

Development of electrochemical sensors based on electrochemical coating for environmental application

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SUSNANO

Summer School 22-25 March 2023, TIRANA

Plan of presentation

Introduction

Electrochemical grafting

Oxidation methods

Reduction methods

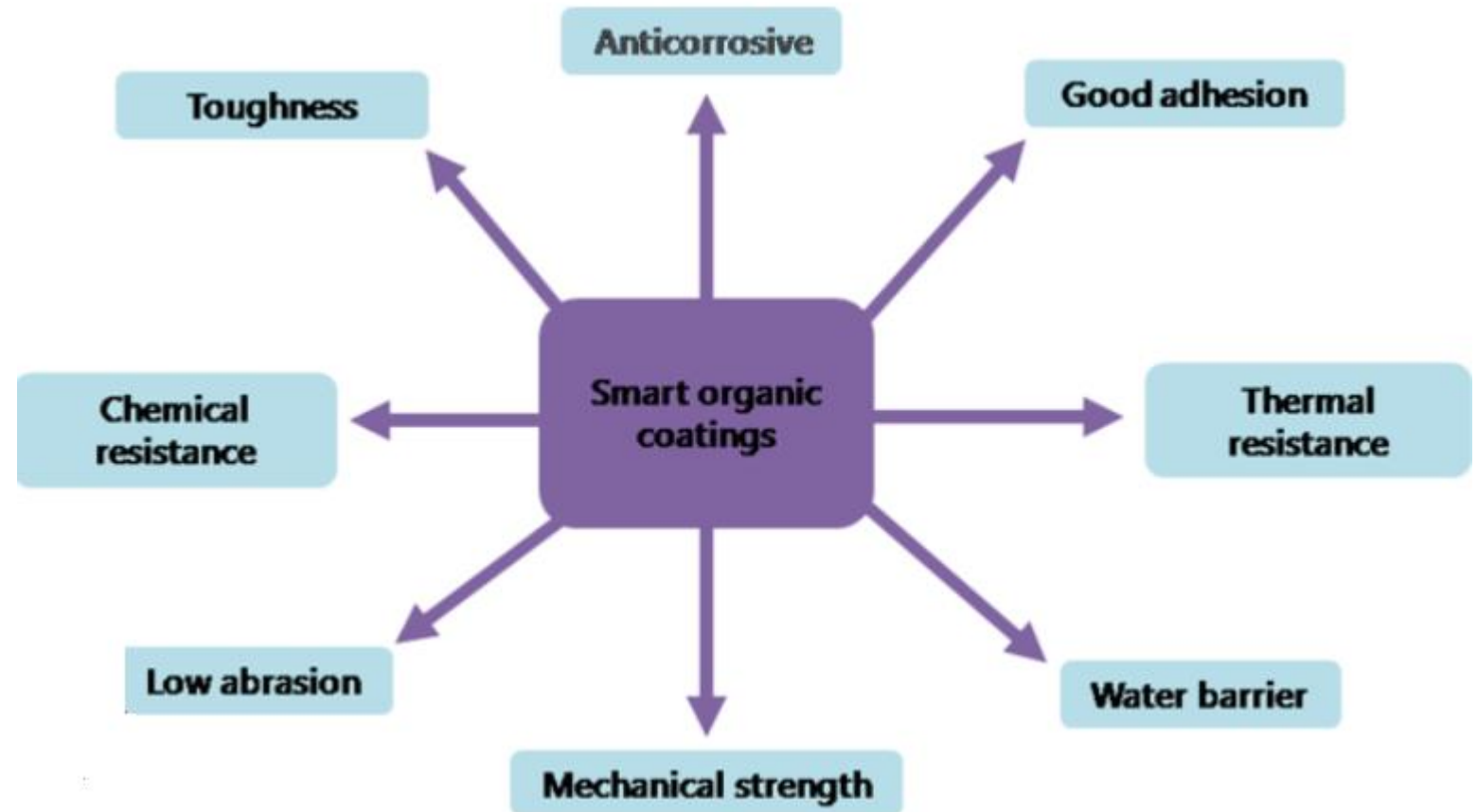
Aryl diazonium salts

Electrochemical sensors for environment

Conclusion

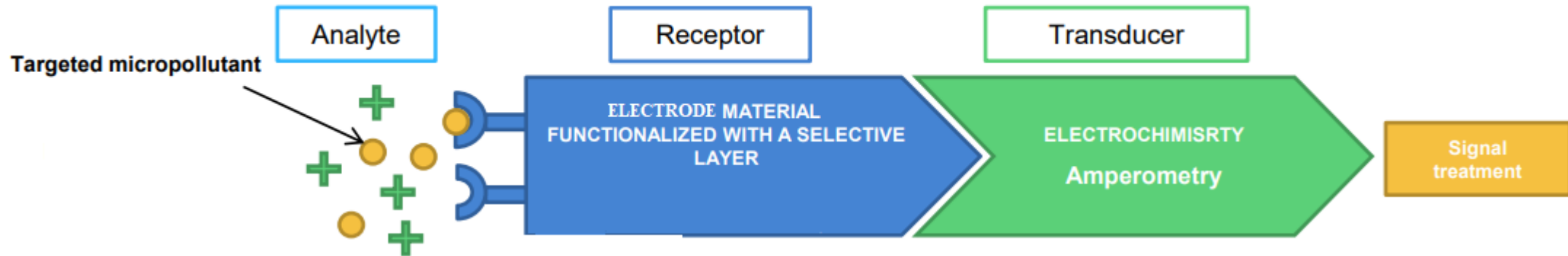
Why chemical or electrochemical grafting is important?

Coating a material with an organic layer, 1 nm to several hundreds of nm, permits to obtain a composite material that retains its mechanical properties but shows the surface properties of the organic layer. The grafted layer imparts properties like: wetting, adhesion, dispersion, chemical sensing, resistance against corrosion, catalytic activity, controlled cell adhesion etc.



Why surface modification is important for electrochemical sensors?

ELECTROCHEMICAL SENSORS



The performances of the sensor device rest primarily on the ability of the active surface to specifically and selectively recognize the target species. Chemically modified electrodes present the advantage that sensitivity and selectivity can be regulated by the incorporation of a convenient functional group onto the electrode surface. A metal ion can interact through the amino groups, the amide nitrogen and/or the carboxylic group present or other ligands.

Long term stability and reusability are also important issues and depend on the surface and interface chemical strategies followed to construct the sensing layer.

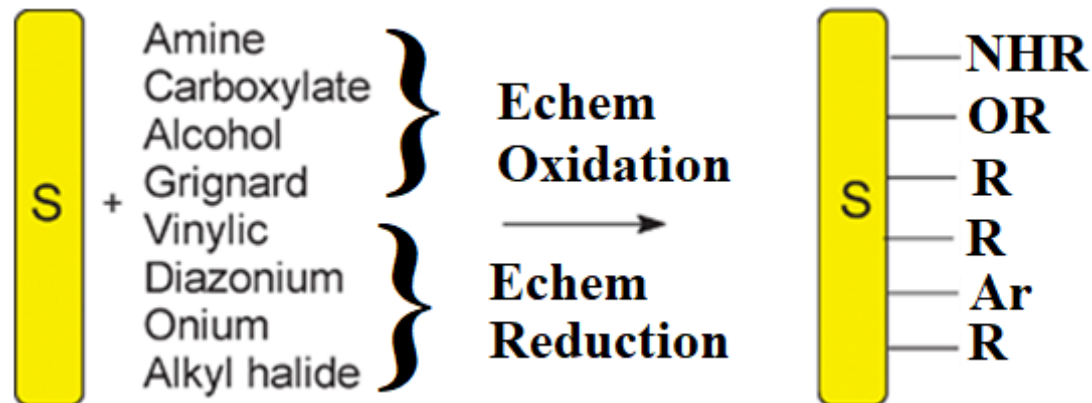
Control over the stability of the active layer usually requires covalent attachment to the transducer while this active layer must be able to suppress or limit non-specific recognition of interferents.

Electrochemical grafting

Electrografting refers to the electrochemical reaction that permits organic layers to be attached to solid conducting substrates.

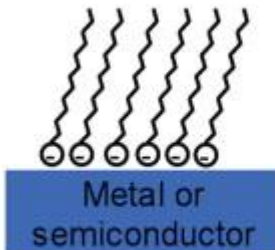
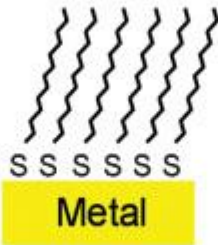
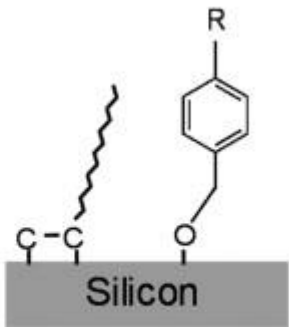
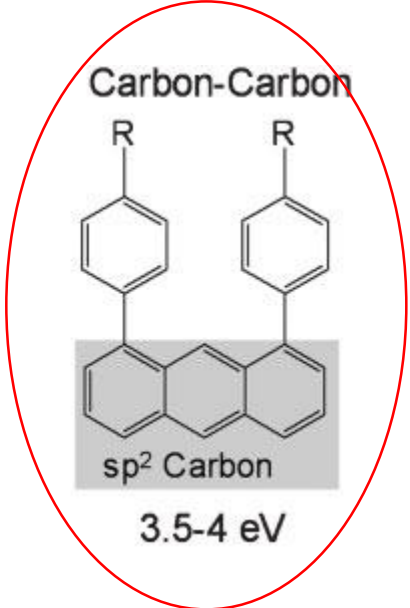
These methods are interesting as they provide a real bond between the surface and the organic layer. Electrografting applies to a variety of substrates including carbon, metals and their oxides, but also dielectrics such as polymers.

Since the 1980s several methods have been developed, either by reduction or oxidation, and some of them have reached an industrial stage.



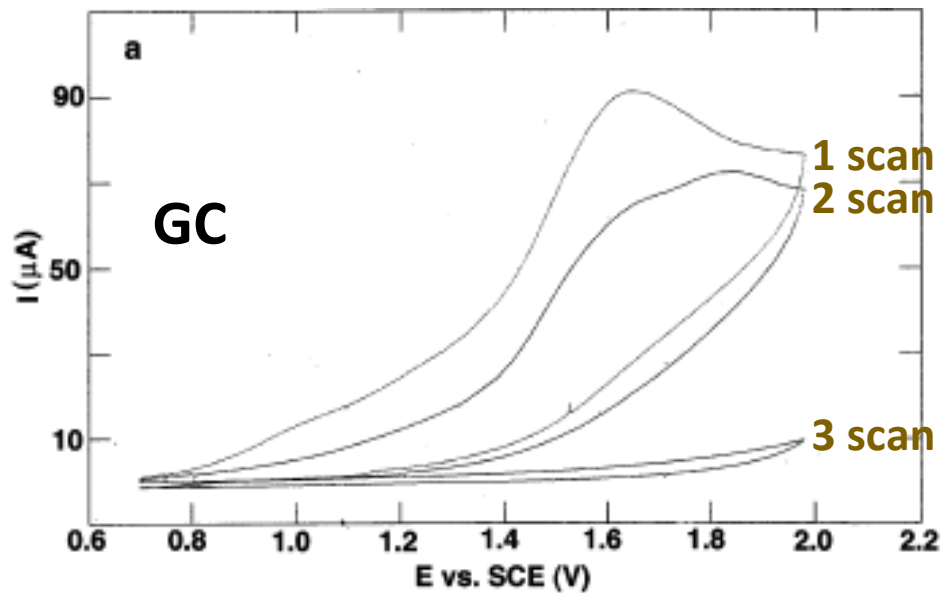
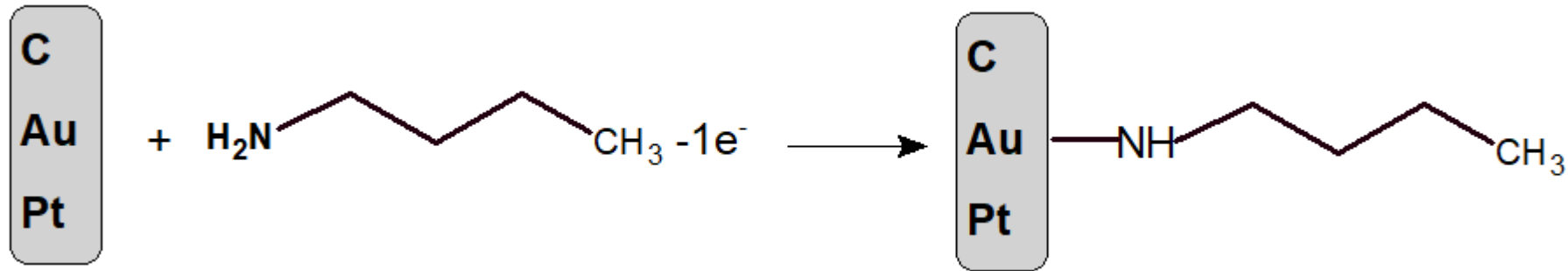
S – carbon, metals including coinage metals, Semiconductors, Polymers

Comparison of the stability of the bond between substrate and organic layer

Layer Type	Langmuir-Blodgett	Self-Assembled Monolayer	Si-C and Si-O	Carbon-Carbon
				
Surface Bond Energy	<0.5 eV	~1.9 eV	3.5-4 eV	3.5-4 eV

The substrate-organic molecule bond can vary from very weak to very strong (as strong as C-C bonds) and covalent grafting provides much more stable films over temperature and potential excursions and for post modification reactions when some times are needed quite harsh conditions.

ELECTROGRAFTING OF AMINES



5 mM n-butylamine + 0.1 M NBu_4BF_4 in DMF

Scan rate = 0.1 V s^{-1}

Pinson et al. *J. Electrochem. Soc.*, 1990. 137, 1757.

Pinson et al. *Langmuir*, 2004, 20, 8243.

One can observe a large irreversible wave which decreases on the second scan and almost disappears after 5 min electrolysis at potential 1.9 V/SCE

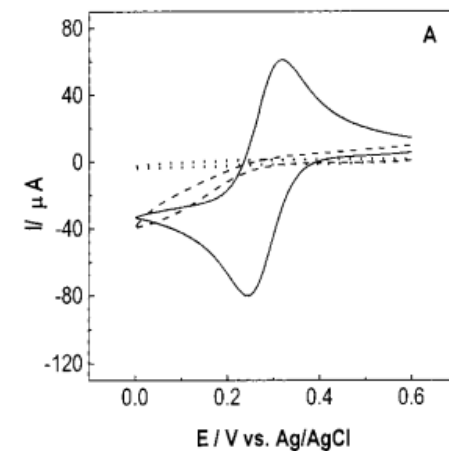
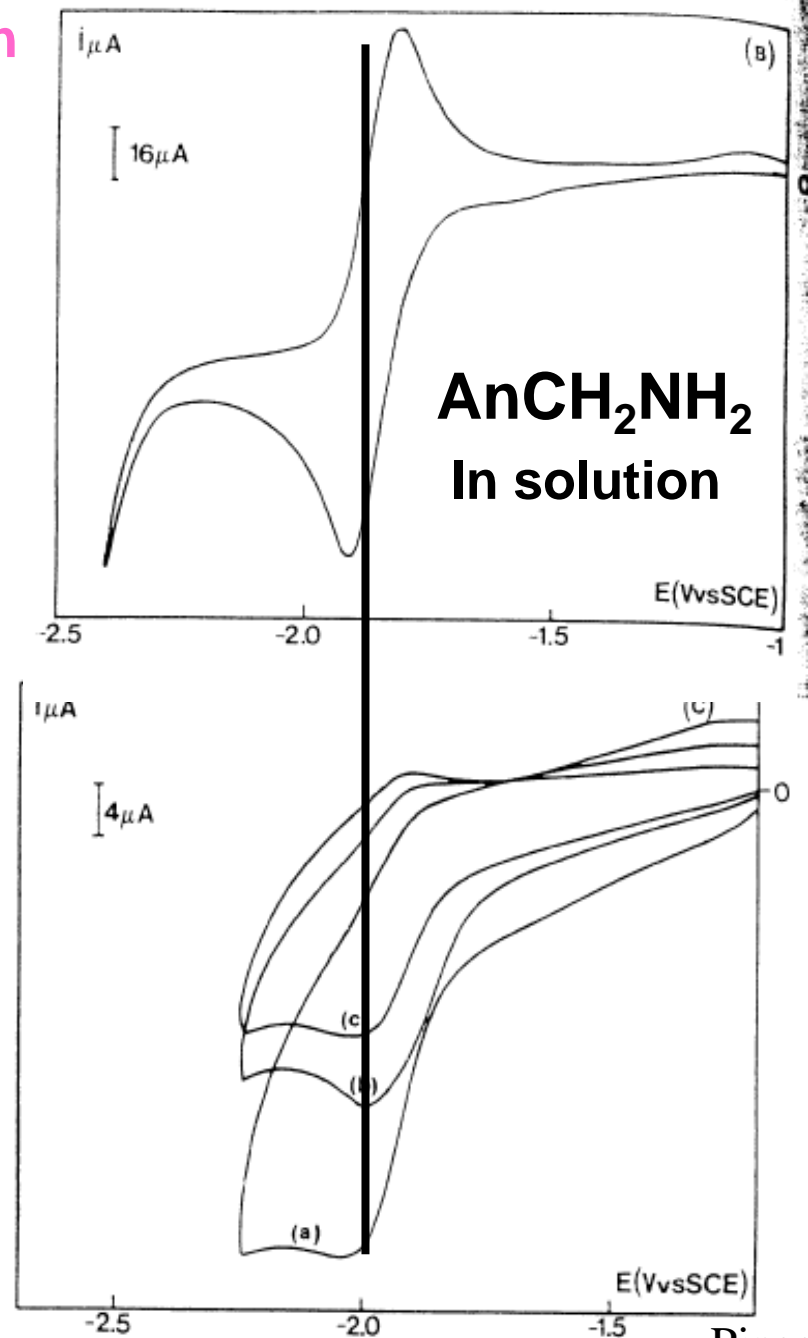
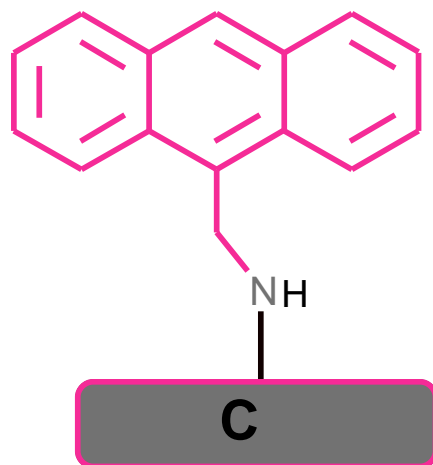


Figure 3. Cyclic voltammograms on bare (—) and 4-ABA-modified GCE (---) in (A) 5 mM $\text{Fe}(\text{CN})_6^{3-}$.

Electrochemical Characterization of the grafted layer from AnCH_2NH_2



The integration of the current of the redox peaks is used for the estimation of surface concentration (Γ) for attached groups.

$$\Gamma = 7 \times 10^{-10} \text{ mol/cm}^2$$

CHARACTERIZATION SURFACE ANALYSIS METHODS

XPS (X-Ray Photoelectron Spectroscopy)

IRRAS (Infra Red Reflection Absorption Spectroscopy)

ATR IR (Attenuated Transmission Reflection Infra Red Spectroscopy)

TofSIMS (Time of flight Secondary Ion Mass Spectrometry)

AFM (Atomic Force Microscopy)

STM (Scanning Tunneling Microscopy)

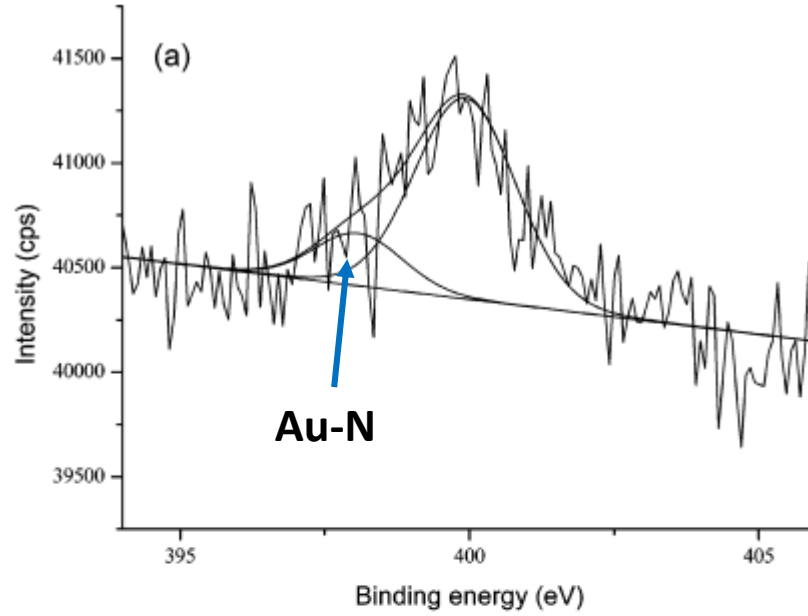
RBS (Rutherford Back Scattering)

SEM (Scanning Electronic Microscopy)

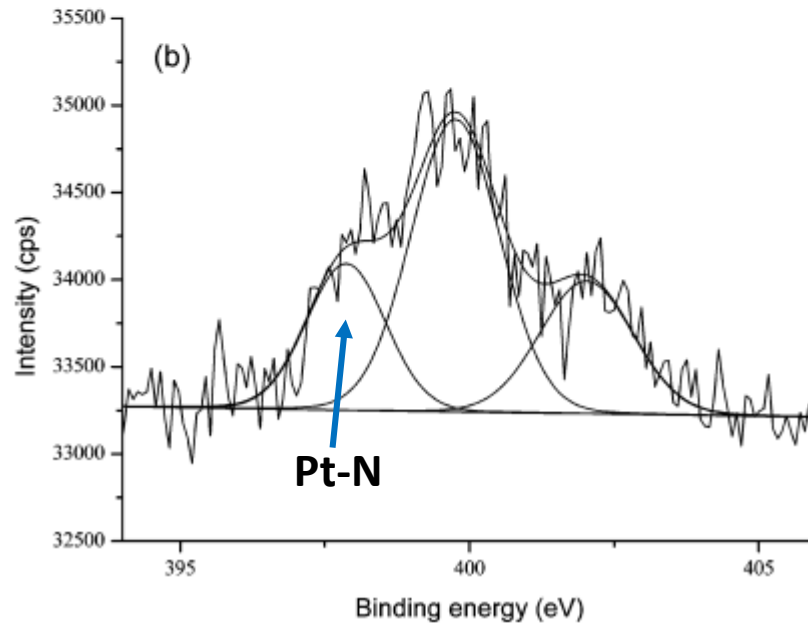
TEM (Transmission Electronic Microscopy)

etc.

XPS characterization of the grafted layer – Formation of metal – N bond

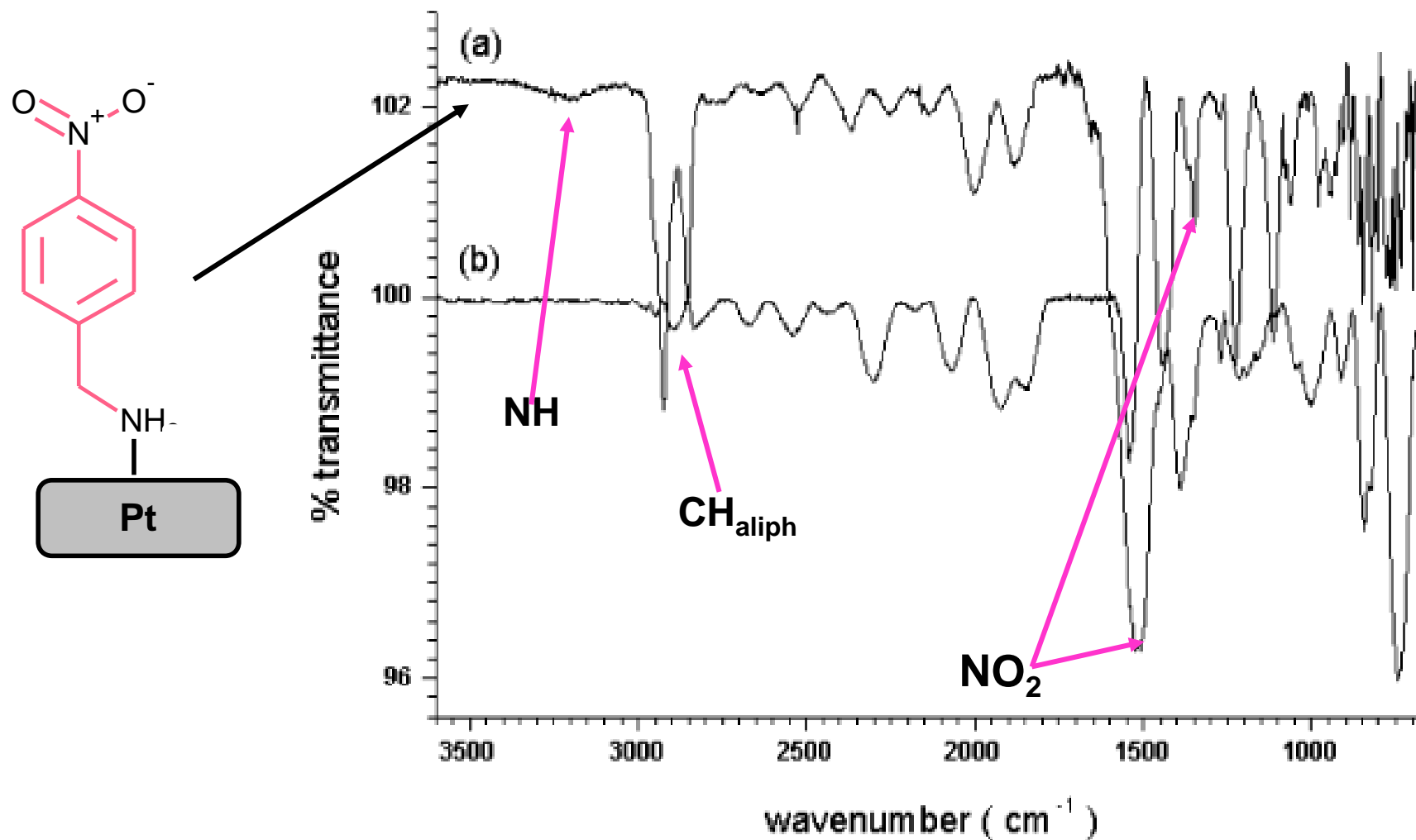


N1s high resolution spectrum



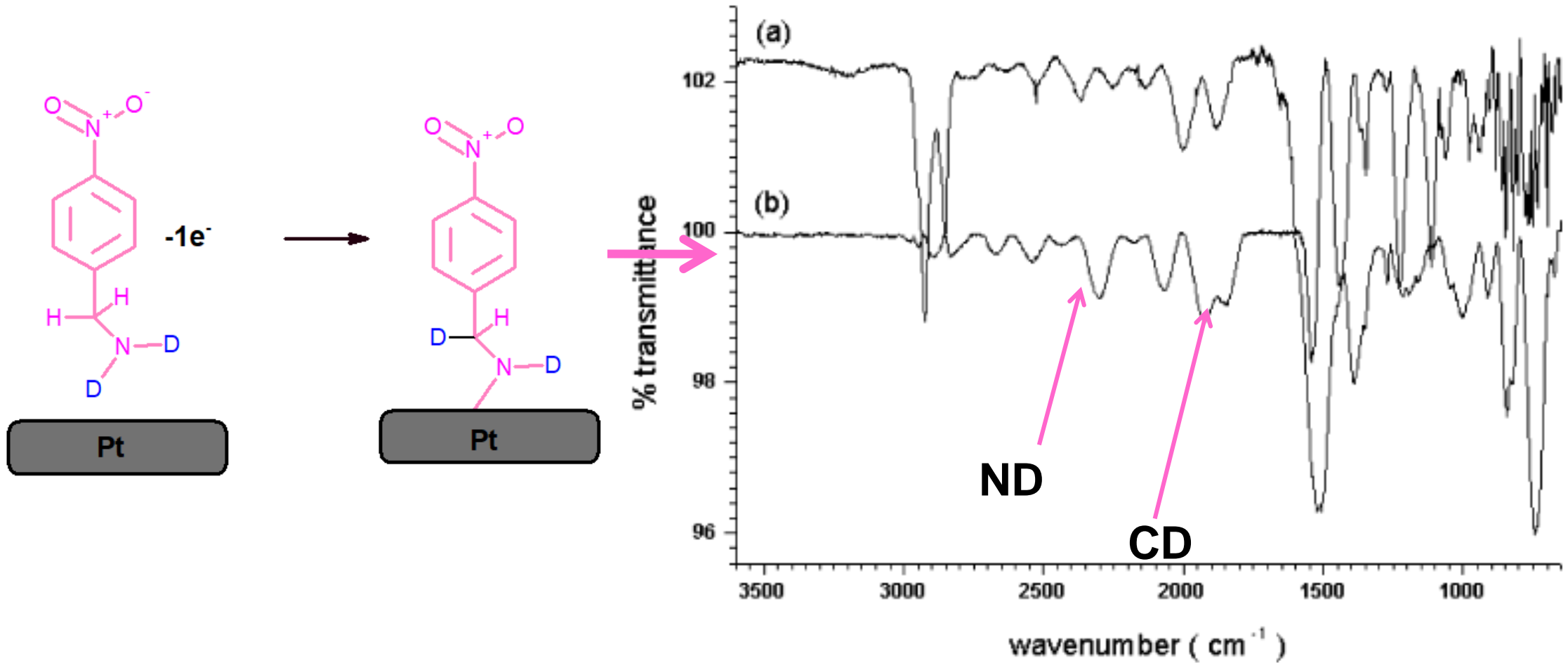
Pinson et al. Langmuir, 2004, 20, 8243.

IRRAS characterisation of the grafted layer



IRRAS spectra of Pt modified with a) -NHCH₂C₆H₄NO₂ and b) -NDCHDC₆H₄NO₂ groups

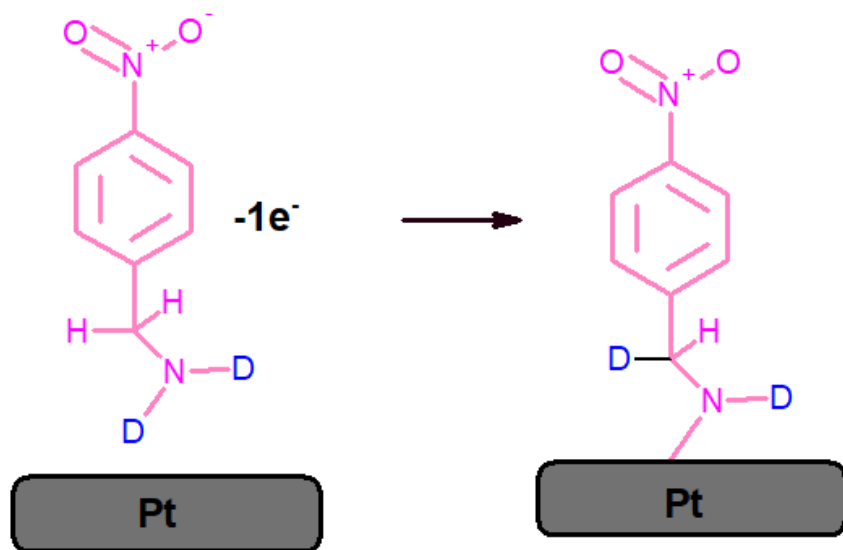
Grafting $\text{ND}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2$



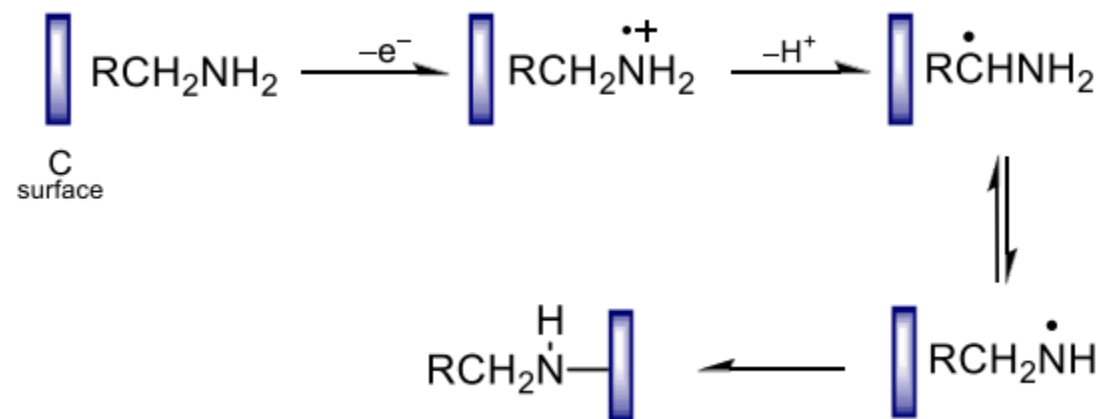
IRRAS spectra of Pt modified with a) $-\text{NHCH}_2\text{C}_6\text{H}_4\text{NO}_2$ and b) $-\text{NDCHDC}_6\text{H}_4\text{NO}_2$ groups

Electrografting reaction mechanism

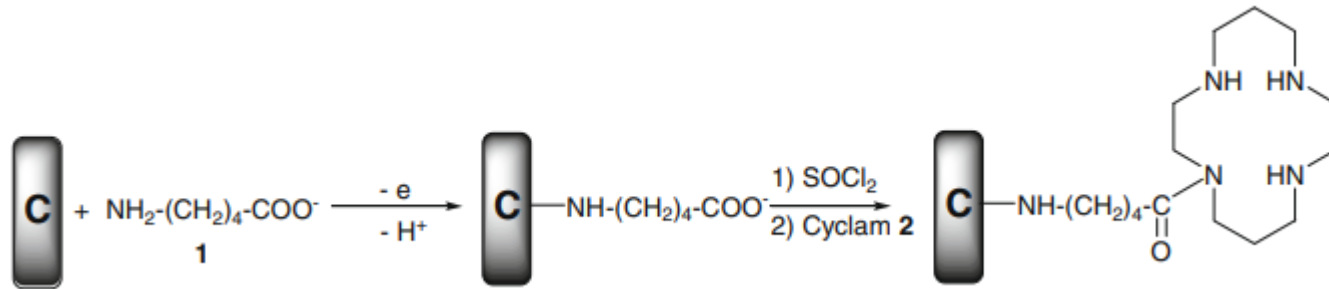
Starting from $-ND_2$ one obtains CD-ND grafted layer



The grafting mechanism of aliphatic amines is established by using deuterated amino derivatives. They showed that the radical obtained after the deprotonation reacted with the electrode surface. After the oxidation of the deuterated primary amine and the formation of the radical cation, the α C atom was deprotonated to form a carbon-centered radical; an equilibrium shift then produces the corresponding aminyl radical which binds to the substrate surface.



Use of alkylamine grafted layer for lead ion detection



The covalent immobilization of cyclam on the carbon fibres allowed the use of the modified electrode in a flow analytical system. The flow sensor exhibited high sensitivity toward lead with a limit of detection of 2.5×10^{-8} mol/L.

Cyclam: 1,4,8,11-tetraazacyclotetradecane

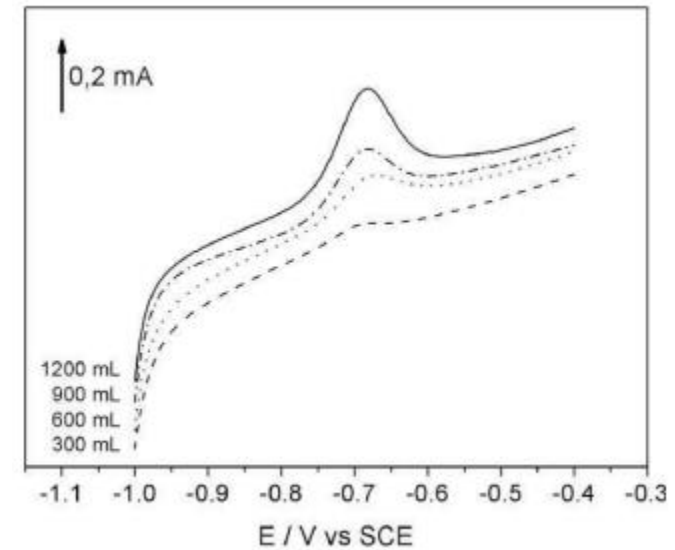
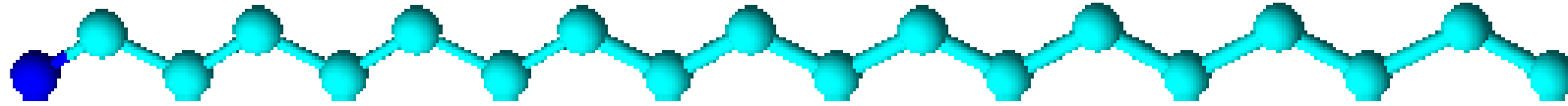
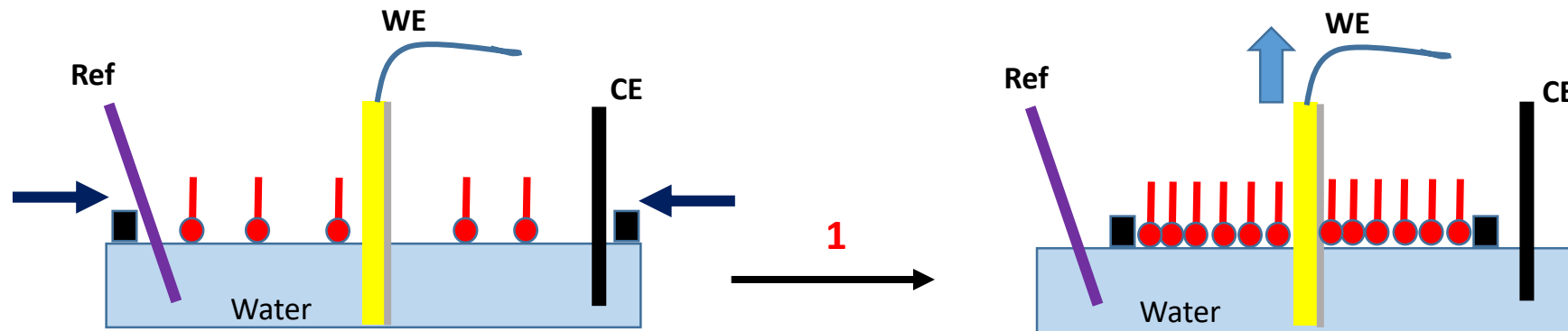


Fig. 9. Voltammograms of Pb^{2+} trapped on a graphite felt electrode after a preconcentration with a 2.5×10^{-8} M lead solution. LSSV analysis was performed in a 0.1 M aqueous solution of LiClO_4 (reduction at -1 VSCE for 5 min and then the potential was varied from -1 to -0.4 VSCE). Scan rate: 0.1 V/s .

Electrografting and Langmuir–Blodgett: Covalently Bound Nanometer-Thick Ordered Films on Graphite



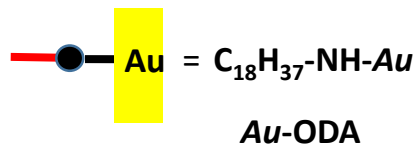
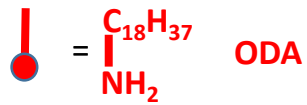
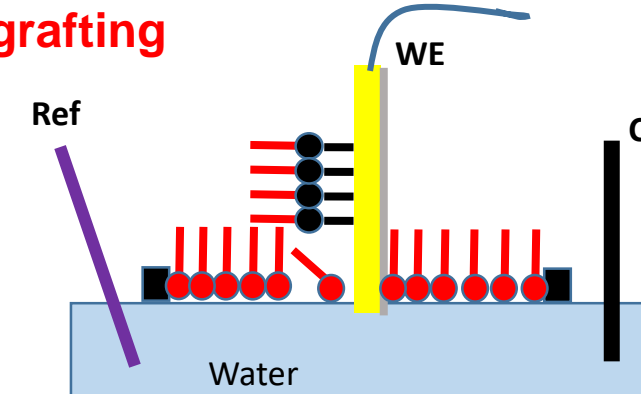
ODA: Octadecylamine



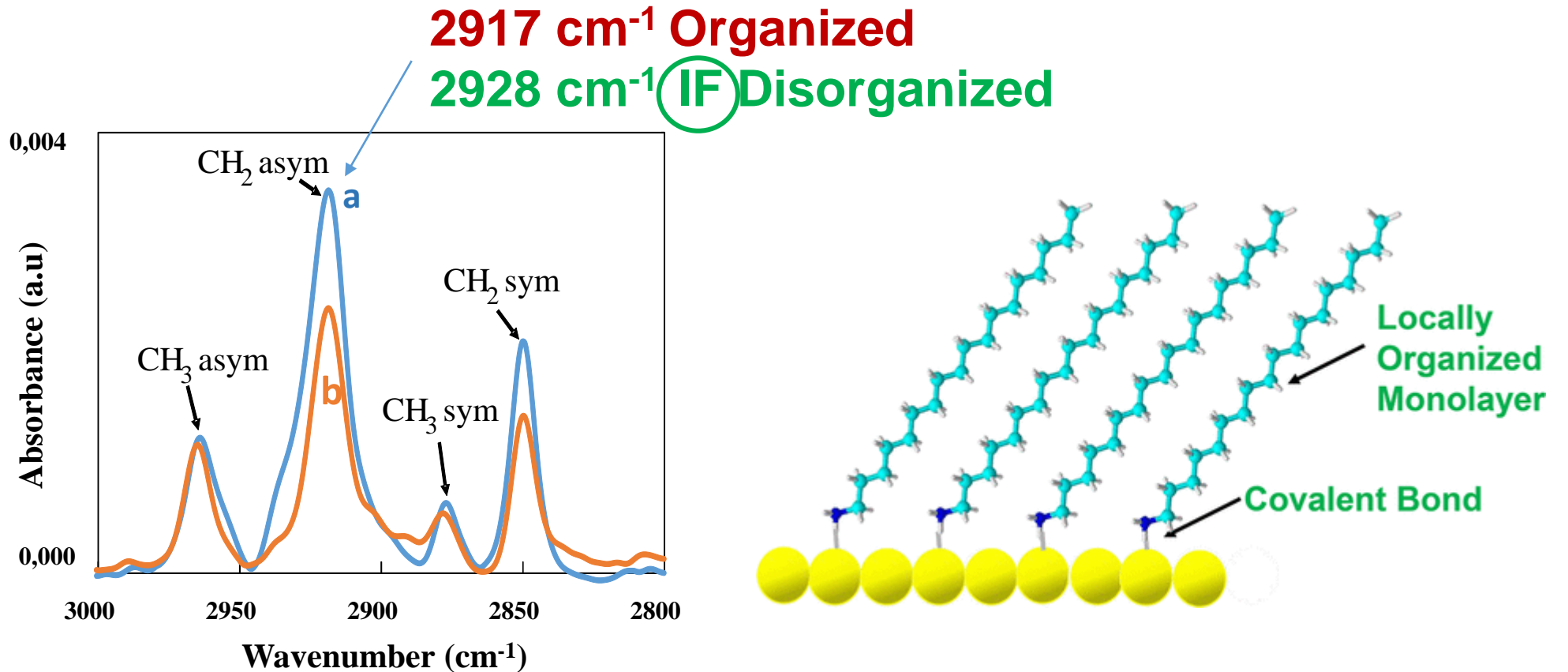
1 = Compression of the film



2 = Transfer and Electrografting



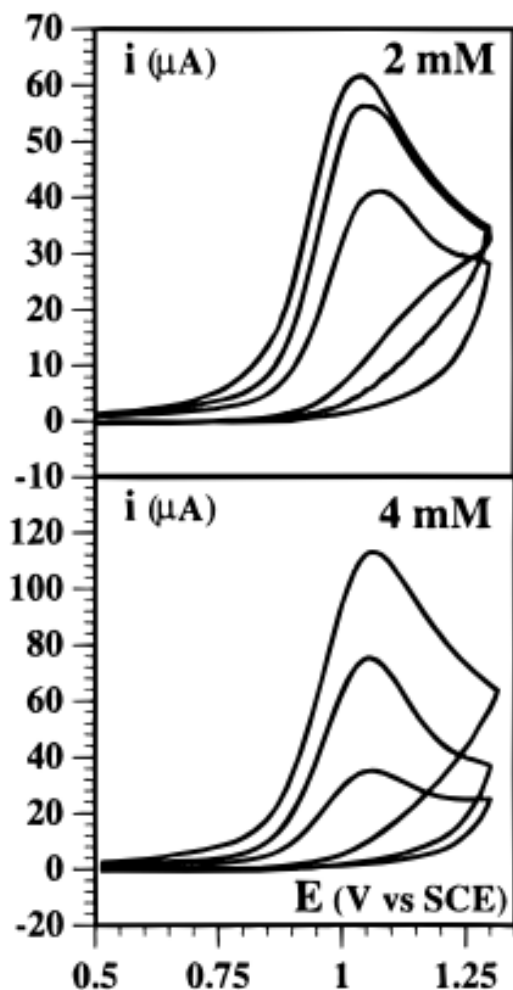
IRRAs spectrum of ODA grafted layer identical to Thiol SAMs on Au



**BUT
RESISTS US**

IRRAS spectra of a) $Au-SC_{18}H_{37}$
b) $Au-ODA_G$

ELECTROCHEMICAL OXIDATION OF CARBOXYLATES



Carboxylate compounds used electrochemical grafting
R – COOH where R structure is given below:

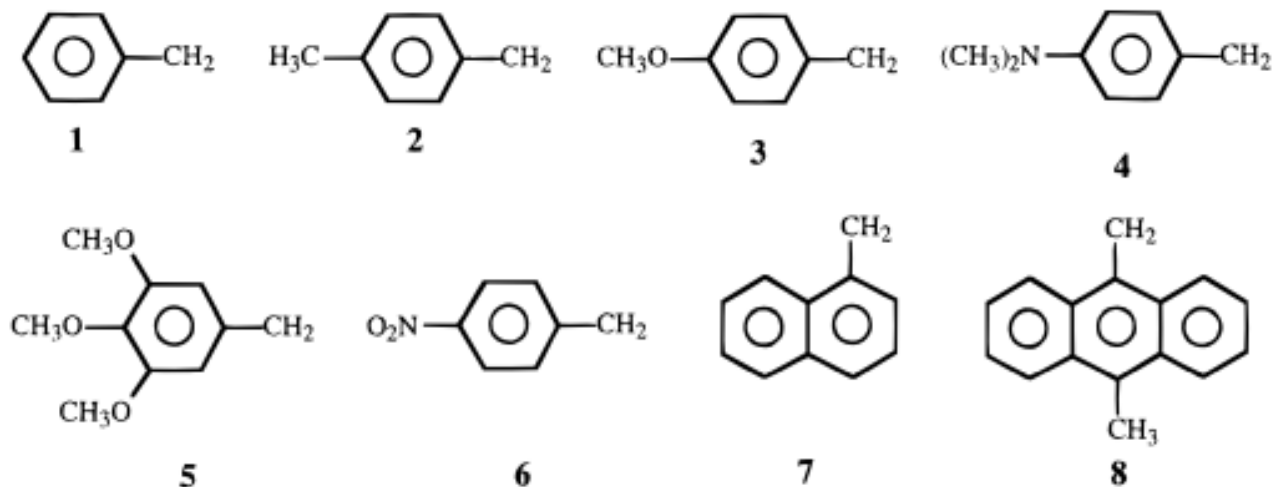
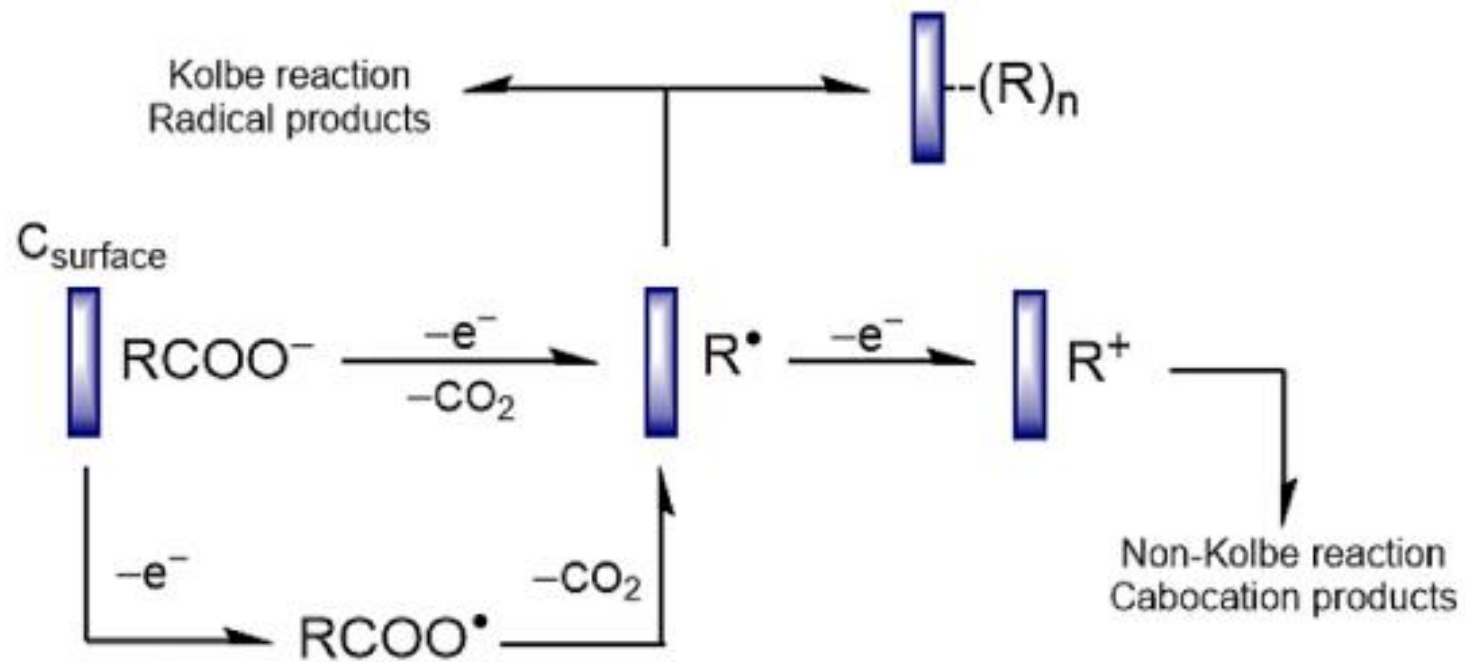


Figure 1. Repetitive cyclic voltammety of 1 in acetonitrile + 0.1 M n-Bu₄N(PF₆) at a glassy carbon electrode. Scan rate: 0.2 V/s. The solution is agitated between each of the successive cycles.

ELECTROCHEMICAL OXIDATION OF CARBOXYLATES

Reaction mechanism



Direct cathodic electrografting of vinylic polymers

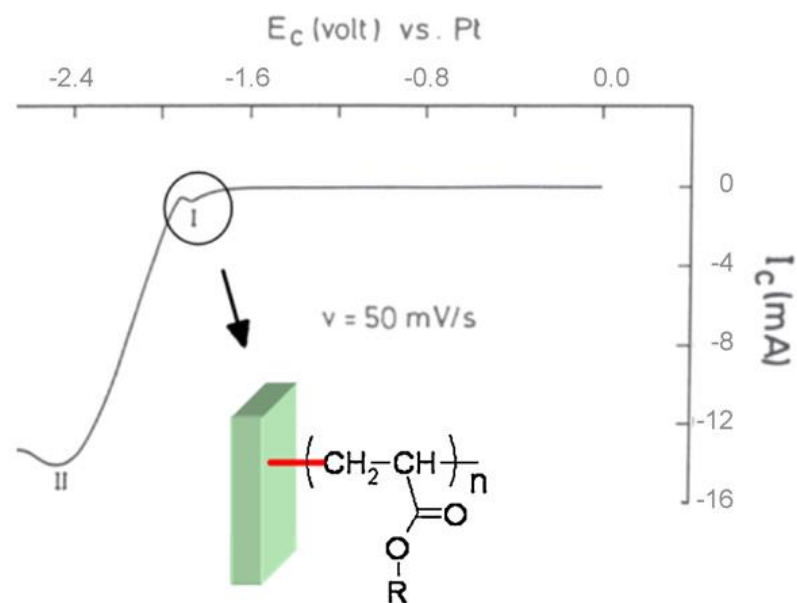
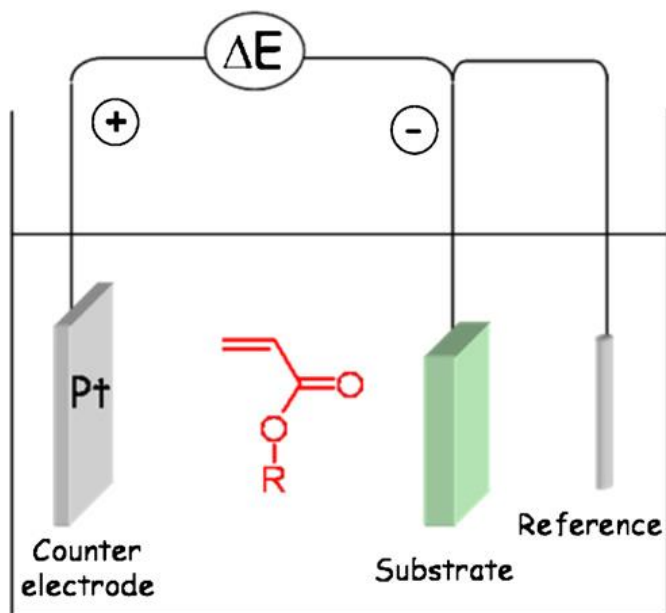
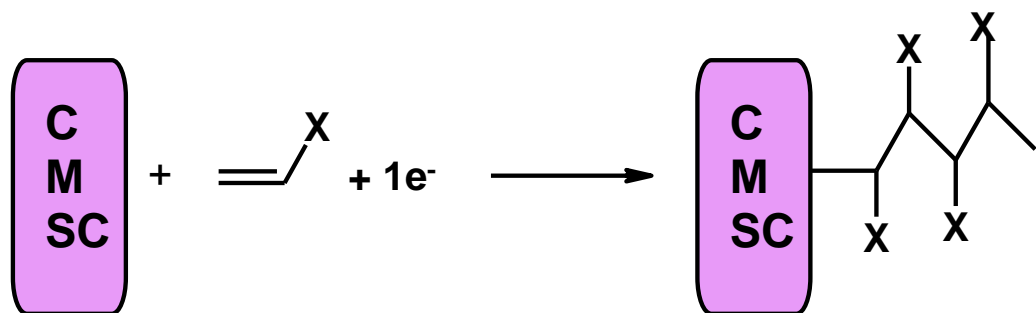
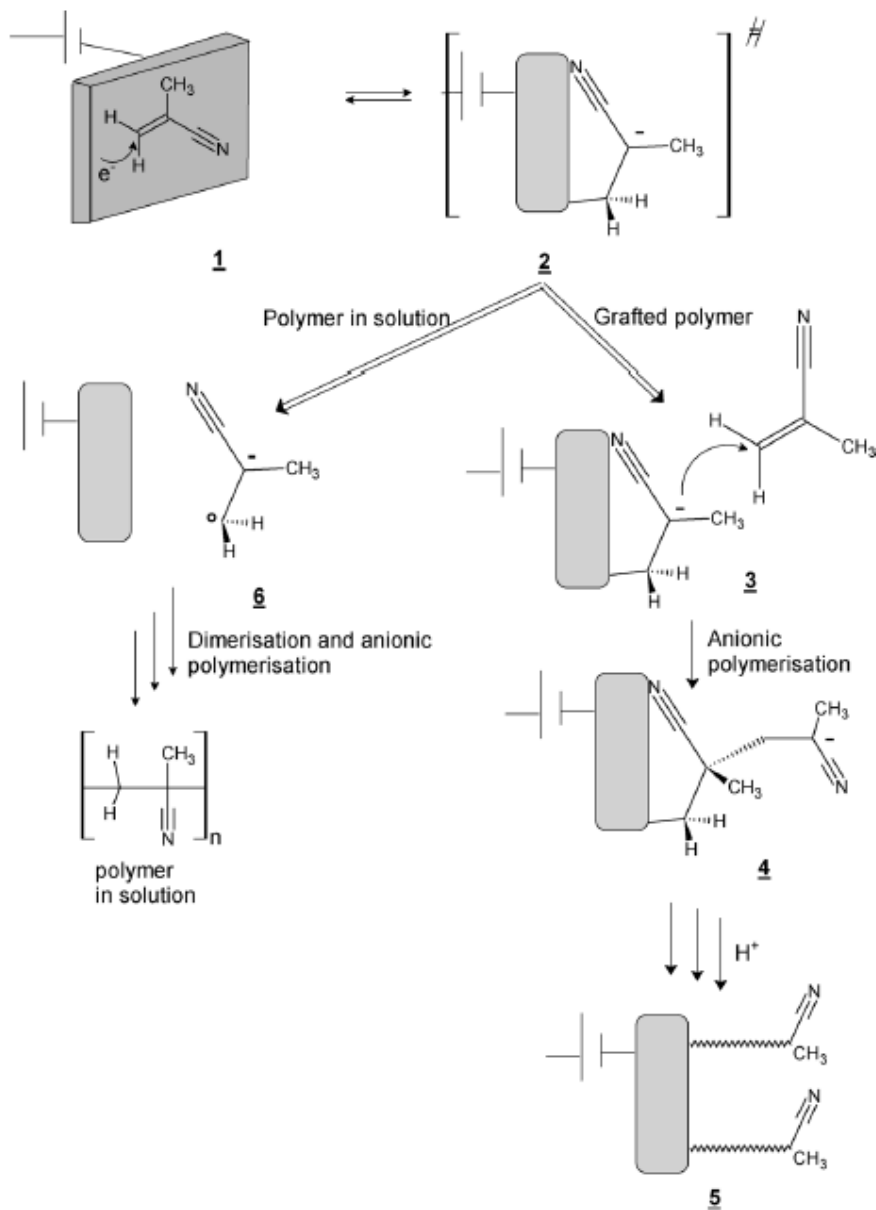


Fig. Electrochemical set-up and voltammogram typical of the electrografting of acrylates.

The conducting substrate to be coated must be cathodically polarized in an **oxygen-** and **water-free** solution of the monomer and a conducting-salt in an organic solvent, under a **dry** and **inert** atmosphere.

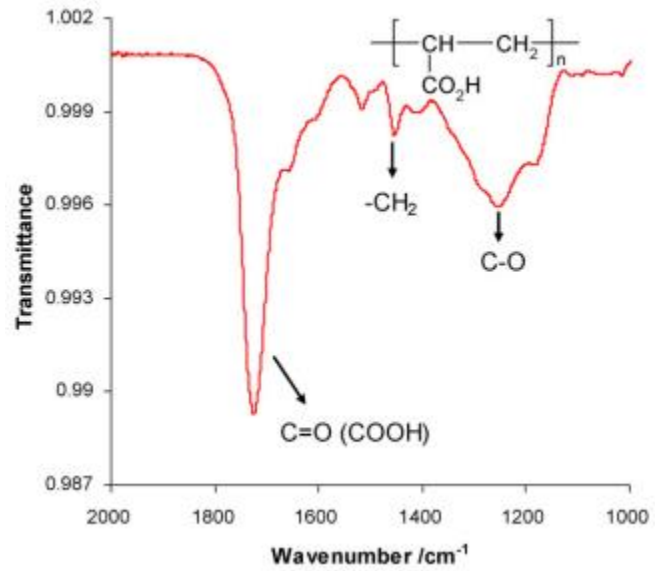
Mechanism of the electroreductive grafting of vinylics



However, Cathodic Electrografting (CE) suffers from several drawbacks which obviously limit its practical use, particularly in industrial conditions: due to its anionic mechanism, CE requires strictly anhydrous conditions.

The applied potential is highly cathodic (around $-2.5\text{ V/ Ag}^+/\text{Ag}$), which might be detrimental for substituted monomers bearing fragile groups.

Modification of Gold surface with PAA and its use for Cu ion removal



Gold surface grafted with Polyacrylic acid film (PAA)

Modification of Gold surface with PAA and its use for Cu ion removal

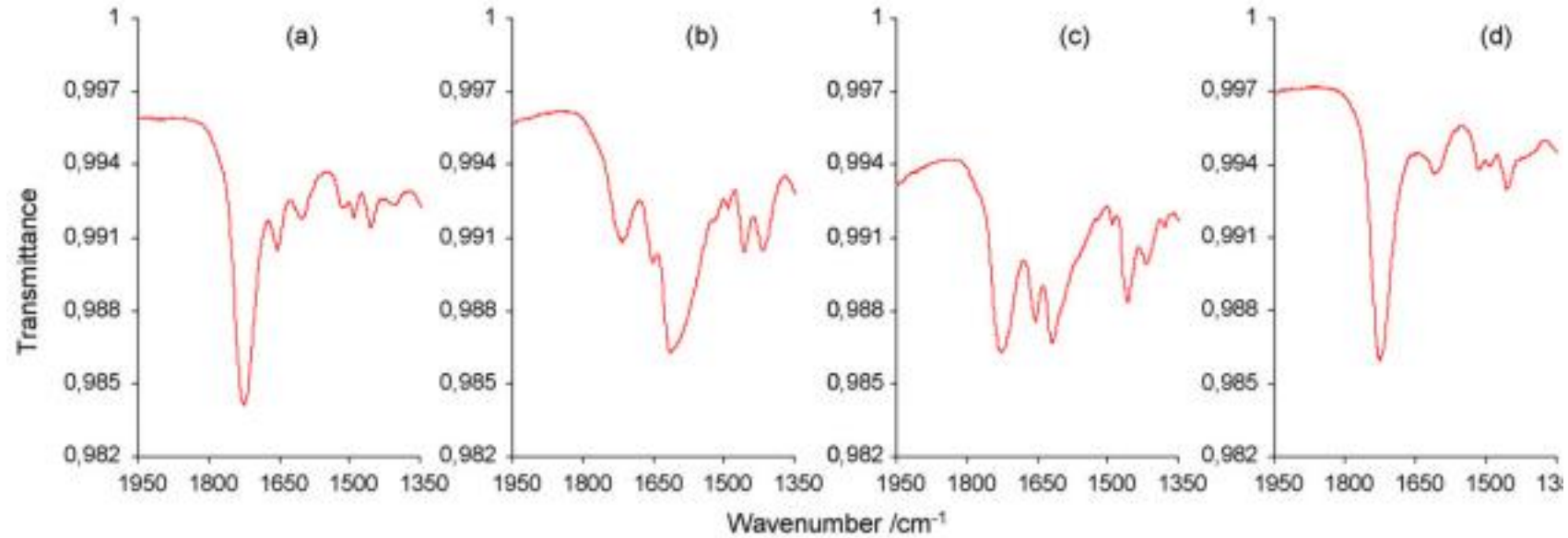


Fig. 7. Treatment progress of copper ions from the PAA film upon local electrochemical acidification, (a) initial situation, (b) complexation with Cu^{2+} ions 64 mg/L, (c) partial release of copper ions, and (d) complete release of copper ions.

ELECTROGRAFTING OF IODONIUM SALTS

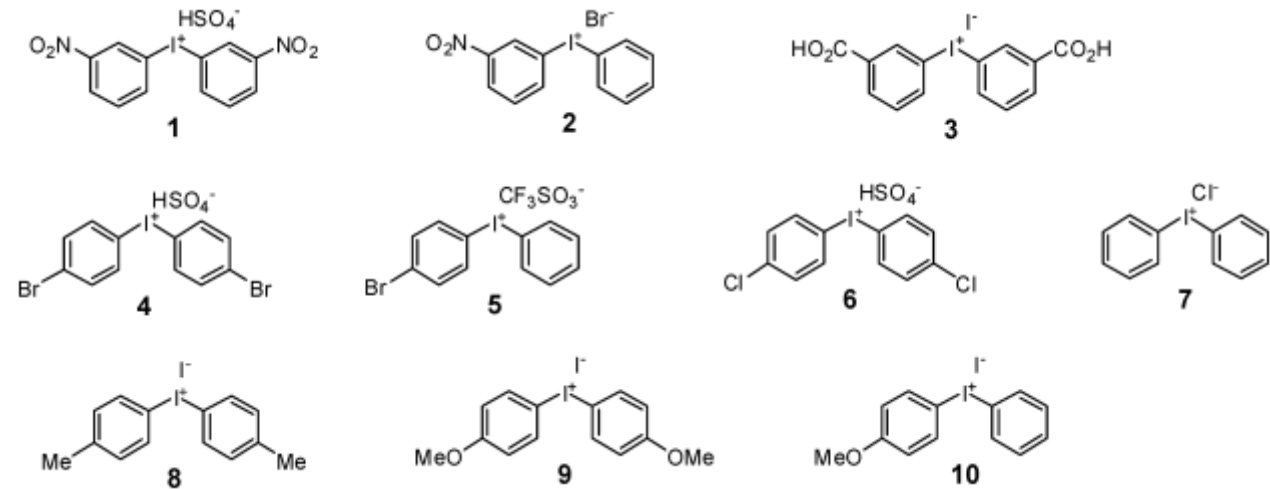
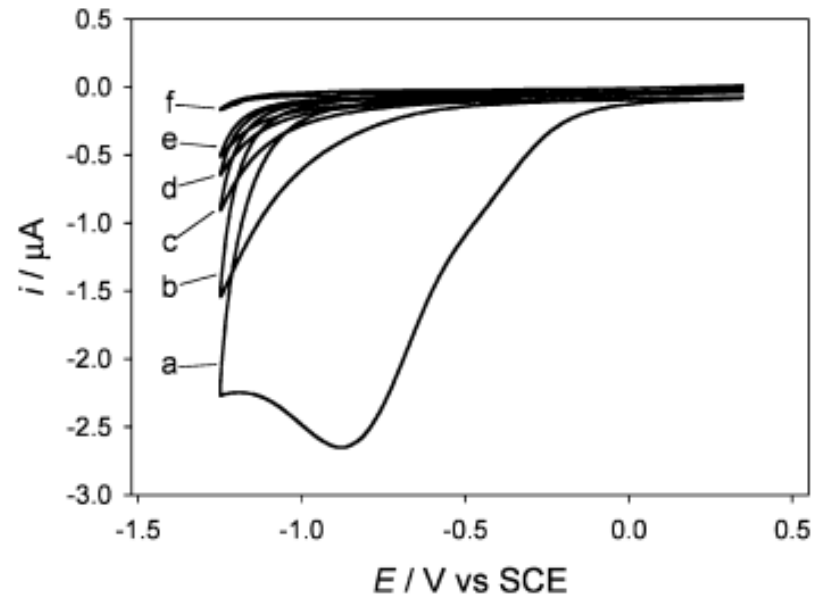
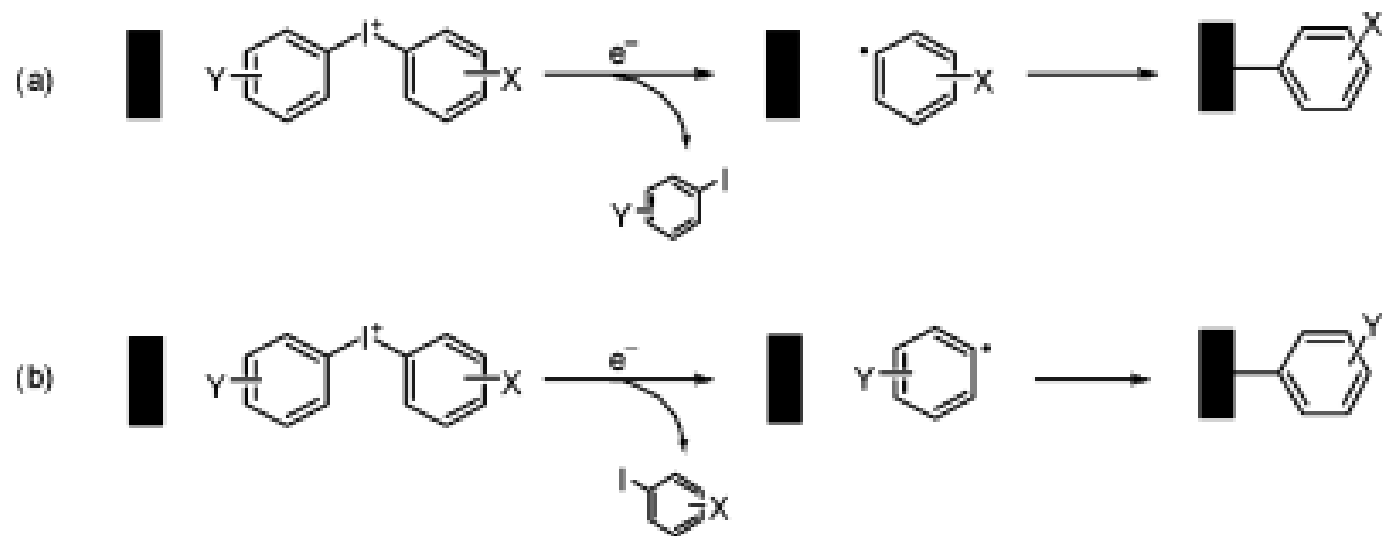


Figure 1. Cyclic voltammograms of 2 mM **4** in 0.1 M Bu₄NBF₄/MeCN recorded at a freshly polished glassy carbon electrode at a sweep rate of 0.2 V s⁻¹; sweep no. 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), and after potentiostatic electrolysis at E_{p,c} - 0.2 V for 300 s (f). The solution was stirred between cycles.

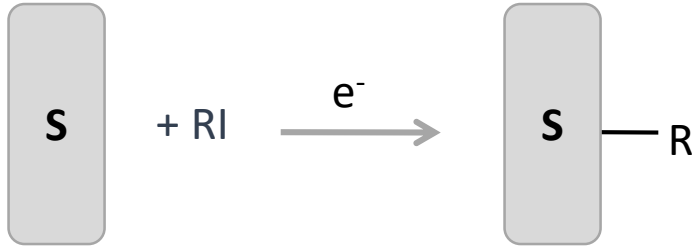
Scheme. Investigated Diaryliodonium Salts

Mechanism of the reaction



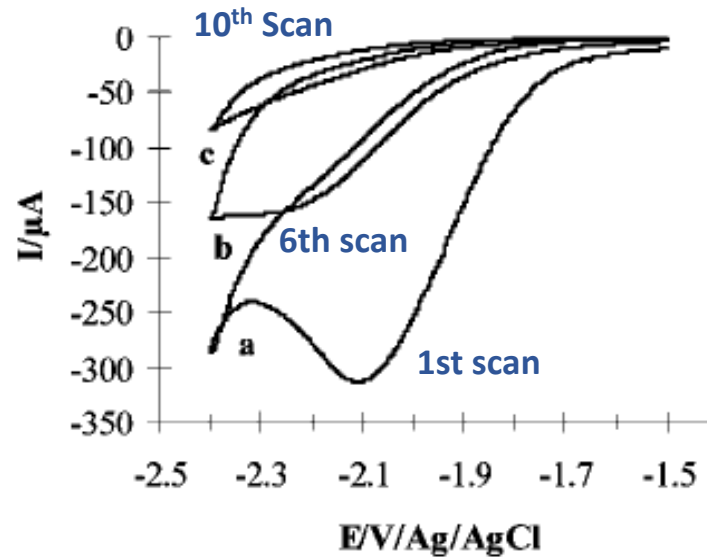
Scheme. Electrochemical Cleavage Reactions of Diaryliodonium Salts (Y) X or H)

Direct grafting of alkyl halides by electrochemistry



multilayers

$I(CH_2)_2C_6F_{13}$



Competition of R^\bullet :
grafting on the surface
and
reduction to anions

The grafting of alkyl halides takes place at very negative potentials which limits the use of this reaction.
Is it possible to achieve the same reaction at more convenient potentials?

Direct grafting of aryl halides by electrochemistry

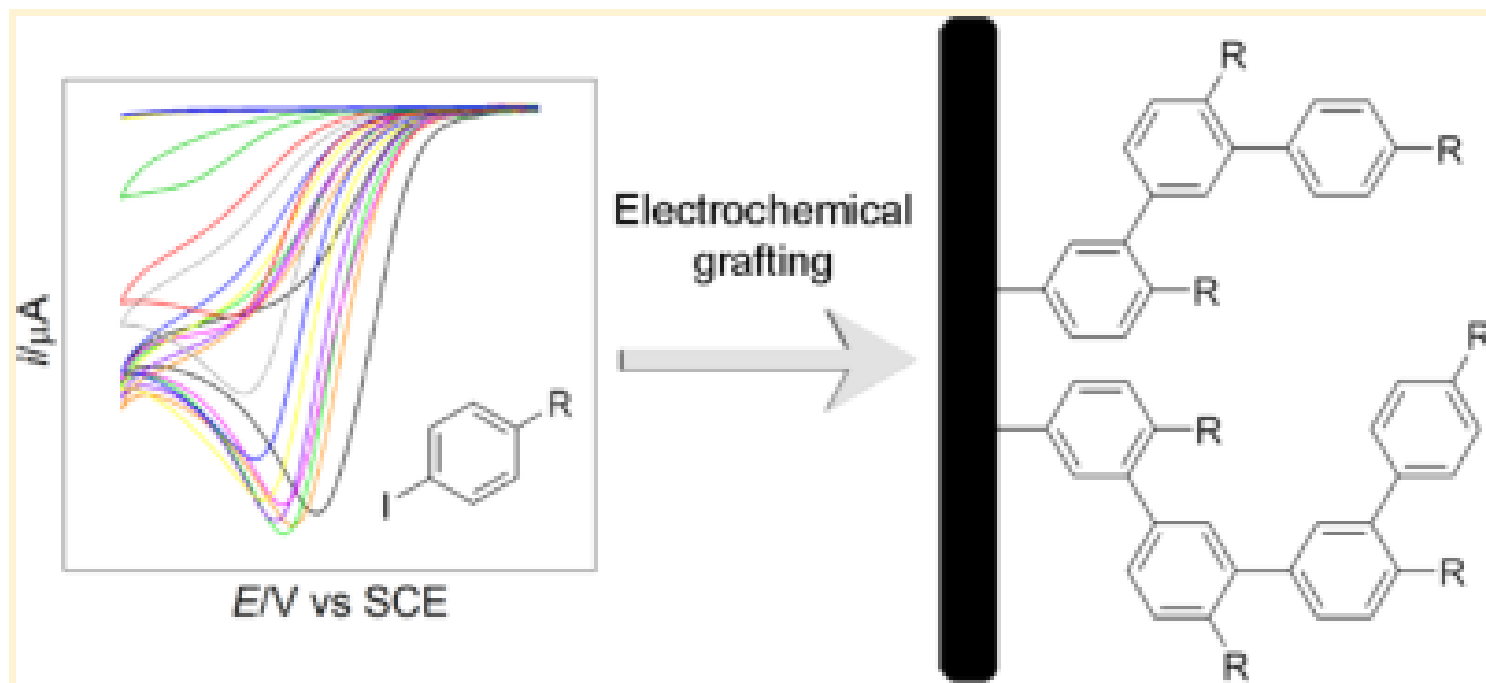
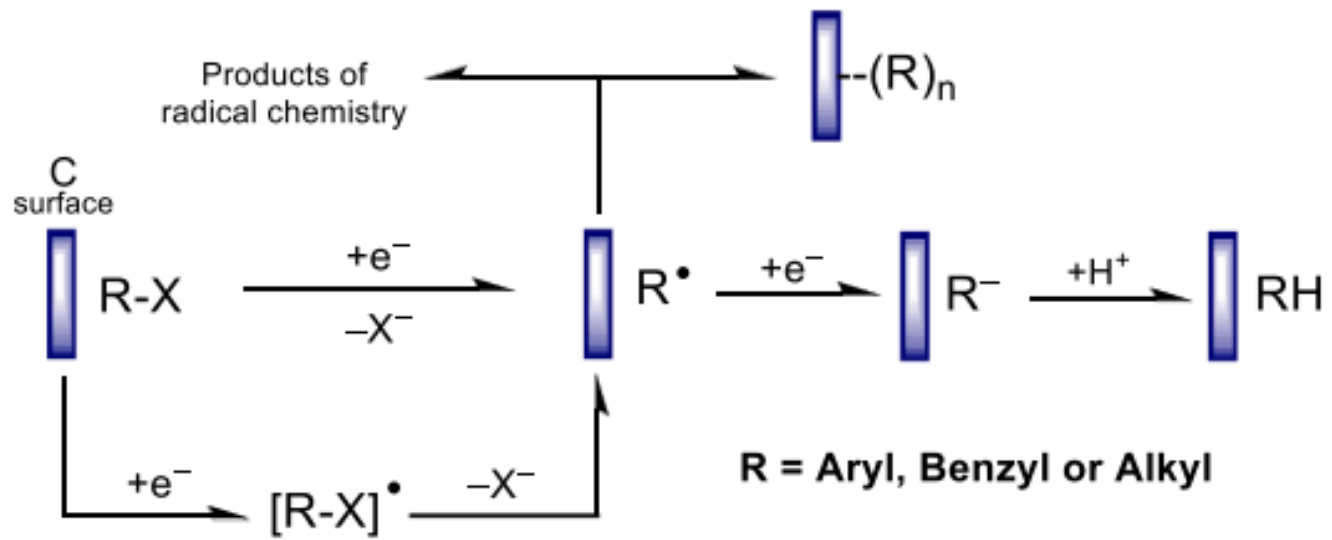
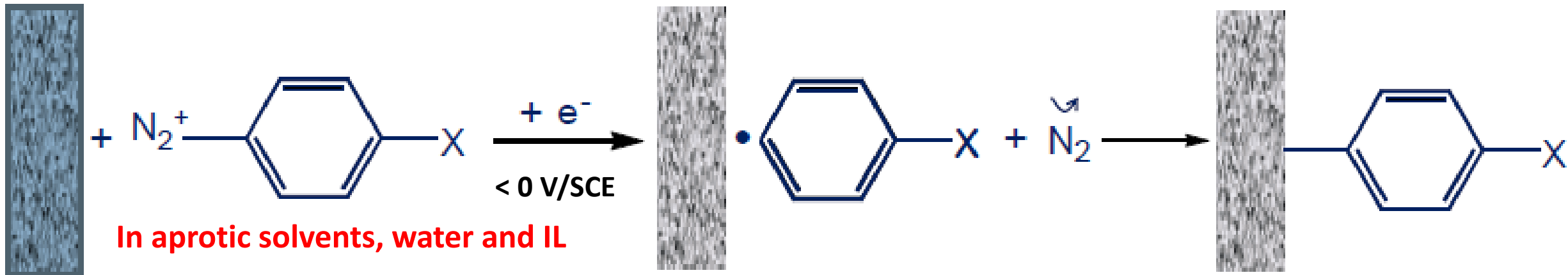


Fig. Cyclic voltammograms (CV) recorded at a GC electrode using $v = 0.1 \text{ V s}^{-1}$ on 2 mM iodobenzene in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{MeCN}$

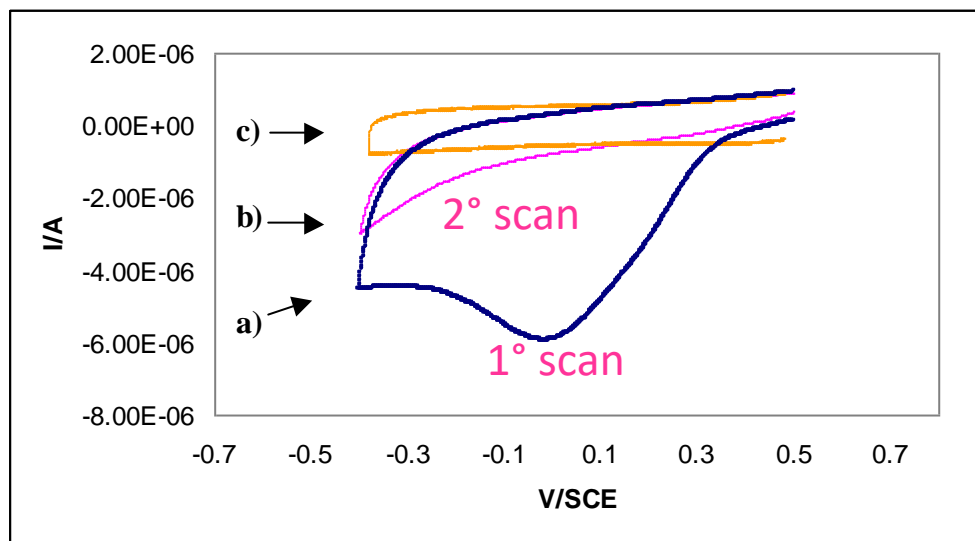
Mechanism of the reaction



Surface modification by reduction of aryl diazonium salts

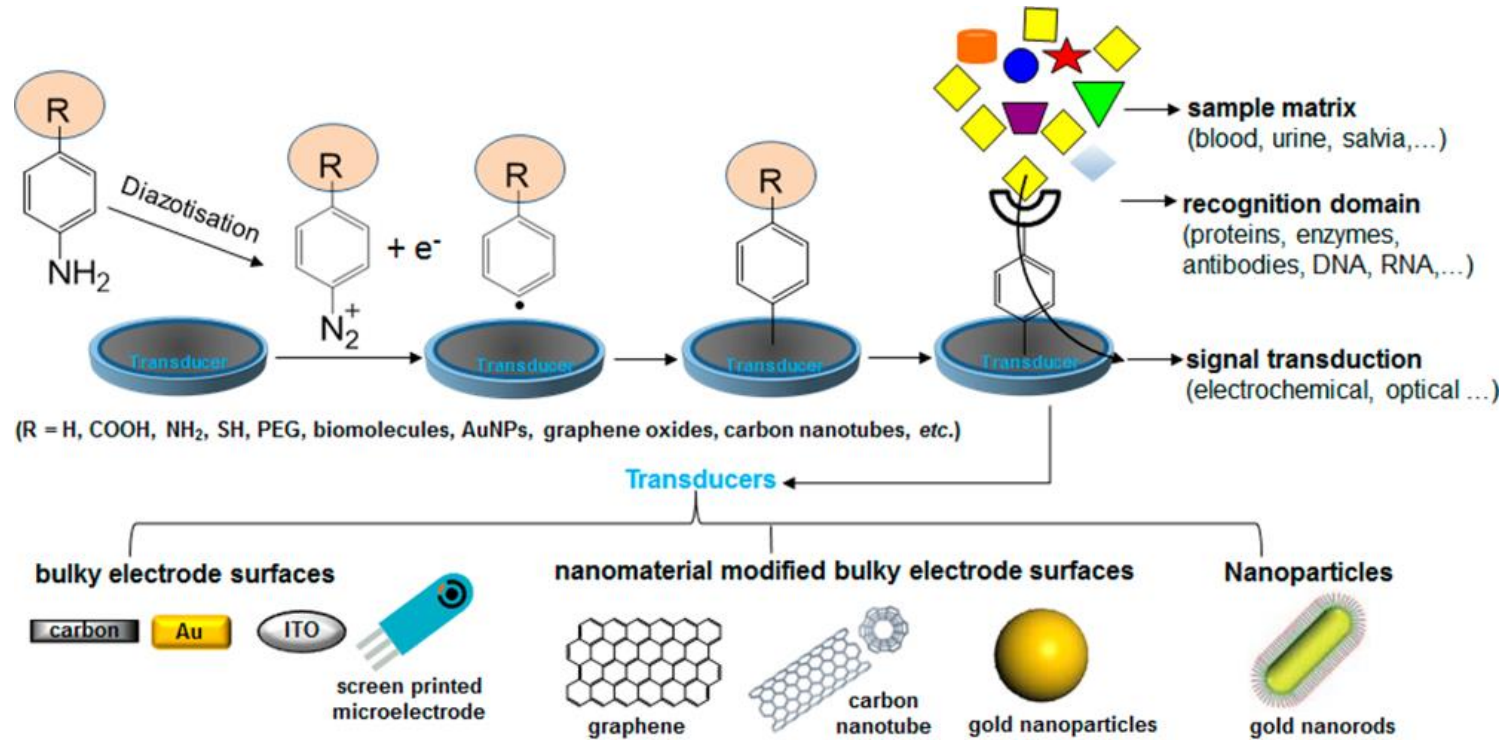


The radical is produced « on » the electrode.
It is not reduced at the potential at which it is formed



The disappearance of the peak on the 2° scan is characteristic of electrografting of Aryl Diazoniums

Diazonium salts are grafted at massive and nanometer size electrodes



Advantages over other surface coupling agents

Easily synthesized (isolated or not), rapid reaction time scale (second to minute), various choices of reactive functional groups, compatibility with wide range of materials, and strong aryl-surface covalent bonding. Therefore Diazonium Salts are considered as EXCELLENT COUPLING AGENTS due to the stability of the grafted layer and the versatility of substituents that are attached to the benzene ring.

Disadvantages: Multilayered disordered films that unable precise control over the surface composition and surface morphology

Grafting of different substrate surfaces

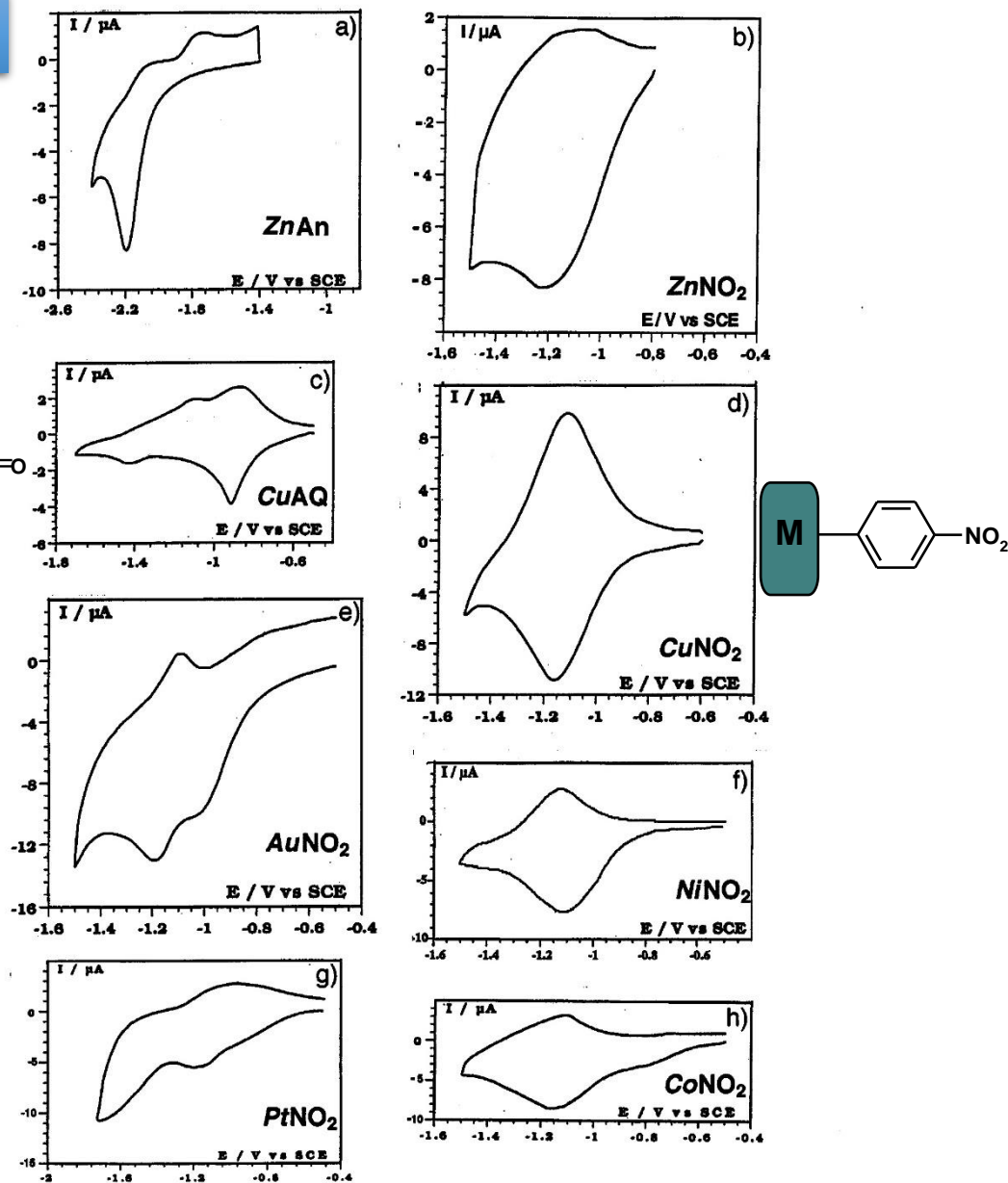
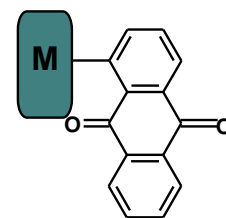
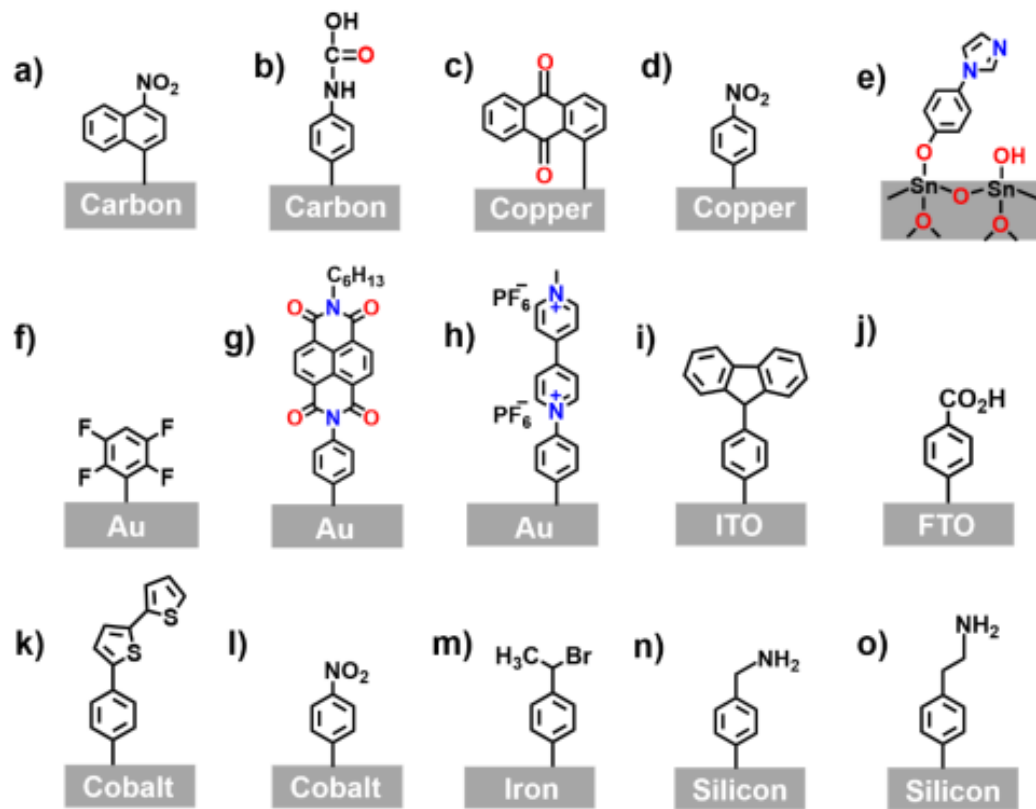


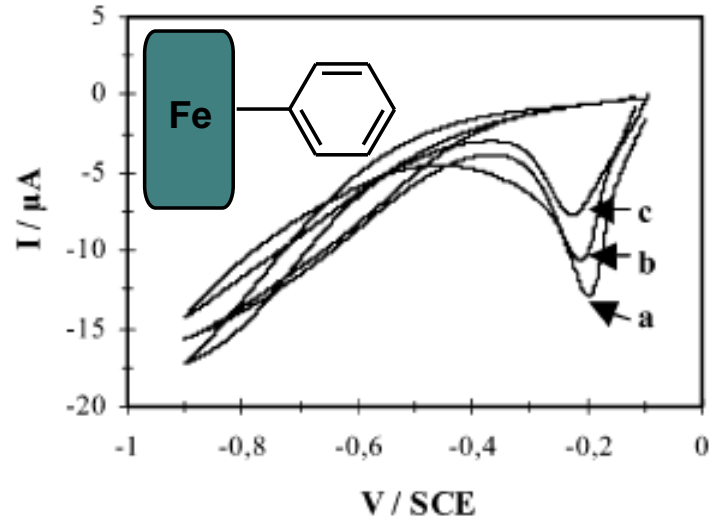
Figure 2. Cyclic voltammograms of modified metallic surfaces: (a) anthryl groups bonded to zinc, *ZnAn*; (b) nitrophenyl groups bonded to zinc, *ZnNO₂*; (c) anthraquinone groups bonded to copper, *CuAQ*; (d) nitrophenyl groups bonded to copper, *CuNO₂*; (e) nitrophenyl groups bonded to gold, *AuNO₂*; (f) nitrophenyl groups bonded to nickel, *NiNO₂*; (g) nitrophenyl groups bonded to platinum, *PtNO₂*; and (h) nitrophenyl groups bonded to cobalt, *CoNO₂*.

The parameters controlling the thickness of the layer obtained by electrochemical or spontaneous reduction of diazonium salts

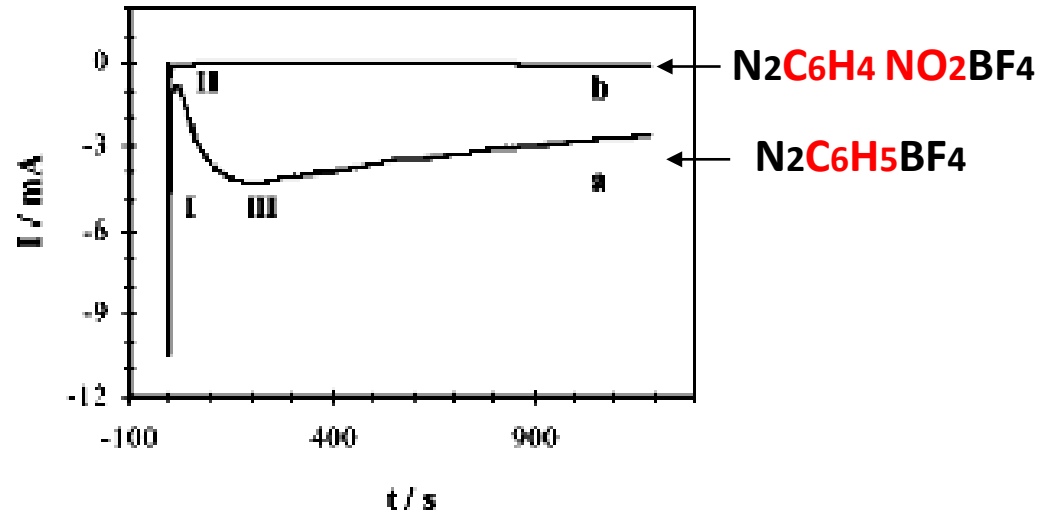
- Concentration of the solution of the diazonium salts
- Potential of electrolysis
- Time of electrolysis, Immersion time
- Nature of the diazonium salt and of the substrate
- **Steric hindrance of the radical**

Steric effects

No steric hindrance - Formation of Micrometric PolyPhenylene layer



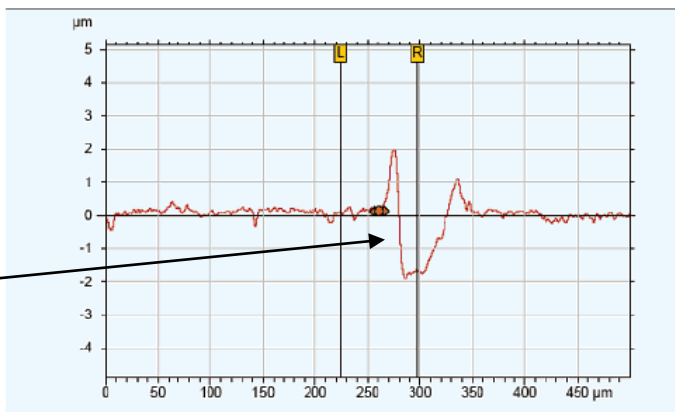
a) 1st; b) 4th and c) 12th scan



Fe / ACN

No steric hindrance- - Formation of Micrometric PolyPhenylene layer

Profilometry



TofSIMS

Table 2. ToF-SIMS Spectrum of a Polyphenyl Film Obtained by Electrodeposition on Iron^a

m/z	assignment
77	$C_6H_5^+$
91	$C_6H_5CH_2^+$
105	$C_6H_5CH_2CH_2^+$
115	$C_6H_5CH=CH=CH^+$ or isomer
128	$C_6H_5CH=CH=CH=CH^+$ or isomer
152	$[C_6H_5-C_6H_5-2H]^+$
228	$[C_6H_5-C_6H_4-C_6H_5-2H]^+$
304	$[C_6H_5-C_6H_4-C_6H_4-C_6H_5-2H]^+$

^a Polyphenyl fragments.

Figure 4. Profilometry of a PP film electrodeposited onto an iron plate. Electrolysis for 20 min at -1.1 V/SCE in an ACN + 0.1 M NBu_4BF_4 + 10 mM $^+N_2C_6H_5$ BF_4^- solution.

SEM

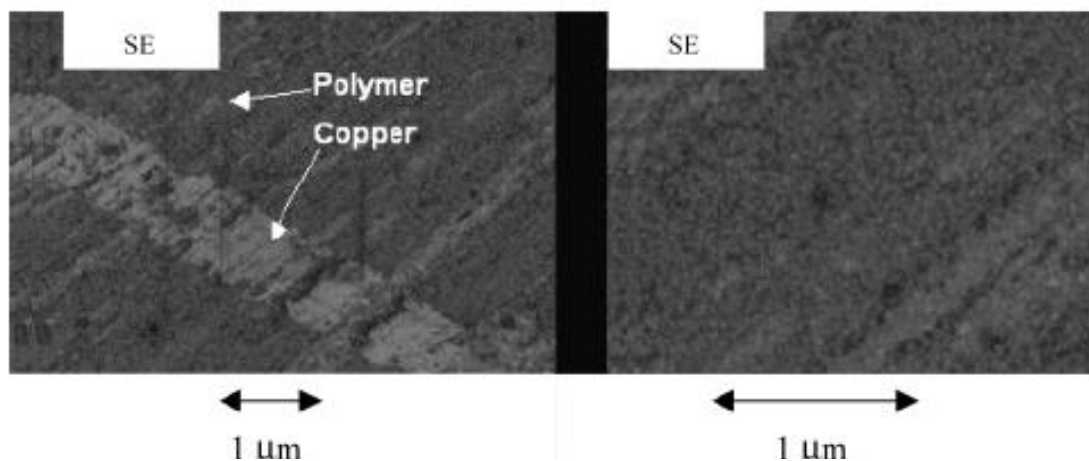
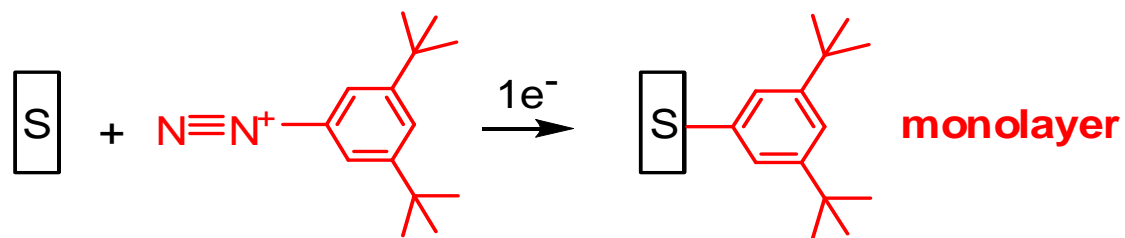
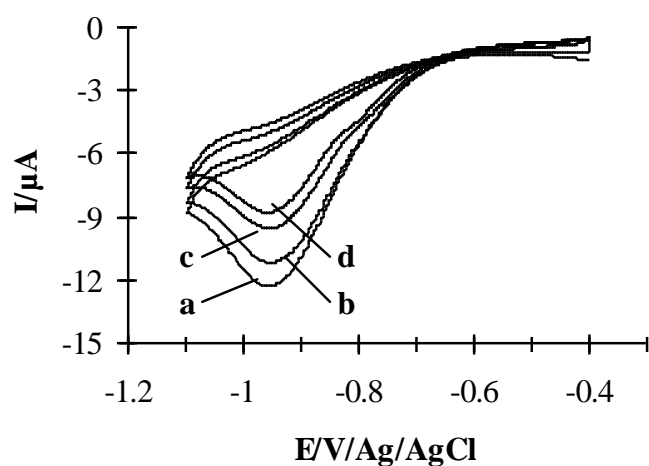


Figure 6. SEM of a PP film on a copper surface. SEs. Left: scratched surface.

Effect of the steric hindrance of aryl radicals on the grafting-monolayer formation



S = Cu, Au, SiH, HOPG and graphene

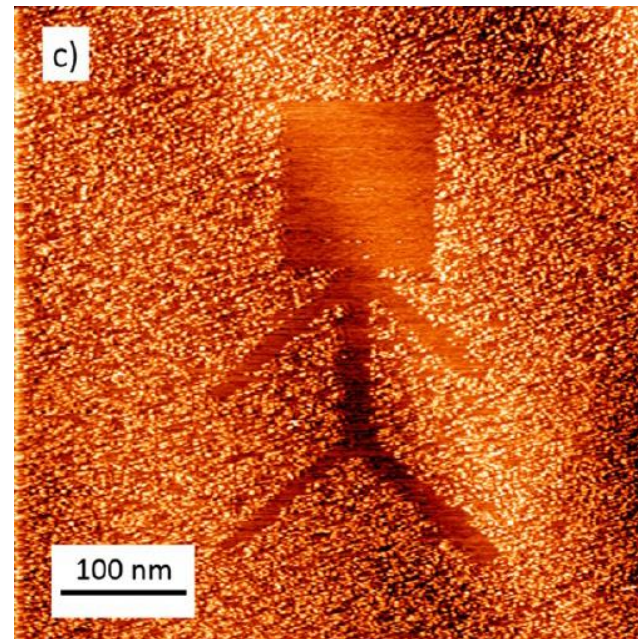
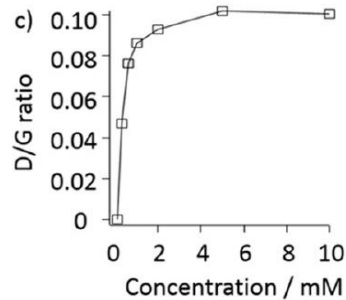
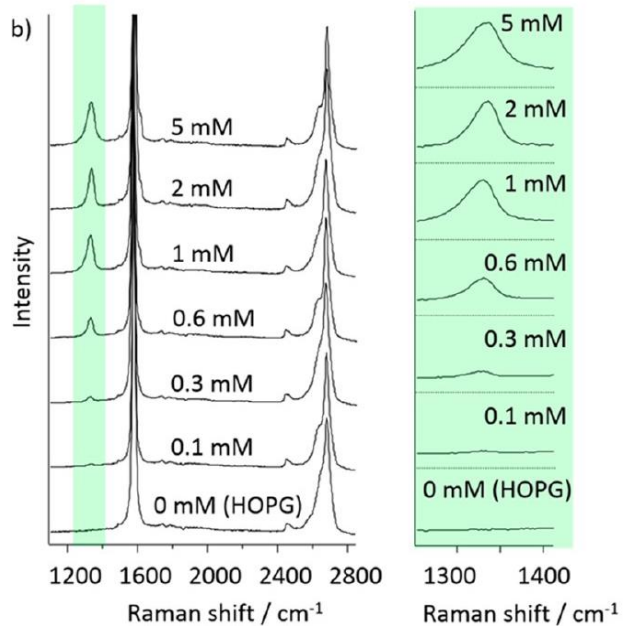
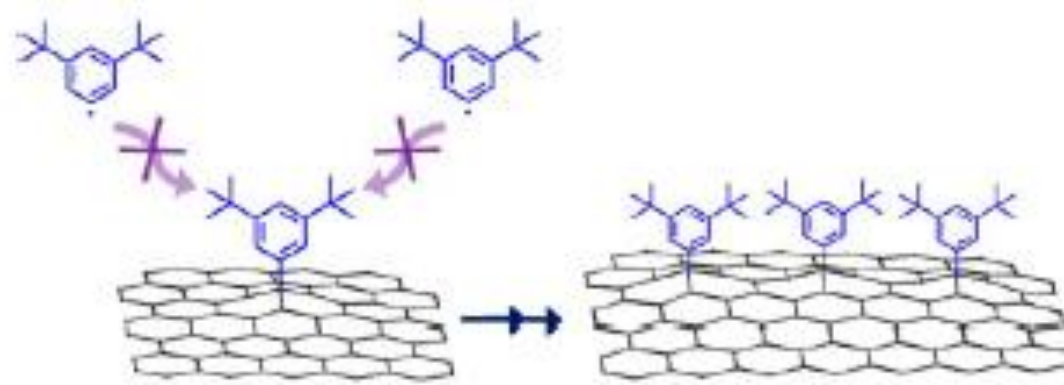
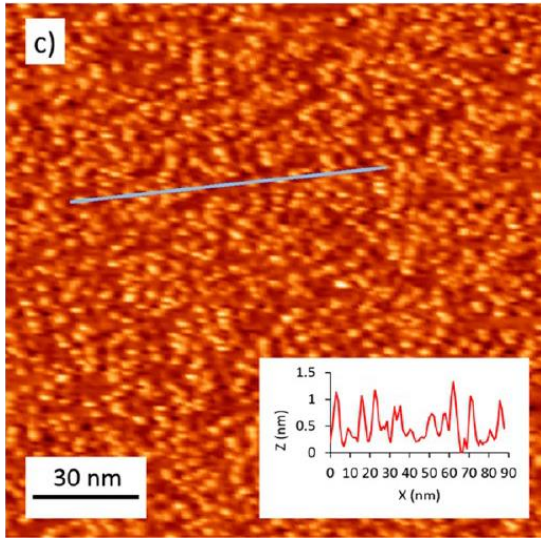
a) 1st; b) 2nd; c) 5th and d) 10th scan.

Table 1. Modification of Surfaces by **1** by Chronoamperometry^a

substrate	time (s)	E (V _{Ag/AgCl})	layer thickness (nm)
Cu	30	-1.2	1.3, $\sigma = 0.6$
Au	300	-1.4	1.0, $\sigma = 0.3$
SiH	150	-0.5	1.6, $\sigma = 0.1$

^a [1] = 4 mM in ACN + 0.1 M NBu₄BF₄.

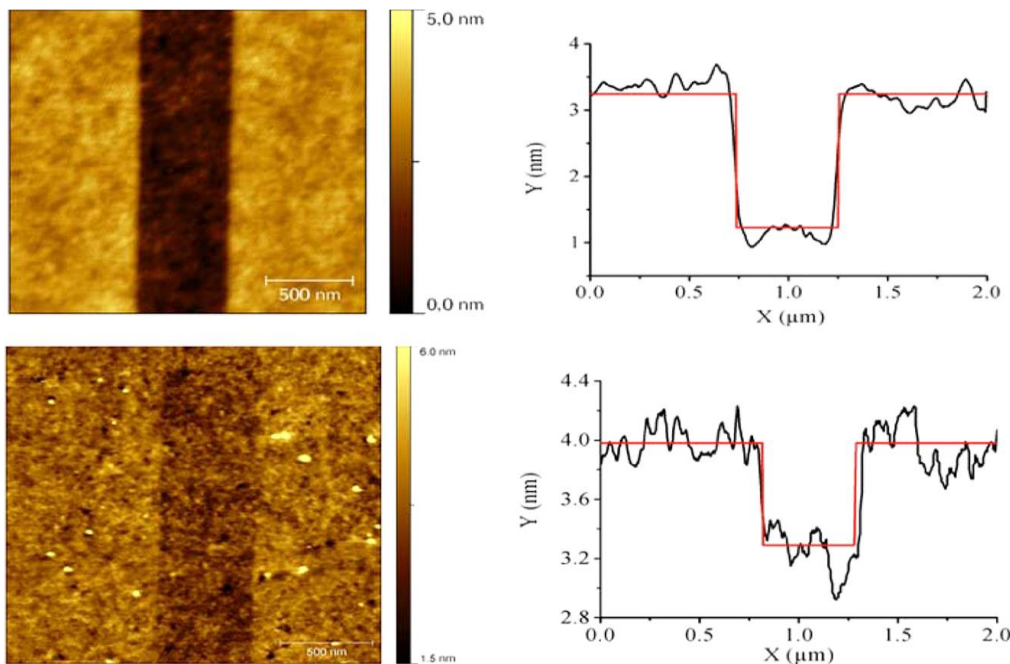
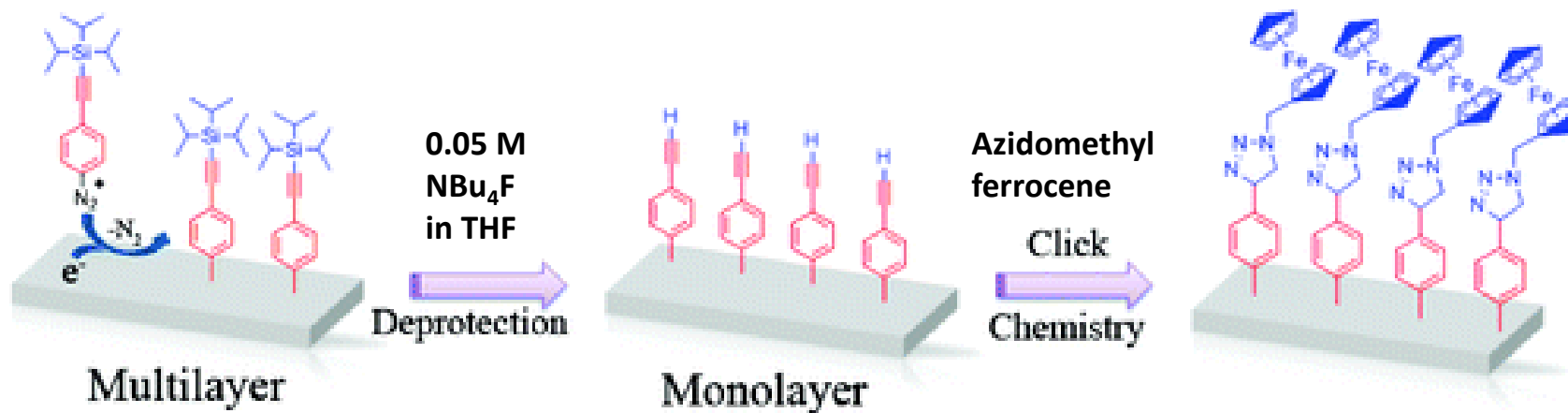
STM and Raman Spectroscopy characterization of 3,5-bis-t-butylphenyl mono layer



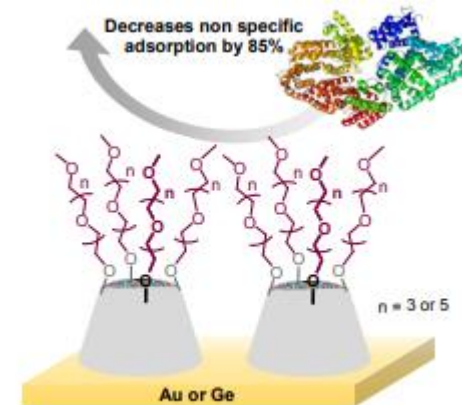
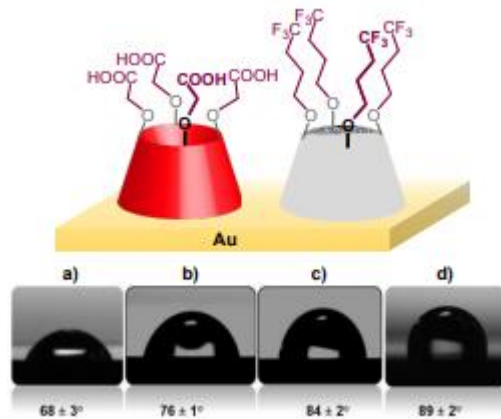
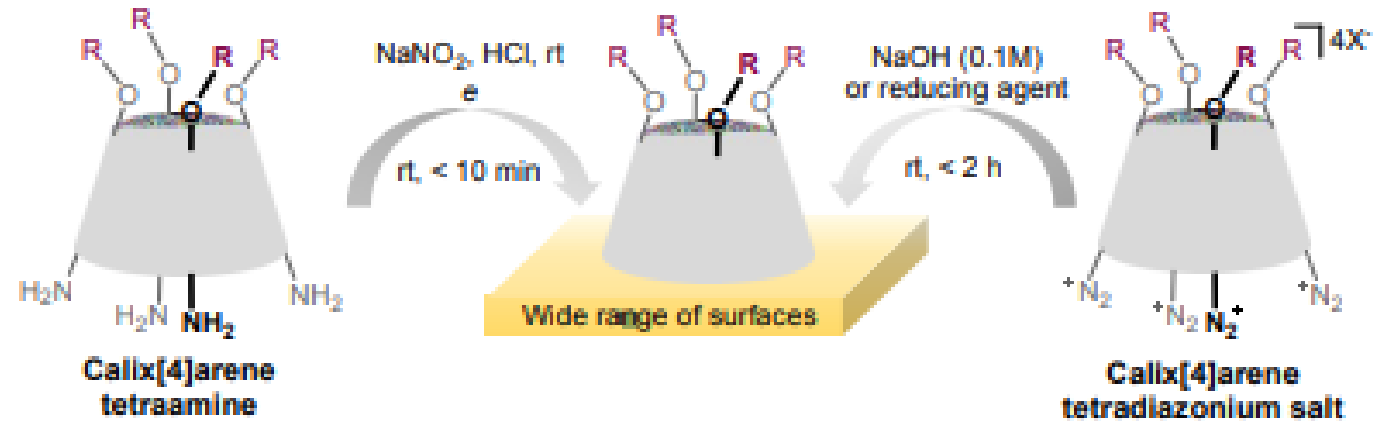
Regenerating pristine sp^2 hybridized carbon atoms on HOPG

Effect of the steric hindrance of aryl radicals on the grafting

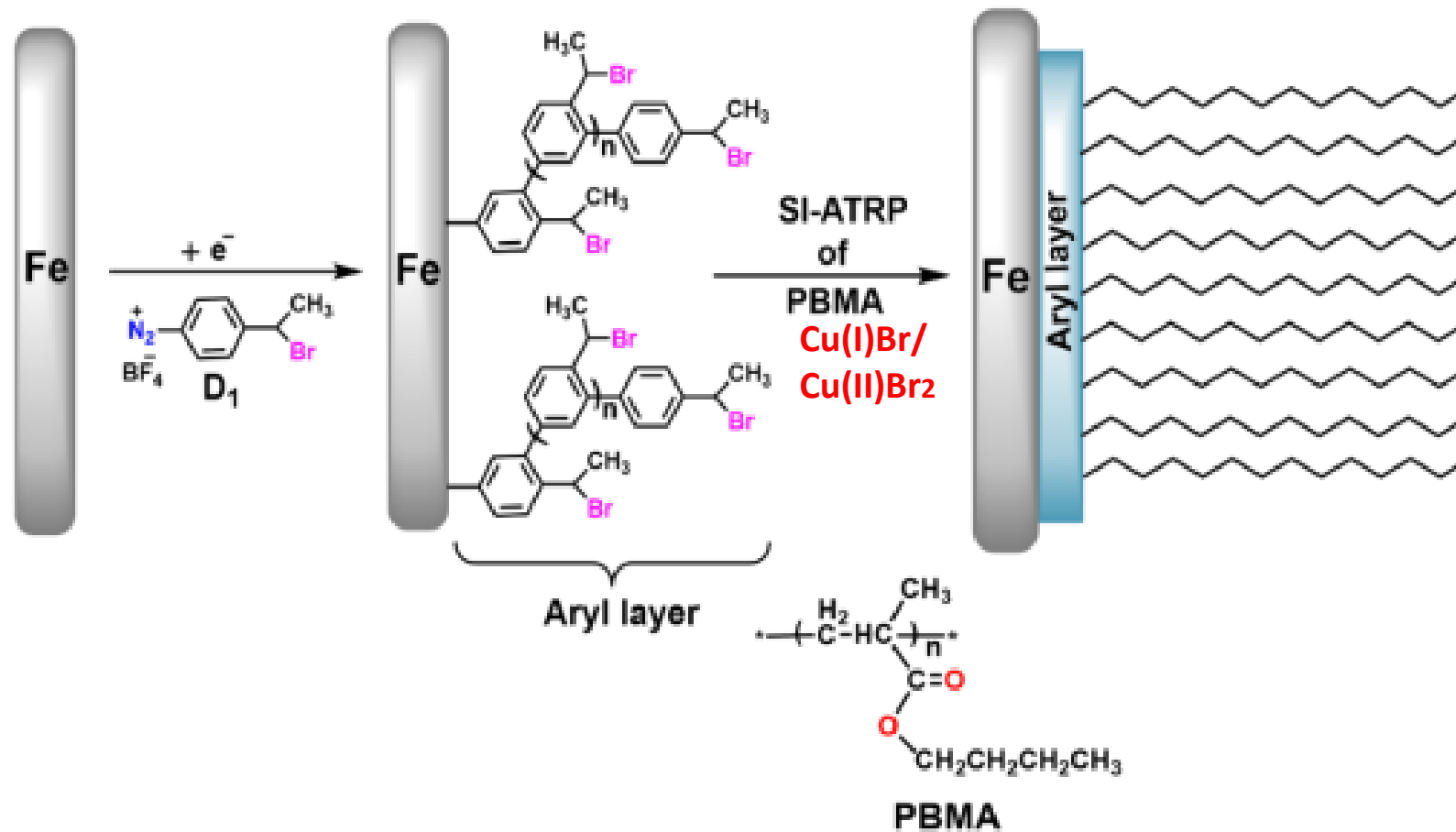
Electrochemical grafting of Triisopropylsilyl (TIPS)-protected ethynyl aryl diazonium salt



Use of calixarenes bearing diazonium groups for the development of robust monolayers



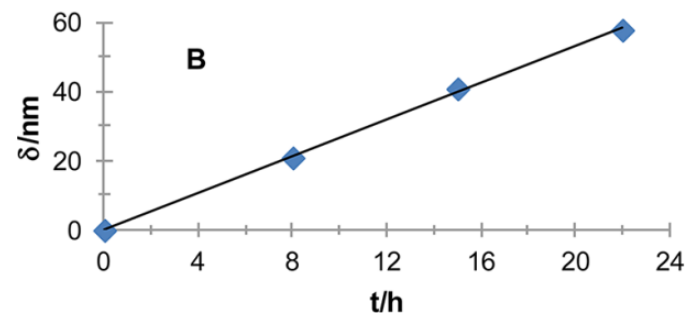
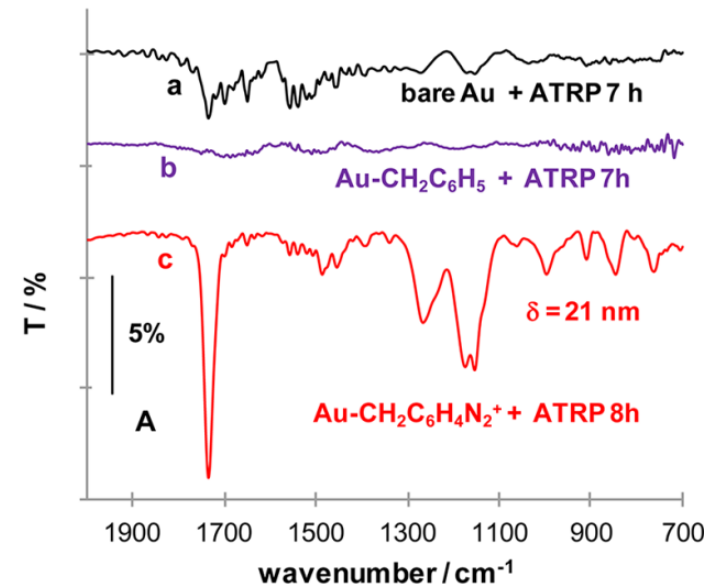
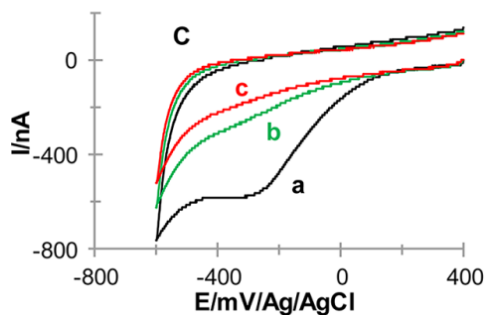
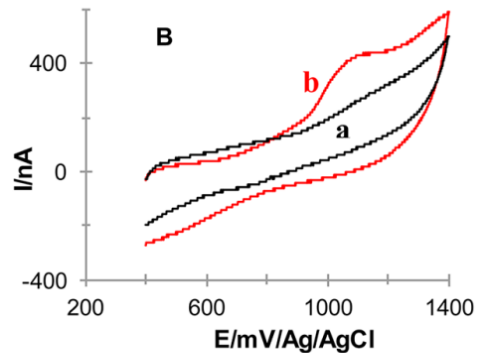
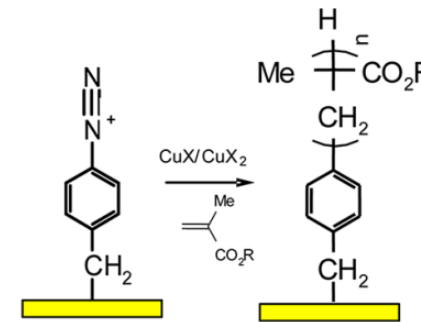
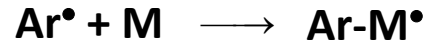
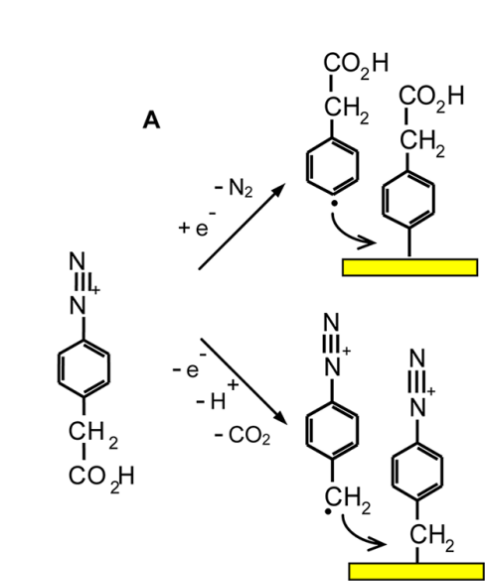
The use of functional group as initiators of SI-ATRP (Surface Initiated Atom Transfer Radical Polymerization)



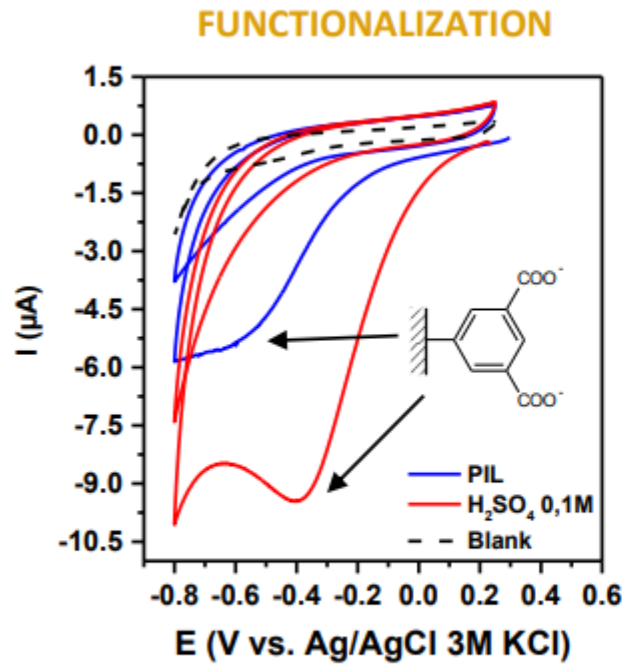
Matyjaszewski et al. Nature Chemistry 2009

Chehimi et al. Langmuir 2005; Daasbjerg et al. Langmuir 2010;

ATRP initiated via active surface diazonium groups



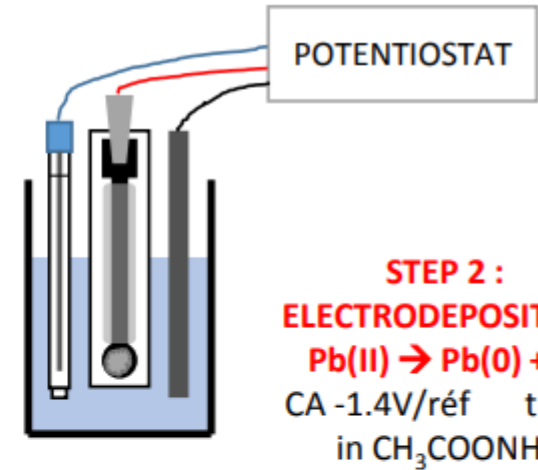
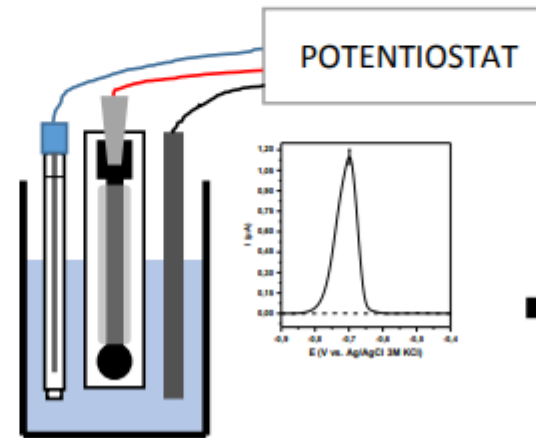
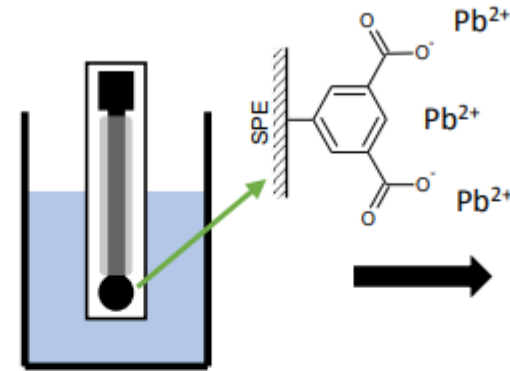
Use of 3,5-dicarboxybenzene diazonium salt for Pb²⁺ ion detection



STEP 1 : Pb(II) ADSORPTION
 Preconcentration
 5 min in CH₃COONH₄
 + Pb(II)

STEP 3 : ELECTROCHEMICAL DETECTION
 Pb(0) - 2 e⁻ → Pb(II)
 SWV in CH₃COONH₄

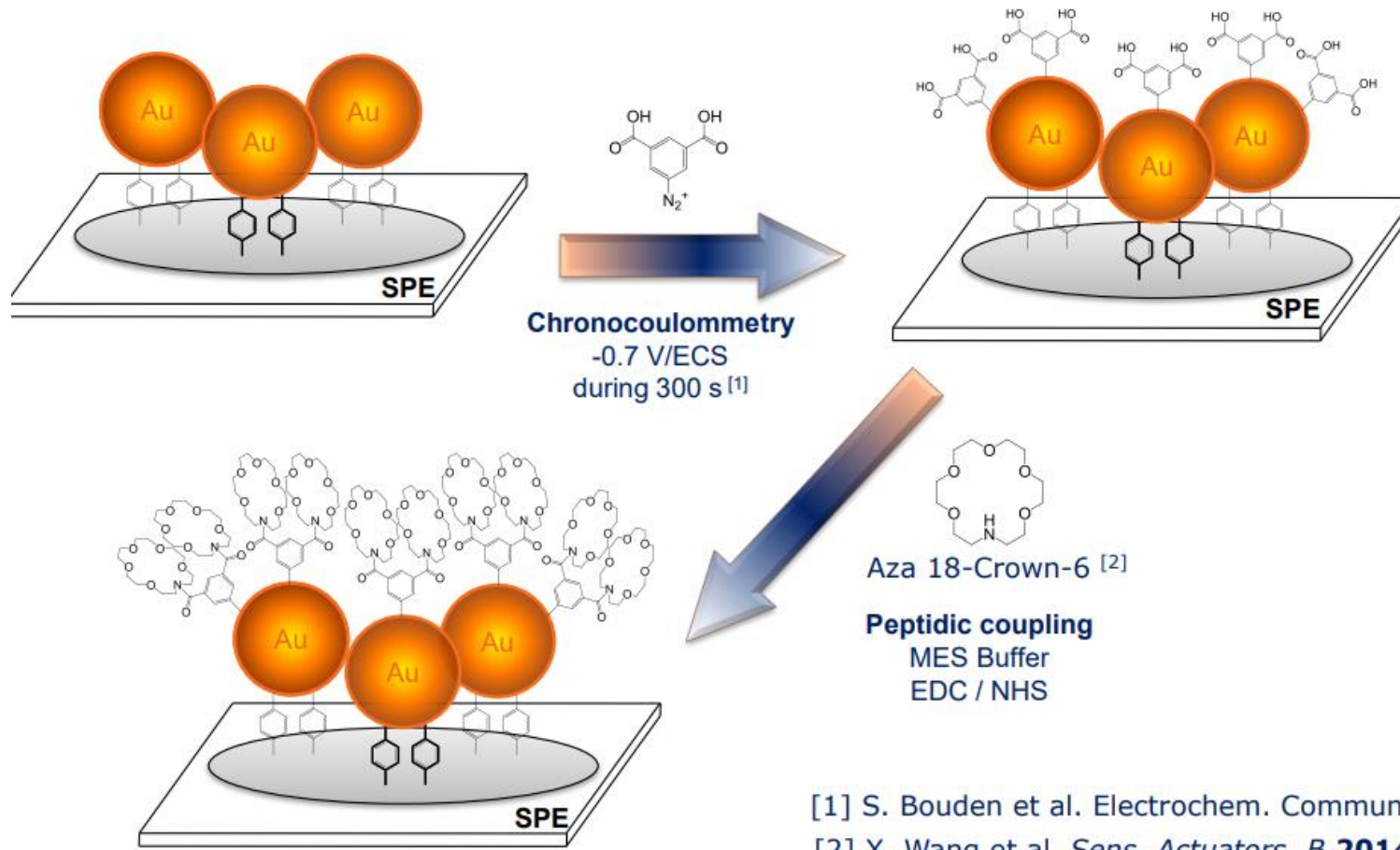
ANALYTICAL METHOD



STEP 4 : REGENERATION
 Ultrasonication 1 min
 in H₂SO₄ (pH 1)

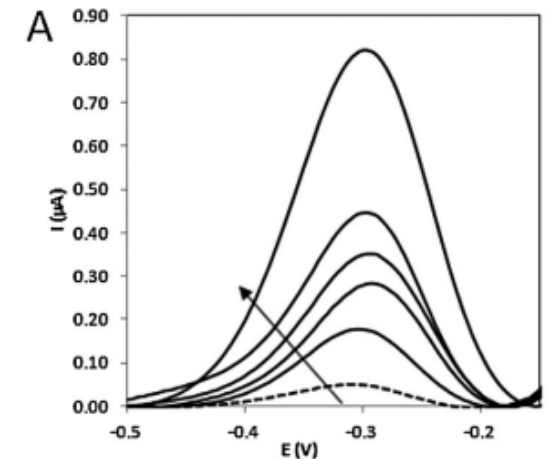
ELABORATION OF NANOSTRUCTURED SPE BASED ON DIAZONIUM SALTS ELECTROCHEMICAL GRAFTING

2 steps functionalization by aza 18-crown-6 ether

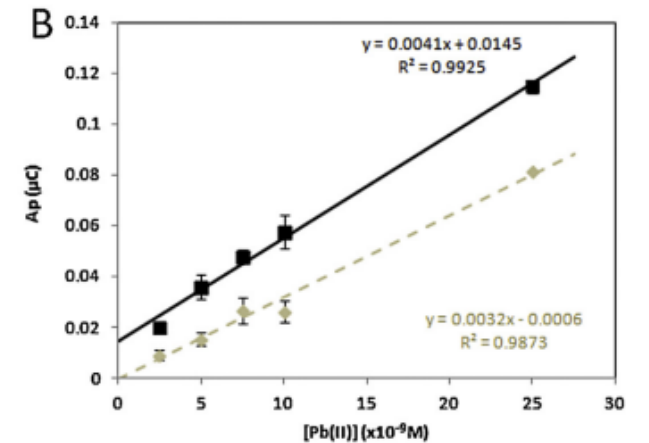


[1] S. Bouden et al. *Electrochem. Commun.* **2014**, 41, 68.

[2] X. Wang et al. *Sens. Actuators, B* **2014**, 193, 413.



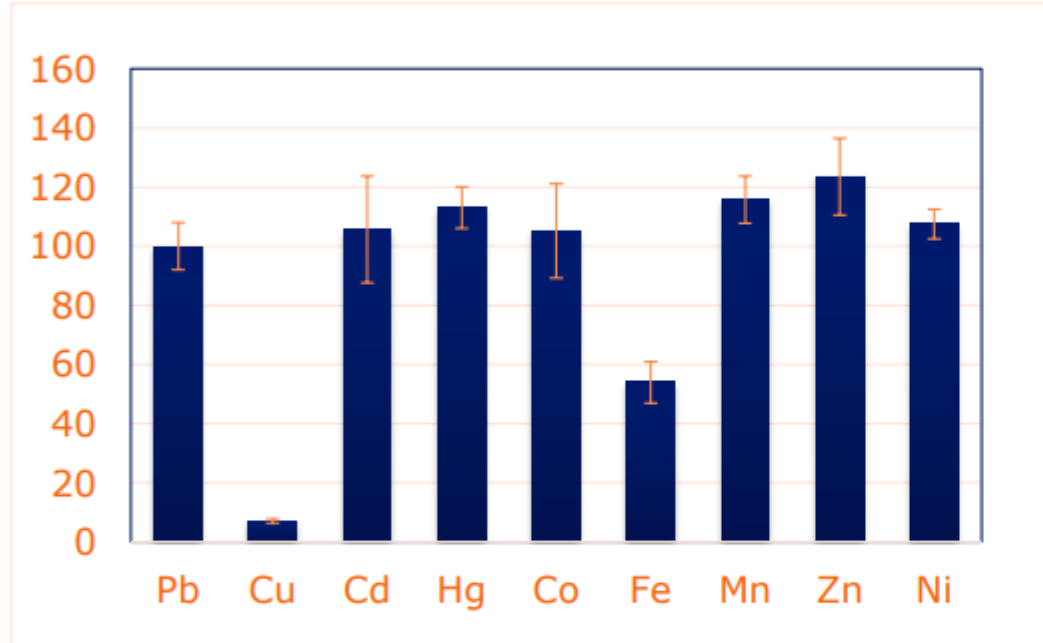
(A) SW voltammograms obtained using SPE-Ph-AuNPs-COOH



Calibration curves obtained using SPE-Ph-AuNPs-COOH (black) or SPE-COOH (grey) for Pb (II) in CH₃COONH₄ (0.1 M) 2.5 10⁻⁹, 5 10⁻⁹, 7.5 10⁻⁹, 10 10⁻⁹, 25 10⁻⁹ M

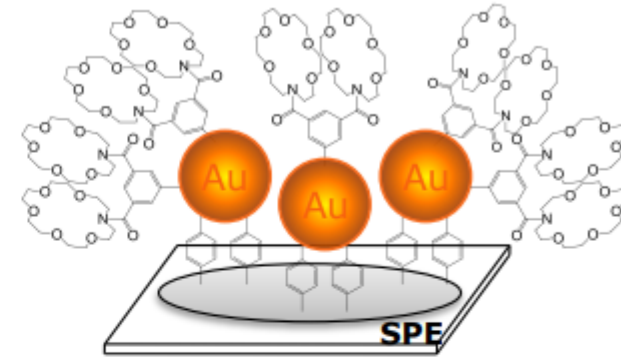
Detection of Pb(II) in the presence of a 100 fold excess of other metals:

Relative intensity of the Pb(II) signal
 I_p/I_{p0}



Pb(II) 10^{-7} mol.L⁻¹
Accumulation time: 10mn
Ammonium acetate 0.1 M, pH 7.

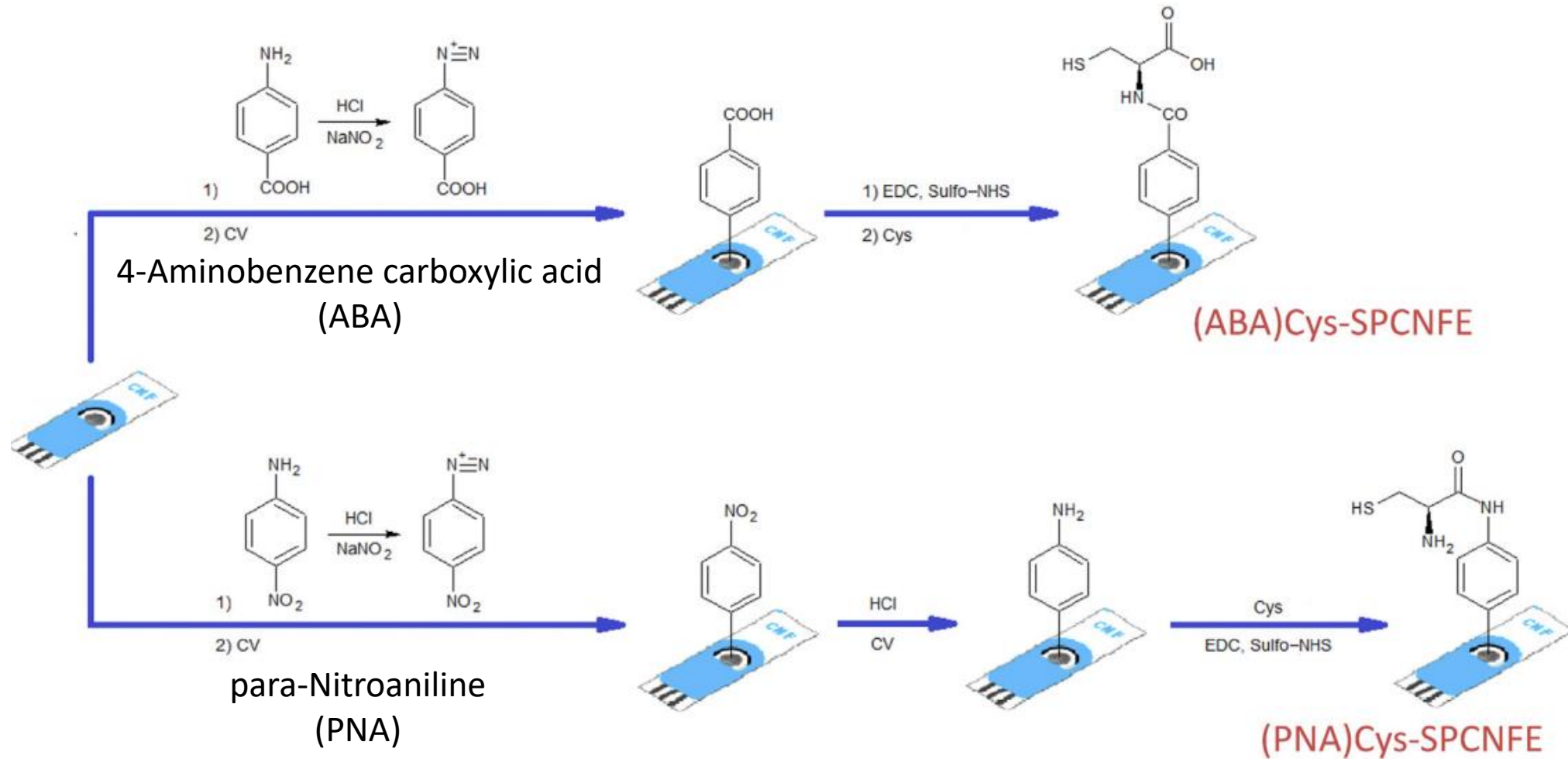
SW-ASV: Deposition Potential -0.75 V for 5 s ;
pulse amplitude 25 mV, ΔV 4 mV.s⁻¹, freq. 25 Hz.
Ammonium acetate 0.1 M, pH 7.



➔ Interference of Cu(II), Fe(II)

H°: Formation of a sandwich complex
between 2 ligands and a metal ion.

Use of grafted layer for simultaneous detection of Cd and Pb ions



Simultaneous Pb(II) and Cd(II) calibration curves were performed at the optimal experimental conditions from 1 to 150 $\mu\text{g/L}$ using both (ABA)Cys-SPCNFE and (PNA)Cys-SPCNFE.

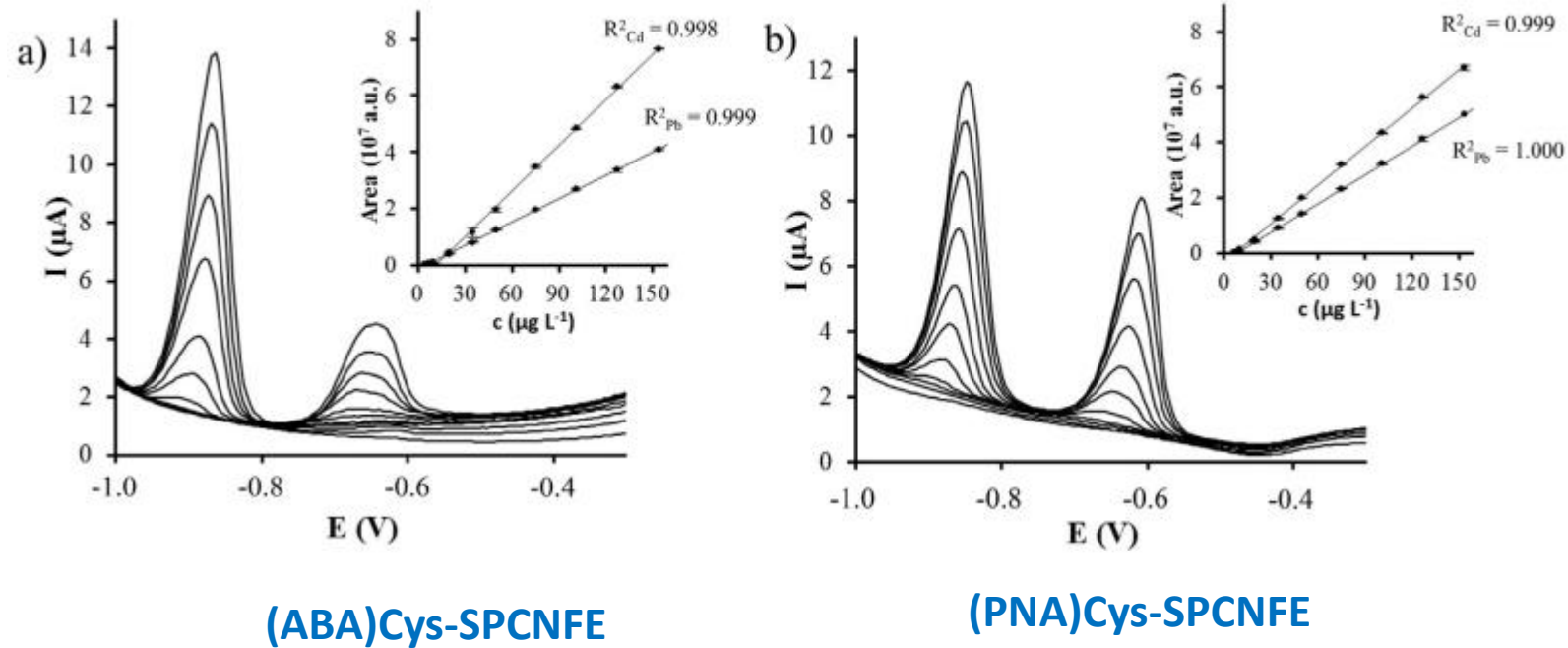
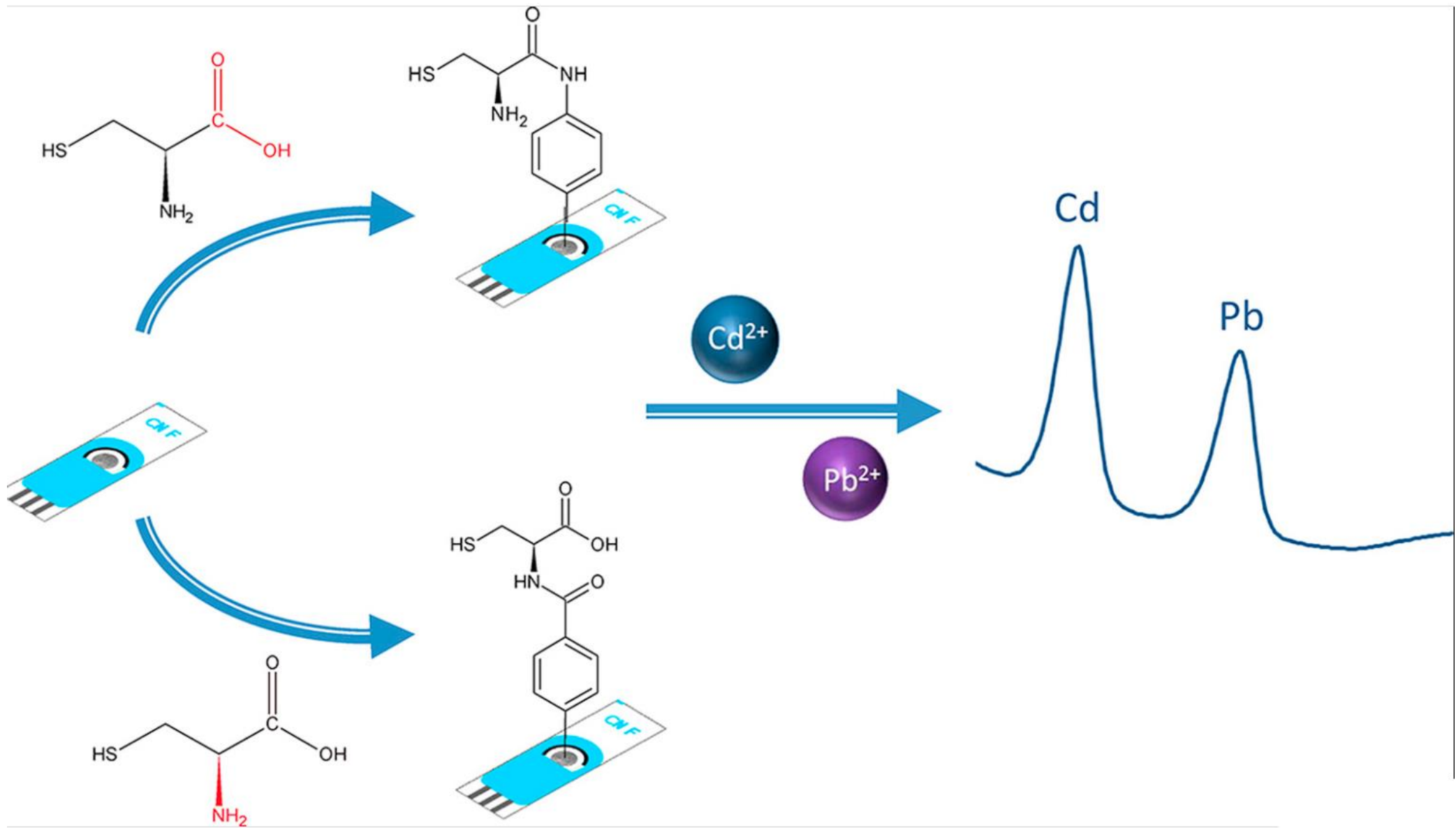
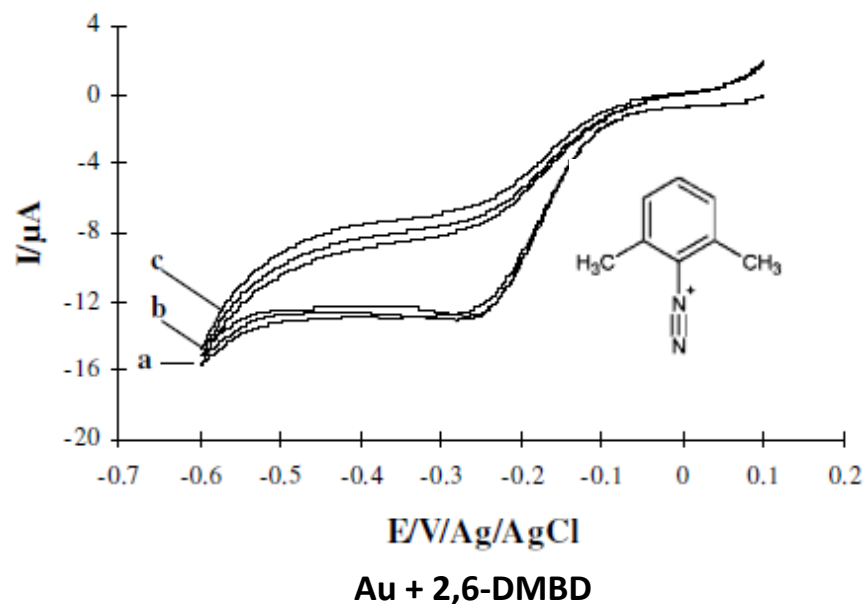
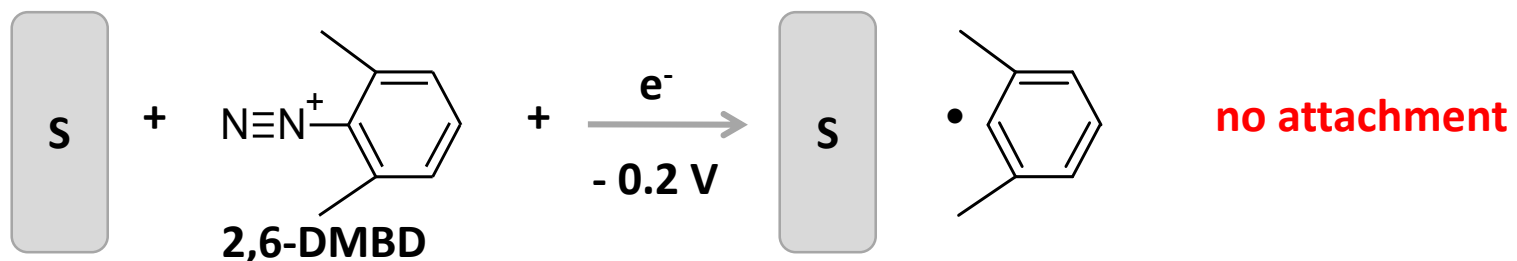


Fig. Two separate and well-defined peaks were obtained for both considered metal ions. Similar shapes and intensities were obtained for Cd(II) using both sensors whereas in the case of Pb(II) a more gaussian-shaped peak with higher intensities was observed using (PNA)Cys-SPCNFE.



Grafting of the aryl radical can be blocked

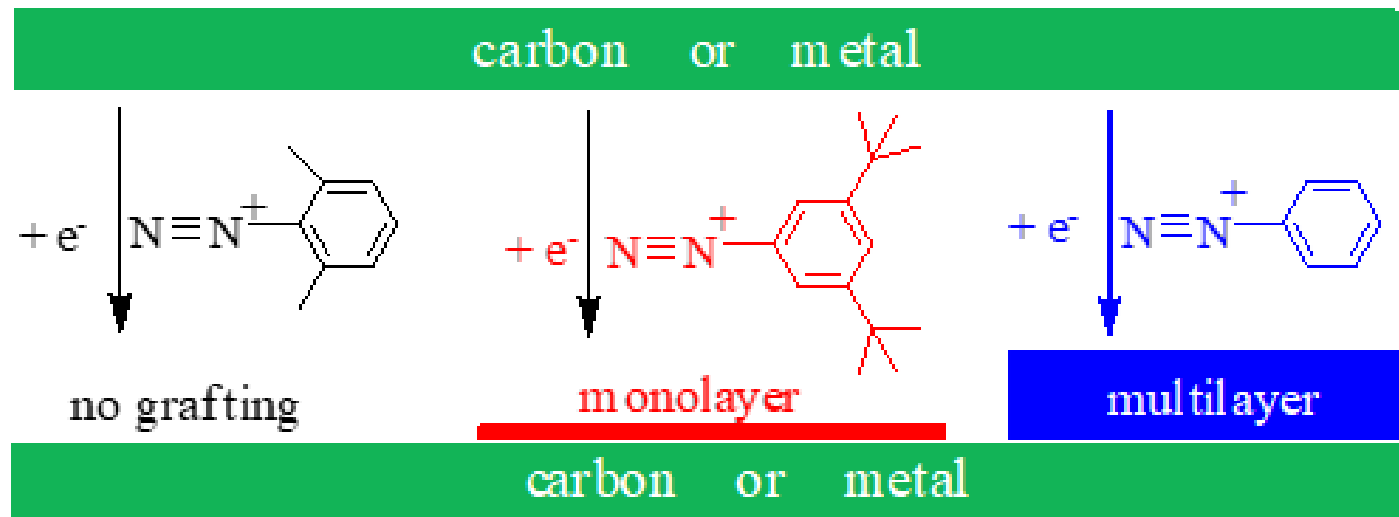


Cu displacement (Å) 0.63
Bonding energy (eV) 0.52
> 50 % lower than **for** the phenyl radical

**thickness not measurable by ellipsometry
no IRRAS signal**

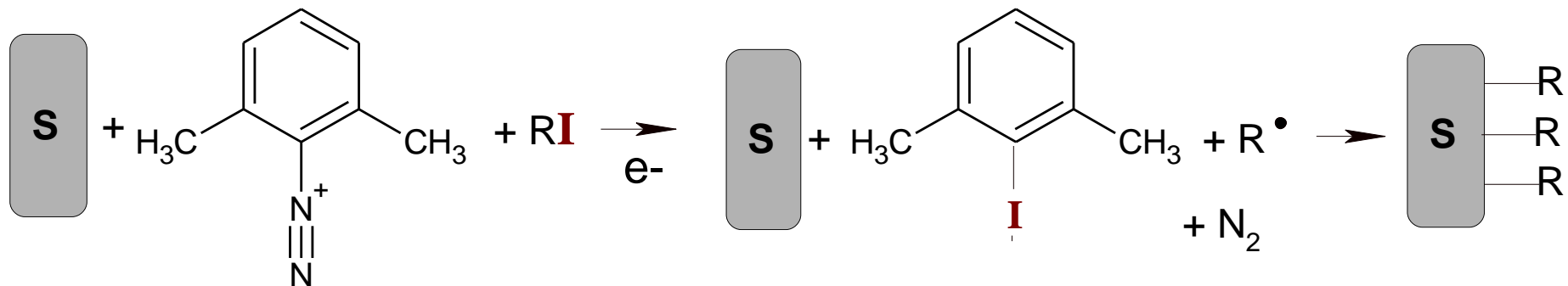
INITIAL ATTACK OF THE RADICAL on the SURFACE
is VERY SENSITIVE to STERIC HINDRANCE

TWO BULKY *t*-Bu GROUPS ARE NECESSARY to LIMIT THE
GROWTH of the LAYER To a MONOLAYER



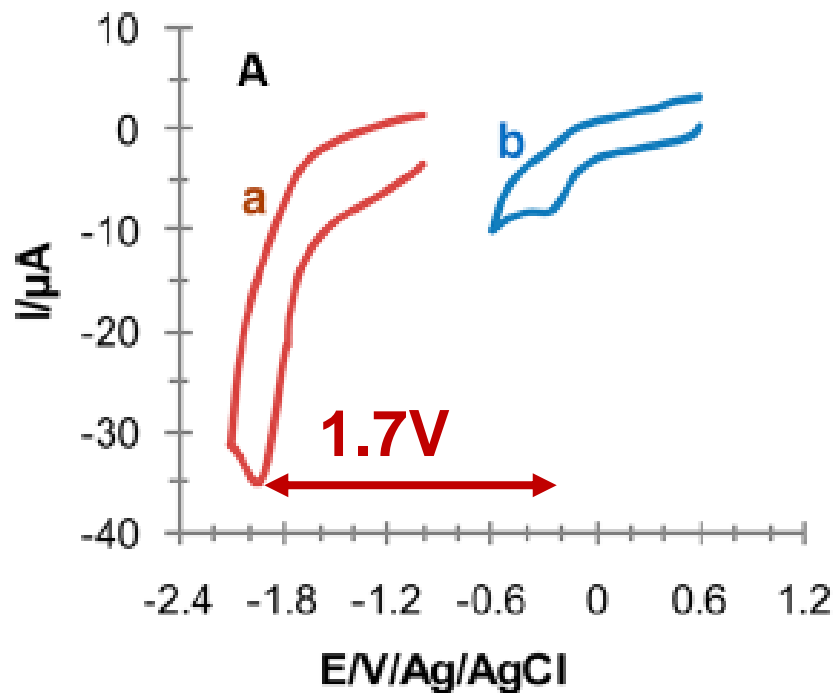
The relation between molecular structure and film morphology
By careful selection of diazonium reagents one can obtain attached films
with different structure and morphology

Indirect Electrografting of Alkyl Halides

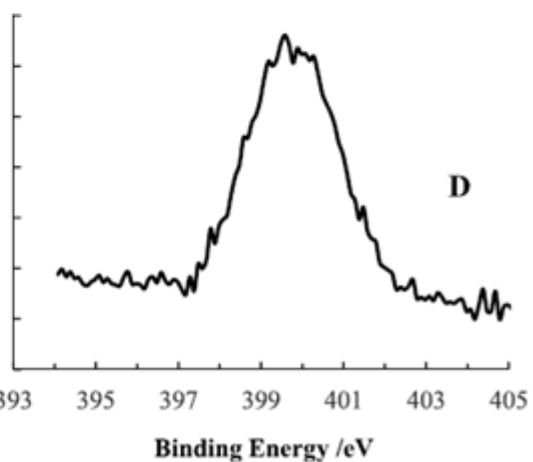
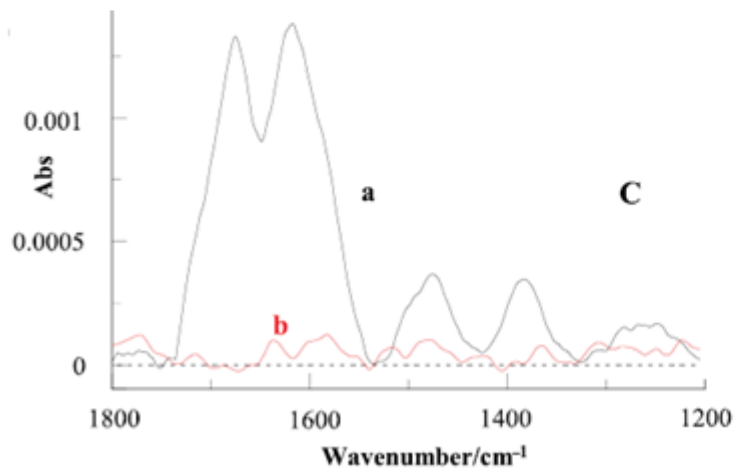
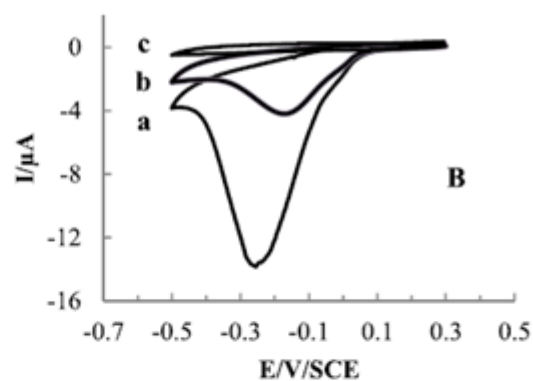
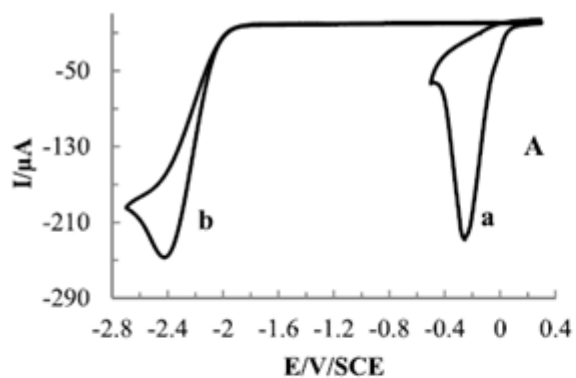


Also with RBr

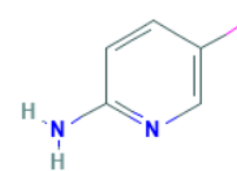
$\Delta E_p = 2.4 \text{ V}$



Indirect grafting of aryl iodides by diverting the reactivity of aryl radicals derived from 2,6-DMBD



5-Iodo-2-aminopyridine.

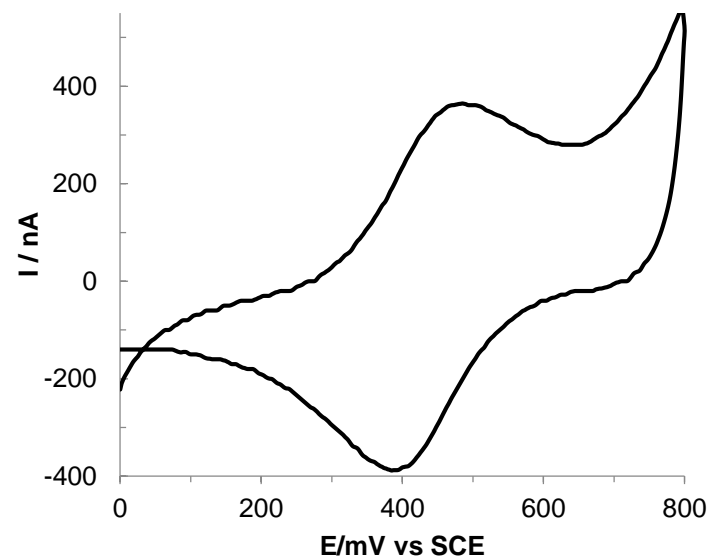
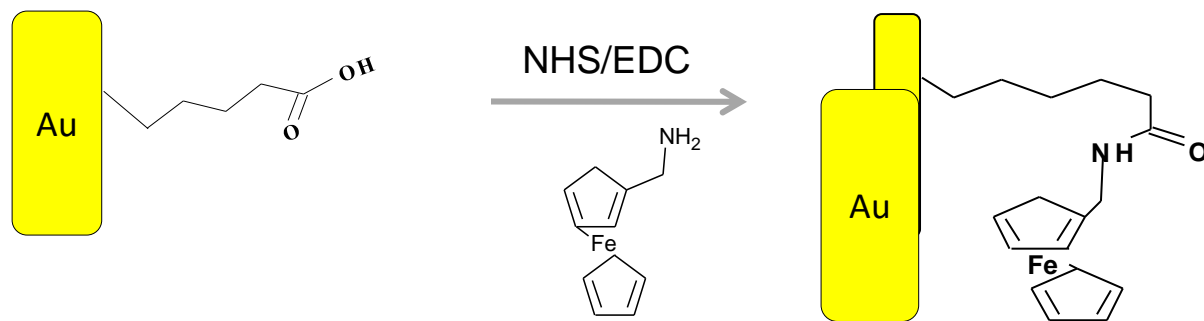


This method permits a gain of potential $> 2\text{V}$ compared to their direct electrografting.

The grafting of some aminopyridines is much easier via their iodo derivative than from their diazonium salt.

Indirect grafting of RBr by diverting the reactivity of aryl radicals derived from 2,6-DMBD

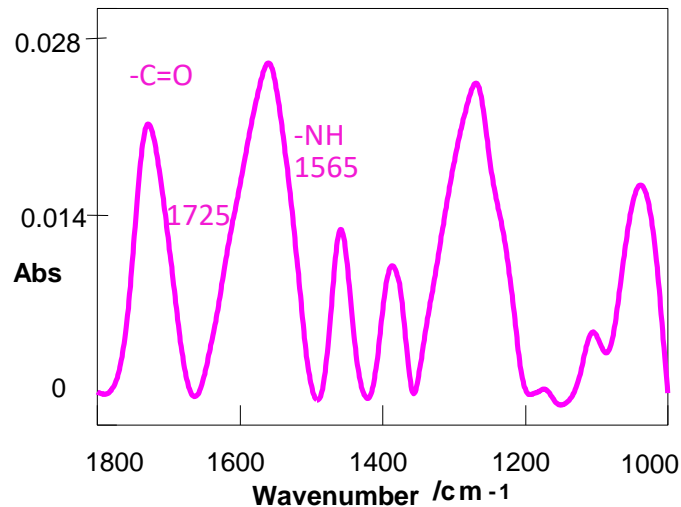
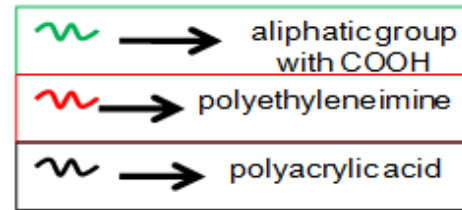
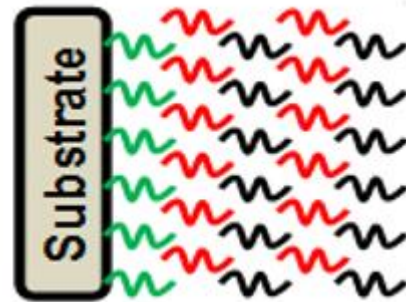
Post-modification of grafted alkyl layers from R-Br



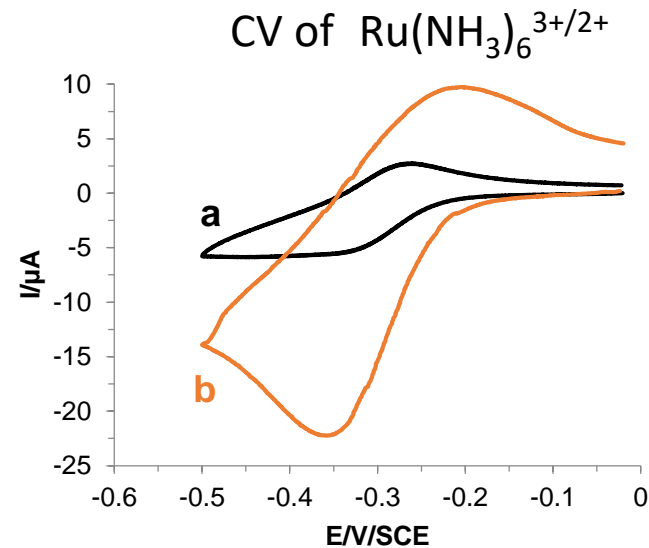
Surf. conc.: $\Gamma = 5 \pm 0.2 \times 10^{-10} \text{ mol/cm}^2$

Indirect grafting of RBr by diverting the reactivity of aryl radicals derived from 2,6-DMBD

Layer-by-layer formation on grafted alkyl layers



Au-C₅H₁₀COO-PEI-PAA



a = Au bare

b = Au-C₅H₁₀COO-PEI-PAA

Indirect electrografting of polymers via diazonium salts

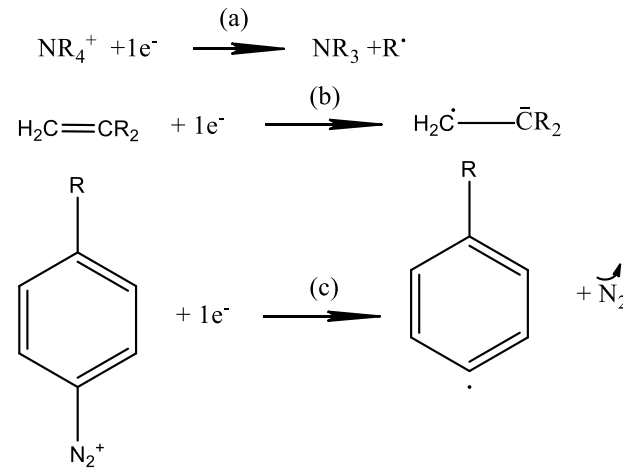
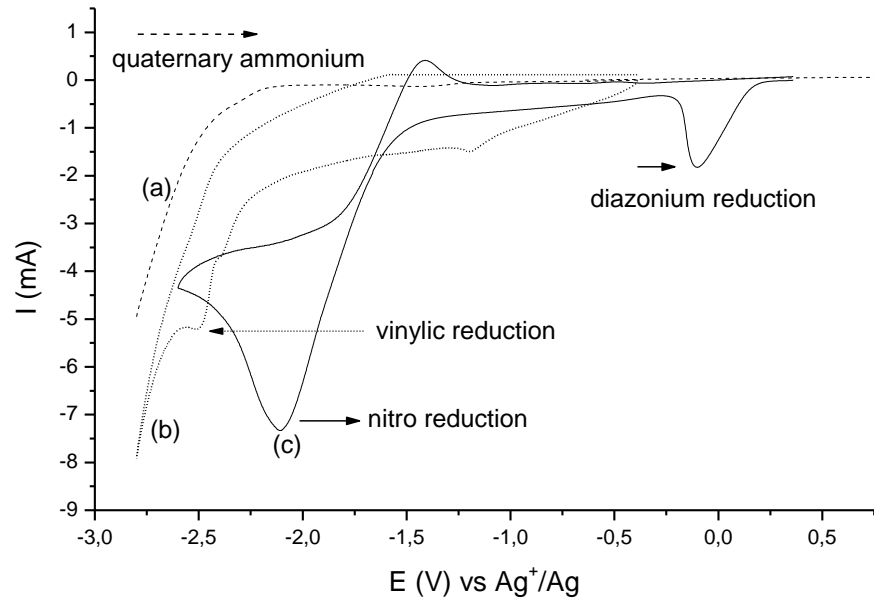
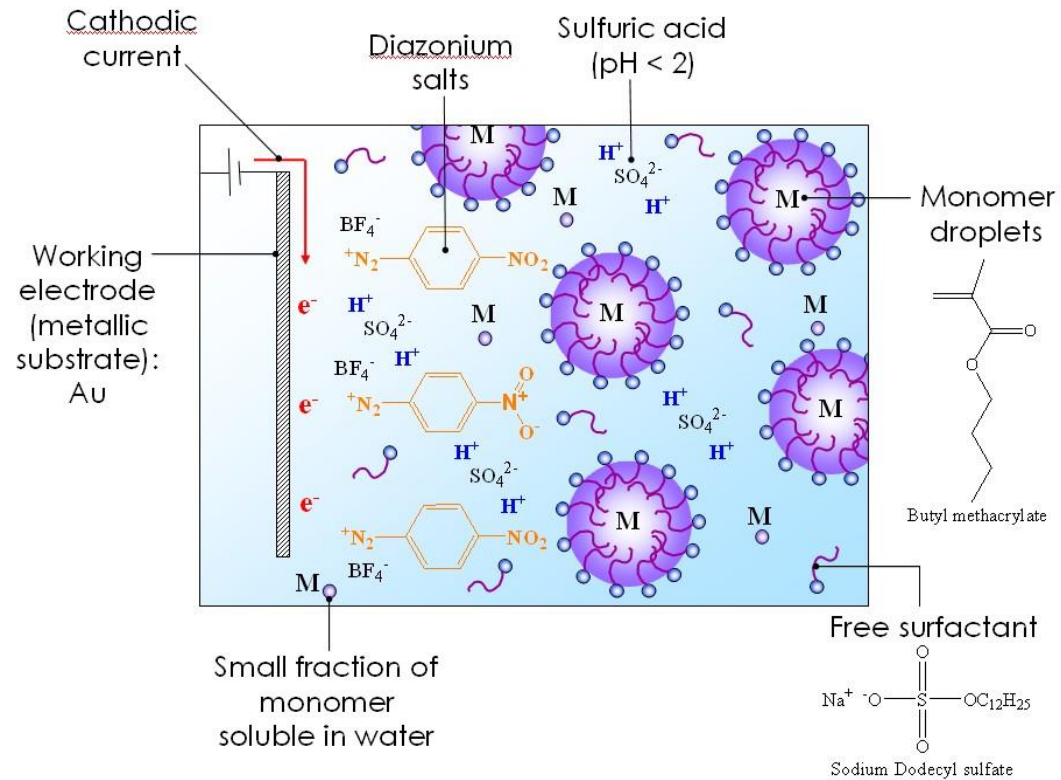


Figure Cyclic voltammetry in acetonitrile

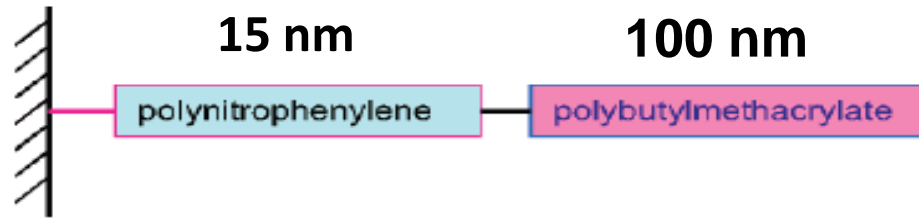
- (a) tetraethyl ammonium perchlorate TEAP ($5 \cdot 10^{-2}$ M), TEAP + vinylic monomer
- (b) and (c) nitrobenzene diazonium tetrafluoroborate NBDT (10^{-4} M). $v=50 \text{ mV s}^{-1}$.

Surface Electroinitiated Emulsion Polymerization (SEEP)

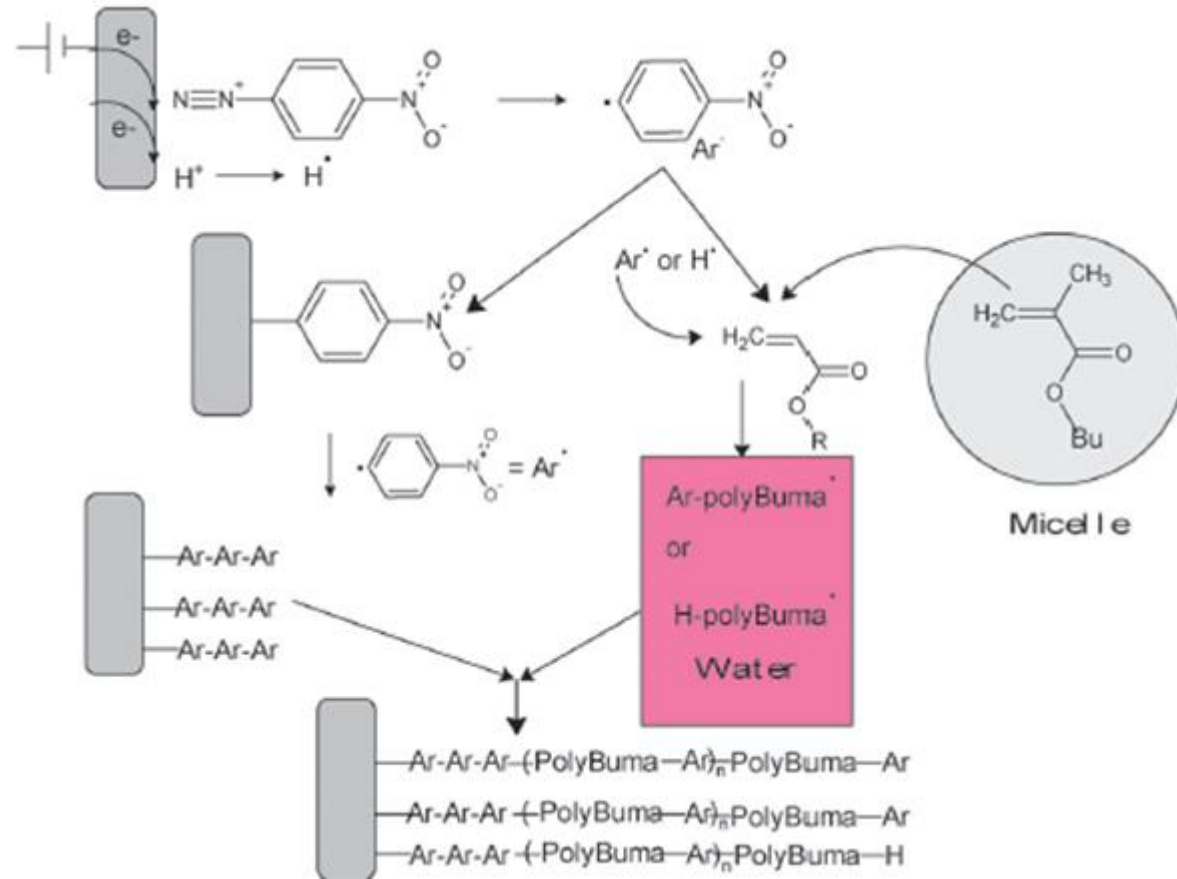


Scheme Composition of the initial miniemulsion system in the electrochemical cell

Simplified film structure



Mechanism of electrografting by SEEP



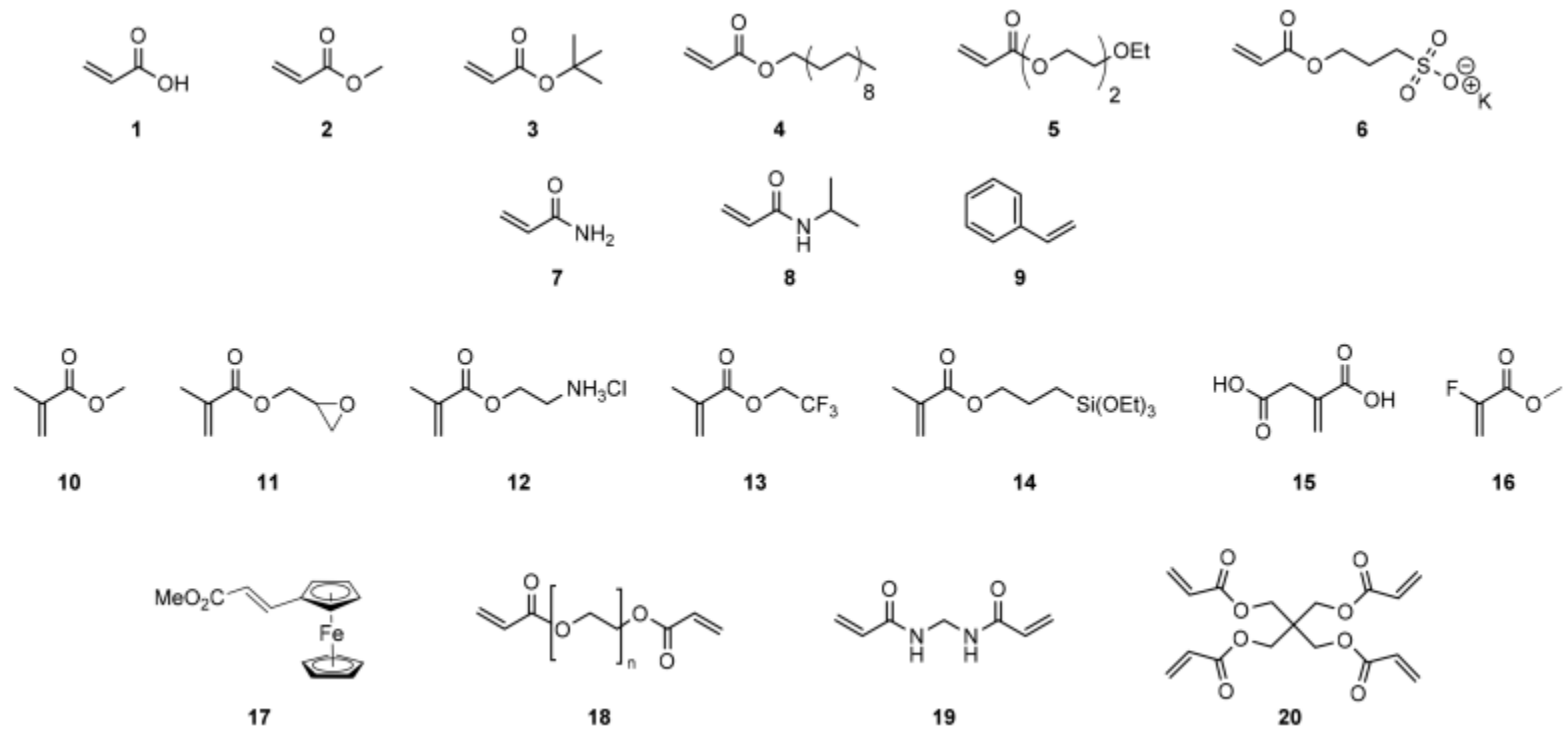
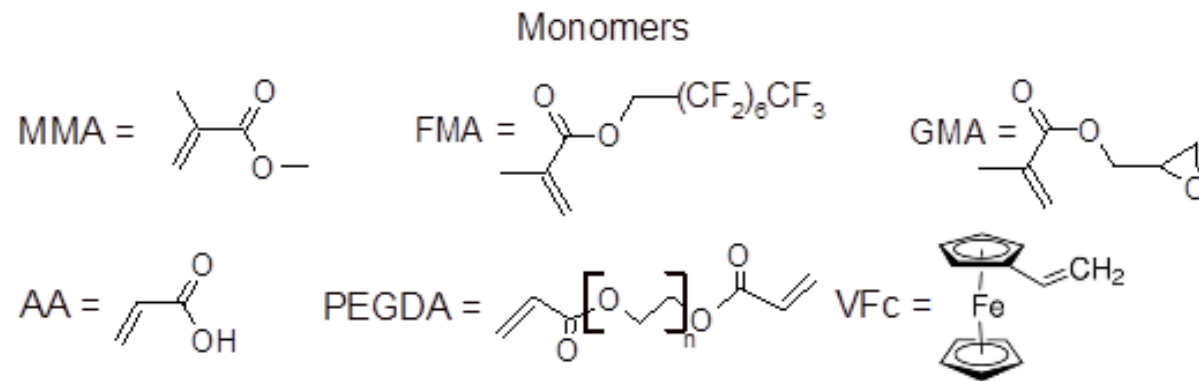
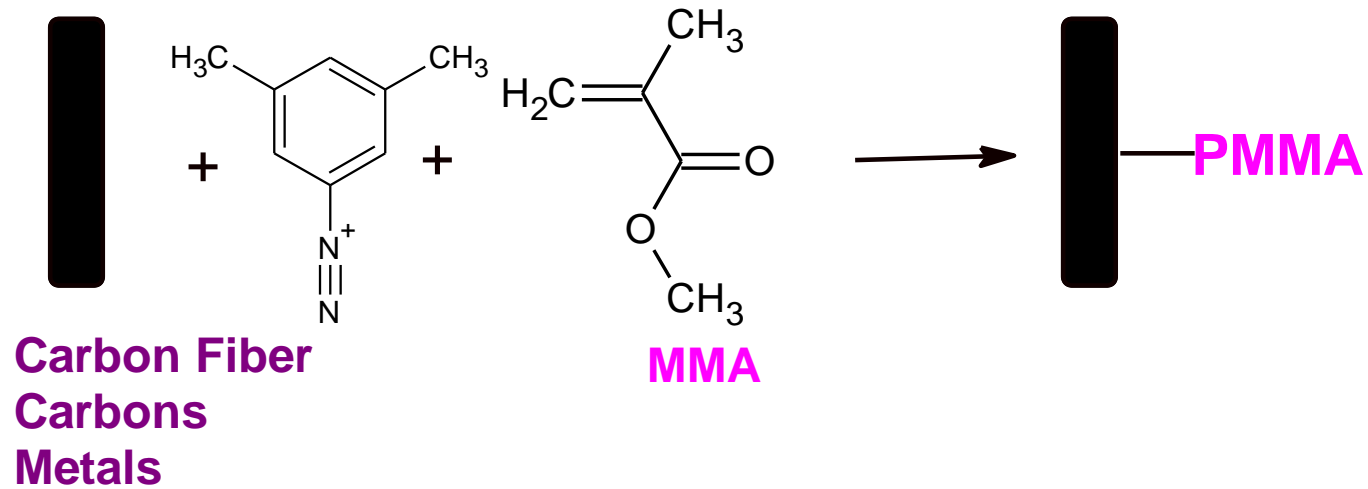


Figure. Divers monomer structures used for SEEP

Unsubstituted acrylates and methyl acrylates (ester and amide derived) showed excellent generality with thick surface bound-polymer films being generated in situ

Direct polymer grafting via Diazonium salts



CONCLUSION

Strongly Electro -Grafted films of various organic molecules onto different substrates either by oxidation or reduction

Very easy to implement (only a conventional potentiostat)

Rapidity, simplicity, absence of catalyst, control of the film thickness

Aryl diazonium salts apart the formation of strongly attached organic films are used as coupling agents for further postmodification of the receptor surface.

Many applications in environmental sensing

Acknowledgments

Prof. Jean Pinson
Prof. Catherine Combellas
Prof. Frédéric Kanoufi
Mr. Jérôme Médard
Dr. Philippe Decorse XPS



Prof. Avni Berisha
Ass. Prof. Flamur Sopaj
Dr. Dardan Hetemi
Dr. Imer Sadriu



Thank you very much for your attention!

Ju faleminderit shumë për vëmendjen tuaj!