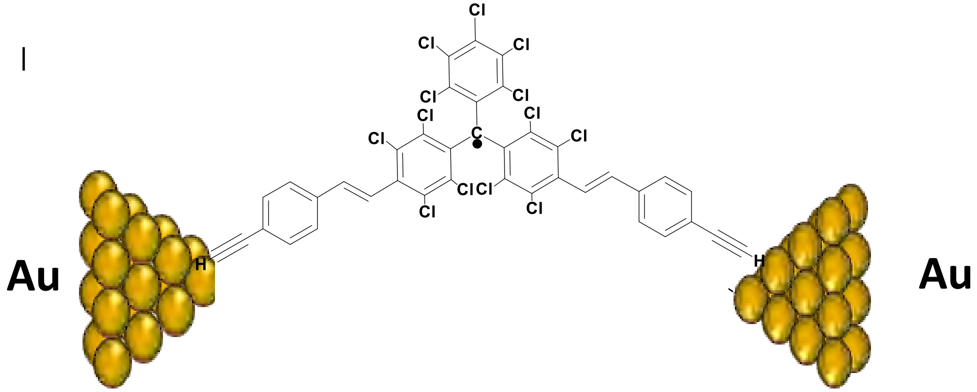
🟢 = chlorine atoms **(PTM)**

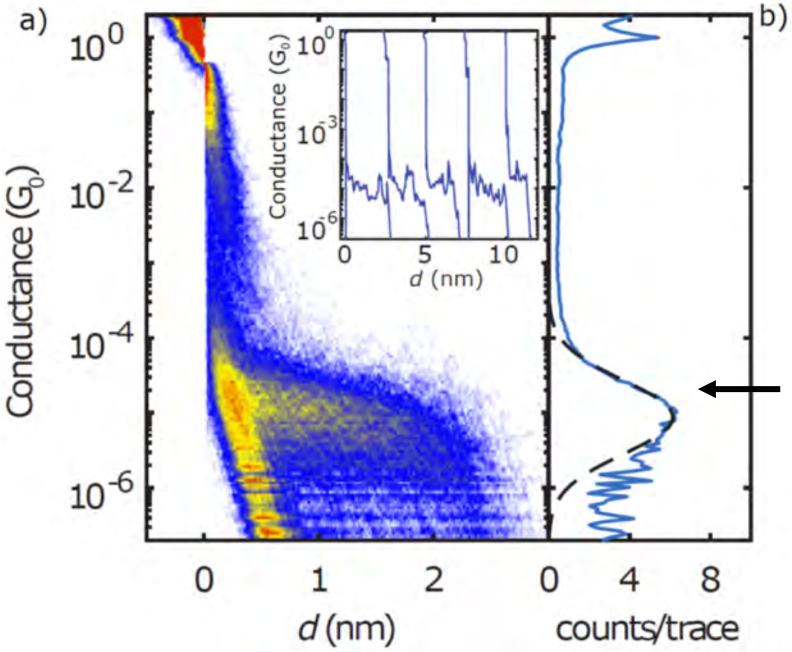
○ = hydrogen atoms **(TTM)**

Electrical properties of PTM radical-based materials

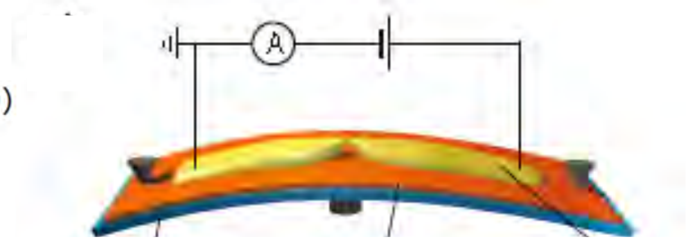
Transport through a single PTM radical molecule







MCBJ



The most probable conductance value was 8.8×10^{-6} G$_0$

In collaboration with H.S.J. van der Zant (Delft Univ. Tech)

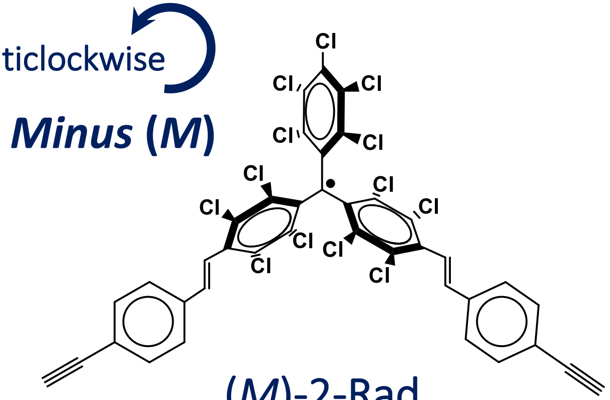
F. Bejarano et al, *J. Am. Chem. Soc.* 2018, *140*, 1691

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

Resolution of the racemic mixture of disubtituted 2-Rad PTM radical

anticlockwise

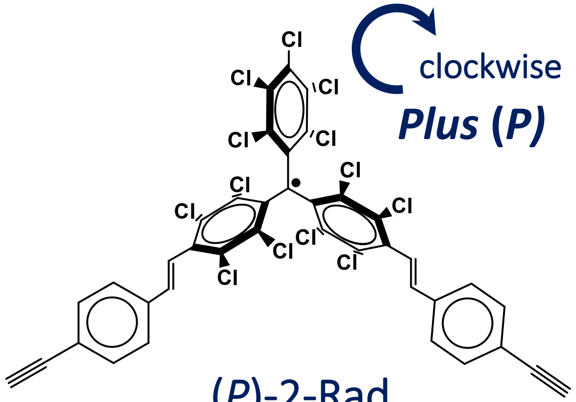
***Minus* (*M*)**



(*M*)-2-Rad

clockwise

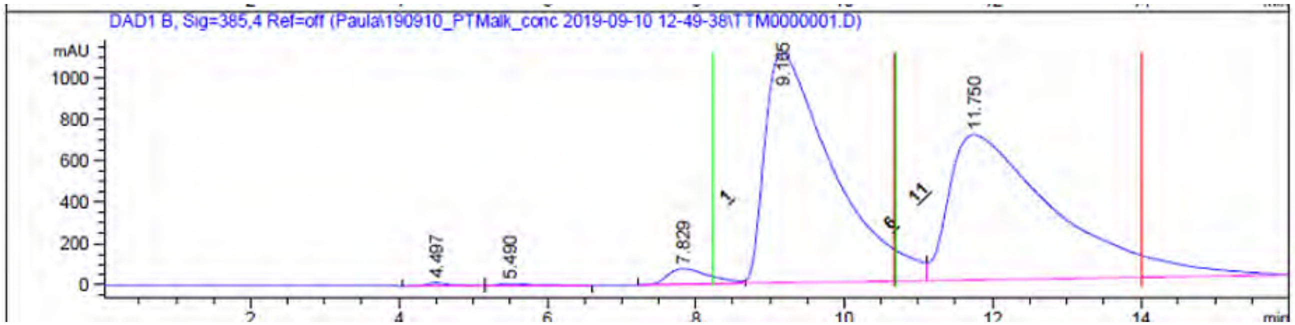
***Plus* (*P*)**



(*P*)-2-Rad

“propeller” conformation of the PTM● moiety

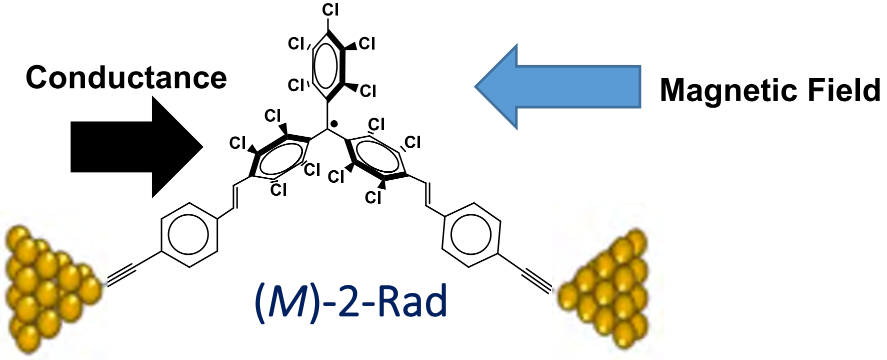
Chiral stationary phase (CSP) HPLC



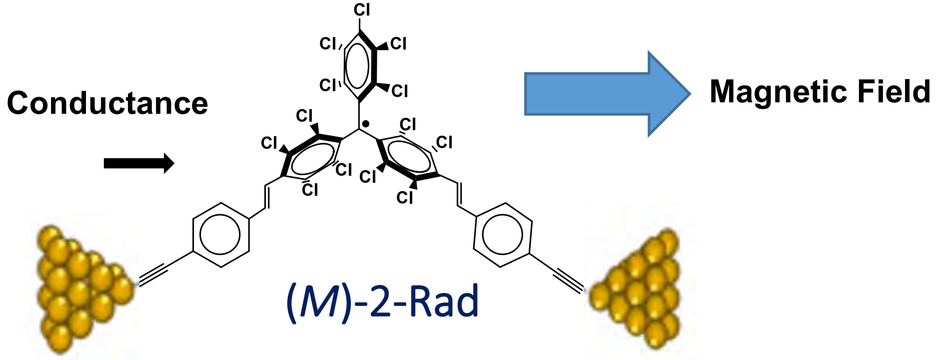
After the resolution of the racemic mixture by CSP HPLC, the conductance through the two possible enantiomers can be explored

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

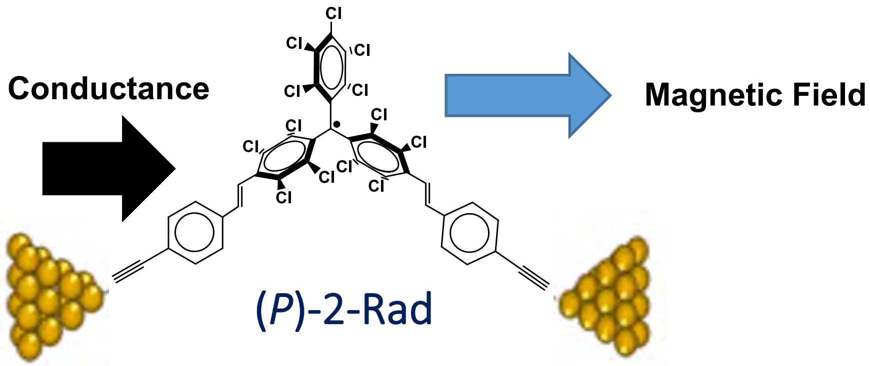
Evaluation of the chiral-induced spin selectivity (CISS) effect using a chiral single radical molecule with EMBJ



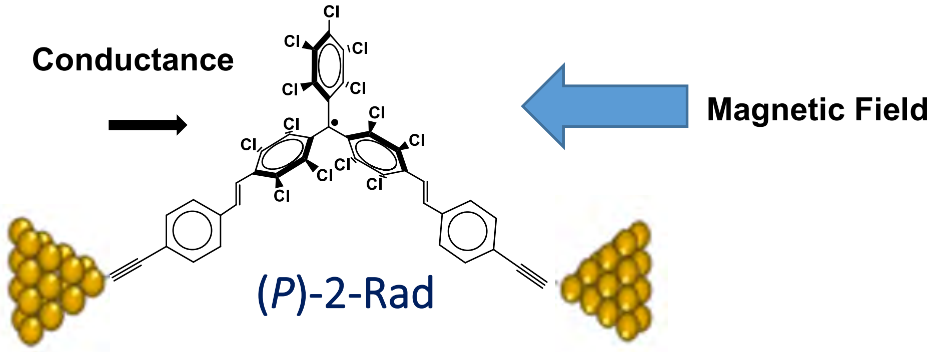
(*M*)-2-Rad



(*M*)-2-Rad



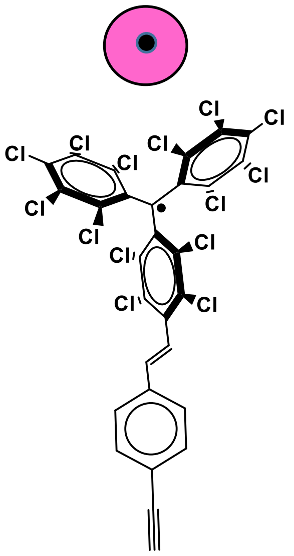
(*P*)-2-Rad



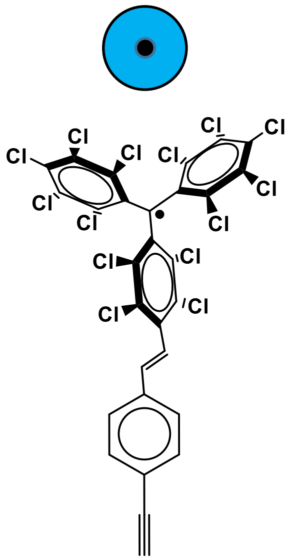
(*P*)-2-Rad

Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

Transport through a racemic PTM radical SAM

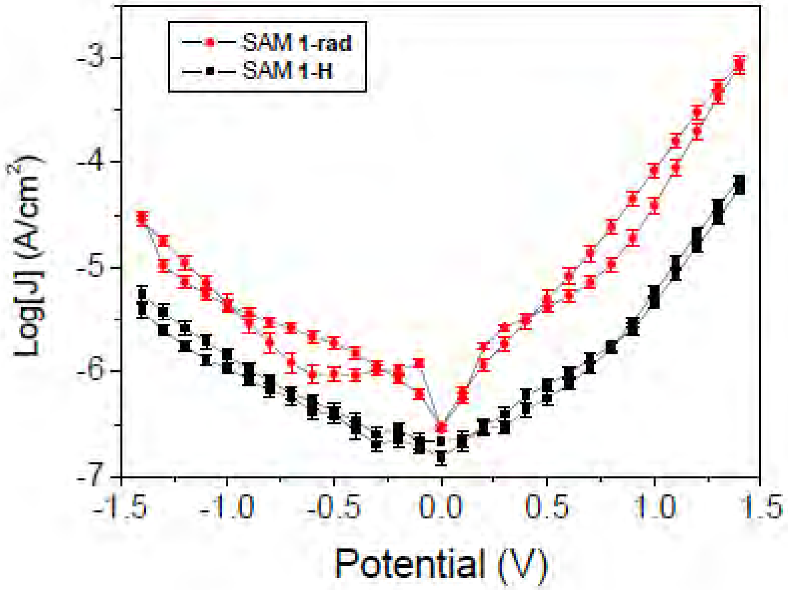


(*P*)-1-Rad

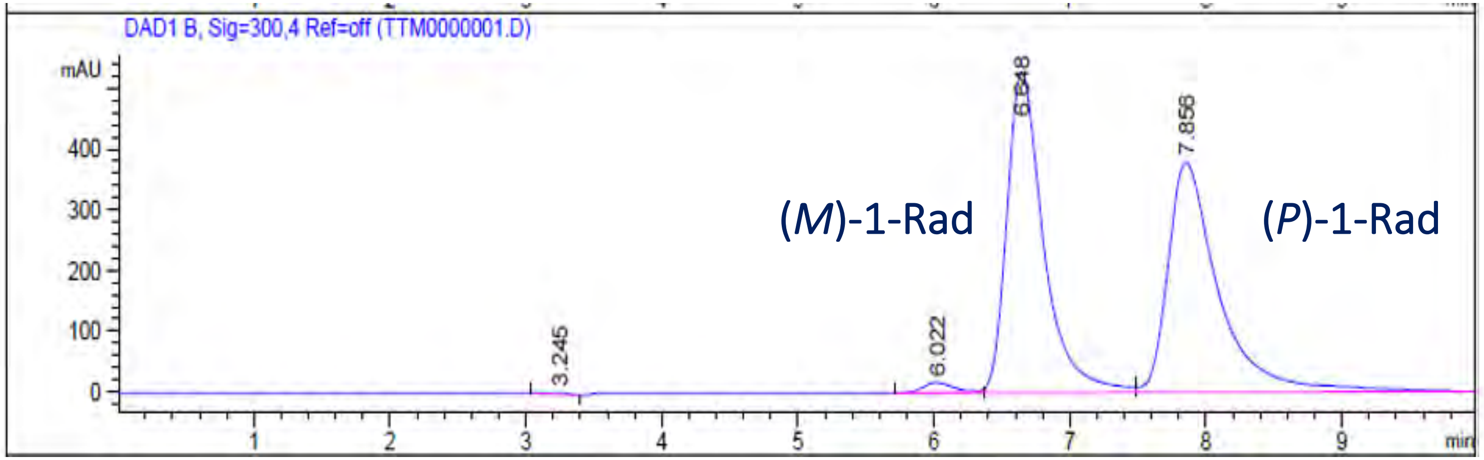


(*M*)-1-Rad

SAM with racemic mixture of radicals

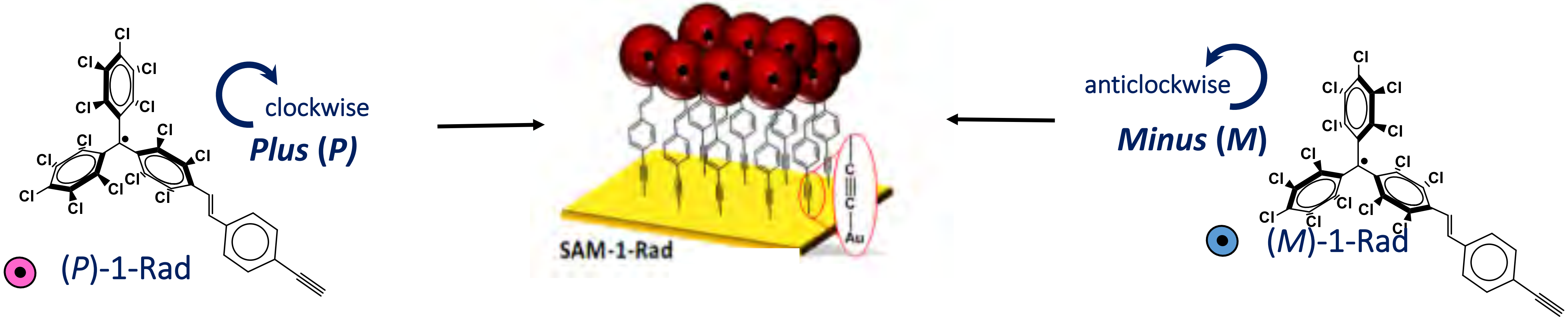


Resolution of the racemic mixture of 1-Rad by CSP HPLC.

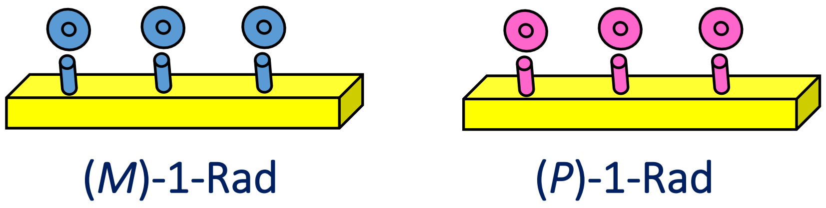


Spin filtration with intrinsic chiral organic radical-based materials due to CISS effect

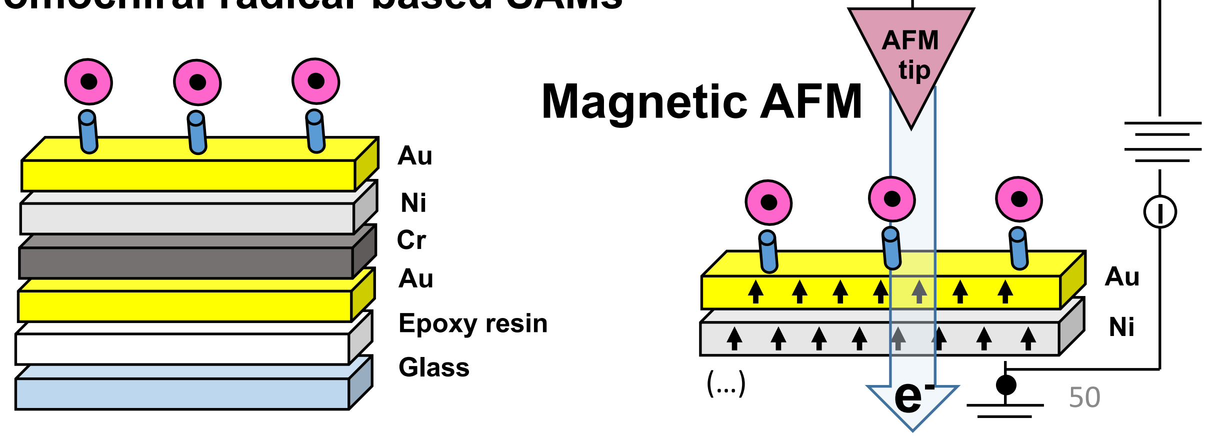
Chiral-induced spin selectivity (CISS) effect with a homoquiral radical Self Assembled Monolayer



(1) Preparation of magnetically active homochiral SAMs for the evaluation of the chiral-induced spin selectivity (CISS) effect with a radical SAM.

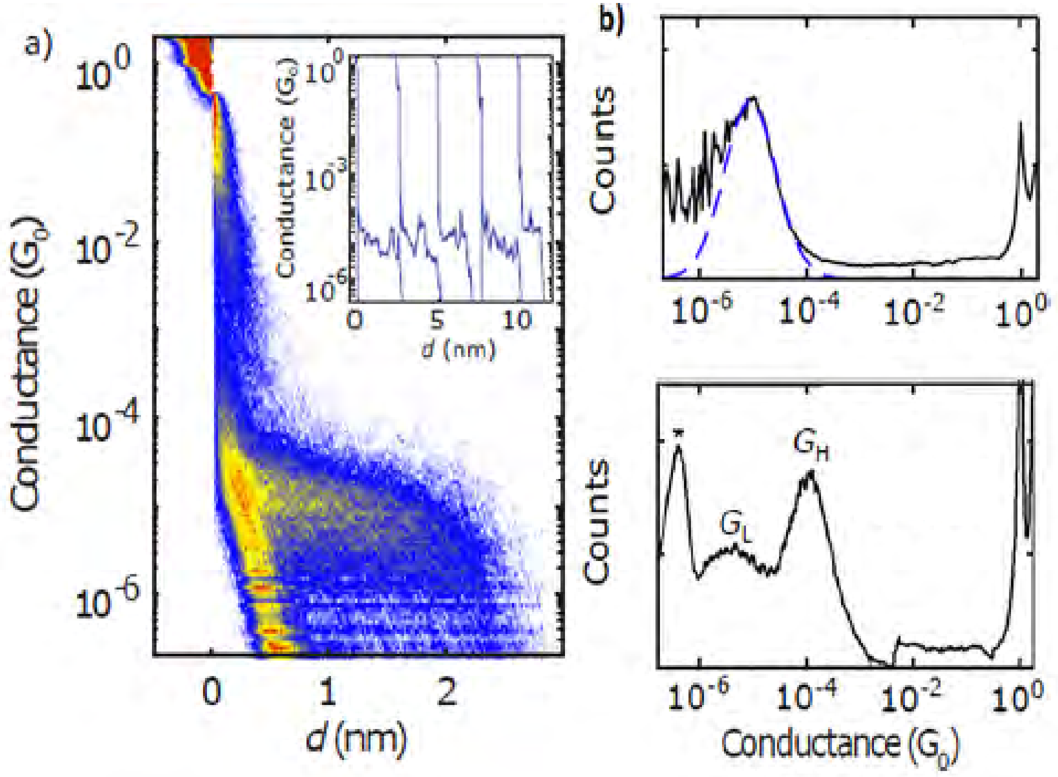


(2) The transmission of spin orientations at r.t. through homochiral radical-based SAMs

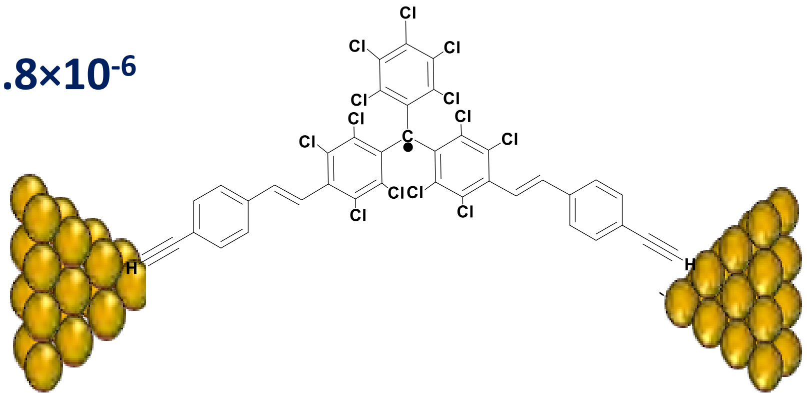


Electrical properties of PTM radical-based materials

Molecule/electrode contact dependance of transport through single PTM radical molecules

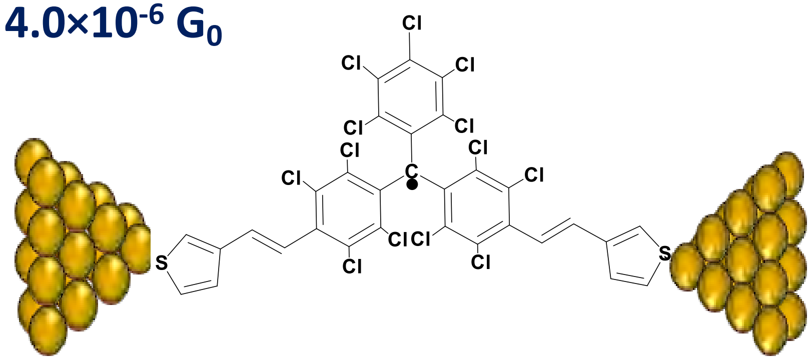


$G \doteq 8.8\times10^{-6}$



Conductances are more localized, a signature of a stronger Au-C bond with a more-defined conformations

$G_H = 1.0\times10^{-4}\ G_0$
$G_L = 4.0\times10^{-6}\ G_0$



Conductances are more spread, a signature of a weaker Au-S bonds with ill-defined molecule-metal contacts

σ Au-C bonds are more robust and have less variability in conductance values ¡¡¡¡

F. Bejarano et al, *J. Am. Chem. Soc.* 2018, *140*, 1691